SHORT TERM SCIENTIFIC MISSION (STSM) SCIENTIFIC REPORT

This report is submitted for approval by the STSM applicant to the STSM coordinator

Action number: CA17107
STSM title: Sustainable UV stabilizer for textile protection
STSM start and end date: 11/01/2021 to 22/01/2021
Grantee name: Laetitia Marrot

PURPOSE OF THE STSM:

The STSM aims at assessing the suitability of bio-carbon as UV stabilizer for the textile protection. Producing bio-carbon from agricultural and wood wastes is a way to provide added value to low-value by-products. In this project, bio-carbon will be produced from hemp stem residues (Cannabis sativa L.) issued from hemp farming. Hemp is an annual plant that grows under various climate and soil conditions. Hemp was selected because it is largely undervalued in Slovenia where the plant is grown for cooking and medicinal oil (cannabidiol), products extracted from the seeds and leaves. The hemp stem, including fibres and shives, represents about 70 % of the plant's dried weight and is likely to end up as low-value products or waste. The parameters used for the carbonization (under nitrogen atmosphere) process of biomass (particle size, gas environment, pyrolysis rate, heating duration and stages, final pyrolysis temperature, chemical and physical activation) have an influence on the bio-carbon structure and properties. Within the STSM, we will study several carbonization process parameters and we will perform an in-depth analysis of the effect of biomass carbonization processes on the strcutural and chemical properties of bio-carbon needed for UV protection. Potential for side applications like energy production will be considered as well.

DESCRIPTION OF WORK CARRIED OUT DURING THE STSM

Prior to the STSM, 10 bio-carbon samples have been produced at the InnoRenew CoE with a tube furnace following different processing routes. The size of the particles have been measured at the InnoRenew CoE. The samples have then been characterized by the following tests in the frame of the STSM at CIRAD:

- Moisture content, volatile and ash matters determination

The moisture, volatile and ash contents of the biochar materials were determined in accordance with the EN 1860-2 standard. The volatile matter of a fuel is the condensable and non-condensable vapor released when the fuel is heated.
For the moisture content (MC), 1.0 g of each biochar material was heated in the oven at 105°C until obtention of a constant mass. Then samples were cooled in a desiccator and their mass were measured to determine the moisture content.
For the volatile content, approximately 0.5 g of the oven-dried mass (Moven-dried) of each biochar materials was heated in an electric furnace for 7 minutes at 900°C without oxygen. Then samples were cooled in a desiccator and their mass were measured (MResidue). The volatile content was calculated as follows:
Volatile content (%)=[100×(M_(Oven-dried)-M_Residue)/M_(Oven-dried) -MC]×100/(100-MC)
For the ash content, approximately 0.5 g of the oven-dried mass (Moven-dried) of each biochar materials was heated in an electric furnace with air. The temperature was successively increased from ambient to 250 °C in 30 min, from 250 °C to 500 °C in 30 min, from 500 °C to (710 ± 10) °C in 60 min, and was maintained at 710 °C for 2 hours until obtention of a constant mass. Then samples were cooled in a desiccator and their mass were measured (Mash). The ash content was calculated as follows:

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Ash content (%)=[100×M_Ash/M_(Oven-dried)]×100/(100-MC)

- Elemental analysis (content of C, H, N and O)

Elemental analyses were carried out with an ElementarVario Macro tube CHN analyzer according to the ASTM D 5373 standard. Prior to analysis, the samples were packed in a tin foil and two tests were performed for each sample. Carbon, hydrogen and nitrogen contents were respectively determined using the quantification of CO_2, H_2O and N_2 (after reduction of NO_x) produced by the combustion of the samples. Oxygen content was calculated by difference, taking into account the ash content (%). Atomic H/C and O/C ratios of hemp and its biochars were determined from these measurements.

- Calorific Values

The calorific value was carried out according to the EN ISO 18125 standard, using an Automated Isoperibol Fixed Bomb Parr 6200 bomb calorimeter, under O_2 atmosphere to ensure the complete combustion of the sample. Higher heating value and Lower Heating Value were determined.

- UV ageing with xenon lamp at 254 nm for 24 and 72 hours
- Preliminary analysis of the effect of bio-carbon particles ageing were assessed through the measurement of the absorbance in the UV range with UV-VIS spectroscopy before and after ageing
- Two samples were left to the IEM lab in Montpellier to assess the feasibility of measuring pore volume and surface area by the adsorption-desorption technique with N_2 gas on a ASAP-2020 porosimeter from Microméritics.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

The hemp biocarbon materials were produced at the InnoRenew CoE by pyrolysis under an inert N_2 atmosphere. Several pyrolysis temperatures and heating rates were followed, as stated in the Table 1.

Table 1. Processing routes of the biocarbon materials.

Sample reference	Pyrolysis Temperature (°C)	Heating rate (°C/h)	Pyrolysis duration (min)
P600-R2000-T30	600	2000	30
P800-R2000-T30	800	2000	30
P1000-R2000-T30	1000	2000	30
P600-R2000-T60	600	2000	60
P800-R2000-T60	800	2000	60
P1000-R2000-T60	1000	2000	60
P400-R200-T30	400	200	30
P600-R200-T30	600	200	30
P800-R200-T30	800	200	30
P1000-R200-T30	1000	200	30

The compositions of the hemp biochars measured at the CIRAD institute indicated:
1) A clear augmentation of the fixed carbon (FC) content when the pyrolysis temperature was increased while the heating rate and the pyrolysis duration do not have a clear effect on the FC.
2) The ash contents varied between 6.8 and 11.7%. The ash content reflects the mineral matter in the samples. During its growth, the hemp plant absorbs in the soil metals such as copper, cadnium, lead, mercury, etc. The relatively high ash contents found in our biochars were believed to be due to the metal absorption during hemp growth. The blue color of the ashes (Figure 1) suggest the presence of copper in the soil.

Figure 1 Ashes from hemp biochars

3) The volatile content strongly decreased with the temperature increase up to 800°C and then stabilizes above 800°C. The volatile content decreased slightly with a higher heating rate at 600 and 800°C but this observation was not confirmed at 1000°C. The elemental analysis showed that the content of carbon increased at higher carbonization temperature while the contents of hydrogen and oxygen decreased. Losses in hydrogen and oxygen are linked to the breakage of large hydrocarbon molecules of biomass to form smaller molecules like water, carbon monoxide and dioxide and other liquid and gaseous $C_xH_yO_z$ compounds beside solid carbon during the carbonization.

The H/C and O/C ratios of the hemp biochar decreased when temperature increased, and variations were too low to conclude on the influence of the heating rate or pyrolysis duration. Low H/C and O/C ratios correspond to high HHVs. Indeed, the Higher Heating Values (HHV_{mf}) for all biochars are high (higher than 27 MJ/kg). As a comparison, the average HHV for crop biomass lays around 15 MJ/kg. For a same temperature, this thermal efficiency HHV seemed to slightly decrease for a higher heating rate.
Hemp stems carbonization showed great potential for its valorization in energy applications (400-600°C). Indeed, carbonizations at 400 and 600°C lead to very low H/C and O/C ratios, associated with high HHVs. The heating rate and pyrolysis duration did not show significant influence regarding the thermal efficiencies of the hemp biochars.

Biochars P400-R200-T30 and P1000-R200-T30 were chosen for their pyrolysis temperatures at 400 and 1000°C to undergo UV ageing. They were left under UV radiation at 254 nm for 24 and 72h. Their absorbance spectra in the wavelength range 300-800 nm were drawn on the Figure 2. The biochar carbonized at 400°C showed a higher absorbance than the one carbonized at 1000°C and the UV ageing increased their absorbances. This observation is promising for their use as anti-UV agents, since it means that their anti-UV property would not decrease during their service life.

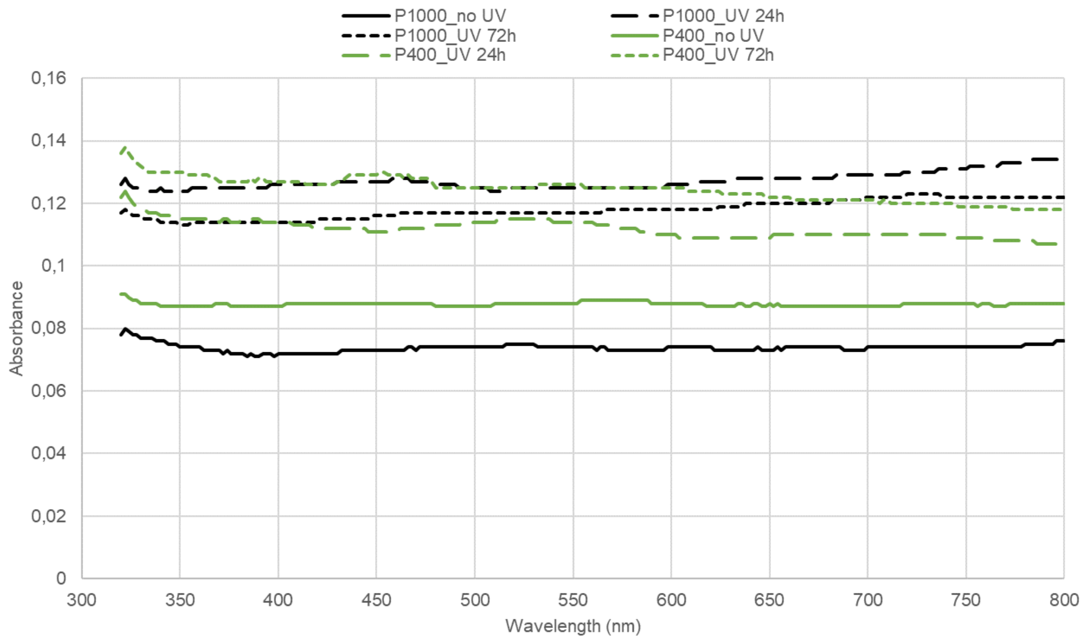

Figure 2 Evolution of the absorbance after UV ageing

The same biochars P400-R200-T30 and P1000-R200-T30 were characterized by gas porosimetry at the IEM institute. The absorption and desorption isotherms with nitrogen gas at 77K are presented on the Figure 3. Presence of micropores and mesopores is highlighted with the type IV isotherms. Surface areas of 4.1687 and 5.3416 m^2/g were found with BET method for biochar carbonized at 400 and 1000°C respectively. This is in good agreement with the pore openings brought by the pyrolysis temperature elevation. However, ultramicroporosity might not be accessible with N_2 and the use of CO2 gas is forecasted for further analysis.

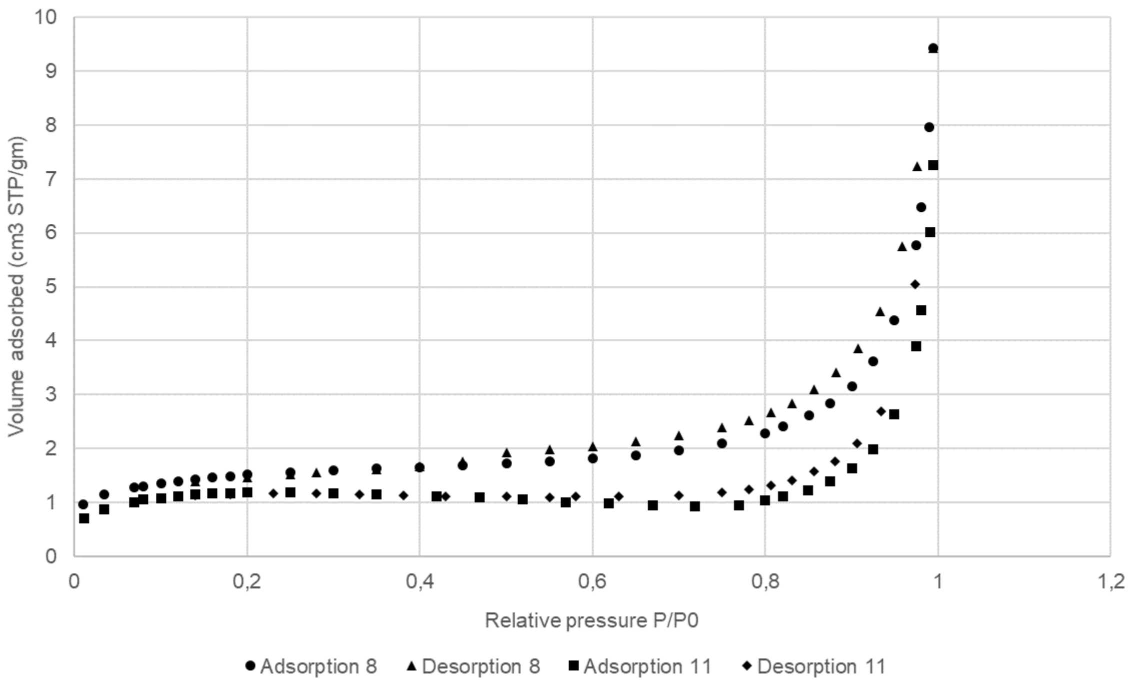

Figure 3 Absorption and desorption isotherms with nitrogen gas at 77K

Complementary experiments (analysis of chemical bonds and graphitic structure by FTIR, Raman and XRD spectroscopies are required to complete the assessment of the potential of hemp bio-carbons for UV protection. They will be carried out at the InnoRenew CoE in the near future.

FUTURE COLLABORATIONS (if applicable)

Other collaboratives experiments are still in progress:
- Mositure content determination, Proximate and ultimate analyses, volatile and ash matters of raw hemp stems, in order to asse the performance of biochar compare to thos of the natice biomass. These analyses are conducted at the CIRAD;
- Additional UV-Visible analyses will be carried out at InnoRenew CoE, on all biochar samples to observed the absorbance spectra in the wavelength range under 300 nm (UVA);
- CO_2 Absrpotion/ desorption to determine the porosity and specific area of the biochar will be carried out soon at InnoRenew CoE;
- FTIR, Raman and XRD spectroscopic analyses, carried out at InnoRenew CoE, will complete the structural analyses of each biochar according to the carbonization process conditions.

The use of hemp biomass and its biochars for energy production will be considered soon for a joint publication in the *Biomass and Bioenergy* journal or *Waste and Biomass Valorization* journal.

The InnoRenew CoE and the CIRAD institute plan to apply for the Proteus Program 2022 (PHC), which aims at developing scientific exchanges between France and Slovenia.