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Addition of biochar in concrete for improved carbon sequestration

Case of Project ‘‘BiBe’’

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Abstract

With the increasing rate of modernization, the CO_2 emission from cement production is bound to increase and so as the built-up areas. There is a potential of sequestering carbon in the civil structures. Biochar, a by-product of pyrolysis of biomass can be utilized in the concrete as an addition and/or replacement to cement. The objective of this thesis was to investigate the carbon sequestration potential of biochar amended concrete; as well as to measure the compressive strength of biochar concrete.

Prepared biochar concretes were cured in water for 28 days and tested for study. The CO_2 concentration data was collected using the CO_2 data logger. The data were displayed and assessed with the help of data logging software – Tiny Tag explorer. As the percentage of biochar increases the amount of carbon adsorbed is also observed to increase. Additionally, it is also important to assess the influence of biochar in compressive strength of concrete. High amount of biochar addition resulted a decrease in strength of a concrete. However, the results indicated clearly that biochar amended concrete can be an effective alternative to capture carbon and reduce the carbon footprint of a cement industry.

Keywords

Biochar, Adsorption, Pores, Feedstock, Pyrolysis, Surface area, CO_2

CONTENTS

LIST OF ABBREVIATIONS

GHG = Greenhouse Gas

IPCC = Intergovernmental Panel on climate change

CO_2 = Carbon Dioxide

GCP = Global Carbon Project

HTC = Hydrothermal carbonization

EPA = Environmental Protection Agency

OPC = Ordinary Portland Cement

NDIR= Non-Dispersive Infrared

PPM = Parts Per Million

1 INTRODUCTION

Climate change caused by the anthropogenic emission of greenhouse gases poses a severe threat to the earth's ecosystems. Emissions of greenhouse gases such as carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) traps heat in the atmosphere and warm the planet. Among them, carbon dioxide acts as a main greenhouse gas responsible for climate change (Marescaux et al. 2018). Cement industry plays a significant role in global carbon emission. Cement industry is a highly energy intensive process. Approximately 1 tonne of CO_2 is emitted per tonne of clinker production during the calcination process (Norcem 2021). Other significant amount of emission generates from the burning of fossil fuels to heat the kiln up to extreme temperature. In 2015, cement industry generated around 2.8 billion tonnes of CO_2, the equivalent of more than any individual country except China and the US (Hausfather 2021). Therefore, it is essential to reduce cement carbon footprint and develop a sustainable method to capture and store CO_2 to combat climate change.

Intergovernmental Panel on climate change (IPCC 2018) considers several pathways to limit the average global warming to 1.5 °C compared to pre-industrial levels. Several research papers were addressed on the utilization of biochar in various environmental applications such as soil health improvement (Novak et al. 2009), energy production (Xiong et al. 2017) and mitigate global climate change (Woolf et al. 2010). With the creation ‘‘mega construction projects’’ there is a need for substitution of cement with a supplementary material especially produced from biomass that has the potential to act as a carbon sink. This thesis is a part of project ‘‘BiBe’’ and within the project it has been decided that the thesis shall investigate the carbon sequestration potential of biochar concrete when biochar is used as a partial replacement to the cement. When biochar is utilized as partial replacement to cement, the strength of the concrete cannot be neglected. So, the additional objective of the thesis is to measure the compressive strength of the biochar concrete. Moreover, the environmental benefits of biochar concrete will be discussed.

In order to reach those goals, this research will address the following key questions:
“How would the different biochar percentage in a concrete affect the amount of CO_2 concentration inside the container?”
“How would the biochar addition influence the compressive strength of a concrete?”

While “biochar application in concrete’’ is a wide and relatively new topic, this study will just focus on ability of biochar amended concrete to capture carbon in a ‘‘controlled environment’ ’and its effect on the strength of concrete.

”BiBe - New applications of biochar as building material” is a two year (1 Dec 2020 – 31 Dec 2022) joint project administered by South-Eastern Finland University of Applied Sciences along with Business services Miksei Ltd acting as a partial implementers. The aim of the project is to investigate the use of biochar as an additive in construction materials and reduce the carbon footprint of the concrete production. The project studies possible application for biochar in construction sectors, i.e., concrete structures, tiles, walls, and noise abatement structures. These applications are studied in laboratory and pilot scale considering the environmental impacts and physical and chemical performance of cementitious materials.

2 THEOREOTICAL BACKGROUND

2.1 Introduction to biochar

Biochar is a type of black carbon produced from a carbonaceous material through the application of heat or chemicals in an enclosed container with little or no oxygen (Deem & Crow 2017). Organic materials from agriculture and other forest wastes (biomass) are burned in a zero or low oxygen environment to produce biochar. Although, biochar looks like common charcoal, it is unique because of its production process and long-term carbon sequestration properties. In addition to carbon capture, biochar also can improve soil fertility, builds nutrient retention capacity in soil, and reduce the need for chemical fertilizers (CharGrow 2019).

Every feedstock and methodology of creating biochar provides different physical and chemical properties of the product (Laine et al. 1991). However, there are some universal physical structures of biochar. The key physical properties are the large surface area (340 m^2/g), water holding capacity and high porosity (0.21 cm^3/g) (Manariotis et al. 2015). As shown in Figure 1, almost 70 percent of biochar composition is carbon whereas the remaining percentage consists of nitrogen, hydrogen, oxygen, ash, and sulphur.

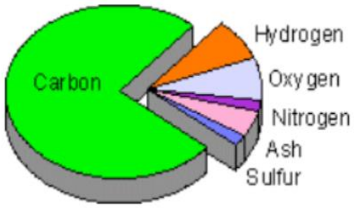


Figure 1 Elemental composition of Biochar (B4SS Project 2018).

From a chemical viewpoint, chemical properties of biochar depend highly on feedstock and pyrolysis conditions. The defining characteristic of biochar is its carbon content consisting primarily of aromatic compounds characterized by rings of six C atoms linked together without oxygen (O) and hydrogen (H), the otherwise more abundant atoms in living organic matter (Lehmann & Joseph 2009).

2.2 Biochar Feedstocks

According to the World Bank (2022), in 2018, the world population, 7.6 billion people, produced two billion tonnes of waste per year. Our global waste is predicted to grow by 70 percent by 2050. In 2016, it was estimated that 1.6 billion tonnes of carbon-dioxide-equivalent were generated from the treatment and disposal of waste (World bank 2022). Therefore, waste-to-biochar conversion could be an option for the environmental sustainability.

Appropriate biochar feedstocks include crop residues (both field residues and processing residues such as fruit pits, nut shell, bagasse, etc), as well as food, forest waste and manures. Biochar's heterogenous properties can be contributed to the wide availability of possible feedstock that can be utilized as biomass. In 2010, the global estimation of feedstock by Woolf et al. (2010) is ~2.27 Pg C/year (Petagram of Carbon), available for transformation process into biochar.

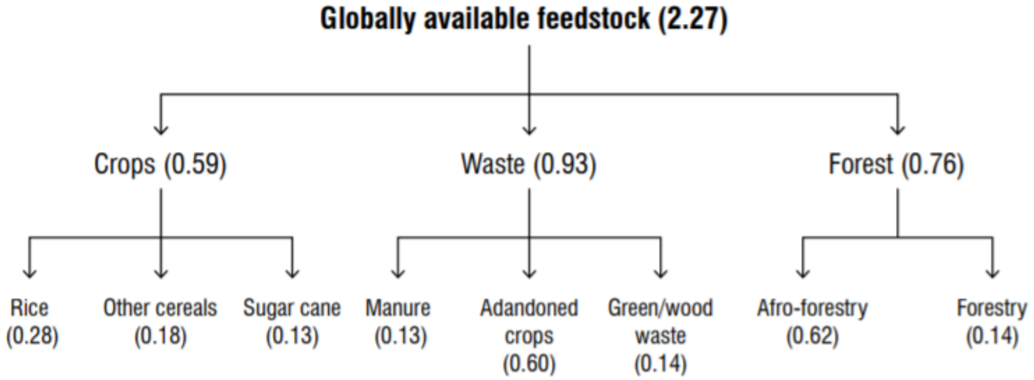
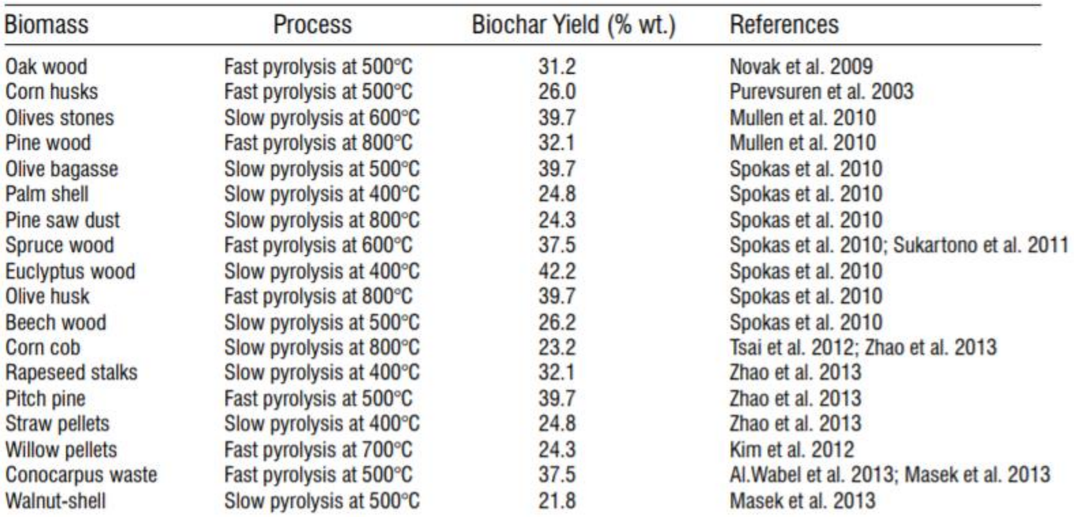


Figure 2 Globally available annual feedstock (in Pg C/year) and their distribution in different biomass (Khaled & Erriquez 2020)

Biochar selection for specific application may require selection of feedstock as well as production techniques to produce biochar with desired characteristics. For instance, Gupta et al (2018) discussed the potential of using biochar as a building material to capture and 'lock' atmospheric carbon in civil infrastructure. The study found biochar produced from food waste, rice waste and saw dust possess honeycomb-like pore structures on the surface of biochar attributing to the release of volatiles from the feedstock creating more pores and/or received from the biological capillary structure of biomass. Figure 3 shows different feedstocks with the amount of biochar yielded with pyrolysis technique.



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. 2011
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

Figure 3 List of biochar yield from different feedstock (Khaled & Erriquez 2020)

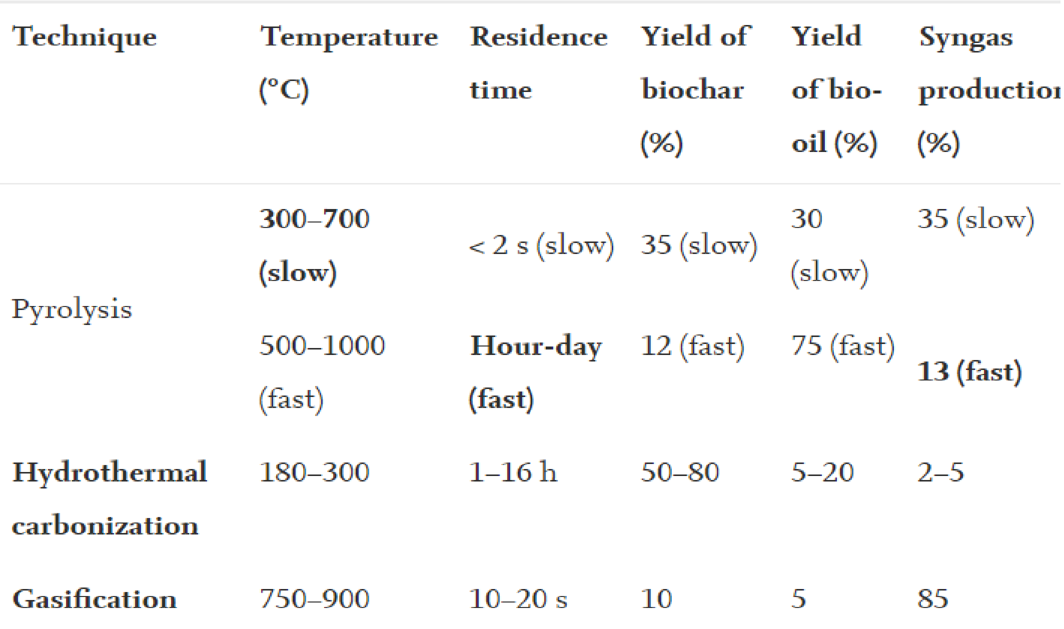
Converting waste to biochar not only solves waste management problem but it can also be utilized as a by-product from energy production from discarded biomasses.

2.3 Biochar production methods

Biochar production varies depending on the process. The equipment's used for making biochar can be as simple as an ancient campfire or as complex as advanced bio-refinery. Thermochemical conversion is a common technique for biochar production that includes pyrolysis, hydrothermal carbonization, gasification and torrefaction (Pang 2019). Whichever the method, the core process is to burn biomass in the absence or limited supply of oxygen.

2.3.1 Pyrolysis

Pyrolysis is a process for decomposing organic materials (biomass) thermally under oxygen-free conditions in the temperature ranging from 250–900 ^{0}C (Yaashikaa et al. 2020). Pre-treatment of feedstock is essential to improve the efficiency of pyrolysis (Rezaei et al. 2019). The feedstock undergoes pre-drying inside the feeder which evaporates the moisture in biomass using excessive hot and dry airflow. Pyrolysis process can be divided into slow and fast depending on factors such as heating rate and retention time at the highest temperature (Al Arni 2018).



Technique	**Temperature (°C)**	**Residence time**	**Yield of biochar (%)**	**Yield of bio-oil (%)**	**Syngas productio (%)**
Pyrolysis	**300–700 (slow)**	< 2 s (slow)	35 (slow)	30 (slow)	35 (slow)
	500–1000 (fast)	**Hour-day (fast)**	12 (fast)	75 (fast)	**13 (fast)**
Hydrothermal carbonization	180–300	1–16 h	50–80	5–20	2–5
Gasification	750–900	10–20 s	10	5	85

Figure 4 Thermochemical conversion techniques and their process conditions (Yaashikaa et al. 2020)

Fast pyrolysis is currently the most popular method. Fast pyrolysis method takes second to complete and yields 65 percent liquid product(bio-oil). The rest of the yield is 20 percent biochar and 15 percent syngas (Jahirul et al. 2012). Fast pyrolysis process requires high heating (500to 600 ◦C) and heat transfer rates (10–200 K/s) and a very short reaction time (0.5–10 s) (Rasaq et al. 2021).

Slow pyrolysis, also called conventional carbonization, produces biochar by heating biomass at low to moderate temperatures for a relatively long reaction time (Zhu et al. 2018). As seen in Figure 4 slow pyrolysis process generates high yields of charcoal. Slow pyrolysis is often considered as the most feasible production process to produce highly reliable and consistent quality biochar. A longer residence time in slow pyrolysis allows the large quantity of vapor to purge which increases the yield of biochar (Raza et al. 2021).

2.3.2 Gasification

Gasification process converts biomass into syngas containing carbon monoxide, hydrogen, carbon dioxide, methane, and smaller quantities of higher hydrocarbons by supplying controlled amount of oxidizing agent at high temperature(>700°C) (Lamb et al. 2020). The oxidizing agent used in gasification can be air, steam, or mixture of these gases. Air gasification produces syngas with low heating values of 4–6 MJ/Nm^3, while gasification with oxygen and steam produces syngas with high heating values of 12–18 MJ/Nm^3 (Couto et al. 2013). The average biochar yield of gasification process is about 5-10 wt% of dry biomass which is comparatively lower than the yield obtained during fast pyrolysis (Yaashikaa et al. 2020).

2.3.3 Hydrothermal carbonization

Hydrothermal carbonization (HTC) converts biomass into a coal like product, called hydrochar, representing high carbon content and high calorific value. The process takes place in high pressure water vessel at elevated temperatures (generally ranging from 180-250 ◦C) and reaction pressure (more than 1 atmospheric pressure) to maintain the water in a liquid form for few hours (0.5-8h) in absence of oxygen (Sivaprasad et al. 2021). This type of thermo-chemical conversion, also referred to as wet pyrolysis (or wet torrefaction), allows the treatment of substrates with elevated moisture content, up to 75%–90%, without requiring a drying pre-treatment step (Lucian et al. 2017). This may be cost effective biochar production for biomass with high moisture content since it requires water. Also, the char yield of low-temperature biomass HTC (< 300 °C) was 67% depending on the feedstock properties, reaction temperature and pressure (Wang et al. 2014).

3 ENVIRONMENTAL BENEFITS OF BIOCHAR AND ITS ADDITION TO THE CONCRETE AS A CEMENT REPLACMENT

3.1 Biochar as a potential CO_2 adsorbent

The porous nature and unique surface area properties of biochar contributes to its efficient CO_2 adsorption potential. A study by Creamer et al (2014) showed that biochar produced from sugarcane bagasse and hickory wood effectively captured CO_2. In the study, bagasse biochar produced at 600 °C showed the most adsorption of CO_2 (73.55 mg g^{-1} at 25 °C). The adsorption was mainly controlled by physisorption where CO_2 interacts with biochar surface through polar bonds on either end of its linear shape. Both dispersion and induction contribute to the attraction of CO_2 to carbon surface, depending on the surface property. The author suggested that the larger surface area of biochar contributed towards the CO_2 adsorption under normal atmospheric temperature. Some studies showed that modified biochar has shown enhanced CO_2 adsorption potential. Metal impregnation (metal nitrate salts of sodium, magnesium, calcium, nickel, iron, and aluminium) on the surface of biochar improved the capturing of CO_2 (Dissanayake et al. 2020). Metal impregnated biochar CO_2 adsorption experiment was carried out in a Thermogravimetric analyser that records the variation in sample weight and a surface area analyser observed the formation of basic sites on the biochar surface that promoted the adsorption of CO_2. The study reported a higher CO_2 uptake by a magnesium-loaded biochar (82.0 mg/g) than the virgin biochar (72.6 mg/g) at 25 °C and 1 atm.

3.2 Biochar concrete buildings as a sink for captured carbon dioxide

Concrete is the second most consumed material after water. Each year 4.4 billion tons of concrete are being produced globally (Hilburg 2019). In the production process of concrete, the construction industry emits massive amount of CO_2 in the atmosphere. About one ton of CO_2 is released in the atmosphere in the production of 1 ton of Portland cement (Worrell et al. 2001). Biochar utilization in soil as carbon sequestration materials has been explored in several studies

(Muhammad et al. 2017; Papageorgiou et al. 2021). With the increase in concrete consumption, there is a potential of sequestering carbon civil infrastructure if biochar can be effectively utilized as admixture in cementitious materials. Depending on the feedstock and pyrolysis conditions, a tonne of dry feedstock has the potential to reduce net greenhouse gas (GHG) emission by approximately 870kg CO_2equivalent (CO_2-e), of which 62–66% are from carbon capture and storage by the biomass feedstock of the biochar (Roberts et al.,2009). However, if the biochar formed is saturated with CO_2 prior to its deployment in the concrete, it is possible to sequester an additional amount of emissions of about 300 kg CO_2 equivalent per tonne dry feedstock, which corresponds to CO_2 adsorption of 7 mmol (CO_2) per gram of biochar (Wei et al. 2012). Biochar with a high surface area and porous nature can be a potential material to capture and store CO_2 by adsorption in its pores. For example, the high pH and high-water retention capacity in pores of biochar reduces the amount of free water in the concrete. The absorbed water is released during the hardening of concrete promoting secondary hydration by internal curing (Choi et al. 2012); this can result in stronger concrete and sequestration of carbon (in the form of biochar) in concrete.

3.3 Reduction in waste and landfilling

Annually, the world generates 2.01 billion tonnes of municipal waste among which approximately 33 percent is not managed in a sustainable way (World bank 2022). With the rise in population, the global waste is expected to reach 3.40 billion tonnes by 2050. Appropriate management of this waste has become a challenging concern. One viable method to manage the waste is to convert it into biochar and utilize them in construction sector.

Biochar uses not only encourages waste recycling but also indirectly reduces the land area required for dumping massive amount of waste. In 2018, a study by Environmental Protection Agency (EPA) reported 18.1 million tons of wood waste. Among them, 3.1 million tons were recycled, and 2.8 million tons were combusted for energy recovery. However, 12.1 million tons of wood waste were disposed in landfill that year. Conversion of wood waste to biochar for construction use could potentially reduce the land area requirement for wood waste. On the other hand, it could also prevent emissions of harmful gases i.e., methane into the atmosphere which is an additional benefit besides preventing leaching of arsenic, chromium, and copper from treated woods into the soil that would affect the local ecosystem.

3.4 Biochar benefits as a partial replacement to cement

Cement, being the main binding material that holds concrete together has been used since ancient times. With the increasing rate of modernization, the CO_2 emission from cement production is bound to increase. Ordinary Portland Cement (OPC) is globally industrialized by combustion of range of raw materials such as limestone and clay causing rapid depletion of these resources. Moreover, the production process of cement requires massive energy to heat the kiln (≈1450 °C) contributing to almost 40% of CO_2 emission (Tayeh et al. 2019). Such enormous release of CO_2 gas could cause several environmental hazards such as climate change and ozone depletion. Therefore, supplementary materials such as biochar as a partial replacement of cement in concrete can decrease the consumption of cement in civil infrastructure which in turns reduces the emission of CO_2 (Suarez-Riera et al. 2020). The other significant change with biochar utilization in cement as replacement was observed in human health. The potential health risk associated with environmental exposure (via air, soil and drinking water) as a result of cement production significantly decreased when a portion of cement particles was replaced by biochar (Campos et al. 2020).

4 MATERIALS AND METHODS

4.1 Biochar production

The biochar sample was produced by pyrolysis of pine wood, birch wood and pine wood chips. Although, slow pyrolysis is less sensitive to moisture content of feedstock, it is recommended to remove at least 80% of the moisture content for high quality char production (Antal & Grønli 2003). Therefore, the feedstocks were ensured that they were adequately dried before combustion. Pine wood and birch wood biochar were prepared through slow pyrolysis method. During the process, feedstocks (pine and birch wood pieces) were heated in a furnace at a high temperature of 450 ˚C with limited oxygen exposure. Other feedstock (pine wood chips) was combusted through a fast pyrolysis process at a temperature of 800 ˚C with limited oxygen. Figure 5 (Left) shows the SoilCare companies' biochar prepared from bigger pine and birch wood pieces. It also shows Carbo culture companies' biochar prepared from small pine wood chips.

Figure 5 On the left is the SoilCare biochar blocks before and after grinded. On the right is the Carbo Culture pine wood chips biochar before and after grounded (Tuominen 2021).

The prepared biochar's were naturally cooled at room temperature and then grounded into fine particles. SoilCare Oy biochar's were grinded by an electronically controlled IKA grinder MF 10.2 Impact grinding head in Xamk premises. After grinding the biochar was sieved with a 2mm sieve. Finally, the biochar's were stored in an airtight bag to avoid contamination by pollutants in the indoor environment.

4.2 Properties of cement and sand used

Portland Cement (CEM II 42.5N) with a 28-day normal strength of 42.5 MPa was used in the study provided by Finnsementti Oy (Finnsementti 2022). The physical and chemical composition of cement were in accordance with the standard SFS-EN 197-1 and are CE marked. Locally available natural sand with maximum particle size of 4 mm were used as aggregates.

4.3 Ingredients mix proportion and specimen preparation

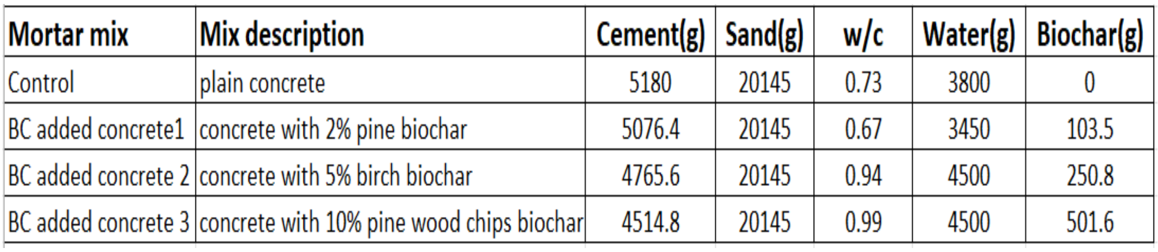
A plain concrete (control) was first prepared adhering to the recommended recipe for standard application. Aggregates were passed through a 4 mm sieve. Water was added at the ratio of 0.73 to the cement as reported in Table 1.
The ratio is calculated by taking the weight of the water and dividing it by the weight of the cement

Table 1 Reference plain concrete (PC) mix proportions with respect to cement weight.

Mix	Cement	Aggregate	Water
Plain concrete	1	3.8	0.73

Three other concrete cubes (with biochar) were cast with a W/C ratio of 0.67, 0.94 and 0.99 as reported in Table 2, considering the water absorption properties of biochar that has ability to absorb water more than its weight (Renewables Plus 2020).

Table 2. Mix proportion of different components in different types of concrete mix



Mortar mix	Mix description	Cement(g)	Sand(g)	w/c	Water(g)	Biochar(g)
Control	plain concrete	5180	20145	0.73	3800	0
BC added concrete1	concrete with 2% pine biochar	5076.4	20145	0.67	3450	103.5
BC added concrete 2	concrete with 5% birch biochar	4765.6	20145	0.94	4500	250.8
BC added concrete 3	concrete with 10% pine wood chips biochar	4514.8	20145	0.99	4500	501.6

In the specimen, biochar was used as a substitute to cement (by wt % of cement in concrete). The materials (sand, cement & biochar) used in the preparation were weighed, following the indicated quantities in Table 2 after weighing the materials, water was manually added for approximately 5 minutes. The mixture was mixed manually with an electric handheld device (see Figure 6) until the ingredients are homogenously combined. The solution was then transferred to a wooden mold as seen in Figure 7.

Figure 6 Mix in process (Tuominen 2021).

Figure 7 Specimen molding - At the top is 10 wt% biochar mixture and at the bottom is a plain concrete (Tuominen 2021).

4.4 Specimen preparation and curing conditions

Four concrete samples were prepared for CO_2 sequestration and compressive strength tests (Figure 8).

- cubes, 100 mm × 100 mm × 100 mm, for CO_2 sequestration tests.
- cubes, 150 mm × 150 mm × 150 mm, for compressive strength tests.

Figure 8 Concrete cubes with different percentage of biochar (Tuominen 2021)

The molds were filled with concrete and compacted immediately using a compacting hammer. The molds were stroked in a uniform manner over the cross-section area to remove pockets of entrapped air. The molds were covered with a sheet of polyethylene, and they were left for a dry curing for a period up to 48 hours, at a temperature of (20 ± 5) °C till demolding. Finished the setting time, the specimens were demolded and immersed into the water for 28 days curing at room temperature (21 C). Sample preparation and preservation precedure were performed in compiance with the European standard SFS-EN 12390-2:2019.

4.5 Experimental plan strategy

4.5.1 Carbon dioxide sequestration test

SKC Tedlar sampling bag (Figure 9) made of ethylene polymer plastic with maximum capacity of 5litres was used as a container.

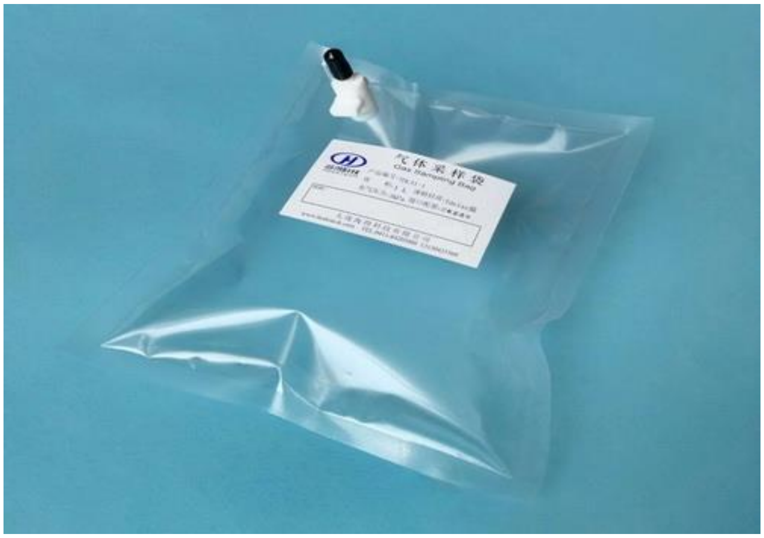


Figure 9 SKC Tedlar sampling bag

The edge of the sampling bag was cut open, so that the concrete cubes and loggers could be placed inside it. Different percentage of biochar amended cubes were placed inside the sampling bags. After concrete cubes and loggers were positioned inside the bags, the cut was thermally laminated leaving a small cut to inject the CO_2 gas pipe. After injecting some amount of CO_2, the cut was covered with a Gaffer tape making sure no air could escape. The containers were checked manually to ensure that there were no leaks in order to measure CO_2 strictly within the container.

TGE-0011 CO_2 data logger as shown in Figure 10 with measuring range 0-2000 pmm (Parts Per Million) and 0-5000 ppm were fixed inside each container to monitor the concentration of carbon dioxide. The logger uses an independently calibrated dual wavelength Non-Dispersive Infrared (NDIR) sensor to measure the CO_2 concentration inside the container. Since the logger had its measuring range limitation, a small amount of nitrogen was injected inside the container so that it would dilute the content of CO_2 and the logger would be able to read the starting level of CO_2 inside the container (Lehesvaara 2022).

Figure 10 TGE-0011 carbon dioxide sensor (Gemini Data Loggers 2017).

The test was carried out for approximately 7 days. The experimental setup is shown in Figure 11. Next, the loggers were stopped and connected to the computer to download the results.

Figure 11 Experimental setup that was used for the identification of the carbon sequestration property

4.5.2 Compressive strength test

Compressive strength was measured at 28-day age of concrete. The specimen selected for testing were water cured according to standard SFS-EN 12390-2:2019. The cubes were gently placed in the loading unit. The load was applied to the top surface of concrete cubes with the rotary grinder. The maximum load of the machine applied to the specimen is expressed in kilonewton and the compressive strength is reported in MPa. For the test, three specimens from each concrete batch were used and the average value was calculated from the results. Also, the effect of biochar addition at different water-cement ratio (W/C) on compressive strength of hardened concrete was also assessed.

The compressive strength is calculated with the following equation 1:

$$CS = \frac{F}{A} \tag{1}$$

Where, *CS* is the compressive strength, *F* is the load at which the cube breaks, and *A* is the initial cross-sectional surface area.

5 RESULTS AND DISCUSSION

5.1 Carbon dioxide sequestration results and discussion

The results of possible CO_2 adsorption by biochar mixed concrete cubes are tabulated in Table 3. The adsorption potential of each biochar concrete was calculated in percentage. The results are calculated in a table format below:

Table 3 Adsorption percentage of carbon dioxide (CO_2) by each biochar concrete

Specimen Description	**Initial concentration of CO_2 (ppm)**	**Final concentration of CO_2 (ppm)**	**Percentage adsorption of CO_2 (%)**
Blank container (without concrete)	4999	4999	0
Concrete (Cement + 0% biochar)	1999	66	96.69
Concrete (Cement + 2% pine biochar)	4990	150	96.99
Concrete (Cement + 5% birch biochar)	2630	10	99.62
Concrete (Cement + 10% pine wood chips biochar)	1996	1	99.95

From the above Table 3 it can be observed that all the subjected concrete with and without biochar absorbed CO_2. An increase in CO_2 adsorption percentage can be seen with the increase in biochar content in the concrete. A replacement of 2 wt% biochar resulted to slight increment in adsorption potential biochar concrete. Likewise, a considerable increment can be observed in the concrete with 5 wt% and 10 wt% biochar. Improved carbon dioxide sequestration can be observed compared to control in 10 wt% biochar concrete in which the adsorption percentage was increased by 3.26%.

For all the biochar samples studied, there had been an immediate CO_2 adsorption (see Appendix 1/1, Appendix 1/2, Appendix 1/3, Appendix 1/4**)**. With the increase in time, CO_2 desorption was also observed in the test. 0 wt% and 2 wt% biochar concrete adsorbed approximately 80% of carbon dioxide within three hours. On the other hand, 5 wt% biochar concrete adsorbed 90.4 percent CO_2 in an hour and 10 wt% biochar concrete adsorbed 90% of CO_2 in two hours. The fast adsorption may have had happened due to the pores size present in biochar. The pores might be an optimal size to adsorb the CO_2 molecules (0.33 nm) and pore constriction is larger than the diameter of CO_2 therefore, they acted as a quick adsorbent. The pores are gradually filled with CO_2 and later some CO_2 are desorbed as well. A similar study has been proposed by Ghani et al. (2013) that supports the assumption about immediate adsorption made in this study. The study suggests the presence of three groups of micropores in a rubber-wood-sawdust-derived biochar, depending on their accessibility through constrictions. The first group adsorbs the CO_2 molecule immediately and also desorbs quickly, which suggests that the constrictions have a much larger than diameter of CO_2.

Additionally, the high pressure inside the airtight container due to the injected CO_2 gases could also be reason behind immediate adsorption. Due to the pressure inside the container, the CO_2 gas may have inclined to cling to the adsorbent. After a few hour, the adsorption was observed to be slow. Perhaps, the pressure reduced as some amount of CO_2 gas was adsorbed by the sample. The blank sample (see appendix 1/6) which was prepared to see the air tightness observed no reduction in carbon dioxide since there was no adsorbent to adhere. Therefore, the size and pressure of an airtight container may have influenced CO_2 gas to be adsorbed in the sample quickly.

Adsorption of CO_2 by control sample could be contributed to the carbonation of the cementitious materials (IVL Swedish Environmental Institute 2021). The carbon dioxide in the container is exposed to the surfaces of the concrete. The exposed CO_2 penetrates the voids of the concrete and reacts with the moisture and form calcium carbonate ($CaCO_3$) that causes the decrease in carbon dioxide concentration.

Comparing the table, the biochar amended concrete shows high CO_2 adsorption rate. Apart from carbonation, the other influencing factor for the increment of CO_2 sequestration potential is due to the higher surface area of biochar. Biochar produced at higher temperature has better sorption capacity because at higher temperature the surface area of biochar is enhanced (Newalkar et al. 2014). The biochar utilized in this study was pyrolyzed at higher temperature i.e., pine wood chips biochar (10 wt% in concrete) was prepared at 800 ˚C. A similar finding has been reported in a study by Lee et al. (2011) that shows the higher CO_2 adsorption capacity due to the availability of surface area. Carbon dioxide tends to softly bound on the surface of biochar through physisorption (Physical adsorption). Therefore, biochar surface area was also a substantial factor for CO_2 adsorption.

Similarly, the increase in pyrolysis temperature causes the release of volatile matter and promotes the porosity development (pore volume) in biochar which plays an important role in adsorption of gas (Gupta et al. 2018). A larger pore volume of biochar provides active area for the interaction between CO_2 and biochar in the concrete that increases the CO_2 sequestration ability of biochar concrete. However, pore size of biochar used in the test were not determined as there are certain range for efficient carbon adsorption (usually micropores with a diameter of <2nm) (Brewer et al. 2012). Therefore, without knowing the pore size distribution of biochar it may not be suitable to assume that higher carbon dioxide adsorption trend occurred due to the biochar pores.

5.2 Compressive strength tests results and discussion

Figure 9. presents the 28-days compressive strength of four concrete cubes with various proportion of biochar mixed under water curing at room temperature. The result shows that concrete containing biochar showed an increase in compressive strength. The addition of 2% biochar resulted in the improvement of strength compared to biochar free one, in which the strength of concrete was increased from 19 MPa to 19.23 MPa. However, further increasing of biochar content reduces the compressive strength of concrete. 5 wt% of biochar reduced the strength by 0.07 MPa compared to plain concrete. A significant reduction in strength can be observed in 10 wt% biochar concrete i.e., 5.17 MPa which represents approximately 27% reduction compared to control.

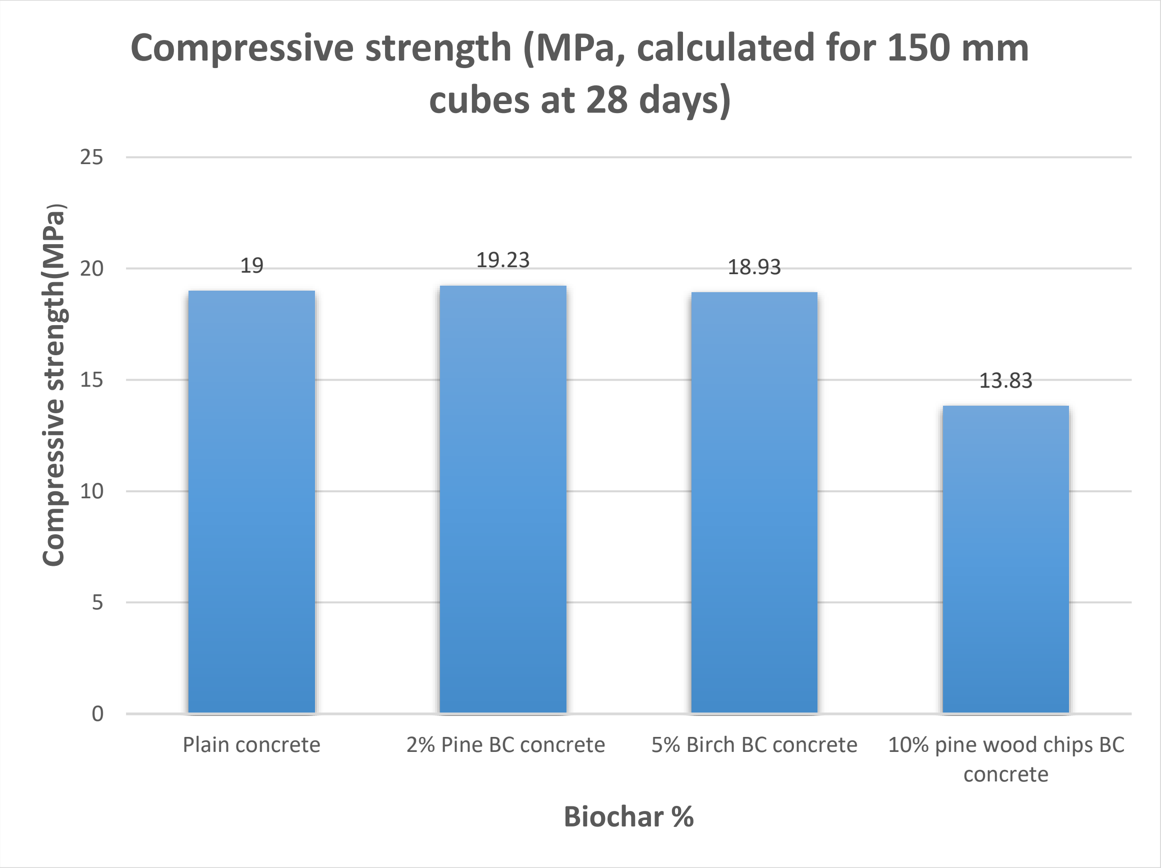


Figure 12 Compressive strength of concrete cubes for mixes 0%, 2%, 5%, and 10% biochar under water curing condition at 28 days.

Containing a small amount < 5 wt% of fine biochar particles as a cement replacement in concrete has properties close to and slightly better than the control specimen. One of the reasons for the increment in strength of the concrete can be attributed to the high-water retention and filler effect of biochar. On the other hand, a small amount of BC (2% in this case) reduces the local w/c ratio of concrete, a parameter to achieve higher strength and durability of a concrete. Besides that, the porous nature of biochar also contributes to better internal curing action of biochar -cement composites (Akhtar et al. 2018; Gupta et al. 2018). The honeycomb like pore structure acts as a water filled reservoir supplying water from the beginning of mixing to enhance the degree of hydration whenever needed in the concrete.

However, in case of samples containing biochar 5wt% and 10 wt%, the strength development is lowered at 28 days. A noticeable reduction can be observed in pine wood biochar concrete due to its low cement content and high w/c ratio (0.99). A similar finding has been reported by Panda et al. 2020, that shows reduction in concrete strength with the increase water-cement proportion. The increase in water content results wider spacing between the cement aggregates hindering the compaction of concrete and further increases the dampness levels. The other reason for strength reduction may be attributed to the agglomeration of biochar particles in the concrete especially at 10 wt% and 5 wt% dosage as seen in Fig 13.

This uneven dispersion of particles also may affect the strength by creating weak zones in concrete (Gupta et al. 2018).

Figure 13 Agglomeration of biochar in the concrete (Tuominen 2021)

6 CHALLENGES AND SUGGESTIONS FOR FURTHER RESEARCH & DEVELOPMENT

One of the main challenges of CO_2 sequestration experiment was selecting the right device for the experiment. The logger used for the experiment had its limitations i.e., the range was 0-5000 ppm. In the experiment we had injected some amount of CO_2 gas inside the container. The gas concentration exceeding the logger range were not detected by the logger. Therefore, the initial concentration was only recorded when the gas concentration inside the container is within the logger range. Similarly, the CO_2 instrument did not measure pressure variations. As we injected the gas inside the container, the pressure was assumed to be higher and during the adsorption the pressure was expected to decrease. A pressure sensor could have been used to support the assumption and study the relationship between pressure and CO_2 gas inside the container.

However, the device was suitable for first time user and was effective in measuring CO_2 concentration in PPM despite of few challenges.

Another challenge of this experiment was finding the right container. The Tedlar PVF gas sampling bag that was cut and later thermally laminated and taped were meant to be airtight. However, there was a chance of air leakage. Two blanks (see Appendix 1/5, Appendix 1/6) were prepared for the test among which one showed a slow reduction of CO_2 after 27 hours of observation whereas the other remained airtight throughout the experiment. The reason for gas reduction might be an accidental leak in the container. Also, the loggers were extremely sensitive, and the experiment was needed to be performed in a regulated conditions as recommended by the logger manual (Gemini Data Loggers 2017).

Having said that, a deeper study is required to research on the CO_2 sequestration potential by biochar concrete. A similar test which will use gas tight bag with normal air at normal pressure having CO_2 concentration about 400 ppm could be carried out. This will help logger to record precise initial level of cardon dioxide, thus the reliable results can be achieved. Further studies can be performed on calculating CO_2 adsorption potential by biochar concrete in a real-life environment rather than a lab environment. Perhaps a room walls with biochar added concrete in a real environment with ideal atmospheric pressure can be an considered for further research. Moreover, a way of calculating adsorbed carbon dioxide gas directly from the concrete after a certain time could be considered as further step instead of fixing logger inside the container. However, it is equally important to study whether biochar that contains adsorbed CO_2 influence the strength of concrete by carbonation.

Feedstocks and parameters used in the production of biochar are also an important factor for making a biochar concrete. This study used three different biochar feedstocks produced at different pyrolysis conditions. Pine wood chips biochar that was pyrolyzed at high temperature (800 ˚C) showed effectiveness in capturing carbon from the container compared to other biochar that were pyrolyzed in low temperature(450˚C). This is most likely due to pyrolysis temperature. At elevated temperature, the surface area and pore volume are enhanced that increases the adsorption capacity. However, it is essential to further research on the pyrolysis temperature residence time and heating rate that would improve the CO_2 adsorption potential of biochar. Also, further study on several feedstocks ability to improve the strength and adsorption potential of a biochar concrete needs to be performed as the key properties of biochar are highly variable and depend on mostly on feedstock type.

7 CONCLUSION

Using biochar as an additive or replacement to cement allows the use of agriculture and forestry waste to sequester carbon in concrete. Biochar utilization in construction sector also represents a potential alternative to reduce carbon footprint of cement industry.

Addition of 2 wt% biochar utilization in concrete was found competent in terms of carbon adsorption potential and compressive strength. Addition of biochar more than 2 wt% has decreased the compressive strength of the concrete. However, it is interesting to note that despite the decrease in compressive strength on the 5 wt% biochar concrete sample, it still fulfilled the compressive strength requirement for residential concrete i.e., > 17 MPa (Nevada Ready Mix 2022). Moreover,10 wt% biochar concrete that has low compressive strength compared to plain concrete can be possibly utilized in other civil infrastructure where strength and durability considerations are less important than structural materials such as yard tiles, flowerpots, concrete bowls, door stop and so on to reduce the carbon footprint of construction industry.

In summary, it can be concluded that a ‘‘regulated amount’’ of biochar as replacement to cement in concrete not only improves the carbon sequestration potential but also the compressive strength of the concrete. The mix of biochar in concrete has achieved the objective of this research.

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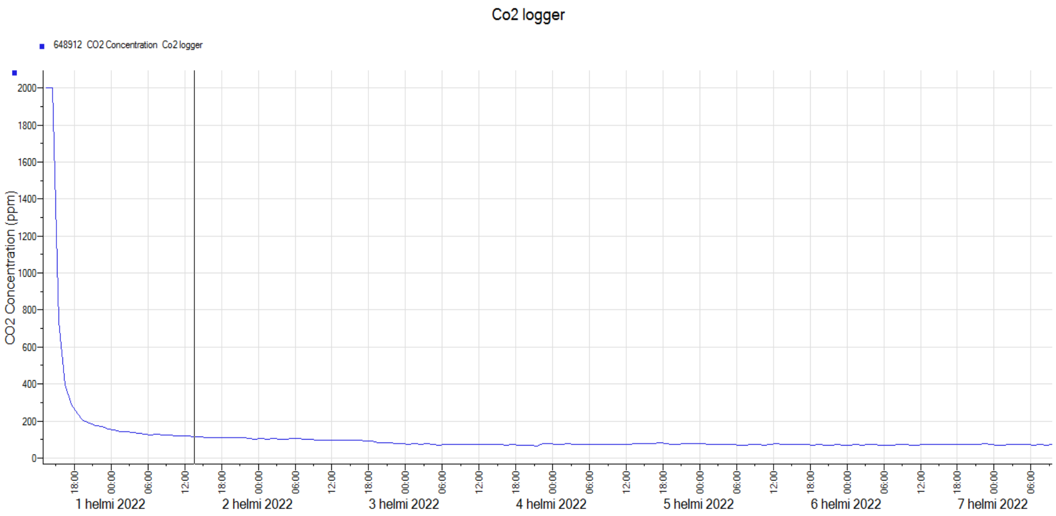
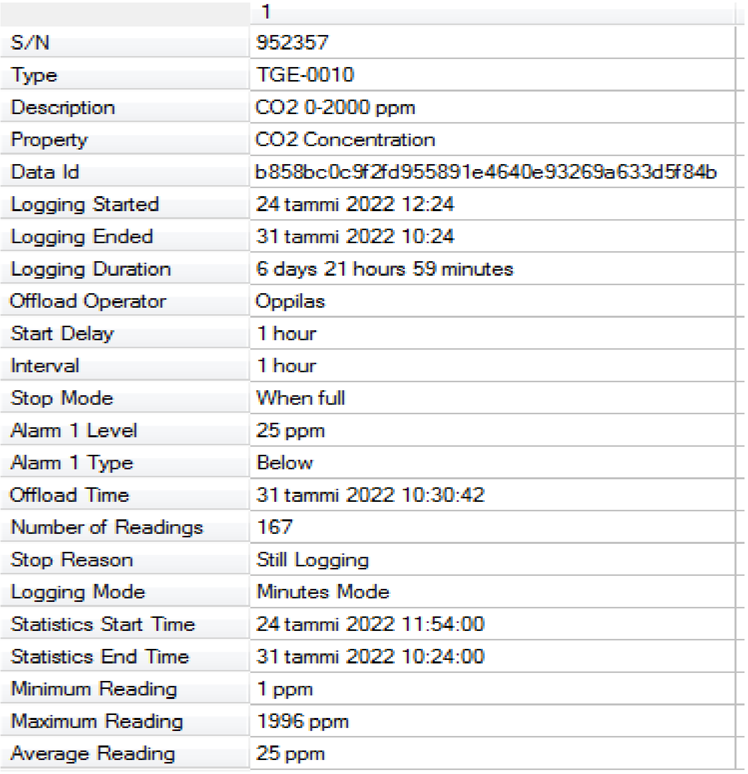
APPENDICES

Appendix 1/1

a. 0% biochar concrete CO2 adsorption result in a graph

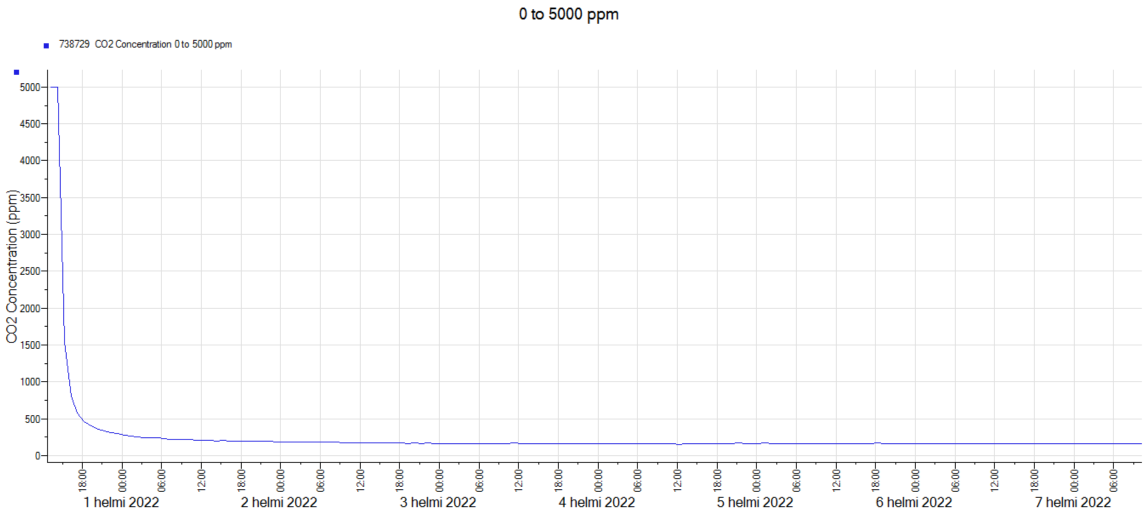


b. 0% biochar concrete adsorption CO2 adsorption result in a sorted table form

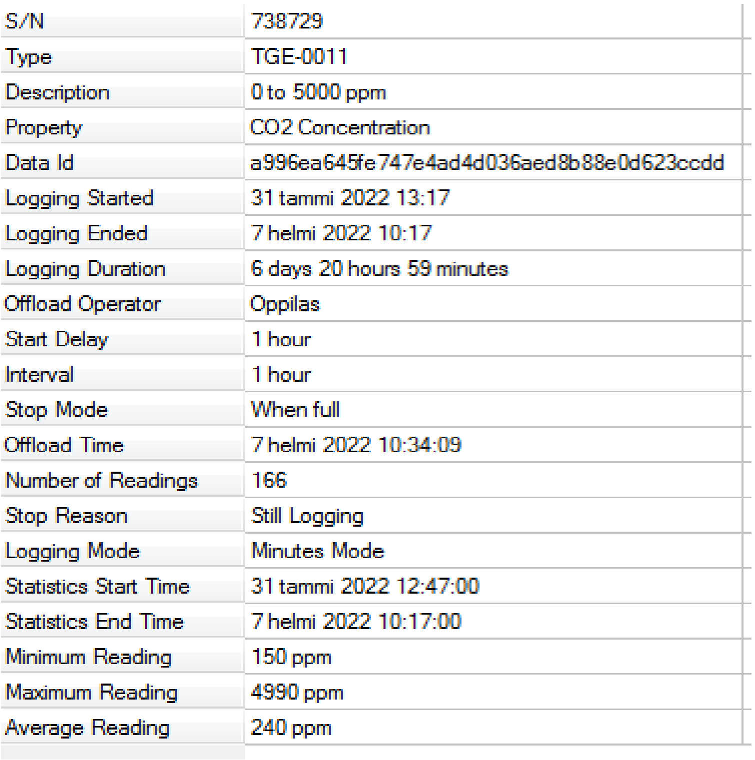


	1
S/N	952357
Type	TGE-0010
Description	CO2 0-2000 ppm
Property	CO2 Concentration
Data Id	b858bc0c9f2fd955891e4640e93269a633d5f84b
Logging Started	24 tammi 2022 12:24
Logging Ended	31 tammi 2022 10:24
Logging Duration	6 days 21 hours 59 minutes
Offload Operator	Oppilas
Start Delay	1 hour
Interval	1 hour
Stop Mode	When full
Alarm 1 Level	25 ppm
Alarm 1 Type	Below
Offload Time	31 tammi 2022 10:30:42
Number of Readings	167
Stop Reason	Still Logging
Logging Mode	Minutes Mode
Statistics Start Time	24 tammi 2022 11:54:00
Statistics End Time	31 tammi 2022 10:24:00
Minimum Reading	1 ppm
Maximum Reading	1996 ppm
Average Reading	25 ppm

a. 2% biochar concrete CO2 adsorption result in a graph

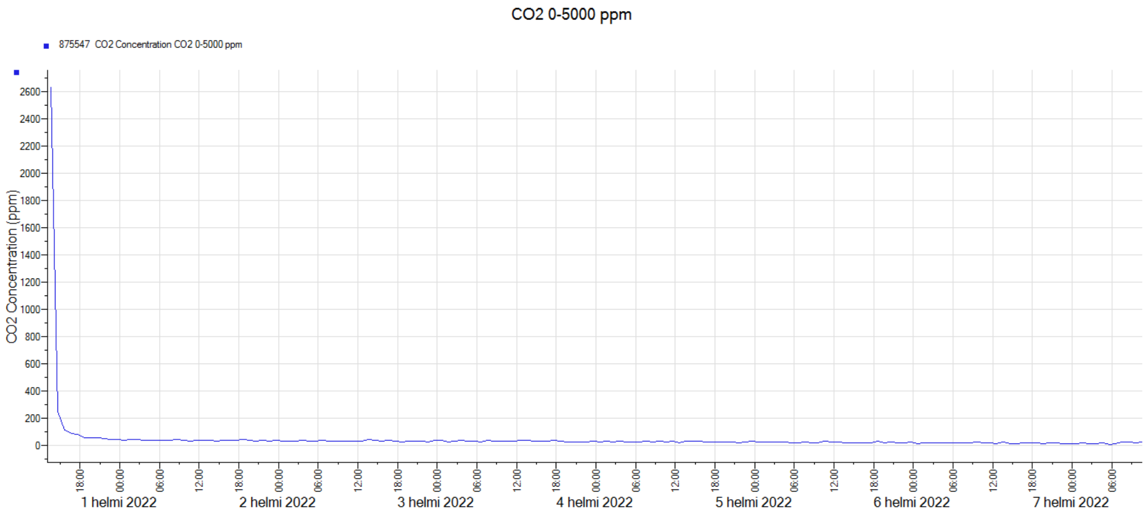


b. 2% biochar concrete CO2 adsorption result in a sorted table form

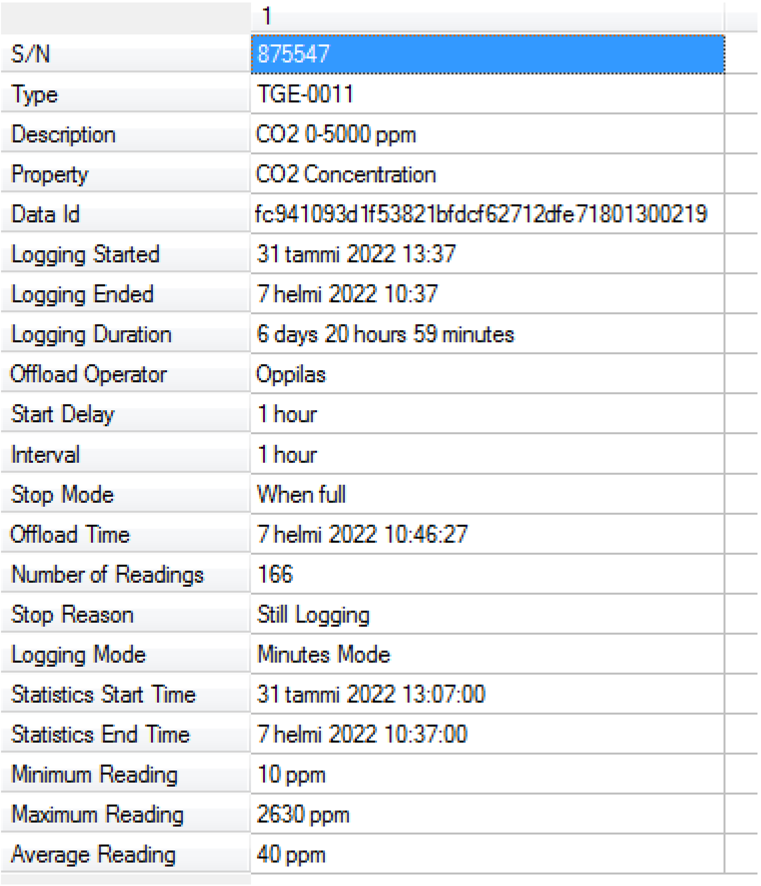


S/N	738729
Type	TGE-0011
Description	0 to 5000 ppm
Property	CO2 Concentration
Data Id	a996ea645fe747e4ad4d036aed8b88e0d623ccdd
Logging Started	31 tammi 2022 13:17
Logging Ended	7 helmi 2022 10:17
Logging Duration	6 days 20 hours 59 minutes
Offload Operator	Oppilas
Start Delay	1 hour
Interval	1 hour
Stop Mode	When full
Offload Time	7 helmi 2022 10:34:09
Number of Readings	166
Stop Reason	Still Logging
Logging Mode	Minutes Mode
Statistics Start Time	31 tammi 2022 12:47:00
Statistics End Time	7 helmi 2022 10:17:00
Minimum Reading	150 ppm
Maximum Reading	4990 ppm
Average Reading	240 ppm

a. 5% biochar concrete CO2 adsorption result in a graph

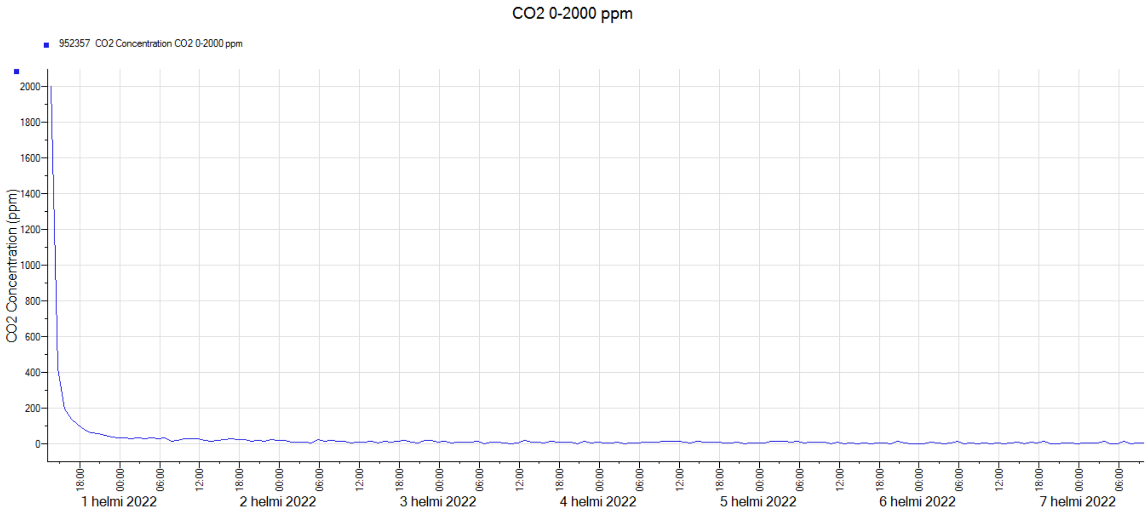


b. 5% biochar concrete CO2 adsorption result in a sorted table form

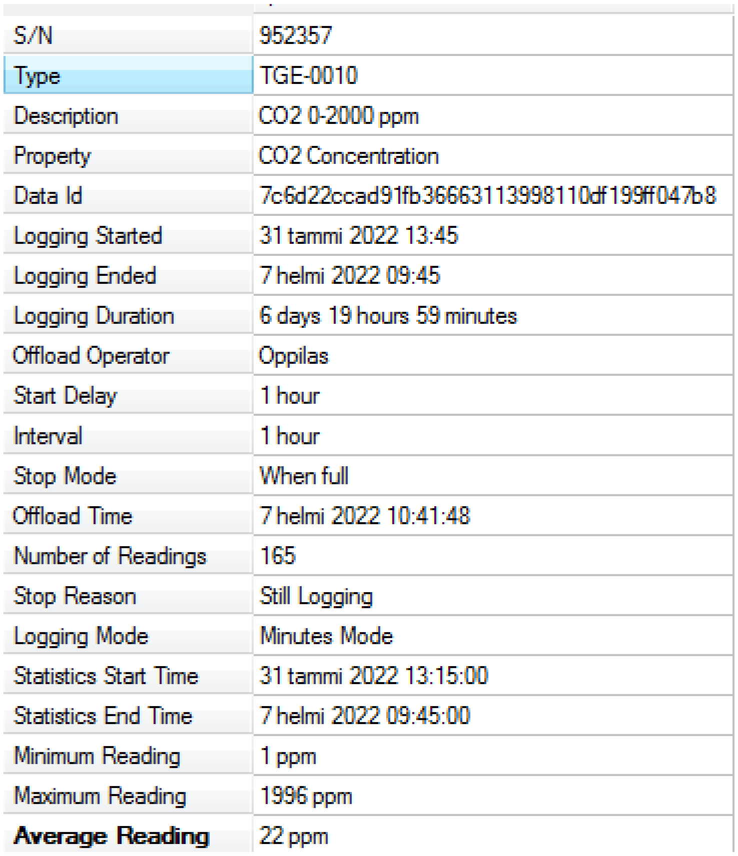


	1
S/N	875547
Type	TGE-0011
Description	CO2 0-5000 ppm
Property	CO2 Concentration
Data Id	fc941093d1f53821bfdcf62712dfe71801300219
Logging Started	31 tammi 2022 13:37
Logging Ended	7 helmi 2022 10:37
Logging Duration	6 days 20 hours 59 minutes
Offload Operator	Oppilas
Start Delay	1 hour
Interval	1 hour
Stop Mode	When full
Offload Time	7 helmi 2022 10:46:27
Number of Readings	166
Stop Reason	Still Logging
Logging Mode	Minutes Mode
Statistics Start Time	31 tammi 2022 13:07:00
Statistics End Time	7 helmi 2022 10:37:00
Minimum Reading	10 ppm
Maximum Reading	2630 ppm
Average Reading	40 ppm

a. 10% biochar concrete CO2 adsorption result in a graph



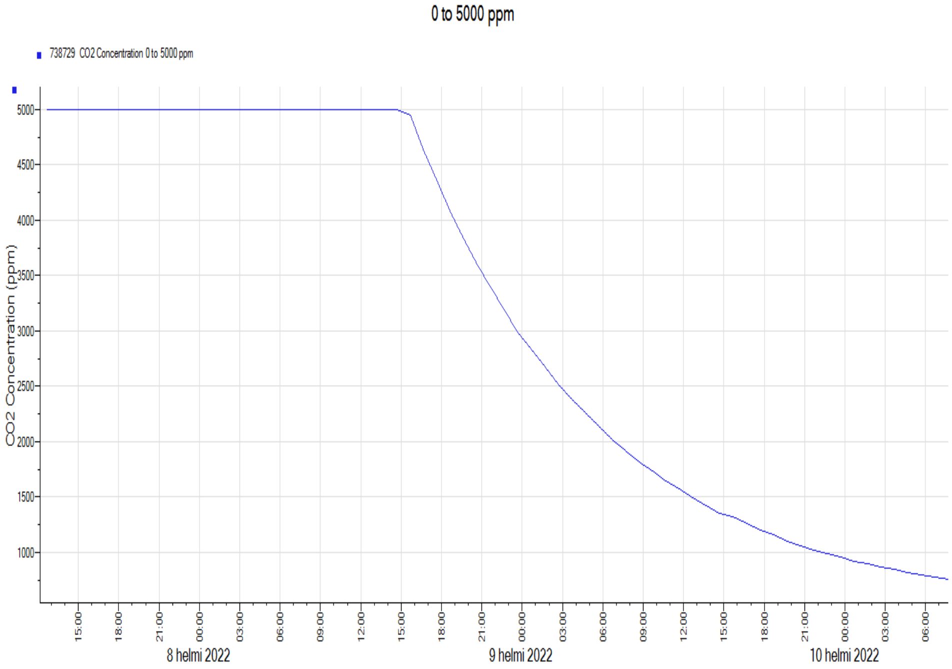
b. 10 % biochar concrete CO2 adsorption result in a sorted table form



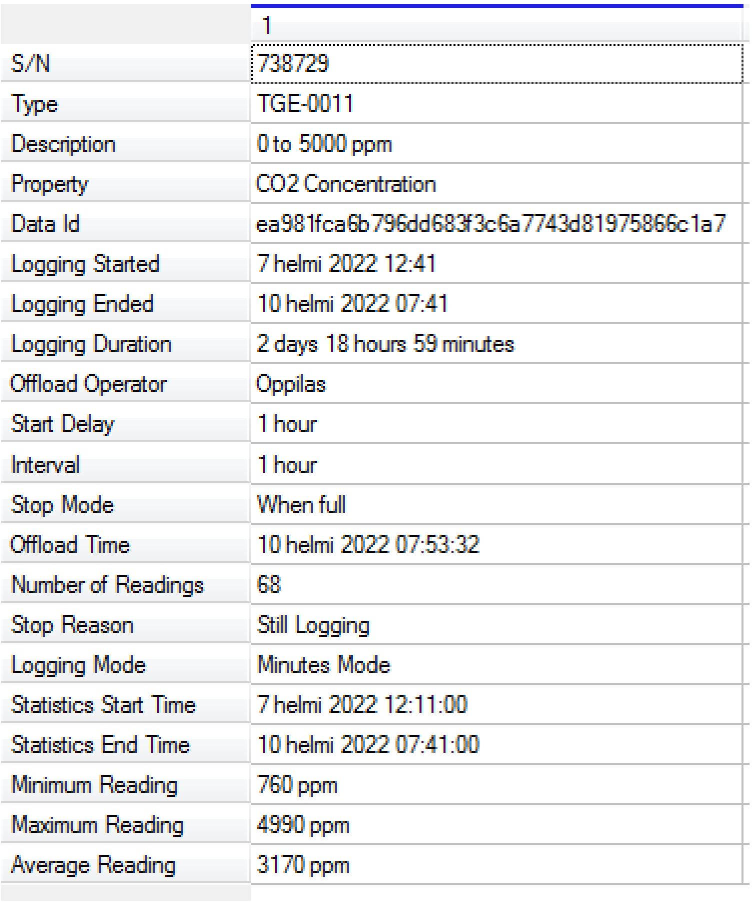
S/N	952357
Type	TGE-0010
Description	CO2 0-2000 ppm
Property	CO2 Concentration
Data Id	7c6d22ccad91fb36663113998110df199ff047b8
Logging Started	31 tammi 2022 13:45
Logging Ended	7 helmi 2022 09:45
Logging Duration	6 days 19 hours 59 minutes
Offload Operator	Oppilas
Start Delay	1 hour
Interval	1 hour
Stop Mode	When full
Offload Time	7 helmi 2022 10:41:48
Number of Readings	165
Stop Reason	Still Logging
Logging Mode	Minutes Mode
Statistics Start Time	31 tammi 2022 13:15:00
Statistics End Time	7 helmi 2022 09:45:00
Minimum Reading	1 ppm
Maximum Reading	1996 ppm
Average Reading	22 ppm

Appendix 1/5

a. Blank sample test result (Attempt 1)

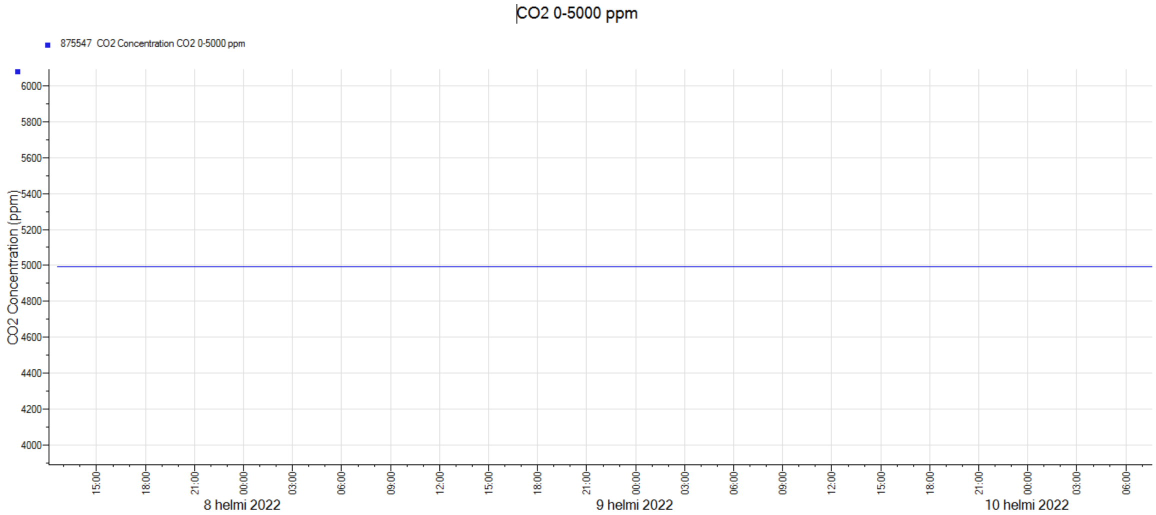


b. Blank sample test result in a sorted table form

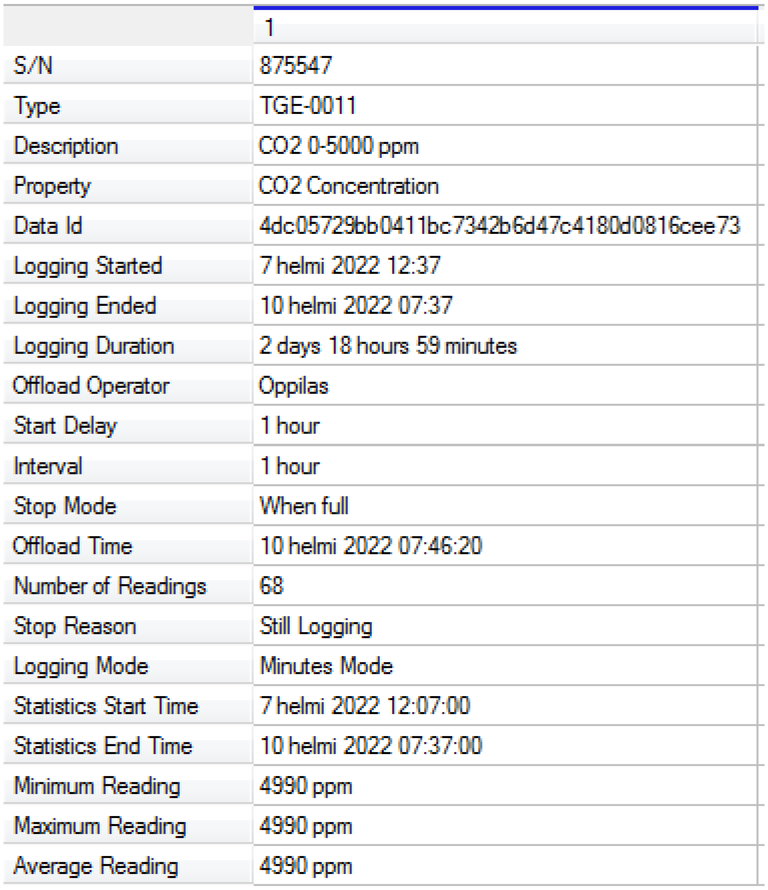


	1
S/N	738729
Type	TGE-0011
Description	0 to 5000 ppm
Property	CO2 Concentration
Data Id	ea981fca6b796dd683f3c6a7743d81975866c1a7
Logging Started	7 helmi 2022 12:41
Logging Ended	10 helmi 2022 07:41
Logging Duration	2 days 18 hours 59 minutes
Offload Operator	Oppilas
Start Delay	1 hour
Interval	1 hour
Stop Mode	When full
Offload Time	10 helmi 2022 07:53:32
Number of Readings	68
Stop Reason	Still Logging
Logging Mode	Minutes Mode
Statistics Start Time	7 helmi 2022 12:11:00
Statistics End Time	10 helmi 2022 07:41:00
Minimum Reading	760 ppm
Maximum Reading	4990 ppm
Average Reading	3170 ppm

a. Blank sample test result in a graph (Attempt 2)



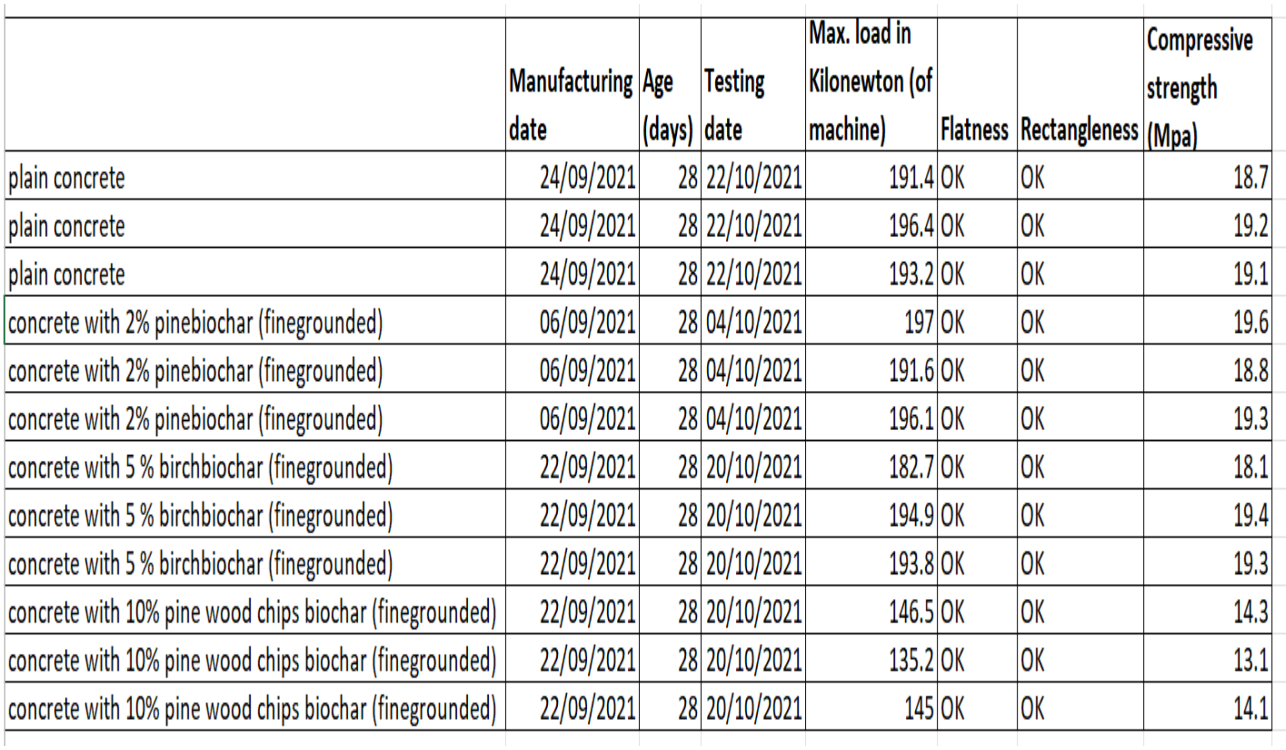
b. Blank sample test result in a sorted table form



	1
S/N	875547
Type	TGE-0011
Description	CO2 0-5000 ppm
Property	CO2 Concentration
Data Id	4dc05729bb0411bc7342b6d47c4180d0816cee73
Logging Started	7 helmi 2022 12:37
Logging Ended	10 helmi 2022 07:37
Logging Duration	2 days 18 hours 59 minutes
Offload Operator	Oppilas
Start Delay	1 hour
Interval	1 hour
Stop Mode	When full
Offload Time	10 helmi 2022 07:46:20
Number of Readings	68
Stop Reason	Still Logging
Logging Mode	Minutes Mode
Statistics Start Time	7 helmi 2022 12:07:00
Statistics End Time	10 helmi 2022 07:37:00
Minimum Reading	4990 ppm
Maximum Reading	4990 ppm
Average Reading	4990 ppm

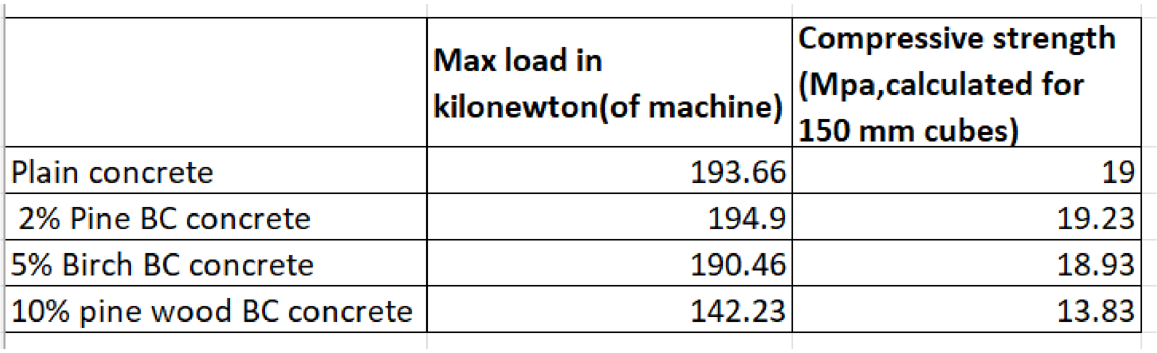
Appendix 1/7

a. Compressive strength test results of the specimen in Mpa,100 mm cubes.



	Manufacturing date	Age (days)	Testing date	Max. load in Kilonewton (of machine)	Flatness	Rectangleness	Compressive strength (Mpa)
plain concrete	24/09/2021	28	22/10/2021	191.4	OK	OK	18.7
plain concrete	24/09/2021	28	22/10/2021	196.4	OK	OK	19.2
plain concrete	24/09/2021	28	22/10/2021	193.2	OK	OK	19.1
concrete with 2% pinebiochar (finegrounded)	06/09/2021	28	04/10/2021	197	OK	OK	19.6
concrete with 2% pinebiochar (finegrounded)	06/09/2021	28	04/10/2021	191.6	OK	OK	18.8
concrete with 2% pinebiochar (finegrounded)	06/09/2021	28	04/10/2021	196.1	OK	OK	19.3
concrete with 5 % birchbiochar (finegrounded)	22/09/2021	28	20/10/2021	182.7	OK	OK	18.1
concrete with 5 % birchbiochar (finegrounded)	22/09/2021	28	20/10/2021	194.9	OK	OK	19.4
concrete with 5 % birchbiochar (finegrounded)	22/09/2021	28	20/10/2021	193.8	OK	OK	19.3
concrete with 10% pine wood chips biochar (finegrounded)	22/09/2021	28	20/10/2021	146.5	OK	OK	14.3
concrete with 10% pine wood chips biochar (finegrounded)	22/09/2021	28	20/10/2021	135.2	OK	OK	13.1
concrete with 10% pine wood chips biochar (finegrounded)	22/09/2021	28	20/10/2021	145	OK	OK	14.1

b. Average compressive strength test result of the specimen in Mpa,100mm cubes.



	Max load in kilonewton(of machine)	**Compressive strength (Mpa,calculated for 150 mm cubes)**
Plain concrete	193.66	19
2% Pine BC concrete	194.9	19.23
5% Birch BC concrete	190.46	18.93
10% pine wood BC concrete	142.23	13.83

Appendix 2

LIST OF FIGURES