# **B**IOCHAR ADDITION TO A LIME-HEMP INSULATING PLASTER



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# **BIOCHAR ADDITION TO A** LIME-HEMP INSULATING PLASTER

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# **ABST**RACT

 $CO_2$  emissions in 2018 reached the highest level in the human history. Architecture design has become an important tool to deal with current environmental problems; the use of no toxic materials and the energy consumption control in buildings life-cycle are strategies that significantly reduce anthropogenic emissions. Biochar, a biomass charred through pyrolysis, allows the capture and storage of carbon. Charcoal stores 50% of its C content for centuries, while biomass combustion and natural decomposition release ~90% of C within 5-10 years.

In this research, biochar is used as a building material, in addition to a lime-hemp insulating plaster. Possible improvements of the mixture in different experimental fields are reported, such as mechanical strength, humidity control or electromagnetic absorption.

Our findings suggest that the presence of biochar in a composite improves some of its mechanical and physical properties, offering room for future studies to deepen biochar characteristics in the building sector.

# INTRC DUCTION

The aim of this chapter is to illustrate the themes and the concepts followed to redact this thesis.

The first part wants to familiarize with the  $CO_2$  emissions problems; continuing with a discussion about sustainability and natural materials.

# "+400%" CO<sub>2</sub> Emissions

In 2018 the highest emissions level was registered in the history of human being.



Fig.1 In 2018 the presence of CO<sub>2</sub> in the atmosphere is 4 times bigger than 1960.

In the last decades some relevant topics have arisen in the building sector, due to the increase of pollution and waste production caused by human activity.

The application of toxic, non-recyclable materials and the  $CO_2$  emissions produced during the building life cycle, encourage the use of renewable materials and more efficient energy measures.

In 2018 the highest emissions level was registered in the history of human being. (Fig.1)

The main reason of this phenomena is high energy consumption, resulting from a growing global economy.

The largest impact is caused by human activity through carbon emissions like coal, oil, gas and cement. The remaining percentage is represented by agriculture management and deforestation; indeed, the crops and trees reduction jeopardized the  $CO_2$  natural cycle<sup>1</sup>.

A fundamental concept is introduced: Green Building.

For the World Green Building Council-WGBC-"a Green Building is a building that, in its design, construction or operation, reduces or eliminates negative impacts and can create positive impacts, on our climate and natural environment. Green buildings preserve precious natural resources and improve our quality of life".

The benefits of Green Buildings are environmental, economic and social. It is possible to reduce negative environmental impacts, by using less energy, renewable sources, natural and recyclable materials. Furthermore, the concept can offers a number of economic and financial benefits reducing energy consumption, costs of maintenance and construction. Many of these benefits concern human health and wellbeing, such as increasing cognitive function, improve working performances, but also support healthier, happier productive and more life.

In this thesis, the mentioned concepts are an inspiration to study and apply a natural by-product of biomass, as a construction material: biochar. The application consists in the addition of biochar in a natural lime-hemp plaster, recording the potential performance improvements. The insulating plaster is a product of EdilCanapa and the added biochar is produced by Laterizi Reato s.r.l.

<sup>&</sup>lt;sup>1</sup> Photosynthesis adsorbs  $CO_2$  from the atmosphere. Carbon is embodied in plants which act as carbon "sinks".

STATE OF THE ART

This chapter illustrates the origin and the properties of biochar, describing the process through which the biomass is transformed in charcoal, syngas and biooil, and analyzing the different charring conditions that establish the products quality. Furthermore, are mentioned the efficiency of the whole process, from the transportation to the final use, and the pyrolysis unit's available in Italy.

# **1.1 WHAT IS BIOCHAR ?**

Biochar is a carbon rich product created by molecolar cracking of biomass, in a zero or low oxygen conditions at temperatures between 300 and 1000 C°, through a process called pyrolysis. It is, essentially, fine-grained charred charcoal. Biochar is a charcoal, mainly used as a soil amendment, it comes from waste organic matter, or harvested biomass.

Biochar is a dark material, composed by small particles, light and highly porous; it is composed by carbon (> 50%) and ash; however, the overall composition is various, depending on the biomass used as feedstock, and the production conditions<sup>1</sup>. Its use as a soil amendment is due to specific properties :

Cations Exchange Capacity (CEC);

Fertilization;

Sequestration of heavy metals and pesticides; Microbial activity;

Retaining of water and nutrients.

The material encouraged researches and applications in different fields.

Indeed, in the last decade, biochar was also applied as a building material:

• clay-biochar plaster, for insulation and breathing properties, maintaining humidity levels in both summer and winter and preventing mold;

• biochar-concrete bricks, with a low weight density and high porosity;

• biochar for asphalt, that can improve the flow-induced crystallization ability.

These are just a few examples of the numerous applications of biochar as a building material. The interest in biochar has led to the

foundation of the "International Biochar Initiative" (IBI): a no-profit association that provides a platform for fostering stakeholder collaboration, good industry practices, environmental and ethical standards to support biochar systems that are safe and economically viable, aiming for sustainability and reducing the effect of climate change. In November 2015, the IBI released version 2.1 of the standardized product definition and product testing guidelines for biochar that is used in soil (IBI, 2015). The IBI Biochar Standards provide guidelines to ensure that biochar is safe to produce and use, but do not provide parameters for production and feedstock handling, nor thresholds or terms for defining the sustainability of the feedstocks or biochar products<sup>2</sup>.

Moreover, a European industrial standard about the characteristics of biochar has been developed. The European Biochar Certificate (EBC) ensures a sustainable biochar.

Users of biochar and biochar-based products will benefit from a transparent and verifiable monitoring and independent quality control. These standards guarantee ecologically sustainable procurement and production of biomass feedstock for biochar production, compliance with emission standards and environmentally safe storage. Biochar quality is comprehensively monitored and documented<sup>3</sup>.

<sup>&</sup>lt;sup>3</sup> The European Biochar Certificate, Website: http://www. european-biochar.org/en.



<sup>&</sup>lt;sup>1</sup> The transformation conditions can deeply modify the properties of the final product. Some parameters that influence the biochar properties are: temperature, pressure, heating rate and residence time.

<sup>&</sup>lt;sup>2</sup> International Biochar Initiative, Resources, Biochar Standards. Website: https://biochar-international.org/.

#### 1.1.1 Origin of Biochar

Biochar is not a new material: the first finding of this material derives from pre-Columbian populations. Indeed, in the Brazilian Amazon region were discovered several areas in which soils have different characteristics from the ones nearby, the latter have acid pH, rich of kaolinite with a low cation-exchange capacity (CEC)<sup>4</sup> and therefore not very fertile.

The first scientific publication is written by the soil scientist Wim Sombroek in 1962, the book *Amazon Soils - A reconnaissance of the soils of the Brazilian Amazon region*, in which he proved the existence of fertile dark earth in Amazon, created between 3000 and 5000 years ago. This specific soil is called in Portuguese "Terra Preta do Indios", or Indian Black Earth<sup>5</sup>.

Terra Preta do Indios, has black color, alkaline pH, is rich of nutrients and particularly fertile. This highly fertility is due to the relevant presence of carbonaceous material, that is able to retain the soil nutrients in particles. The latter, was produced from past human activities, like cooking or fires, and from the voluntary addition in soils during thousands of years. The addition occurred through the slash-and-char technique: the biomass resulting from the slashing of the crops was not burned, but was charred, obtaining a charcoal that could be used as an amendment. More in detail, Terra Preta is characterized by high pH, high concentration of nutrients such as N, P, K, and Ca, and up to 70 times more biochar than surrounding soils; it contains more carbon (up to 150 g C/kg)

in comparison to the soils without charcoal (20-30 g C/kg). Moreover, the Terra Preta soil is 1-2 m deep, while the surrounding soils are only 10-20 cm deep<sup>6</sup>. Petersen et al. (2001) reported that Amazonian Dark Earths in Açutuba were under continuous cultivation without fertilization for over 40 years<sup>7</sup>.

Nevertheless, biochar alone is not responsible for the formation of these highly fertile soils; research shows that nutrients in Terra Preta soils were incorporated in the form of human and animal excrements, aquatic and terrestrial biomass, and food residues such as mammal bones, fish bones, and turtle backs<sup>8</sup>.

In the twentieth century, biochar was used for numerous applications: in Japan during the 1910s pyrolyzed biochar made out of carbonized rice husks, called *kuntan*, was applied as a component of growth media for hydroponics. Furthermore, *kuntan* was used for water purification, and as an absorbent material for moisture and gas. During World War I, poison gas was introduced to the

<sup>5</sup>Already in the 19th century Smith (1879) and Hartt (1885) reported the existence of dark soil in the Amazon territories.
<sup>6</sup> Lehmann J., *Terra Preta de Indio*, Cornell University, 2009.
<sup>7</sup> Ibidem.

<sup>8</sup> Biochar for sustainable soils. Website: https://biochar. international/.



<sup>&</sup>lt;sup>4</sup> Kaolinite is a clay mineral with a low cation-exchange: CEC is a measure of how many cations can be retained on soil particle surfaces. This is one of the ways that solid materials in soil alter the chemistry of the soil. CEC affects many aspects of soil chemistry, and is used as a measure of soil fertility, as it indicates the capacity of the soil to retain several nutrients.

battlefields, and activated biochar was used as a component of gas masks, for its adsorbent properties.The various evidences and past applications of charcoal has been the starting point for the recent studies on biochar.

#### **1.1.2 FEEDSTOCKS**

The variety of biochar is due to the high number of possible feedstocks that can be used as biomass. Any crop residue and animal manure can be turned into biochar; in this way energy is produced as a by-product<sup>9</sup>. The global estimation of feedstock by Woolf et al. (2010) is  $\sim$ 2.27 Pg C/year<sup>10</sup>, available for transformation process into biochar. (Fig.4) The calculation can't be accurate, considering that the yield of biochar changes according to the biomass used and that the pyrolysis conditions influence the final result. In Fig.5 the yield of different feedstock is showed. Biomass can be classified in primary if it is organic, in secondary if it is inorganic and in tertiary if it is fluid. Another classification is in natural biomass, formed processing natural matter.

Vassilev et al. (2013) classified biomass in different groups depending on the source: woody, agricultural, aquatic, human and animal waste, industrial waste biomass. The majority is woody biomass which includes stems, branches, leaves, barks, lumps, chips of different trees.

The main source of woody biomass are forest areas.

<sup>9</sup> Bhattacharya I., Yadav J. S. S., More T. T., Yan S., Tyagi R. D., Surampalli R. Y., Zhang T. C., Biochar, in: Surampalli R. Y., Zhang T. C, et al. *Carbon Capture and Storage - Physical, Chemical, and Biological Methods*, American Society of Civil Engineers (ASCE), 2015. p. 422.
 <sup>10</sup> Petagrams (Pg) of Carbon. 1 Pg =1015 grams= 1 billion

metric tonnes. (Pg) of Carbon. (Pg) = 1013 grants = 1 billion



Fig.4 Globally available annual feedstock (in Pg C/year) and their distribution in different biomass.

Biomass	Process	Biochar Yield (% wt.)	References
Oak wood	Fast pyrolysis at 500°C	31.2	Novak et al. 2009
Corn husks	Fast pyrolysis at 500°C	26.0	Purevsuren et al. 2003
Olives stones	Slow pyrolysis at 600°C	39.7	Mullen et al. 2010
Pine wood	Fast pyrolysis at 800°C	32.1	Mullen et al. 2010
Olive bagasse	Slow pyrolysis at 500°C	39.7	Spokas et al. 2010
Palm shell	Slow pyrolysis at 400°C	24.8	Spokas et al. 2010
Pine saw dust	Slow pyrolysis at 800°C	24.3	Spokas et al. 2010
Spruce wood	Fast pyrolysis at 600°C	37.5	Spokas et al. 2010; Sukartono et al. 201
Euclyptus wood	Slow pyrolysis at 400°C	42.2	Spokas et al. 2010
Olive husk	Fast pyrolysis at 800°C	39.7	Spokas et al. 2010
Beech wood	Slow pyrolysis at 500°C	26.2	Spokas et al. 2010
Corn cob	Slow pyrolysis at 800°C	23.2	Tsai et al. 2012; Zhao et al. 2013
Rapeseed stalks	Slow pyrolysis at 400°C	32.1	Zhao et al. 2013
Pitch pine	Fast pyrolysis at 500°C	39.7	Zhao et al. 2013
Straw pellets	Slow pyrolysis at 400°C	24.8	Zhao et al. 2013
Willow pellets	Fast pyrolysis at 700°C	24.3	Kim et al. 2012
Conocarpus waste	Fast pyrolysis at 500°C	37.5	Al.Wabel et al. 2013; Masek et al. 2013
Walnut-shell	Slow pyrolysis at 500°C	21.8	Masek et al. 2013

Fig.5 List of biochar yield from different feedstock.

The second largest source includes a wide range of agricultural crops: stalks, straw, shells of these crops are used. Agricultural biomass and woody biomass are widely used for energy production in different parts of the world.

Classification of the biomass can give an estimation on the cellulose or lignin component in it. For example, it is expected that industrial and animal waste biomass contains more sulfur as compared to woody and agriculture biomass. Prediction of elements can help in comparing the energy content in biomass which is important in the selection of biomass for pyrolysis. Classification on the basis of lignin and cellulose is helpful when a certain type of product is desirable after the pyrolysis<sup>11</sup>.

#### **1.1.3 BIOMASS TRANSFORMATION TECHNIQUES**

The techniques used for the transformation of biomass into energy are called bioenergy conversion technologies. Energy rich products can be obtained through the conversion of the organic matter; therefore, it is important to choose the appropriate method to save energy with the minimum environmental consequences.

The methods can be classified into two groups: biochemical conversion and thermochemical conversion. The first involves biological catalyst to produce energy from biomass; the second involves heat and a chemical catalyst. The main process involved in biochemical conversion is fermentation, widely used to obtain methanol and biodiesel, while for thermochemical conversion combustion, gasification and pyrolysis are the most used. The biochemical conversion is the less expensive and more environmentally friendly, but thermochemical conversion is the most  $popular^{12}$ .

Biochar is mainly produced through pyrolysis, that permits to change different parameters according to the product's characteristics needed. However, this is not the only process for the production of this material: the different methods for the production of biochar can be divided in conventional and current techniques.

#### **1.1.3.1 CONVENTIONAL TECHNIQUES**

These methods can be used for a small scale production, following the pyrolysis principle. These techniques permit to obtain a good quality biochar and are still used locally. Biochar production with conventional techniques is on a domestic scale.

CARBON ZERO EXPERIMENTAL BIOCHAR KILN

It is a kiln, isolated with firebrick and closed with a 200-liters barrel of steel. The biomass is covered up and heated from beneath. In the lower stove part, the wood fires, where a maximum pyrolysis temperature of 320 °C it is reached. The wood for fire is dependent upon the moisture content: additional heat is needed otherwise, as the exothermic reaction releases heat. Using a pilot model with a retort volume of  $\sim 5 \text{ m}^3$ , the kiln can process up to 1 ton of air-dried, chipped woody biomass per hour, with a conversion efficiency of woody biomass to biochar being 30-33% and  $\sim$ 1.4-1.7 MWh of chemical energy in the syngas produced. Straw and grasses have lower lignin content and hence a lower conversion efficiency to biochar ( $\sim 17\%$ )<sup>13</sup>. The advantages to this approach are numerous.

<sup>&</sup>lt;sup>11</sup> Tripathi M., Sahu J.N., Ganesan P., "Effect of process parameters on production of biochar from biomass waste through pyrolysis: A review", in: *Renewable and Sustainable Energy Reviews*. Elsevier, Amsterdam 2016. p. 469. <sup>12</sup> Ivi. p. 470-471.



Fig.6 Scheme of carbon zero experimental biochar kiln.

A not too big support flame is required to keep the gases ignited. A cylindrical tube-like structure called "the blower" is mounted at the top of the afterburner, from where injection of the air steam takes place. The firebrick is placed at a height of 3/4 of the top of the afterburner barrel for the deflection of the gas stream, and it must mix well with some air to keep the ignition. The thermocouple probes further extend into the retort from the bottom and top to maintain the temperature. (Fig.6)

#### Two barrel charcoal retort

This combination is where the smaller vessels are filled with different biomass. The biomass has to be dried up in order to make the charring process effective. The vessel has to be placed upside down, two bricks are laid upon which filled vessels are placed. Then the vessel is filled to the top. After that, the bigger drum is placed upside down on the smaller vessel containing the biomass. This to ensure that the vessel is sealed entirely. Holding the inner container tightly to the bottom of the larger container and turning it back making sure that the content doesn't spill out. The entire burning process lasts for a minimum of 30 minutes. After that the pyrolysis of the biomass starts. The gases escape during the heating process in between the barrel, the vessel emerges along with fire which further heats the vessel<sup>14</sup>. (Fig.7)



Fig.7 Scheme of two barrel charcoal retort.

#### Two barrel charcoal retort with afterburner

In this technique a tank containing the biomass for charring is used. The principle is similar to the one mentioned above, the only difference is the size. One of the containers is used as the retort- with a lid and a bottomwhich is placed at the bottom and one, placed above, acts as the afterburner.

This barrel has only a cylindrical bottom and the top is removed. The afterburner is placed above the retort. (Fig.8)

<sup>&</sup>lt;sup>13</sup> Bhattacharya I., Yadav J. S. S., More T. T., Yan S., Tyagi R. D., Surampalli R. Y., Zhang T. C., op.cit, p. 427.



Fig.8 Scheme of two barrel charcoal retort with afterburner.

#### Terra Preta Pot

It is used to make biochar from agricultural waste residues. The same pot can be used at home to cook or to warm a domestic area. It can be described as a pot inside a pot, which suits the concept of micro-pyrolizer. It is made from plastic and clay materials, or it is manufactured by a skilled potter. Thus, it is possible to make biochar maintaining local pottery traditions<sup>15</sup>. (Fig.9)



Fig.9 Scheme of terra preta pot.

#### **1.1.3.2 CURRENT TECHNIQUES**

The modern pyrolizers vary in size, from laboratory scale (milligrams units' capacity) to industrial equipment (capacity of several tons/hour).

North In America the largest fast pyrolizers 250 tons process or 200 of biomass/day<sup>16</sup>. dry tons Pre-dimensioned studies from small to large scale pyrolizer systems are necessary to value costs of the biomass processing at a large-scale central facility, over small-scale processing facility situated near to biomass source. For a large-scale central processing facility, the additional costs are transportation, storage and handling cost<sup>17</sup>.

#### COMBUSTION

Combustion is the oldest and the most common technique to convert the energy stored in the biomass into heat. It consists in burning – at 800-1000°C- the organic matter in the presence of oxygen. The result of this process is the complete oxidation of the biomass, converting almost all the chemical energy in thermal energy and with a paltry amount of ash. Combustion can be applied to every type of biomass, only if the humidity in the material is less than 50%; above this limit the direct combustion is not worth it, considering the cost of the process. Moreover, it is possible to have a pre-treatment of the biomass to increase the efficiency after combustion. The first step of this technique is the combustion of the vapors, which burns as flames; the proportion of oxygen in the air and the biomass fuel are an essential factor to obtain an efficient process. The residual material, in form of charcoal, is burnt to give more heat. The main products are carbon dioxide and water vapor. Tars, smoke and alkaline ash particles are also produced, it is important to control the emissions of these products for an environmentally acceptable system. The weaknesses are: more indoor and outdoor pollution than fossil fuels, risk of monoxide poisoning and requires regular maintenance and a lot of space for the fuel storage<sup>18</sup>(Fig.10)

<sup>&</sup>lt;sup>15</sup> Bhattacharya I., Yadav J. S. S., More T. T., Yan S., Tyagi R. D., Surampalli R. Y., Zhang T., op.cit., p. 428.

<sup>&</sup>lt;sup>16</sup> Ivi, p. 429.

<sup>&</sup>lt;sup>17</sup> Ibidem.

<sup>&</sup>lt;sup>18</sup> Tripathi M., Sahu J.N., Ganesan P., op.cit., p. 471.



Fig.10 Scheme of the combustion process.

#### GASIFICATION

Gasification is a thermochemical process in which the carbon contents of biomass are converted into gaseous fuels, in the presence of oxygen, air, nitrogen, carbon dioxide, steam or some mixture of these gases at high temperature (700-900°C). Unlike combustion, it is a partial oxidation of biomass which extracts the energy and form gaseous products. In this process, the intrinsic chemical energy of carbon present in the biomass is converted into combustible fuel gases which can be used more efficiently and easily than raw biomass. The gas produced is generally referred as bio-syngas (synthetic gas), which mainly consist in CO,  $CO_2$ ,  $H_2$  and  $N_2$ .

The residues after gasification are char, ash, tar and some oil. Gasification is a very efficient method to produce  $H_2$  from the biomass not only at the laboratory scale but also for the large-scale hydrogen production. Most of the problems faced in the production of biochar from biomass,

generally, come from its composition. It is a fact that O/C ratio is very important for a high gasification efficiency. Low O/C ratio biomass on gasification leads to high efficiency.

Torrefaction can be considered a pretreatment before conventional gasification to improve the quality of the product, considering that it reduces the O/C ratio of the organic matter. It is a low temperature process -200 to 300°C - requiring a heating speed of about 50°C/min, depending upon the composition and type of the biomass. The latter, in general, is a low energy density hydrophilic material but upon torrefaction it becomes a hydrophobic solid with improved calorific value. The solid product of the torrefaction process contains approximately 30% more energy per unit mass compared to regular biomass, making the solid biochar a more energy dense material. Porosity of the biochar formed after torrefaction is also high compared to conventional gasification.

Biomass is a difficult material to grind or mill; energy consumption for milling biomass is found to be reduced by three to seven times on torrefaction. (Fig. 11)



Fig.11 Scheme of the gasification process.

# **1.2 PYROLYSIS**

Biochar, as mentioned before, is created with a process called pyrolysis, a smoldering and chemical process that burns biomass at high temperatures and with low presence or totally absence of oxygen, without combustion.

Pyrolysis consist in two phases: primary pyrolysis, in which, due to the heat, the biomass is evaporated and decomposed into different chemical groups; the secondary pyrolysis is the main process in which the organic matter is converted into syngas, bio-oils and bio-char<sup>19</sup>.

The low energy gas (8 to 15 MJ kg<sup>-1</sup>) is composed by methane, hydrocarbons, carbon monoxide and dioxide.

The liquid compound (15 to 30 MJ kg<sup>-1</sup>) is generally termed bio-oil.

<sup>19</sup> Bhattacharya I., Yadav J. S. S., More T. T., Yan S., Tyagi R. D., Surampalli R. Y., Zhang T. C., op.cit., p.428-29.



Fig.12 Scheme of the pyrolysis process.

The high energy (20-30 MJ kg<sup>-1</sup>) solid biochar, that contains a quantity of C from 50% to 90%, includes volatile carbon, moisture, fixed carbon and ash.(Fig.12)

The three products derived from the pyrolysis processes have different structure and properties depending on the feedstock used, the conditions and the process.

During the pyrolytic process the chemical structure of the final biochar is influenced by temperature, heating rate and pressure. Considering these parametres, pyrolysis is classified in fast, slow or intermediate; other categories are flash, vacuum, and microwave

pyrolysis.

#### **1.2.1 Origins of Pyrolysis**

Pyrolysis is a composite word and derives from the Greek language: "pyro" that means fire, plus "lysis" that means decomposition.

It is hard to define the first trace of pyrolysis since it is a process that can occur in nature, usually when a land comes in contact with lava or a fire accident.

The first traces of pyrolysis for charcoal production have 5500 year, and were found in the south of Europe and in the Middle East World. With the rise of the Bronze Age, this technique spread all over the world.

Pyrolytic process was known through Egyptian for wood coal production and, after through the charcoal pile during the XX century. Biochar was made at places where suitable raw material was abundant. Therefore, an easier way to provide the necessary heat was used: biomass was put together with an airtight layer of earth and a small part of the biomass was burned. The air-flow was controlled through little openings in the earth layer, to keep a productive balance between burning and pyrolysis. Bricks and kilns were also produced during this process. Thanks to the good insulation and airflow control lot of biochar was obtained. In the 1930s, transportable, cylindrical metal kilns were developed in Europe and became widespread in the 1960s in developing countries. In 1971, efforts where shifted to enhance bio-oil and syngas production, and to reduce charcoal to a by-product (Antal, Gronli 2003)<sup>20</sup>.

Nowadays, thanks to the studies on the properties and the possible applications of biochar, this transformation process can be considered and exploited in different cases.

#### **1.2.2** Types of Pyrolysis

The pyrolytic process, also called bioenergy conversion<sup>21</sup>, is able to determine the final conditions -thermal, electrical and mechanical - of the biomass treated, reducing the costs and the energy consumption respect to the combustion existing processes.

Different types of pyrolysis depend on specific operating parameters fixed for the process and on the different proportion of products – oil, gas or solid- obtained.

The classification is made considering the heating rate<sup>22</sup>, the residence time and the temperature.

Starting with the traditional ones, slow, intermediate and fast – all made in anaerobic conditions- in this chapter, are explained the pyrolysis types, following the less conventional transformations.

<sup>&</sup>lt;sup>20</sup> Meyer D., Biochar-A survey, Tampere University of Technology, 2009.

<sup>&</sup>lt;sup>21</sup>Tripathi M., Sahu J.N., Ganesan P., op.cit.,p.470.

<sup>&</sup>lt;sup>22</sup> Heating rate, is the ratio of British thermal units of fuel consumed to kilowatt hours of electricity produced. Hence, the lower the heat rate, the higher the conversion efficiency. Online Dictionary.

#### FAST PYROLYSIS

Fast pyrolysis is characterized by short residence time (0,5-10s), proceeds with a temperature of 800-1200 °C, at a rapid heating rate condition of 10-200 °C/s. The feedstock is added in the pyrolizer when it reaches the desired temperature, not at the beginning nor at the end. This type of pyrolysis produces 60-75% of liquid product, 15-25% of biochar and 10-20% of non-condensable gaseous product.

Fast pyrolysis produces more bio-oil than gaseous or char compound because the exposure time is minimized and heating rate is high.

The pH is low (3.1) that makes the bio-oil corrosive and can be used as a fuel.

Currently, the food and chemical industry uses this technology to produce flavors.

#### INTERMEDIATE AND SLOW PYROLYSIS

The slow pyrolysis, also named carbonization pyrolysis, has a temperature of 500-900°C, stay at 0.1 to 10°C/s for a time ranging between 5 and 300 min. It is demonstrated that with slow pyrolysis more char is produced. Biomass is introduced in the reactor at the beginning of the process. Thanks to  $O_2$  absence, a low amount of  $CO_2$  is produced, and biomass is pulverized into char, producing more solid matter in relation to the liquid and gaseous one.

Intermediate pyrolysis is something between slow and fast pyrolysis. So, while the fast produces high amount of liquid and the slow a large quantity of char, the intermediate stays in the middle and produces a char for soil fertilization, thanks to his dryness, and a bio-oil of excellent quality. This permits to use the oil for boilers and engines. Final products in slow pyrolysis are: 30% liquid, 35% solid and 35% gas, while for the intermediate the amount of liquid increases reaching 50% and the rest is solid and gas at 25% each.

Slow pyrolysis is the favorable process

#### FLASH PYROLYSIS

Flash pyrolysis is an alternative to fast pyrolysis, with a temperature between 800 - 1200 °C and has a residence time of 0.1-1s. This kind of pyrolysis has a very high heating rate ( >500 °C/s ), yielding a lot of liquid product and not much char. Furthermore, the oil compound produced contains ash that causes an increase of viscosity, that doesn't allow its industrial use.

#### VACUUM PYROLYSIS

The most important element in this kind of process is the pressure, that needs to be low - 0,01-0,02 MPa - with a total absence of oxygen and with a temperature of 450-600°C  $^{23}$ . The heating rate is similar to the slow pyrolysis.

Vacuum is used to remove the vapors from the reactor, in which most liquid product is produced and char has porous structure.

<sup>23</sup> Tripathi M., Sahu J.N., Ganesan P., op.cit., pp. 471-473.

#### Fig.13 Operating conditions for different types of pyrolysis.

	Fast	Slow	Intermediate	Flash	Vacuum	Hydro
Temperature (°C)	800-1200	500-900	500-700	800-1200	450-600	350-600
Heating rate (°C/s)	10-200	0.1-10	1-10	>500	0.1-1	10-300
Residence time (s)	0.5-10	300-18000	0.5-20	0.1-1	0.001-1	>15
Pressure (MPa)	0.1	0.1	0.1	0.1	0.01-0.02	5-20
Particle size (mm)	<1	5-50	1-5	< 0.5	-	-

Pyrolysis can be optimized depending on the feedstock used and the operating conditions desired. Therefore, it is possible to obtain more char with slow pyrolysis, or more bio-oil with fast pyrolysis.

Another important characteristic of this process is the use of any kind of waste and biomass - wet or dry, hard or soft - and the low production of sulfur and  $NO_x$  gases, harmful to the environment.

The process can be cost efficient if a large pyrolysis plant is used and there is no need for previous or subsequent transformations of the product.

#### **1.2.3** Impact of process conditions on biochar properties

Final biochar quality and properties are closely related to the operating parameters, temperature, reaction time, pressure, particle size and heating rate. All these influence the hemicellulose, cellulose and lignin proportion, that determine the amount of stable carbon in char, and the carbon content. Another important element to consider is the quantity of ash that, in some cases, can influence the char yield.

#### TEMPERATURE

Temperature is one of the most important variables that influences biochar physicochemical properties<sup>24</sup>.

Increasing the temperature, carbon content, surface area and porosity rise, leading to a higher CCS<sup>25</sup> capacity of the biochar<sup>26</sup>. Biochar quantity production depends on more aspects like feedstock and composition. (Fig.14)

#### HEATING RATE

This operating condition has a relevant role in reactivity and composition of biochar. Indeed, it can modify the surface area and morphology. The amount of biochar product and its chemical composition are strictly connected to the heating rate: surface area increase with a fast heating rate, and a higher oxygen content is the result of a slow one. With an high heating rate the macro pores (>2 mm diameter) presence increases and consequently absorption capability, with a raise of the surface area. However, if the pores are too large the surface area decreases. Low heating rate is the best parameter to obtain a noticeable quantity of biochar.

With the slow pyrolysis is associated a low heating rate (10 °C/min) a higher portion of solid matter is produced;

<sup>26</sup> Brown, R., Biochar production technology, in *Lehmann, J., Joseph, S. (Eds.), Biochar for Environmental Management Science and Technology.* Earthscans, UK 2009. Pp. 127–146.

Fig.14 Comparison of temperature effect on char yield for different biomass.

Authors	Biomass	Temperature range (°C)	Biochar yield (%)
Williams and Nugranad	Rice husk	400-600	33-25.5
Aysu and Kusuk	Ferula orientalis L	350-600	40.26-26.29
Zhang et al.	Corncob	400-700	34.2-20.2
Sanchez et al.	Sewage slug	350-950	52-39
Ayhan Demirbas	Olive husk	450-1250	44.5-19.4
Ayhan Demirbas	Corncob	450-1250	30.6-5.7
Shabangu et al.	Pine	300-450	58-26

 <sup>&</sup>lt;sup>24</sup> Physicochemical properties: in general, are specific gravity, melting temperature, thermal expansion, electrical and thermal conductivity, corrosion resistance.
 <sup>25</sup> CCS: Carbon Capture Sequestration.

with a high heating rate (10-200  $^{\circ}$ C/s) the bio-oil yield increases.

#### RESIDENCE TIME

Residence time is the amount of time a matter stays in a system - in this case the biomass - so, long residence time means it may last from 30 min to several hours, and short residence time that the process lasts only a few seconds. Usually, with the long residence time is associated a low pyrolysis temperature and a bigger amount of char product.

#### Pressure

Pressure is strictly related to the biochar particles morphology. Indeed, Cetin et al. (2004) observed that biochar particles produced under a pressure of 0.50 MPa (5 bar) have larger cavities with thin cell walls compared with biochar produced under atmospheric pressure. From 10 to 20 bar, larger particles with perforations are formed; the particles turn into droplets and the volatile content is removed. Droplets coalesce to form larger particles. From 5 to 10 bar, with a high temperature (>600 °C) there is a

phenomenon of swelling, due to the volatiles that tend to escape. At higher pressure (10-20 bar), swelling decreases: when a higher pressure is reached, biochar tends to stretch elastically causing a decrease in swelling. Surface area increases slightly proportionally with the increase of pressure until 10 bar; above this level the contribution of mesopores and macropores is too high and the surface area decreases.

High pressure influences the quantity of char production and its quality, the C presence increase when the pyrolytic process is executed under high pressure.

#### PARTICLES SIZE

There is no much information about particles due to undergoing research.

Nevertheless, it is known that increasing the particle size through the raise of temperature, it is possible to obtain a higher biochar yield, because the vapor inside the pores has to cover a larger distance causing cracking of the mass and secondary reactions and producing a bigger amount of char<sup>27</sup>.

<sup>&</sup>lt;sup>27</sup> Tripathi M., Sahu J.N., Ganesan P., op.cit., pp.474-475.

## **1.3 BIOCHAR PROPERTIES**



#### Fig.15 CO<sub>2</sub> cycle.

The main application of biochar is as soil fertilizer, thanks to specific properties of this material. The reason why biochar is important as a soil amendment is not only a consequence of its ability to increase the crop yield. Globally, soil holds more carbon (1,100 Gt) than the atmosphere (750 Gt). The following scheme illustrates the connection between the two, through the C-cycle. (Fig.15)

The carbon cycle consists in the exchange of carbon between soil and the atmosphere: CO<sub>2</sub> is absorbed by the plants, then O is released in the atmosphere and carbon is absorbed by the soils through photosynthesis. When plants die, the biomass gradually releases the inner carbon in the atmosphere, offsetting the absorbed carbon.

Plants release  $\sim$ 90% of the carbon dioxide. This is a balanced cycle. In Lehmann et al. (2006) it is reported that the exchange of the whole carbon on the earth between atmosphere and soils takes approximately 14 years; the increase of carbon due to anthropogenic pollution led to an increase of C in the atmosphere with respect to soil. Charring the biomass, 50% of the carbon content of biomass is immediately released, with a stable biochar residue. Indeed, during pyrolysis, charcoal reaches a stable aromatic structure <sup>28</sup>.

<sup>&</sup>lt;sup>28</sup> The higher is the pyrolysis temperature, the stabler is the product: between 250°C and 350°C, a complete depolymerization (pyrolysis) of the cellulose occurs, resulting in significant mass loss and creation of an amorphous C matrix; at 330°C, the first aromatic structure starts to build; above 350°C, polyaromatic graphene sheets begin to grow, with consequent reduction of the amorphous-C matrix. Above 550-600°C, carbonization begins: most of the remaining non-C atoms are removed and graphene sheets continue to grow, eventually coalescing.



Fig.16 Stabilization of the carbon at different pyrolysis temperature: above 350°C, polyaromatic graphene sheets begin to grow, with consequent reduction of the amorphous-C matrix. Above 550-600°C, carbonization begins, and graphene sheets continue to grow and coalescing. The higher is the pyrolysis temperature, the stabler is the product.

The stability of biochar allows to store the remaining carbon for centuries, after 100 years the carbon content of the charcoal is around 40% <sup>29</sup>.

Charcoal has a long residence time in soil, the components of carbon in biochar persist approximately 10-1000 times longer than residence times of most soil organic matter. Biochar can be considered a carbon sink: it removes the carbon dioxide from a short term cycle, integrating it in a long-term cycle. (Fig.17)

Charcoal is also used in soils for particles sequestration: charcoal produced through pyrolysis of organic matter, is negatively charged, contributing to electrostatic adsorption of positive ions.

The capability of this material to adsorb and store particles is due to the cation exchange capacity (CEC). High CEC allows to immobilize cations such as nutrients, heavy metals, pesticides, herbicides and hormones; it also reduces  $N_20$  and CH<sup>4</sup> in soils, dangerous substances for crop development and for the environment. Due to its porous structure and alkaline ashes contents, the determinatvvvion of CEC is challenging.

Biochar is composed by macro pores, mesopores and micropores. The conditions of pyrolysis and the type of feedstock strongly influence the dimensions of pores. The surface area and the pore volume of biochar increase proportionally with temperature, reaching a maximum at  $\sim$ 700°C, after which they decrease. This is due to the number of micropores, responsible for most of the surface area<sup>30</sup>. When the temperature is higher than  $\sim$ 700°C the micropores increase their size, coalescing: the consequence is the formation of macro pores and the decrease of the surface area.

<sup>&</sup>lt;sup>29</sup> Lehmann J., Gaunt J., Rondon M., "Biochar sequestration in terrestrial ecosystem-A review", *Mitigation and Adaption Strategies for Global Change*, Springer, 2006. p. 406.

 $<sup>^{30}</sup>$  Specific surface area (SSA) is a property of solids defined as the total surface area of a material per unit of mass (m²/kg) or solid or bulk volume (m²/m³ or m⁻1). Biochar has an SSA of several hundred m² g⁻1 to a thousand m2 g⁻1.

The higher the surface area, the higher the quantity of gases and water that can be retained in the biochar.

Water retaining is an important property to obtain an efficient fertilization of soils. Water is conserved in the pores, this brings to a crop development considering the consistent presence of moisture in the soil. The ability of biochar to absorb water can reach 5 times its weight.

Another characteristic of biochar is the C:N ratio. The higher is the temperature of pyrolysis, the larger is the C:N ratio. For example, in pecan biochar, the C:N ratio is 244. Nitrogen immobilization occurs generally when organic residues possessing a C:N ratio greater than 32 are added to soils.

A high C:N ratio, allows a higher stability<sup>31</sup>. High inputs of fertilizers and pesticides and their long persistence in the soil adversely affect the soil microflora, disturbing soil health and reducing the total bacterial and fungal biomass. Biochar increases the pH of soils so provides a suitable habitat for a diverse group of soil microorganisms. Enhancing the microbial activity, the plant productivity is higher and the soil healthier. The biochar stability and its capacity to capture and store particles may play a global warming mitigation role.

<sup>31</sup> Bhattacharya I., Yadav J. S. S., More T. T., Yan S., Tyagi R. D., Surampalli R. Y., Zhang T. C., op.cit., p. 433.



Fig.17 % C remaining from biomass decomposition after 100 years and after pyrolysis; range C remaining after decomposition.

# **1.4 PRODUCTION PROCESS**

It is important to consider the high variety of charring processes that can be applied for the transformation of biomass into biochar, such as gasification, pyrolysis, torrefaction. There are numerous models of gasifiers and pyrolizers, different in size, charring conditions and consumption. The process is chosen according to the availabile biomass and the requested yield. For instance, gasification is more profitable for syngas yield.

The three products (syngas, bio-oil, biochar) have diverse applications:

Syngas is a mixture of carbon monoxide, carbon dioxide, and hydrogen. It is composed by the elements volatilized during the charring process. Syngas from pyrolysis is a combustible gas and can be used for the production of power for the production of hydrogen, ammonia, methanol, and synthetic hydrocarbon fuels (bio-fuels). It can be also used as an energy source for the pyrolysis, this application allows to reduce the costs of the charring process.

BIO-OIL is a dark brown liquid product. It has a higher density than biomass, which reduces storage and transport costs. Bio-oil is not suitable for direct use in standard internal combustion engines, but can be upgraded to either a special engine fuel or (through gasification processes) to a syngas and then bio-fuel. Bio-oil can be used for co-firing, as it can be easily handled and burned. Other applications are: chemical, pharmaceutical and cosmetics industries, materials technology.

BIOCHAR is mainly used as a soil amendment. Other uses are: water filtration for heavy metals and pollutants; as a building material for thermal insulation, humidity control and electromagnetic shielding.

According to the multitude of parameters, the the costs and profits are changeable. It is difficult to estimate the efficiency of the different pyrolysis methods: it is more realistic to describe and evaluate one example of charring process.

In the following section, the pyrolysis process used for the production of Bioton biochar is analyzed. The method used by the company Laterizi Reato s.r.l aims to produce biochar, mainly for water depuration, and syngas for the cogeneration of the process. The first step is the storage of the biomass. It is composed by virgin wood of poplar, turkey oak and fruit trees. Most of the used biomass (A) is not grown for this purpose, but is the waste that is not useful for other applications. A low percentage of the biomass is grown specifically for the charring process, purchased and chipped by the company.

The cost of the biomass changes according to the origin. The chipped wood (B), with humidity <30%, can range between 40-60  $\notin$ /ton (10-15  $\notin$ /m<sup>3</sup>); while the remaining biomass is obtained without a cost. After the storage, the biomass is milled, reaching a size <30mm. The cost of the milling process is 35-40  $\notin$ /ton. The milling machine is electric; part of the energy is produced by a photovoltaic plant.

The pyrolysis is carried out with a pyro-gasifier PG350 (maximum capacity 350kg/h), with a consumption of 280-300 kWh, produced by the Indian company Ankur. To achieve an efficient process 250 kg/h are pyrolyzed, producing 500/550 Nm<sup>3</sup>/h of syngas, with 1511 Wh/ Nm<sup>3</sup>. The syngas yield is 1:25 by weight.

250kg of biomass produce an amount of gas that corresponds approximately to 200 kWh. The heat of the process is used to dry biomass and to warm up the charring chamber. The heat and power losses are lower than 5%. The gas is condensed to create a substance similar to bio-oil. The whole biomass is transformed in biochar, syngas or heat, and the self powering system (syngas is used to power the plant) permits to reduce the losses. The biochar yield is 10% the weight of the input biomass. After the pyrolysis, the material is ready to be used. In this case the product is used as a water filter for heavy metals and pollutants. It is important to underline that the charring plants are still not globally widespread. This implies that the transportation costs and pyrolizer availability are strongly influenced by the distances.

Considering the low number and limited scale of existing pyrolizers, the efficiency of a commercial scale unit can only be estimated.

All the information is supplied by Pierluigi Reato, founder of Laterizi Reato s.r.l.



Fig.18 Production process scheme of bioton biochar.



# **1.5 BIOMASS TRANSORMATION UNITS AVAILABILITY**

To analyze the feasibility of the process for the industrial production of biochar it is important to study the availability of machines that currently produce syngas, bio-oil and biochar, and their targets. According to the application of the products, different machines are used: pyrolyzators, gasifiers, pyrogasifiers. Differents machines lead to differents quality products and different percentage of biochar, hence it is essential to take into account the diversity between the pyrolysis units to esteem the amount of charcoal currently produced.

The company Ecco Soluzioni located in Vimercate (MB), is specialized in pickup and disposal of garbage, and in the last years a pyrolysis unit has been installed in for the production of biochar. In Mondovì (CN) a Swiss company installed two pyrolyzators, the production is focused on syngas, while the biochar obtained is not pure, as it is rather a bio-oil.

The Laimburg Experimentation Center and Unibz (University of Bolzano) started a project called wood-up, financed by the European Regional Development Fund (ERDF). The Alto Adige Sud Tyrol burns around one million cube meters of biomass every year to produce 1300 GWh, 12% of the energy requirement of the region, and 2000 tons of biochar produced are discarded each year. The goal of the project is to reutilize the charcoal as a fertilizer to enhance the production of biomass, optimizing the whole cycle. An important step is the analysis of the efficiency, different companies are taking part in this initiative and both gasifiers and pyrolizators are used for the production of syngas

Fig.19 Position of the pyroylisis units in Italy.

and charcoal. The project is still on-going, results will show the possible economic and environmental improvements.

Nowadays 36 gasification and pyrolysis units are used in Alto Adige.

Romana Maceri is a company based in Rome, focused on stockage and recycle, of paper, plastic, glass and wood. Apyrolyzator produces syngas is utilized to power the process and biochar is used as a filter for liquids. As mentioned in the previous paragraph, the Laterizi Reato s.r.l owns two pyrogasifiers, and the production is focused on the yield of biochar used as a filter for polluted water, while syngas is used to power the entire process.

The total of the pyrolyzation units currently working in Italy are 42, various in inputs materials, charring methods, and products obtained. The locations and the low number bring to a high transportation costs, directly proportional with the distance between the biomass collection site and the pyrolyzation site.

All the information is supplied by Pierluigi Reato, founder of Laterizi Reato s.r.l.

**STATE OF THE ART** 

# **ZANTERIORITY** Research about biochar as a building material is still widely open. In this chapter are d researches that can

presented patents and researches that can be essential to discern the possible uses of biochar in buildings.

# **2.1 INTRODUCTION**

The anteriority was carried out using different tools: World of Science, Orbit, Science Direct, Google Scholar, Google Patents, Pico Polito.

Keywords: biochar; biochar applications; biochar as a construction material; biochar  $CO_2$  adsorption; biochar plaster; carbon plaster; carbon building application; charcoal building material; building electromagnetic shielding; shielding effectiveness; wave absorbing; permittivity.

Three patents and eight applications have been detected. The patents were found in Google Patent, while the applications were found on the sources Science Direct and Pico Polito.

The first patent analyzes a clay-composite brick with the addition of biochar, explaining the preparation method and the results. Natural wood biomass was charred for this application. The results show the improvement caused by biochar regarding compressive strength, water retention and porosity of the final product.<sup>1</sup>

The second and the third patent are included in the same study. Therefore, these are published as one patent regarding the application of biochar as a mortar and as a and as an interspace layer for a filled wall. In the first case a binder, an aggregate and biochar are combined. Replacement of 2% river sand by biochar resulted in increase of compressive strength of mortar by 24% and 15% at 7 days and 28 days respectively, 4% replacement of sand showed about 20% increase at 7 day while slight increase of strength at 28 day is observed compared to plain mortar. 6% sand replacement does not impact the strength of mortar. Moreover, a partial sand replacement of charcoal does not affect the flexural strength of the mixture.

2% and 4% replacement of sand by biochar significantly reduce sorptivity of mortar compared to plain mortar<sup>2</sup>.

The second case consists in the measurement of the CO<sub>2</sub> adsorption of a wall filled with biochar-coated pellets. The used biochar is yielded from wood waste. The pellets are created with water and plaster in a ratio of 1:3, and then mixed with biochar. Two different configurations of wall panels were tested - one type with a cavity thickness of 15mm and another type with a 30mm cavity. A typical indoor partition wall can measure 6m wide and 3m high, if three layers of the experimental panel (with 30 mm cavity) are applied (since a wall can be 110 mm thick), with a concentration of 1000 ppm, the entire wall can potentially adsorb 30 g of CO<sub>2</sub> within the first 10 minutes and 3,24 kg of CO, in two months. After this period either the panels are replaced, or the biochar will lose the capacity of capturing gases in its particles<sup>3</sup>. The various researches illustrate different characteristics of biochar: the electromagnetic shielding property in cement composites mixed with charcoal: the flow-induced crystallization of biochar in asphalt; the improvement in compressive strength of biochar-based mortar; the low thermal conductivity and moisture adsorption given by the use of biochar as a filler; the humidity control and the prevention of molds and microbes in biochar internal plaster; and the lightness of biochar bricks.

<sup>&</sup>lt;sup>1</sup> Lu Lun C., *Biochar-Clay Composite Brick*, international patent n. CN106955670A, 2017.

<sup>&</sup>lt;sup>2</sup>Shuan M., Wei H., Souradeep G., Jing Yeng C., International Publication Number WO 2018/203829 Al, International Patent Classification: C04B 18/10 (2006.01) E04C 2/02 (2006.01), World Intellectual Property Organization, 2018. pp. 8-25.

<sup>&</sup>lt;sup>3</sup> Ivi. Pp. 25-32.

# PATENT 1 TITLE: BIOCHAR- CLAY COMPOSITE BRICK

The object of the present invention is to provide a composite clay bricks biochar and its preparation method, a biological biochar-clay composite brick with good mechanical properties and water permeability, having good adsorption properties of pollution. CN106955670A China 18 August 2017 Chen Baoliang Lu Lun

#### MATERIALS

Water; wood biomass; clay; biochar.

#### PROCESS

The first step is premixing biomass and water. The wood is preferred but straw, rice husks and bamboo can be used as well. The wood needs to be crushed and sieved.

Clay is added to the mix. Preferably kaolin or montmorillonite clay is used.

The mixture is rolled into a ball, placed into a mold and then dried in a constant temperature environment. The temperature is 40-60°C for 2-6 h.

The composite is burnt in a kiln to obtain the biochar-clay composite brick. Pyrolysis is performed at the temperature of 500 to 900°C for 2 to 6 hours.

Three types of mixture were made

Example 1

The timber is pulverized and sieved.

1 unit of wood is sieved with 2.5 units of water;

1 unit of composite is mixed with 6 units of clay;

The drying conditions are 40°C for 6h;

The heating rate of the kiln is 10°C/min with a temperature of 800°C for 6h.

Example 2

1 unit of wood is sieved with 3 units of water;

1 unit of composite is mixed with 7 units of clay;

The drying conditions are 60°C for 6h;

The heating rate of the kiln is 10°C/min with a temperature of 700°C for 6h.

Example 3

1 unit of wood is sieved with 4.5 units of water;

1 unit of composite is mixed with 10 units of clay;

The drying conditions are 60°C for 5h;

The heating rate of the kiln is 10°C/min with a temperature of 800°C for 4h.

Biochar clay bricks loss rate, compressive strength, porosity and water retention were calculated.
#### TESTS

The absorption capability of the bricks was tested by adding 200ml of methylene blue solution, then putting all in a shaker, at a temperature of 25°C at 120 r/min, a fixed time-point sampling of measuring the concentration of contaminants.

It was found that the sample employed 78h to complete the methylene blue solution absorption.

#### RESULTS

The porosity was tested:

- the samples were measured in length;
- the volume(V) was calculated;
- these were dried at a temperature of 105°C for 24h, to obtain the sample dry mass (M1);
- these were cooled into a vertical tank;

• the samples were immersed in distilled water for 24h;

• at the end, these were dried with a wet towel and the mass absorbent of the sample (M2) was immediately weighted;

The formula used to calculate porosity was p = (M2-M1)/V.

	Loss Rate (%)	Compressive Strenght (MPa)	Water Retention (g/cm <sup>2</sup> )	Porosity (-)
Example 1	4,12 >	20 0	,96	0,402
Example 2	3,74 >	20	0,92 0	,365
Example 3	4,05 >	20	0,81 0	,331

Fig.1 Results of the different examples.

Preparation method is simple and quick, the process is made without additional reagent. It does not require sophisticated equipment.

Biochar clay bricks may be prepared according to the need (as a filler or as a water permeable pavement bricks to remove contaminants in storm water runoff)<sup>4</sup>.

The physical properties of the product suggest the use of the bricks to lighten walls and increase the porosity of the partition.

<sup>&</sup>lt;sup>4</sup> Lu Lun C. patent n.CN106955670A, 2017, China.

# PATENT 2 TITLE: MORTAR WITH BIOCHAR

The invention relates to the addition of biochar to a mortar. The steps are: combining binder, aggregate and biochar; adding an aqueous solvent to form a mixture. WO2018/203829 AI China, Singapore 8 November 2018 Shuan M., Wei H., Souradeep G., Jing Yeng C.



Cement (CEM 52.5 N); sand < 2.75 mm; biochar (300 °C and 500°C of pyrolysis); heating rate 10 °C/min, residence time 45 minutes, holding time in oven 30 minutes.

#### PROCESS

Mixing of mortar was carried out in a Hobert mechanical mixer at ambient temperature of 30 °C, mixing time between 10-12 minutes. The mortar was then cast into molds on a vibrating table to achieve sufficient compaction. The cast specimens were covered with polythene sheets for the next 22-24 hours till demolding. After demolding, all the samples were transferred to fog room (100% relative humidity) for curing at temperature of  $27 \pm 2$  °C. The samples were cured for 7 days and 28 days before they were taken out for strength and permeability testing.

Mortar mix	Mix description	Cement (g)	Sand(g)	Water(g)	Biochar (g)	Biochar content (% of the total weight)	Superplasticizer dosage (wt.% of cement)	Flow (mm)
Plain mortar_river san (control 1)	d Plain mortar (W/C=0.40)	10,000	27,500	4000			0.35	145
2% sand replacement_BC300	Mortar with 2wt.% sand replaced by biochar prepared at 300°C	10,000	26,950	4,000	550	1.3	0.6	140
2% sand replacement_BC500	Mortar with 2wt.% sand replaced by biochar prepared at 500°C	10,000	26,950	4,000	550	1.3	0.56	138
4% sand replacement_BC300	Mortar with 4wt.% sand replaced by biochar prepared at 300°C	10,000	26,400	4,000	1,000	2.6	0.72	135
4% sand replacement_BC500	Mortar with 6wt.% sand replaced by biochar prepared at 300°C	10,000	25,850	4,000	1,650	4.0	1.3	118

Fig.2 Proportions of the components in different types of mortar mix.

#### TESTS

Compressive strength: testing was conducted on cylinder samples (100 mm(d)x200mm(h)) following the loading conditions stated in BS EN 12390-3:2009. Strength of biochar mortar at different water-cement ratio (W/C=0.50 to 0.35) was tested according to ASTM C109-16. 50mm cube samples.

WATER PENETRATION: a cylinder specimen is loaded on to a calibrated water penetration apparatus. Before the test, the cylinder specimens have been oven dried at 70 °C for 24 hours. The dried specimens were then coated with epoxy on the outer face to prevent leaking of water from the sides. Water pressure of  $5\pm0.2$  bar was applied for 72 hours. After that, the specimens were split into two halves and the maximum penetration depth (in mm) was recorded.

SORPTIVITY: The test was performed on 28 days-old samples based on ASTM C 1585-1 3.50 mm(h)

X 100mm(d) samples were cut from 200mm(h) x 100mm(d) cylinder samples using a high speed concrete cutter. The samples were prepared and conditioned following the procedures stated in the standard. After the drying stage, the sides of the specimens were sealed with a layer of epoxy to prevent absorption (from the sides). The coating was allowed to dry for 24 hours. The test was carried out at  $25\pm2$  °C and relative humidity of  $60\pm5\%$ .

DRYING SHRINKAGE: Drying shrinkage was conducted as per ASTM C596. Fresh mortar was cast into 25x25x285 mm moulds and sealed until demoulding. After that, the samples were immersed in water for 72 hours. The surface of the wet samples was then wiped, and measurement was recorded. The mortar samples were stored in a constant temperature-humidity room (26°C, 65% RH) during the test. Subsequent length measurements were carried out every 1-3 days.

#### RESULTS

COMPRESSIVE STRENGTH: All the mixes were prepared with water-cement ratio of 0.40. Replacement of 2% river sand by biochar resulted in an increase of compressive strength (of mortar) by 24% and 15% at 7 days and 28 days respectively. Increase in compressive strength is similar when BC500 replaces 2% of river sand. 4% replacement of sand with BC300 shows about 20% increase at 7 days while slight increase of strength at 28 days is observed compared to plain mortar. 6% sand replacement with BC300 does not affect the strength of mortar.

FLEXURAL STRENGTH: 2% or 4% replacement of sand by biochar shows similar flexural strength as plain mortar at all ages of mortar, this means that biochar as sand replacement does not affect flexural strength.

SORPTIVITY: 2% and 4% replacement of sand by biochar significantly reduces sorptivity of mortar compared to plain mortar. Coefficient of initial sorptivity, which is caused by transport of moisture through fine capillary pores and gel pores, is reduced by 44% and 25% by sand replacement of 2% and 4% respectively by biochar compared to plain mortar.

WATER PENETRATION: 2% sand replacement have reduced the penetration depth by 56% and 25% respectively, meaning the biochar's enhanced mortar has significantly higher resistance to penetration of water under pressure. 6% replacement shows similar penetration depth as plain mortar.

DRYING SHRINKAGE: the drying shrinkage of control mortar and mortar with 2% and 6% sand replacement by biochar made at 300°C and 500°C was measured. The maximum shrinkage takes place within the first two weeks. The shrinkage stops once the mortar reaches 40-day age. 2% and 5% sand replacement by weight with BC 300 produce similar shrinkage as plain mortar, while 2% sand replacement with BC 500 show slightly lower shrinkage at 80-day age compared to plain mortar.

MECHANICAL STRENGTH: compressive and flexural strength of mortar samples with 2% replacement is similar to control sample with crushed rock sand. It means that use of biochar to replace part of crushed rock sand does not have significant influence on strength<sup>5</sup>.

<sup>&</sup>lt;sup>5</sup> Shuan M., Wei H., Souradeep G., Jing Yeng C, op.cit., pp. 8-25.





Fig.6 Coefficient of sorptivity of the initial and secondary rate.



Fig.7 Depth penetration test results.

## PATENT 2.1 TITLE: WALL FILLING

The patent consists in the measurement of the  $CO_2$  adsorption of a wall filled with biochar-coated pellets.

WO2018/203829 AI China, Singapore 8 November 2018 Shuan M., Wei H., Souradeep G., Jing Yeng C.



#### MATERIALS

Biochar-coated pellets: mixed wood waste biochar, gasified at a temperature of 550-600°C for 3-4 hours, then grinded in laboratory. Pellets are created with water and plaster in a ratio of 1:3, coated with biochar. Pellets have a diameter of approximately 15 mm.

#### PROCESS

First, the biochar-coated pellets were subjected to a process of desorption, to remove the adsorbed carbon dioxide ( $CO_2$ ) and to assess how much  $CO_2$  the biochar can adsorb: 30 g of biochar were heated in a furnace at 500°C for 2, 3 or 4 hours; after the subsequent cooling, the mass of the biochar was determined. This tells the yield of the heating process. 3 g of desorbed biochar sample was placed inside a tank together with a Telaire  $CO_2$  analyzer (model number 7001). 2000  $\pm$  50 ppm of  $CO_2$  were introduced into the tank from a  $CO_2$  cylinder. Readings of the  $CO_2$  concentration was recorded for 4 hours; the goal was to find the heating duration for a high yield and the duration that produces biochar with the highest  $CO_2$  adsorption rate. It was found that a heating duration of 3 hours is the best. The biochar pellets were therefore heated at 500 °C for 3 hours to desorb  $CO_2$ 

Two configurations of wall panel were tested - one with a cavity 15mm thick and another one 30mm. These coincide with thicknesses of coating layers that are commonly used in the building industry.

#### **TESTS CONDUCTED**

ABSORPTION OF  $CO_2$ : The cavity of the wall panel was filled with desorbed biochar pellets in an air-tight enclosed tank. The wall and a small electric fan were placed inside the tank, and a  $CO_2$  sensor were then placed inside each tank. The tanks were then tightly sealed.  $CO_2$  was introduced into the tank through a tube until the carbon dioxide concentration reached 500 or 1,000 ppm<sup>6</sup>. The  $CO_2$  concentration was recorded at 5 minutes interval for 2 hours. In the setup with 30 mm cavity, the total mass of biochar used for the coating was just about 6 g.

#### RESULTS

ADSORPTION OF  $CO_2$ : both types of pellets eventually reduce the  $CO_2$  concentration (in the tanks) to zero. The biochar pellets are able to achieve the reduction in half the time taken by the control sample (plaster pellets). With 1000 ppm of  $CO_2$  the biochar coating is able to reduce the concentration 8 times faster than the control sample. It was found that within the first 10 minutes, biochar coated pellets can potentially remove 0.021 mmol/g and 0.199 mmol/g of  $CO_2$  at starting concentration of 500 and 1,000 ppm respectively. If more  $CO_2$  was introduced into the tank as soon as the total cumulative adsorbed  $CO_2$  reached a plateau, even more carbon would have been adsorbed by the pellets. A typical indoor partition wall is 6 m wide and 3 m high; this can be made up of 180 units of the experimental tested panel. If three layers

of the experimental panel (with 30 mm cavity) are applied (since a wall can be about 110 mm thick), the entire wall can contain about 3.24 kg of biochar. With a concentration of 1000 ppm, the said wall can potentially adsorb 30 grams of  $CO_2$  within the first 10 minutes<sup>7</sup>.



Fig.8 Cumulated CO<sub>2</sub> absorption/absorption in treatment tank (experiment 1).



Fig.9 Cumulated CO<sub>2</sub> absorption/absorption in treatment tank (experiment 2).

Beside patents, various studies and applications have been conducted. These reveal specific biochar properties in different fields.

<sup>&</sup>lt;sup>6</sup> The reason that 500 and 1,000 ppm starting concentrations were chosen is that 500 ppm is the usual indoor concentration

in NUS, and ,000 ppm is commonly accepted as the upper limit to indoor concentration.

<sup>&</sup>lt;sup>7</sup> Shuan M., Wei H., Souradeep G., Jing Yeng C., op. cit. pp. 25-32.

### **RESEARCH N.1**

# CEMENT-BASED ELECTROMAGNETIC SHIELDING AND ABSORBING BUILDING MATERIALS

#### WHAT

The electromagnetic shielding of carbon-filled cement material.

#### WH0

Guan H., Liu S., Duan y., Cheng J.

#### WHERE

School of Materials Science and Engineering, Dalian University of Technology, China.

#### WHEN

2005

#### WHY

This experiment consists in the application, as a filler, of carbon materials to a cement mixture, to obtain electromagnetic shielding and absorption.

#### HOW

The materials used were Portland and high alumina cement. In a Portland cement matrix composite, colloidal graphite at 0.92 vol% with the thickness of about 4.4 mm was added. The applications were carried out using polyester as the base material and colloidal graphite and PVA binder as the coating; addition of 30 wt.% carbon filaments to commercial colloidal graphite; cement composites filled with coke powder.

#### RESULTS

• Graphite powder into a high alumina cement matrix. Shielding effectiveness increases with the increasing of graphite addition. When the volume is increased to 30.0 vol%, a specimen with about 3 mm thickness can give a shielding effectiveness of 10–40 dB in the frequency range 200–1600 MHz;

• Polyester as the base material, colloidal graphite and PVA binder as the coating: when the coating is 0.3–0.4 mm thick, it can have a shielding effectiveness of 11.2 dB at the frequency of 1.0 GHz;

• Addition of 30 wt.% carbon filaments to commercial colloidal graphite: the shielding effectiveness becomes 19.8 dB at 1.0 GHz;

Cement composites filled with coke powder: with 9.18 vol% coke powder, a sample with a 4.8 mm thickness can give a shielding effectiveness of 49–51 dB at the frequency 1.0–1.5 GHz<sup>8</sup>.

<sup>&</sup>lt;sup>8</sup> Guan H., Liu S., Duan y., Cheng J., Cement based electromagnetic shielding and absorbing building materials, in *Cement and Concrete Composites*, Amsterdam: Elsevier, 2006. https://www.sciencedirect.com/science/article/abs/pii/S0958946505001356. Accessed on 21.10.2019.

# RESEARCH N.2 ANALYSIS OF SHIELDING EFFECTIVENESS OF CEMENT COMPOSITES FILLED WITH PYROLYZED BIOCHAR

#### WHAT

The application of biochar as a filler in cement composites

#### WHO

Savi P, Cirielli D., di Summa D., Ruscica G., Natali Sora I.

#### WHERE

Department of Electronic and Telecommunications Politecnico di Torino, Torino, Italy. Department of Engineering and Applied Sciences, University of Bergamo, Dalmine, Italy.

#### WHEN

2019

#### WHY

Obtain an electromagnetic shielding and permittivity of the composite in the X-band 9.

#### HOW

Commercial biochar in the form of granulate charred at 750 °C for 4h is used. Two different mix formulations were prepared using biochar granulate at 1% (B1) and at 10% (B10) by weight of cement keeping constant the ratios of superplasticizer at 1.5% (necessary for an acceptable workability), variating water ratio from 35% (B1) up to 55% (B10). The biochar was mixed together with ordinary Portland Cement (PC) matrix (grade 52.5 R). Moreover, a reference specimen (B0) was realized mixing only cement together with a water and superplasticizer ratios equal to 35% and 1,5% by weight of cement respectively.

The samples preparation consisted of three steps:

• The biochar granulate was mixed with Portland cement and the superplasticizer using a mechanical mixer for 4 minutes, obtaining a homogeneous mixture;

• The obtained composite was poured into rectangular silicone moulds for shielding effectiveness (SE) analysis and into cylindrical moulds for permittivity analysis.

• The specimens were kept at 90  $\pm$  5% relative humidity for the initial 24 hours. The samples were then demoulded and immersed in water; the curing period occurred at room temperature (20  $\pm$  2 °C) for 28 days.

The complex permittivity of cement composites filled with pyrolyzed biochar was measured in the frequency range 1-12 GHz, the shielding effectiveness of the samples was investigated in the X-band (8-12 GHz) measuring the scattering parameters in a rectangular waveguide (22.86 x 10.16 mm).

The complex permittivity was measured on several samples B0, B1 and B10.  $\varepsilon$ 'r represents the stored energy and provides information about the dissipated energy.

The same mix formulation was used to make samples with rectangular shape (thickness 4 mm) to be inserted in the WR90 waveguide holder. The scattering parameters of the empty waveguide and of the one with the samples were measured and the SE evaluated.

#### RESULTS

As shown in Fig.10-11-12, for all composites the  $\varepsilon$ 'r is compared to B1 with respect to the reference plain mortar (B0). At a frequency of 8 GHz, composite B10 shows  $\varepsilon$ 'r value of 17, whereas B1 and the reference composite (B0) displayed 7 and 4, respectively.

As it was expected from the permittivity measurements, composite B10 shows the highest value of SE around 15 dB, whereas the plain cement (B0) and the composite B1 have a comparable value. For general use, the SE is considered good if it ranges from 10 to 20 dB<sup>10</sup>.



Fig.10 Final  $\mathbf{\mathcal{E}}$ 'r for the different samples.

Fig.11 Final SE for the different samples.



GradeExcellentVery<br/>goodGoodModerate<br/>(fair)SE (dB)> 3030-2020-1010-7

Classification of shielding effectiveness for general use.

Fig.12 Detail: final  $\mathcal{E}$ 'r for the different samples.

 $<sup>^{\</sup>rm g}$  In electromagnetism, absolute permittivity, often simply called permittivity, usually denoted by  $\epsilon$ , is the measure of capacitance that is encountered when forming an electric field in a particular medium. More specifically, permittivity describes the amount of charge needed to generate one unit of electric flux in a given medium. A charge will yield more electric flux in a medium with low permittivity than in a medium with high permittivity. It is, basically, a material's ability to store an electric field in the polarization of the medium. (Wikipedia)

<sup>&</sup>lt;sup>10</sup> Savi P., Cirielli D., *Analysis of shielding effectiveness of cement composites filled with pyrolyzed biochar*, Dept. of Electronic and Telecommunications, Politecnico di Torino, Torino, Italy, in collaboration with di Summa D., Ruscica G., Natali Sora I., Dept. of Engineering and Applied Sciences University of Bergamo, Dalmine, Italy. Torino, Bergamo: Research Gate, 2019.

# RESEARCH N.3 BIOCHAR-POLYMER COMPOSITES AND THIN FILMS

#### WHAT

Biochar and activated biochar were used as filler (20 wt%) to produce epoxy resin-based composites. The activated biochar (12.5 wt%) was also used to produce screen printed thin films.

#### WHO

Quaranta S., Savi P.

#### WHERE

Bologna, Italy.

#### WHEN

2016

#### WHY

Analysis of the electrical characteristics of both epoxy resin-based composites with biochar as a filler and screen-printed films.

#### HOW

The used biochar derived from Acer saccharum, charred at 500 °C, activated by KOH<sup>11</sup>. The dielectric properties of the charcoals were tested in the frequency range 1-10 GHz.

The epoxy resin composite contains 20 wt% of carbon powder; the composite, in liquid form, was poured into a cubic mould (approximately 2.5x2.5x1.5 cm) and left resting until completely hardened.

Screen printing was used to deposit the activated biochar as a thin film (thickness  $\sim 10-20 \mu$ m) on FR4 substrate. Ethyl cellulose, which acts as a binder, thickener and dispersion steric stabilizer, terpineol (Sigma Aldrich), which is the solvent, and biochar, were dispersed in 80 mL of ethanol by stirring (2 hours) and sonication (15 hours by using a Ti horn). Ethanol was evaporated under reduced pressure in order to produce a printable paste. Ink's final formulation is comprised of biochar (12.5 wt%), ethyl cellulose (9.4 wt%) and terpineol (78.1%). Several prints having different thicknesses were obtained by printing multiple layers intercalating a drying at 125°C for 5 minutes after the deposition of each printed layer. The final curing was performed in a muffle at 160°C for 150 minutes in air.

#### RESULTS

As a filler in epoxy resin at 20 wt.% (biochar and activated biochar): complex permittivity measurements up to 10 GHz are compared with pure epoxy resin. The values obtained using activated biochar as filler in epoxy resin are approximately twice those obtained with non-activated biochar. The increased real part of permittivity can be reasonably related to the introduction of polarizable functional groups by the alkaline activation treatment.

To prepare screen printed films (activated biochar): the films were electrically characterized.

Sheet resistance in the order of  $k\Omega$  and low frequency inductive behavior caused by charge carriers' different mobility were revealed. Although the inductive behavior it supposed to be concentration independent and the sheet resistance is supposed to decrease with the biochar loading, additional investigation is being currently done on 1,25 and 33 wt% biochar films to verify these assumptions <sup>12</sup>.



Fig.13 Real permittivity of the different materials.



Fig.14 Loss tangent of the different materials.

<sup>12</sup> Quaranta S., Savi P., Biochar-Polymer composites and thin films: characterizations and applications, *2nd International Forum on Research and Technologies for Society and Industry Leveraging a better tomorrow* (RTSI), USA: IEEE, 2016.

<sup>&</sup>lt;sup>11</sup> KOH: Potassium hydroxide. A caustic white deliquescent solid, used as a bleach and in the manufacture of soaps, dyes, alkaline batteries, and many potassium compounds. (The free Dictionary)

# RESEARCH N.4 FLOW-INDUCED CRYSTALLIZATION OF BIOCHAR IN BIO-ASPHALTW

#### WHAT

Addition of different contents of biochar in bio-asphalt and analysis of the flow-induced crystallization.

#### WH0

Zhou X., Adhikari S.

#### WHERE

Wuhan University of Technology, Wuhan, China. University of Waterloo, Ontario, Canada.

#### WHEN

2016

#### WHY

Flow-induced crystallization (FIC) in polymers is an important problem that occurs on a very rapid time scale. This study aims to evaluate the difference of crystallization with the addition of biochar.

#### HOW

The raw material size of waste wood is smaller than 75  $\mu$ m. Bio-oil and biochar were derived from pyrolyzed waste wood at 500 °C with N2. The pyrolysis speed is 2.0 g/s. The base asphalt used in this study was a performance graded asphalt PG58–28. The bio-asphalt was prepared by adding 10% bio-oil to base asphalt. Then, biochar was added into the liquid and BMBA (biochar modified bio-asphalt) was obtained. Biochar dosages of 0%, 2%, 4%, 6%, and 8% were added and the different mixtures were marked by S1, S2, S3, S4 and S5, respectively. BMBA aging was carried out through RTFO (short-term aging), ultraviolet (UV) aging and pressure aging vessel (PAV, long-term aging) procedures. The long-term sample is assumed to simulate 10 years of aging and it is marked by S7. UV aging is in accordance with the UV radiation conditions of Taiyuan city using UV aging tester under 65 W/m2 at 60 °C for 7 days and it is marked by S6. (Fig. 15)

The tests are: X-ray scattering, molecular dynamic simulation, Fourier infrared spectroscopy and microscope experiments.

#### RESULTS

Biochar can improve the flow-induced crystallization ability of bio-asphalt. Moreover, biochar can affect the crystal structure of bio-asphalt. Biochar can improve the high-temperature stability and enhance the FIC. Aging could highly affect the crystallization morphology of BMBA. Moreover, UV effect on aging are more severe than those of PAV. BMBA exhibited the flow-induced crystallization, and the morphology of the crystallization changed with increased shear stress.

Shear stress can improve the complex structure of bio-asphalt, and the crystallinity of the polymer decreased with increases in the shear stress<sup>13</sup>.



Fig.15 Mass ratio of the different specimens.

<sup>13</sup>Zhou X., Adhikari S., Flow-induced crystallization of biochar in bio-asphalt under various aging conditions, in *Science of the Total Environment*, Amsterdam: Elsevier, 2019.

#### **RESEARCH N.5**

# MECHANICAL AND MICROSTRUCTURE PROPERTIES OF BIOCHAR-BASED MORTAR: AN INTERNAL CURING AGENT FOR PCC

#### WHAT

Investigation on the viability of using biochar as a sustainable alternative material to sand in cementitious mortar composites.

#### WHO

Mrad R., Chehab G.

#### WHERE

Department of Civil and Environmental Engineering, American University of Beirut, Lebanon.

#### WHEN

2019

#### WHY

The analysis is carried out to provide guidelines to the effective incorporation of biochar in cementitious mortar and increase the use of charcoal in the building sector.

#### HOW

Type I Portland cement obtained from LafargeHolcim plant in Chekka, Lebanon, was used throughout this study. Natural sand was obtained from a local quarry in Beqaa, Lebanon, and used for the production of all mortar mixes.

The biochar was produced from the slow pyrolysis of municipal solid waste (MSW), treated at temperatures ranging from 300 to 400 °C, in Lebanon.

The biochar was obtained in two size categories: coarse aggregates and powder (filler).

(Fig.16 presents the water absorption capacity of biochar, which is approximately 60% after 48 h of soaking.) .

Biochar particles were measured at relative humidity (RH) conditions ranging from 95 to 0%. Biochar samples were oven-dried for 24 h, saturated in distilled water for 48 h, and left to reach their saturated surface dry conditions (SSD) prior to testing.

The samples were then placed in controlled climatic chambers of different RH for 72 h until stable mass was reached, and mass measurements were recorded.

Fig.17-18 show the water desorption behavior of biochar measured in the lab and from literature review, respectively.

Six different mortar mixtures were prepared with an effective w/c ratio of 0.43 and a binder to fine aggregate mix ratio of 1:3. This included a plain mortar mixture designated as 0.0% and five other mixtures with varying amounts of water-saturated biochar aggregates as a replacement of sand.

The biochar was oven-dried, air cooled, and then submerged in water for 48 h prior to mixing. The sand was oven-dried and cooled for 24 h before mixing. After mixing, the mortar was cast

in 50 mm metal moulds and placed in a closed room to set and harden at 76  $\pm$  2% relative humidity and 23  $\pm$  20 °C for 24 h (prevalent room temperature).

#### RESULTS

Compressive strength decreased with increasing replacement percentage of sand, with biochar under both curing conditions. The reason behind the higher drop in compressive strength for specimens cured in water can be attributed to the porous nature of biochar and its high-water absorption capacity. Since biochar contents beyond that were detrimental to the compressive strength of mortars, only mixes M1 (5%), M2 (10%), and M3 (15%) were considered for the remainder of the experimental program. The inclusion of partially saturated biochar in cementitious mortar composites generally decreases the compressive strength for various curing conditions. It is suggested that the biochar replacement of sand be limited to 15% and be fully saturated prior to inclusion in mortar for better results.



Fig.16 Time-depentent water absortion profile of biochar.



Fig.17 Water desorption profile of biochar at different relative humidity levels (RH%), starting from saturated surface dry.



Fig.18 Water release (g/g of saturated char) from biochar particles, produced at 300° and 500° at different relative humidity.



Fig.19 Compressive strength of mortars.



Fig.20 Compressive strength of mortar cubes for all mixes at 7, 14 and 28 days under air curing conditions.

# RESEARCH N.6 BIOCHAR PAPER: ELEVATING BIOCHAR FROM NOVELTY TO UBIQUITY

#### WHAT

Producing a cardboard with biochar and paper pulp (chardboard), to pack fruits and vegetables, double their shelf life and then compost it in the backyard.

#### WH0

Hans Peter Schmidt in collaboration with the Genesee Center for the Arts based in Rochester, NY.

#### WHERE

Ithaka Institute, Switzerland.

#### WHEN

2018

#### WHY

To produce a sustainable packaging material, with biochar and paper pulp. This project could potentially transform biochar from being a novelty material to one that is ubiquitous in the consumer environment, preventing massive amounts of carbon from returning to the atmosphere, by casting off the chardboard to the soil after use.

#### HOW

A variety of different feedstocks can be used to produce biochar for paper fabrication. The initial test used biochar derived from coffee chaff. This chaff char has the benefit of being relatively uniform in size, as well as being consistent in both availability and composition. Other feedstocks could be used but would require uniformity in size which is an important

criterion for fillers used in paper making.

Filler content in paper varies depending on the type of paper but can reach more than 30. Paper pulp was the only other material used in the prototypes.

#### RESULTS

Biochar used as a filler has the potential to provide a variety of different properties.

• it is compatible with beneficial bacteria: municipalities are struggling to divert more food wastes from landfills, but they are challenged by the odor problem of decaying food waste. Food waste can be disposed of in chardboard containers, with efficient degraders, which would reduce odor and prevent nutrient loss.

• Low thermal conductivity: an interesting property of chardboard is its low thermal conductivity. This is an ideal characteristic for hot or cold food packaging.

• Extend shelf life: certain fruits and flowers are highly susceptible to premature ripening due to ethylene, a natural plant hormone that promotes cell degradation. As biochar can sorb ethylene, added to packaging for fruits can help increase their longevity.

• Anti-static agent - Electrostatic discharge (ESD) can damage electronics components during

shipment. Biochar produced at higher temperatures is conductive so, chardboard can dissipate static as well as protect electronics from mechanical damage, eliminating the need for multiple packaging elements.

•Moisture absorption: the porous nature of biochar increases the absorption of moisture and vapors which can help to keep products fresher, longer and in other applications can provide resistance to fungi or mold formation.

# RESEARCH N.7 BIOCHAR-CLAY PLASTER FOR INDOOR AND OUTDOOR SPACES

#### WHAT

Biochar-clay composite plaster for indoor and outdoor spaces.

#### WHO

Hans Peter Schmidt

#### WHERE

Ithaka Institute, Switzerland.

#### WHEN

2018

#### WHY

The biochar used in building's envelope is not going to re-enter in the atmosphere, because of the stable structure of the charcoal. Furthermore, the use of biochar and clay can give a natural anthracite color to the plaster, without adding colorants or synthetic paintings.

#### HOW

Biochar is added to a clay-sand mixture at a ratio of 30-50%. The biochar-mud mixture contains 50% biochar, 30% sand and 20% clay.

This mixture can be used both for spray plastering and for conventional throw-on techniques. For the bottom and intermediate plaster layers it is recommended to also use larger-dimensioned pieces of biochar (diameter < 25mm), as this makes the plaster less likely to crack. A further layer can be applied within 12-24 hours.

Finest ground char can be used for the top layer.

#### RESULTS

The result is an anthracite-colored plaster. If lighter color is desired, the proportion of finely ground biochar can be reduced to 20-25% for the top layer, and mud-based paint applied as the final coating. Such plaster is easy to apply and is not irritating to the skin of those applying it, meaning that gloves and protective clothing are not needed.

#### **RESEARCH N.8**

# BIOCHAR AS BUILDING MATERIAL FOR OPTIMAL INDOOR CLIMATE -WINE CELLAR

#### WHAT

A new form of plaster made of biochar and clay to achieve an optimal cellar climate for the production of natural wines, because a decisive factor for a good wine is not just temperature, but also humidity.

#### WHO

Hans Peter Schmidt

#### WHERE

Hans Peter Schmidt and the Delinat Institute.

#### WHEN

2018

#### WHY

Biochar-clay plaster means that wine cellar walls would be able to "breathe", adsorb moisture and maintain a stable humidity level 40-70%. The result might be pleasing from a hygiene perspective, but it is important even for the microbial flora.

#### HOW

Biochar is added to a clay-sand mixture at a ratio of 30-50%. The biochar-mud mixture contains 50% biochar, 30% sand and 20% clay. The walls of an old Valais wine cellar were sprayed obtaining a 10 cm thick layer of the new biochar-clay plaster, biochar can be mixed in conventional lime or cement based plasters in equal proportions. Doing so, the biochar can help increase their insulation and water storage capacities.

#### RESULTS

This massive wall coating provides not only good thermal insulation and consequently fewer temperature fluctuations, but is also a great humidity regulator.

In combination with the right ventilation, the machine-sprayed plaster made of clay and biochar is able to keep cellar humidity levels constant throughout the year, preventing and reducing the development of mold and other microbes.

# **1** State of the Art **2** Anteriority

# 

In this chapter the materials used for this research are illustrated: the item CanapaMix2 given by the company, is an insulating plaster used as a matrix; the biochar, given by the company Laterizi Reato srl, is used as an addition to the mixture.

# **3.1 CANAPAMIX2**

Research on natural materials can improve the quality of life and support the preservation of the environment. The insulating plaster used for the study is given by the company EdilCanapa.

EdilCanapa born in Abruzzo, this company employs only natural materials to form an ecological composite: hemp combined with lime.

All their products are 100% natural and recyclable and also the additives have vegetal origin. Hemp is exploited for its wooden part, called shive. It has a molecular structure that makes the material breathable and fire resistant, thanks to the silica inside the pores.

The shive represents the inert body of the conglomerate to which the lime is added as a binder. The combination of lime and hemp gives birth to numerous products, such as external/internal coat, bricks and paintings.

The products are: conglomerates for cladding (CANAPAMIX1), bricks for external and internal infills (CANAPLOCK), bedding mortar (CANAPAMALTA), insulating panels in hemp fiber and hemp shive (CANAPANNELheat-insulating SALUBERPAN), and finishing plaster (CANAPAMIX2), fixative for paints (CANAPAPRIMER), anti-mold and self-cleaning paints (CANAPITTUR), and conglomerates for screeds (CANAPAMAS) 1. Edilcanapa products are lightweight and easy to assemble, reducing installation times, costs and developing a healthy building site with less waste of material than common construction sites.

The aim of this thesis is to evaluate the performance improvements brought from the addition of biochar in a natural matrix material, creating a natural composite material.

Canapamix2 is a premixed plaster, based on NHL5 natural hydraulic lime, crushed hemp and natural additives are mixed with clean water; it can be applied manually or with a machine.

It is used as a thermal breathable plaster for interior and exterior surfaces.

Canapamix2 is sold in 25 kg sacks and has a hazelnut color. Supports must be resistant and clean, on old walls it is essential to perform a pressure or water sandblasting wash until all traces of dirt and ruined parts are eliminated.

Preparation of the mixture:

- Mixing water as a plaster mortar: 80/90%
- Mixing water as a rendering mortar: 95/105%
- Mixing time with a whisk: 3 min
- Mixing time in cement mixer: 4/5 min
- Working time: 45 min
- Waiting time for application of the next layer: 24 hours
- Maximum layer thickness: 15 mm
- Maximum total thickness: 150 mm

Recommended waiting time to apply CANAPASTUCK: 72 hours

Waiting time for paint on shaving: 30 days. Mix preferably in a cement mixer with about 20/22.5 liters of clean water for each 25 kg bag of product for a duration of 4/5 minutes until a homogeneous, lump-free mixture is obtained. Let the mixture rest for a few minutes and mix



<sup>&</sup>lt;sup>1</sup> All EdilCanapa products are described in detail at https:// www.edilcanapasrl.it.

Characteristic	Value/ Description	Measurement unit
Appearance	powder - hazelnut color	-
Grain size	0,6	mm
Workability at 25 °C	45	min
Application temperature	+5 / +30	°C
Theoretical yield	3.0 / 3.5	kg / m <sup>2</sup> x cm thickness
Compressive strenght	1,0 (Category CS I - UNI EN 1015-11)	N / mm <sup>2</sup>
Reaction to fire	Non-flammable combustible material	-
Water absorption	1.18 (Category W0 - UNI EN 1015-18)	kg / m²min <sup>0,5</sup>
Water absorption diffusion resistance(µ)	≤ 15	-
Adhesion	≥ 0,52	N / mm <sup>2</sup>
Thermal conductivity	0.0888 (Category T1 - UNI EN 1745)	W / mK
Specific heat	1500	J / kgK
Density	497	kg / m³

Fig.1 CanapaMix2 data sheet.

# **3.2 BIOTON BIOCHAR**

The biochar used for the applications is offered by the company Laterizi Reato s.r.l.. The biomass used for the pyrolysis is virgin wood, more precisely  $\sim$ 70% poplar,  $\sim$ 30% turkey oak, with residues of willow, plane tree and fruit tree wood. The wood is slashed in chips (< 30mm), then the biomass is poured in the pyro gasifier: a PG350 model that can carbonize 350 kg/h of biomass, with an energy consumption of 250-300 kW/h. It is a downdraft, it means that creates a downward current of air, and an open core: its design is characterized by an opening on the top. For this reason, there is a regular pressure level in the machine, while the temperature and the humidity level are influenced by the seasons and the indoor space control.

The pyrolysis is carried out at a temperature of  $\sim$  550° and the residence time range between 3-6 hours, depending on the requirements of the final product, the outdoor humidity and temperature, and the humidity content of the biomass. The particles size is <20mm and C in the charcoal reaches the 86%.

# **3.3 PARTICLES EXAMINATION**

The analysis of the material's particles with an electronic microscopy was enlightening to understand the structure and the size of the different mixture components. Before the examination, the samples have been heated to eliminate the embodied humidity.

Biochar size range between 5 and 500  $\mu$ m, its surface is smooth, the pieces are stretched and is recognizable a structure with holes: these pass through the whole fragment following the length direction. The gaps have a diameter of ~20  $\mu$ m and characterize the porosity of the material.

smallest fragments are The shattered don't show the porous and structure. however is visible the elongated shape and the flat surface of biochar. Lime-hemp mixture shows the lumpy aspect of the lime and the small filaments of hemp, that works as fiber in the composite. The size of the hemp strands range between 3 and 700  $\mu$ m in length and the diameter can reach 100  $\mu$ m. The surface of lime is rough, while the surface of hemp is fibrous.





Fig.3 Electron microscopy image of the biochar: x1000.

⊢ 20 µm —



Fig.4 Electron microscopy image of the lime-hemp insulating plaster: x5000.

# **1** STATE OF THE ART **2** ANTERIORITY

# **J**EDILCANAPA

**A** EXPERIMENTAL ACTIVITY

In this chapter are illustrated the experimental tests and the relative results: both mechanical and physicochemical characteristics of the composite are analyzed and compared with the matrix product Canapamix2. The results are converted in tables and graphs, facilitating the interpretation of the outcomes.

# 4.1 TARGETS

The aim is to verify possible performance improvements of a lime and hemp insulating plaster, with the addition of biochar. As mentioned before, the mixture is a product of the company EdilCanapa, called Canapamix2: the proportion between lime-hemp mixture and water is s/w 0.9.

The biochar used comes from the company Laterizi Reato S.r.l, made out of charred virgin wooden biomass at a temperature of  $\sim$ 550 °C.

Biochar percentages of 5, 10 and 20% of the mixture total weight are added, according to the anteriority researches.

Various tests have been conducted. The previous physical studies of biochar led us to draw our attention on the humidity control and the electromagnetic adsorption of the product.

The tests include:

**COMPRESSION, BENDING, ADHESION:** these tests are conducted to monitor the physical modifications of the mixture after the addition of biochar, in particular to verify the possible occurrence of negative physical impacts in the final product.

The specimens are compared to the certified product without biochar, to check physical modifications.

**STEAM VAPOR PERMEABILITY AND WATER ABSORPTION:** these applications regard the humidity control. The goal is to verify the capability of biochar to absorb and gradually release the particles of vapor and water; this brings to a lower probability of indoor condensation, implying a preservation of the partitions, healthier internal spaces and the possible use of this product in high humidity level spaces, such as kitchens, toilets and wine cellars;

**ELECTROMAGNETISM ABSORPTION:** outdoor and indoor electromagnetic waves can fill up the charcoal micropores in the partition, this leads to a healthier interior space.

The goal is to obtain a product that guarantees a high humidity control and an electromagnetic absorption, that can be used to build healthier and safer indoor spaces.





# **4.3 APPLICATIONS**

#### **4.3.1 SAMPLES PREPARATION**

#### MATERIALS

BIOTON BIOCHAR, (Laterizi Reato s.r.l) in different percentages of 5–10 and 20%;

CANAPAMIX2, (EdilCanapa) lime and hemp insulating plaster;

WATER, proportion sample/water 0.9.

#### MIXTURE PREPARATION

The mix is made following EdilCanapa instructions: clean water is combined to the Canapamix2 (for every unit of Canapamix2, 1.1 unit of water is added). The mixture is blended mechanically for 4-5 minutes and then left to rest for a while before the application. Biochar is added in the three different percentages of 5%, 10%, 20%.

The preparation of the samples was conducted at the LASTIN Laboratory on the 11th and 12th of November 2019. First of all, the UNI standards were studied as a guideline to follow, in some of the cases. Indeed, for the mechanical and water absorption test a triple pig iron mould was used in reference to UNI EN 196-1:2016 and UNI EN 1015-18:2004. For the steam permeability test, the samples were built in accordance to UNI EN 1015-19:2008, a circular mould from a plastic tube ( $\emptyset$  16cm) with a wooden, square base.

A 30x30 cm wood mould was built for the electromagnetic adsorption test; for the adhesion test four samples of plaster are placed on a brick wall.

Initially, biochar was crushed using a millstone and dried at  $20\pm2$  °C. The next step was the charcoal activation: 500g of biochar at time where put in an oven at 120°C for 30 minutes.

Charcoal activation permits to remove ash, oxygen, water and other components. Moreover, activation led to an increase of the porosity. "Activation" means that the carbon surface has a large number of pores that can absorb gases and nutrients (the activated carbon can have 1500 to 3000 m<sup>2</sup>/g of surface area).

It was observed that the weight of biochar decreases after the treatment  $(20 \pm 4\%)$ , while the volume remained almost the same (from 1.3 m<sup>3</sup> to 1.27m<sup>3</sup> after the pre-treatment).

After the activation the biochar is sifted for 10 minutes, in a sieve with granulometries that range in between 3,15 mm and 0,075 mm. (Fig.1)

The granulometry of the used biochar is <0,5 mm, that represented  $\sim30\%$  of the weight. This allows to use the biochar as a powder in lime-hemp mixture.



Fig.1 The different granulometry of the sifted biochar.

# Monday 11<sup>th</sup>

Number of tray	Biochar weight <b>(g)</b>	Biochar weight after pre-treatment (g)	Weight loss percentage (%)
1_One tray	500	386	22,8
2_One tray	500	395	21
3_One tray	500	420	16
4_Two trays	300+200	376	24,8
Tuesday 12 <sup>th</sup>			
Number of tray	Biochar weight (g)	Biochar weight after pre-treatment (g)	Weight loss percentage (%)
5_Two trays	300+200	390	22
6_Two trays	300+200	380	24
7_Two trays	300+200	372	25,6
8_One tray	200	172	14

Fig.2 Data sheet of biochar pre-treatment.



Fig.4 Mixture process:1) Canapamix2; 2) Canapamix2 with biochar; 3) Mixture adding water.



# DETERMINATION OF MECHANICAL STRENGTH: COMPRESSION AND BENDING

#### TEST EXECUTION DATE: 12/12/2019

PLACE of EXECUTION: MastrLAB, DISEG, Politecnico di Torino.

REFERENCE STANDARD: UNI EN 196-1:2016, UNI EN 1015-11:2007.

#### EQUIPMENT

Centesimal gauge/caliber Digital scale Zwick/Roell zmart.pro static testing machine for tensile, compression, bending, shearing and torsion tests. (Fig.5)

#### SAMPLES PREPARATION

Triple pig iron mould was used in reference to UNI EN 196-1:2016. The three moulds are 40x40x160 mm each and a thin layer of vaseline was applied to prevent the sticking of the mixture.

#### MATURATION

The samples harden in a room at  $20\pm5$  °C and RH  $50\pm10\%$ , for 28 days.

#### PROCESS

All the samples were weighted and measured before the test.

Both of the tests were made twice: two groups of four samples ( $\sim\!40x40x160$  mm each ), with 0-5-10-20% of biochar.

The Bending test was done, obtaining two pieces from one sample. Then, with the two parts, the Compression test was executed.(Fig.6-7)



Fig.5 Zwick/Roell zmart.pro static testing machine.



Fig.6 Bending test.



Fig.7	Compression	test
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# DETERMINATION OF MECHANICAL STRENGTH: COMPRESSION AND BENDING

#### RESULTS

Sample	Code	Biochar %	Sample measures (mm)	Sample weight (g)	N <sub>max</sub>	N <sub>av</sub>
The Martin 30	1_AB	0%	160x40x38,4	158	133,42	110.26
	1_CD	0%	160x40x38,8	158	87,11	110,20
	2_AB	5%	160x40x39,1	156	111,36	107 07
	2_CD	5%	160x40x38,9	155	102,79	107,07
	3_AB	10%	160x40x39	147,2	80,96	0470
	3_CD	10%	160x40x39,9	149	108,5	94,73
	4_AB	20%	160x40x40	160,9	109,92	110 7
	4_CD	20%	160x40x40,7	160,6	129,47	119,7






# DETERMINATION OF MECHANICAL STRENGTH: COMPRESSION AND BENDING

#### RESULTS

Sample	Code	Biochar %	Sample measures (mm)	Sample weight (g)	$N_{\max}$	N/mm²	Compression resistance ( N/mm²)
	1A 1B	0%	160x40x38,4	158	1095,15 1067,01	0,71 0,69	0.64
	1C 1D	0%	160x40x38,8	158	978,81 846,22	0,63 0,54	0,04
	2A 2B	5%	160x40x39,1	156	1070,72 1055,46	0,68 0,67	0.70
	2C 2D	5%	160x40x38,9	155	1486,63 1373,76	0,95 0,88	0,79
	3A 3B	10%	160x40x39	147,2	1418,97 1441,84	0,91 0,92	0.04
	3C 3D	10%	160x40x39,9	149	1508,78 1429,92	0,94 0,89	0,91
	4A 4B	20%	160x40x40	160,9	1416,49 1542,18	0,88 0,96	0.05
	4C 4D	20%	160x40x40,7	160,6	1658,52 1548,75	1,02 0,95	0,95





Fig.9 Compression test results\_Graphs and tables.

# DETERMINATION OF MECHANICAL STRENGTH: ADHESION

#### TEST EXECUTION DATE: 04/02/2020

**PLACE of EXECUTION:** LASTIN, Laboratory for Innovative Technologic Systems, Politecnico di Torino

REFERENCE STANDARD: UNI EN 1015-12:2016

#### EQUIPMENT

Pawls diameter 50 mm 4 clay bricks Digital pull-off tester

#### **SAMPLES PREPARATION**

Two circular shapes of 50 mm were carved in each brick to confine the test area. The original lime and hemp plaster and the plaster with 5-10-20% of biochar were placed in the test area.

#### MATURATION

The samples dried in controlled conditions:  $22\pm5$  °C, RH 50 $\pm10\%$  for 28 days.

#### PROCESS

For each sample two pawls of 50 mm are sealed. After the glue hardening the test was carried out following the UNI EN 1015-12:2016.



Fig.10 Digital pull-off tester.





Fig.11 Adhesion samples.

# DETERMINATION OF MECHANICAL STRENGTH: ADHESION

Sample	Code	Biochar %	Pawls diameter (mm)	Surface (mm <sup>2</sup> )	Break type	Resistance (N)	Resistance (Mpa)	Resistance average (Mpa)	
0:01	P1 P2	0%	50	1962,5	A	6	0.00306	0.00255	
	P 3	E0/	FO	1062 5	A	4	0.00204	0.00055	
0.0	P 4	J %	50	1902,0	В	6	0.00306	0.00255	
0.0	P 5	10%	50	1962 5	А	4	0.00204	0 00220	
1. 1. 1.	P 6	1070	00	1302,0	А	5	0.00255	0.00223	
	P 7	20%	50	1062 5	А	6	0.00306	0 00255	
P 8		ZU /0	50	1902,5	А	4	0.00204	0.00255	

An additional test consisted in applying the plasters on a clay brick wall, to similuate its real use and observe its mechanical behavior.



Fig.12 The different plaster applied on the clay-brick wall.

# **DETERMINATION OF WATER ABSORPTION COEFFICIENT**

#### TEST EXECUTION DATE: 20/12/2019

**PLACE of EXECUTION:** LASTIN, Laboratory for Innovative Technologic Systems, Politecnico di Torino.

#### REFERENCE STANDARD: UNI EN 1015-18:2004

#### EQUIPMENT

Centesimal gauge/caliber Digital scale Distilled water Sealing

#### SAMPLES PREPARATION

Triple pig iron mould was used in reference to UNI EN 1015-18:2004. The three moulds are 40x40x160 mm each and a thin layer of vaseline was applied to prevent the sticking of the mixture.

#### MATURATION

The samples harden in controlled conditions:

 $22\pm5$  °C, RH 95% for 2 days (the mould was put in a basin partially filled with water and sealed.

 $22\pm5$  °C, RH 50 $\pm10\%$  for 26 days.

#### PROCESS

Two groups of four samples with 0-5-10-20% of biochar were realized. Each sample was divided in two parts (final dimension of one sample:40x40x80 mm). (Fig.11)

All the pieces surface were sealed except the bottom one, dipped for 5-10 mm under the free surface of the distilled water.

The absorption level was recorded weighing the mass of the specimen after 10 and 90 minutes from the start of the test. (Fig.12)

 $C = 0,1(M_2-M_1) \text{ Kg/(m^2 min^{0.5})}$ 

C = water absorption coefficient

 $M_1$  = sample mass after 10 min (g)

 $M_2$  = sample mass after 90 min (g)



Fig.13 Divided samples of 40x40x80 mm.



Fig.14 Samples during the water absorption test.

# **DETERMINATION OF WATER ABSORPTION COEFFICIENT**



Sample	Biochar %	Sample weight (g)	Weight 10 min (g)	Weight 90 min (g)	С	C average
1A ——	0%	72,88	87,50	108,71	2,12	01/
1B <b></b>	0%	80,26	94,00	115,61	2,16	2,14
2A ——	5%	75,89	91,50	117,02	2,55	2.51
2B	5%	75,18	91,42	116,12	2,47	– 2,31
3A	10%	72,05	88,60	117,48	2,89	0.00
3B	10%	71,60	87,70	116,15	2,84	2,80
4A ——	20%	79,40	98,80	134,02	3,55	2.95
4B • • • • •	20%	71,86	79,54	121,14	4,16	- 3,00



Fig.15 Water absorption test results\_Graphics and Tables.

# **DETERMINATION OF WATER VAPOR PERMEABILITY**

#### TEST EXECUTION DATE: 09/01/2020

**PLACE of EXECUTION:** LASTIN, Laboratory for Innovative Technologic Systems, Politecnico di Torino

REFERENCE STANDARD: UNI EN 1015-19:2014

#### EQUIPMENT

Centesimal caliber Digital scale Distilled water Sealing  $KNO_3$  Saturated solution of Potassium Nitrate, provides a RH ~93,2%. LiCl Saturated solution of Lithium Chloride, provides a RH ~12,4%.

#### SAMPLES PREPARATION

A circular test vessel (A =  $0.02 \text{ m}^2$ ) was used in reference to UNI EN 1015-19:2014, in which the sample is sealed. (Fig.12) The three moulds are  $40\times40\times160 \text{ mm}^3$  each and a thin layer of vacaline was applied to prevent

The three moulds are 40x40x160 mm<sup>3</sup> each and a thin layer of vaseline was applied to prevent the sticking of the mixture.

#### MATURATION

The 5 samples were dried in controlled conditions:

22 $\pm$ 5 °C, RH 95% for 5 days (each mould was put in a plastic bag and sealed). 22 $\pm$ 5 °C, RH 50 $\pm$ 10% for 23 days.

#### PROCESS

4 samples of 0-5-10-20% of biochar for the high humidity condition and other 4 for the low humidity condition are sealed in the circular vessels.

Each sample was weighted before and after the sealing, to monitor the added weight.

Then an interval of time was fixed for the measures, approximately 20 minutes.

The test was completed when, comparing two measurements in a row, there was no more weight gain (after 255 min).

First, vapour flux was calculated applying the formula  $\Delta G/\Delta t$  (kg/s).

Then, water vapour permeance  $\Lambda$  (kg/m<sup>2</sup>\*s\*Pa) was calculated throw the formula:

$$\Lambda = \frac{1}{((A^* \Delta p)/(\Delta G/\Delta t)) - R_A}$$

where:

 $A(m^2)$  = area of the circular vessel, 0,02.

 $\Delta G(kg) =$  weight variation

 $\Delta t(s) = time variation$ 

- $\Delta p(Pa) =$  difference in the water vapor tension between the ambient air and the saline solution, a value taken from specific statements (1010 Pa)
- $R_{A}^{=}$  water vapour diffusion resistance of the air gap, between the sample and the satured solution (0,048x10<sup>9</sup> Pa\*m<sup>2\*</sup>s/kg for a air gap of 10mm).

### **DETERMINATION OF WATER VAPOR PERMEABILITY**

Permeability  $W_{vp}$  (kg/m\*s\*Pa) was calculated multiplying permeance for the samples thickness t(m):

$$W_{vo} = \Lambda^* t$$

At the end, the resistance coefficient to vapor diffusion  $\mu$  was obtained:

						þ	l = <u>air p</u> sam	ern ple	neability permea	1, bil	94*10 <sup>-10</sup> ity ∧*t								
	Code	Bioch addit	nar ion	Sampl thickn	e ess	Samp weigh	le t (g)	Sa we mi	mple ight 10 n (g)	Sa w	ample eight 30 iin (g)	Sarr weiq min	ple ght 50 (g)	San weiq min	nple ght 90 (g)	San weig min	nple ght 194 (g)	San weig min	nple ght 255 (g)
NO	1_A	0%				409,0	)5	40	9,23	4(	09,19	409	,10	409	,03	408	,57	408	3,42
	2_A	5%		15 m	m	482,3	36	48	2,41	48	82,25	482	,54	482	,32	482	,04	481	,90
	3 A	109	%	~13111	111	435,4	14	43	5,47	4	35,47	435	45	435	,30	435	,24	434	1,93
	4 A	209	%			430,0	)9	43	0,03	42	29,92	429	,89	429	,85	429	,69	429	9,60
0	1_B	0%				422,0	)4	42	2,07	42	22,14	421	,88	421	,82	421	,80	421	,55
	2 B	5%		15 m	~	447,7	<b>′</b> 4	44	7,76	44	47,62	447	,69	447	,57	447	,40	447	7,38
	3 B	109	%	~13111		448,1	1	44	8,13	44	48,07	447	,92	447	,88	447	,76	447	7,74
	4_B	209	%			468,9	98	46	8,93	4(	68,76	468	,76	468	,82	468	,65	468	8,57
	RH 93,	2%	1_A		2_A		3_A		4_A		RH 12,4%		1_B		2_B		3_B	Z	1_B
	∆G (kg	J)	0,00	0063	0,000	)46	0,0005	1	0,00049		∆G (kg)		0,0004	.9	0,0003	6	0,00037	′ (	),00041
	∆t (s)		15 3	300	15 30	)0	15 300		15 300		∆t (s)		15 300		15 300		15 300	1	5 300
	∆p (Pa	ι)	101	0	1010		1010		1010		∆p (Pa)		1010		1010		1010	1	010
	$\Lambda$ (kg/m <sup>2</sup>	²*s*Pa)	2,26	6E-9	1,64	-9	1,79E-9	9	1,71E-9		$\Lambda$ (kg/m <sup>2</sup> *s*F	Pa)	1,71E-	9	1,23E-	91	,19E-9	1	,41E-9
	W <sub>vp</sub> (kg/n	n²*s*Pa)	3,3	9E-11	2,46	E-11	2,68E-	11	2,56E-11		W <sub>vp</sub> (kg/m <sup>2</sup> *s	*Pa)	2,56E-	11	1,84E-	11	1,78E-1	1 2	2,11E-11
	μ		5,7	2	7,88		7,22		7,53		μ		7,54		10,48		10,80	Q	9,17





Fig.16 The circular test vessel built for the water vapor permeability test.

## **ELECTROMAGNETIC FIELD SHIELDING**

In electromagnetic absorption tests the effectiveness of the shielding material is determined by the attenuation: how much the radiation is reduced while passing through the material compared to when there are no obstructions, electromagnetic waves intensity is measured in dB, a logarithmic scale unit. Wi-Fi networks emit 2.4-5 GHz waves, a 5 GHz Wi-Fi connection is more susceptible to obstructions than 2.4 GHz connections, and so will have a slightly shorter effective range, typically, 3-5 meters shorter. Physical obstructions in houses, such as brick walls and metal frames, can reduce the range of a Wi-Fi network by 25% or more.

GPS frequencies are below 2 MHz. Smartphones are some of the most significant sources of EMF radiations. 5G, the fifthgeneration mobile network, emits a frequency range between 600 MHz to 71 GHz. The frequency spectrum of 5G is divided into millimeter waves, mid-band and low-band. 5G millimeter wave frequency are between 24 GHz to 71 GHz; 5G mid-band frequencies are between 2.4 GHz and 4.2 GHz; 5G low-band frequencies are below 1000 MHz. X-rays are used in radiology and can easily penetrate the human body, being dangerous for the organism. These rays' frequencies range between 30PHz-300EHz.

Other electromagnetic generating devices are: microwave ovens, electrical wiring, dimmer switches, plumbing, electrical heating.

In the last decades the intensity of electromagnetic radiations increased and the combination of fields can generate health problems. According to the Physicians for Safe Technology association, people tend to experience symptoms associated with exposure to electromagnetic fields of varying frequencies and power this phenomenon is called electro sensitivity. Some of the symptoms are: tiredness, insomnia, neurological problems, dementia, attention deficit hyperactivity disorder, ear problems, cardiovascular and dermatological problems, infertility, headaches, emotional problems, restless leg syndrome.

However, the symptoms are not necessarily

EM radiation	Frequency	Wave length
LF	30 kHz - 300 kHz	10 km - 1 km
MF	300 kHz - 3 MHz	1 km - 100 m
HF	3 MHz - 30 MHz	100 m - 10 m
VHF	30 MHz - 300 MHz	10 m - 1 m
UHF	300 MHz - 3 GHz	1 m- 10 cm
Microwave	3 GHz - 300 GHz	10 cm - 1 mm
Infrared	300 GHz - 428 THz	1 mm - 780 nm
Visible light	428 THz - 749 THz	780 nm - 380 nm
Ultraviolet	749 THz - 30 PHz	380 nm - 10 nm
X rays	30 PHz - 300 EHz	10 nm - 1 pm
Gamma rays	>300 EHz	< 1 pm

Fig.17 Electromagnetic radiations and relative frequencies.

caused by the field exposures. The World Health Organization report that there is no direct correlation between exposure and symptoms, leading to the suggestion that psychological mechanisms play a role in causing or exacerbating EHS symptoms. Electromagnetic hypersensitivity is not an accepted diagnosis, medically there is no case definition or clinical practice guideline and there is no specific test to identify it, nor there is an agreed-upon definition to conduct clinical research.

It may require both a medical evaluation to identify and treat any specific conditions that may be responsible for the symptoms, and a psychological evaluation to identify alternative psychological conditions that may be responsible or contribute to the symptoms. Studies have shown that symptoms are more closely associated with belief that one is being exposed than with any actual exposure<sup>2</sup>.

#### **C**OMPARISON OF ELECTROMAGNETISM ATTENUATION

As we mentioned, the attenuation of the radiation is given in dB. Fig.4 shows how the field reduction corresponds to the decibel scale, when the measures are carried out in

Factor	Reduction	Decibel
10	90,000%	10
100	99,000%	20
1000	99,900%	30
10000	99,990%	40
100000	99,999%	50

Fig.18 % of radiation reduction related to dB scale.

power density (W/m). To understand the shielding effectiveness of the tested biochar mixture it is essential to compare it with commonly used materials, such as concrete, bricks, glass, drywall and timber. The tests consider the frequencies between 0 and 8 GHz. The results allow a direct comparison to the plaster analyzed in this research. The maximum shielding is given by the glass panel: 3,92 dB of attenuation at 2 GHz<sup>3</sup>.



<sup>&</sup>lt;sup>1</sup> World Health Organization, *About Electromagnetic Fields*. Website: http://emftests.com/what-happens-when-you-are-exposed-to-electromagnetic-fields/.

<sup>&</sup>lt;sup>2</sup> Diagnosis, *Electromagnetic hypersensitivity*, Wikipedia. Website: https://en.wikipedia.org/wiki/Electromagnetic\_ hypersensitivity.

<sup>&</sup>lt;sup>3</sup> U.S. National Institute of Standards and Technology (NIST) and the University of the German Federal Armed Forces, *EMF shielding by building materials, Attenuation of microwave band electromagnetic fields by common building materials,* 2017.



Fig.19 Electromagnetic attenuation of some building materials.

# **DETERMINATION OF ELECTROMAGNETIC WAVES ATTENUATION**

#### TEST EXECUTION DATE: 20/12/2019

**PLACE of EXECUTION:** LACE\_Antenna and Electromagnetic Compatibility Laboratory, DET, Politecnico di Torino.

#### EQUIPMENT

Anechoic Chamber with dissipative material. Electric field: 2,5Hz – 18 GHz (Fig.21) Two ridge horn antennas (1-18GHz) (Fig. 23) Wooden support lined with alluminium sheets The Vector Network Analyzer (VNA) used for measurements of the scattering parameters is Agilent E8361A.

#### SAMPLES PREPARATION

Square wooden moulds of 30x30 cm were made and lined with oven paper to prevent the sticking of the mixture. (Fig. 20)

#### MATURATION

The samples dried in a room at  $22\pm5$  °C and RH 50 $\pm10\%$ , for 28 days.

#### **MEASUREMENTS**

Each sample (0-5-10-20% of biochar) was placed in the anechoic chamber and fixed at the wooden support.

The scattering parameters (reflection coefficient S11 and transmission coefficient S21) were measured with the VNA in the frequency band 1-18GHz.

Final diagrams show the transmission coefficient, S21 expressed in decibel (dB) trasmitted as a function of frequencies.



Fig.20 Square wooden moulds of 30x30 with the different % of biochar.

(From the upper-left side:0-5-10-20% of biochar).



Fig.21 Interior of the anechoic chamber.

# **DETERMINATION OF ELECTROMAGNETIC WAVES ATTENUATION**



Fig.22 Final diagram: dB quantity trasmitted at different frequencies.



Fig.23 Example of Double ridged horn antenna.

# DATA SHEETS

### CANAPAMIX2

Characteristic	Value/ DescriptionM	easurement unit
Appearance	powder - hazelnut color	-
Grain size	<0.6	mm
Workability at 25 °C	45	min
Application temperature	+5/+30	٦°
Density	639	kg / m³
Compressive strenght	0.64 (Cat. CS I - UNI EN 1015-11)	N / mm <sup>2</sup>
Water absorption	2.14 (Cat. W0 - UNI EN 1015-18)	kg / m² min <sup>0,5</sup>
Water absorption resistance	5.7-7.5	μ
Adhesion	≥ 0.52	N / mm <sup>2</sup>
EMF attenuation (1-18GHz)	0-2	dB

# CANAPAMIX2 + 5% BIOCHAR

Characteristic	Value/ DescriptionM	easurement unit
Appearance	powder - anthracite	-
Grain size	<0.6	mm
Workability at 25 °C	45	min
Application temperature	+5/+30	C°
Density	623	kg / m³
Compressive strenght	0.79 (Cat. CS I - UNI EN 1015-11)	N / mm <sup>2</sup>
Water absorption	2.51 (Cat. W0 - UNI EN 1015-18)	kg / m² min <sup>0,5</sup>
Water absorption resistance	7.5-7.9	μ
Adhesion	-	N / mm²
EMF attenuation (1-18GHz)	-	dB

# DATA SHEETS

# CANAPAMIX2 + 10% BIOCHAR

Characteristic	Value/ DescriptionM	easurement unit
Appearance	powder - anthracite	-
Grain size	< 0.6	mm
Workability at 25 °C	45	min
Application temperature +	5 / +30	<u>Э</u> °
Density	592	kg / m <sup>3</sup>
Compressive strenght	0.91 (Cat. CS I - UNI EN 1015-11)	N / mm <sup>2</sup>
Water absorption	2.86 (Cat. W0 - UNI EN 1015-18)	kg / m <sup>2</sup> min <sup>0,5</sup>
Water absorption resistance	7.2-10.8	μ
Adhesion	-	N / mm²
EMF attenuation (1-18GHz)	2-6	dB

## CANAPAMIX2 + 20% BIOCHAR

Characteristic	Value/ DescriptionM	easurement unit
Appearance	powder - anthracite	-
Grain size	<0.6	mm
Workability at 25 °C	45	min
Application temperature	+5/+30	°C
Density	630	kg / m³
Compressive strenght	0.95 (Cat. CS I - UNI EN 1015-11)	N / mm <sup>2</sup>
Water absorption	3.85 (Cat. W0 - UNI EN 1015-18)	kg / m² min <sup>0,5</sup>
Water absorption resistance	7,5-9,2	μ
Adhesion	-	N / mm <sup>2</sup>
EMF attenuation (1-18GHz)	7-29	dB

# **STATE OF THE ART C**ANTERIORITY **J**EDILCANAPA

**4**EXPERIMENTAL ACTIVITY

**D**CONCLUSIONS

#### COMPRESSION AND BENDING

The mechanical tests were carried out to evaluate if the presence of biochar could influence the performance of the composite. There are no significant variations in terms of bending between the different specimens. The biochar does not modifiy the flexural strength of the composite.

The same specimens have been used for the compression test; the mechanical improvements due to the addition of biochar are evident: the samples with 5% of biochar show an increase in strength of  $\sim$ 23%, while the specimens with more biochar (20%, 4A-B-C-D) have an increase of  $\sim$  48%, compared to plain mortar.

It is assumed that this improvement is due to the stretched structure of the biochar fragments, which have a behavior similar to wooden fibers.

Furthermore, biochar fragments smaller than  $\sim 20 \ \mu m$ , are interposed between the lime and hemp particles, strengthening their bonds.

#### ADHESION

The results showed a slight difference between the specimens, the biochar presence does not negatively affect the mechanical resistance of the plaster.

An additional test was carried out to prove the adhesion capacity on a clay bricks wall, simulating the actual application of the insultating plaster.

After the drying period the different plasters did not show craks or structural failures.

#### **POSSIBLE APPLICATIONS**

Adding biochar does not negatively affect the mechanical properties. Hence, it is possible to use the biochar-hemplime plaster for the same applications recommended for the Canapamix2 insulating mortar.



Fig.1 Stretched structure of biochar fragments. Electron microscopy image:x1500.



Fig.2 Stretched structure of biochar fragments. Electron microscopy image:x2000.

#### WATER ABSORPTION COEFFICIENT

The tests show that a larger amount of biochar increase the capillary absorption capacity. The specimens with 5% biochar increases the absorption up to 17% compared to plain mortar, while the specimens with 20% biochar up to 80%.

The graph illustrates a constant growth, which is higher in the segment between 10 and 20%.

Electron microscope images show how the larger fragments maintain the porous structure of the charcoal, increasing the capillarity.

15 days after the test the weight of the samples was recorded to see whether the specimens retained or realeased the absorbed water. The measurements showed that the weight was slightly higher than before the test: almost all the water absorbed was released.





Fig.3 The porous structure of the charcoal. Electron microscopy image:x1500.

#### WATER VAPOR PERMEABILITY

The test was carried out at high and low RH, considering the samples' weight after 255 min from the start of the test in accordance

with Italian Standard UNI EN 1015-19:2014. In both cases  $\mu$  of the plain mortar is lower than  $\mu$  of the biochar samples, i.e. plain mortar: ~5,7 (RH 93,2%); biochar mortar: ~7 (RH 93,2%). However in all samples  $\mu$ <11; this value is the threshold between a high and a middle permeability material.

The addition of biochar causes a decrease of permeability. This phenomen is probably caused by the interposition of biochar fragments between the lime-hemp particles, that obstruct the penetration of vapor through the specimen.



Fig.4 Interposition of biochar fragments between the lime-hemp particles. Electron microscopy image:x3000.

#### **POSSIBLE APPLICATIONS**

The biochar mortar has a good water storage capacity, thus it is a good humidity regulator. It is suggested to apply it as a finish coat, to help keeping humidity levels constant throughout the year and preventing the development of mold and microbes.

Recommended applications are in rooms that require humidity control, such as kitchens or bathrooms, wineries, cellars and medical areas.Hence, the biochar plaster offers a better performance in environments that have occasional RH peaks, but it can't guarantee the same behaviour in rooms with constant high or low RH levels.

20 µn

#### SHIELDING EFFECTIVENESS

The shielding effectiveness of the various samples can be evaluated as  $SE = -10\log(S21)$ . In order to avoid the errors due to measurements setup, the transmission coefficient of the empty window is measured and used as reference. Results are shown in Fig. 23. The plain plaster has an attenuation level close to zero dB, while the composite with the 10% of biochar has a shielding effectiveness of  $\sim$ 5 dB for the whole range. The sample with the 20% of biochar shows the highest value of shielding effectiveness. lowest The peak is 29 dB at 12 GHz.



#### **POSSIBLE APPLICATIONS**

A high electromagnetic waves absorption capacity can interfere in the use of the electronic devices. Therefore, is not recommended the application of materials with a considerable biochar percentage in spaces where it is necessary a stable and powerful transmission.

It is suggested the use of a product with a high biochar presence in areas where an electromagnetic protection is preferred, such as bedrooms and spaces for children.

Other applications can be in the radiology ward or in laboratory where high an low radiations are frequently emitted for experimentations.

#### **RESEARCH ACHIEVEMENT AND PROPOSAL**

Due to the growing impact of human activity, the constant increase of energy consumption and the consequences of the use of toxic and non-recyclable components, the scope for employing environmentally-friendly materials in the building sector is growing. This brought us to investigate a natural composite, which might contribute to improve human health and life quality indoors.

Our research explores the use of biochar as an addition to a natural plaster. According to the literature this by-product can improve some physical performances of the composite. Moreover, stable structure of biochar allows carbon capture and storage (CCS), which reduces presence of  $CO_2$  in the atmosphere<sup>1</sup>.

Considering its porous structure, we decided to add biochar in the final plaster coating, in order to improve the indoor humidity control. Charcoal is presently used in agriculture only and the number of transformation units is small, biochar availability has so far been limited. On the other hand, its properties, in agriculture, have encouraged studies concerning its use in the building sector.

The goal of this research was to examine biochar's mechanical behavior, as well as its water and vapor control, including a focus on electromagnetic field attenuation. The latter is a pressing concern due to the electromagnetic waves' intensification (i.e. 5th generation mobile and wi-fi networks).

#### **Research Limitations**

The lack of research on the use of biochar in the building sector did not allow the individuation of guidelines on the definition of mix design and experimentation parameters. It should also be stressed that test equipment and work space conditions are essential to obtain accurate and reliable results. For instance, the vapor permeability test was carried out without a constant humidity control and with a self-made equipment, which prevented us from complying with UNI EN 1015-19:2004.

#### FURTHER RESEARCH

Considering the error range attributable to the test equipment and the operating activity, our findings are consistent with the original goals. Starting from the results obtained, further research might focus on:

• Mechanical tests: adding a higher biochar percentage (>20%) to the same composite; adding the same biochar percentages (5-10-20%) to different matrixes; using biochar with a higher granulometry and porosity to verify possible mechanical alterations;

• Humidity control: using biochar with higher granulometry and surface area to check possible improvement of absorption capacity;

<sup>&</sup>lt;sup>1</sup> Lehmann J., Gaunt J., Rondon M., *Bio-Char Sequestration In Terrestrial Ecosystems - A Review*, Cornell University, GY Associates Ltd, Centro Internacional de Agricultura Tropical (CIAT), Springer, 2006, pp 405-406.

operating with suitable equipment to confirm the material's behavior;

• Electromagnetic waves attenuation: adding biochar in the composite, varying biochar granulometry and surface area to monitor changes in the electromagnetic absortion level.

A slight variation in the parameters can significantly modify the composite's properties, thus its possible uses. Biochar's changeability enhances its versatility, offering a suitable product for different applications: a slow pyrolysis leads to a larger biochar yield; a higher granulometry increases biochar porosity; pre-treatment influences the absorption capacity.

Future research could explore a number of topics: biochar application in different natural matrixes; use of different biochar typologies (from different feedstocks, pyrolysis parameters and pre-treatments); mix-design variations (% of biochar in the composite, particles size, materials proportion); the possible development of a supply chain, from feedstock purchase to the application of the final product.

In conclusion, this research proves biochar's great capability to attenuate electromagnetic waves and to control humidity, encouraging further research. Future investigations might focus on verifying whether biochar improves the performance of building components in addition to different natural composites.





















- Fig.1 Biochar without pre-treatment.
- Fig.2 Milling process of the charcoal.
- Fig.3 Collecting the pre-treated biochar.
- Fig.4 Preparation of the moulds for the electromagnetic test.
- Fig. 5 Mixing the composite with biochar.
- Fig.6 Moulds preparation for the mechanical test.
- Fig.7 Preparation of the adhesion specimens.
- Fig.8 Measurement of the specimen before the mechanical tests.
- Fig.9 Compression test
- Fig.10 Sputtering of the specimens with gold particles.

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# PAOLO ERRIQUEZ

Think about the generations and say that we want to make it a better place for our children, and our children's children, so that they know it's a better world for them

And think, if they can make the world a better place...

Michael Jackson - Heal the world