ContaminatEd land Remediation through Energy crops for Soil improvement to liquid biofuel Strategies

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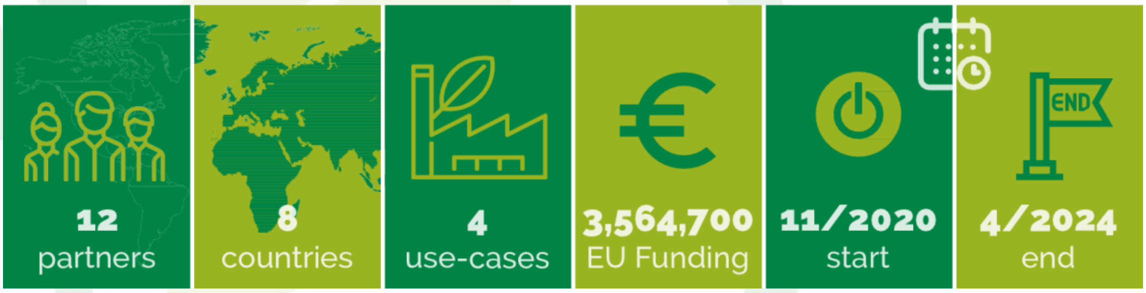
NEWSLETTER

Issue # 3 / December 2023

CONTENTS

1 INTRODUCTION - OVERALL PROJECT PROGRESS



CERESiS project being in its last year of implementation and nearly completed, has achieved significant progress in all three pillars. In terms of the phytoremediation pillar, additional fields have been planted with crops, and harvesting and analysis of the existing biomass species are being finalized. The biomass technologies that are being trialled, namely Supercritical Water Gasification (SCWG), Fast Pyrolysis, MILD Combustion and also, the cleaning and contaminant separation technologies, have shown interesting results and experiments are still running, while the optimization of the fast pyrolysis plant has been completed. The plant will be operated in the next months with many types of contaminated biomass samples to explore their potential in terms of biofuel production. Finally, the Decision Support System (DSS) architecture has been finalized and the focus now is on the development of the DSS platform that will support stakeholders with decisions on the pathways from phytoremediation to biofuel production. More updates are highlighted in the following sections, while the focus of the current Newsletter is on the CERESiS trialled technologies.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101006717

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Fonds Nouvelles frontières en recherche
New Frontiers in Research Fund

Fonds de recherche Société et culture Québec

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Remediation of large, contaminated areas can lead to the production of sustainable, non-iLUC, high quality and high value biomass for biofuels

2 PILLAR 1 – PHYTOREMEDIATION

The work is ongoing and the phytoremediation pillar is on track with 16 field and greenhouse trials planted, using soils from 9 contaminated and brownfield sites in UK, Italy, Brazil, and Ukraine. Furthermore, in the UK, endpoint soil and biomass analysis has been completed at the 4 new identified phytoremediation sites, with all biomass collected to indicate yields and provide contaminated biomass samples for downstream processing. In Brazil, partners are currently carrying out the final harvest and analysis of the soil, biomass, and roots, while information and data have been already provided for the development of the Decision Suppport System. Finally, endpoint analysis of soil and biomass, in experimental and biomass production areas, is nearly completed in Italy, while research for data from phytoremediation trials and use cases (4 identified so far) is ongoing.

3 PILLAR 3 – DECISION SUPPORT SYSTEM

After concluding the CERESiS DSS architecture the focus has been on developing the CERESiS DSS platform. The CERESiS DSS platform is designed as a cloud-native web application that will support decisions on defining, assessing, and optimizing complete pathways from phytoremediation to biofuel production, including partial pathways, depending on the particular interest and requirement of the potential DSS users. At the moment the work is focused on developing the first version of the CERESiS DSS platform and more specifically integrating the supply chain optimization solution, the multi-criteria decision analysis and also developing the Machine Learning models that will support decision support process.

4 FOCUS ON THE TRIALLED TECHNOLOGIES

Supercritical Water Gasification

In the CERESiS project contaminated biomass is converted to a useful biofuel or biofuel precurson, in particular to Fischer-Tropsch fuel. In order to obtain a useful biofuel, a number of process steps need to be conducted. Firstly, the biomass is processed through gasification, since in general, in gasification processes contaminants can be separated, so that they cause no issue in further process steps. In this case the supercritical water

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gasification is used. These experiments are conducted at KIT. This process is operated at high temperatures and pressures and it only requires water as a reactant. Under the chosen conditions the water breaks the biomass down to form gaseous products. This product gas can then be further processed. It needs to be cleaned from compounds like H2S. In CERESiS, this is realized with a Membrane Gas Absorption, where the H2S is separated through a membrane. The cleaned product gas can then be further reformed so that it can serve as a feed for the Fischer-Tropsch synthesis. The Fischer-Tropsch synthesis turns the reformed gas in liquid products, like kerosene, diesel or gasoline. As a last step, these liquids are separated in a distillation column to obtain a clean fuel.

Throughout the past 2.5 years the SCWG process has been successfully developed at KIT, so it is now suitable for the chosen (often dry) biomasses. Throughout the project, the laboratory plant has been reconstructed several times to overcome some experimental issues, like salt and coke formation and low gasification efficiencies. Learnings that can be drawn from the past experiments are:

- Process effluent can be recycled to significantly reduce the needed amount of fresh water.
- Process effluent can be free from heavy metals.
- Little differences in the gasification of the different CERESiS biomasses are observed. Thus, the SCWG process is equally suitable for all of them (independent of lab-plant configuration).
- Salt and coke deposition can limit the operation duration. This issue can be overcome with appropriate process design.

The final lab-plant configuration consists of a two-stream concept where the cold biomass slurry is heated by mixing it with hot supercritical water. In this configuration, long term operation of more than 100 hours and carbon gasification efficiencies of about 97% could be reached.

Fast Pyrolysis

Fast Pyrolysis (FP) is used in the CERESiS project for the production of biofuels and biofuel precursors from contaminated biomass. FP process is used for the conversion of the organic contaminants and the separation or confinement of the inorganic contaminants in a concentrated form.

CERESiS partner, CNR, performed preliminary experiments to assess the performance of the Fast Pyrolysis reactor for bio-oil production. Based on the results obtained, the plant has been upgraded by increasing the power supplied in order to achieve high temperatures (up to 600 °C) and faster heating rates.

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An experimental campaign was started to define the optimal operating conditions of the FP reactor. Phalaris from the University of Tuscia (UoT) was selected as feedstock for assessing the need of feedstock pre-treatments, drying and palletization. The results showed that bio-oil yield was not affected by drying and pellettization, however bio-oil quality in terms of water and solid content was improved by drying and pellettization, respectively.

Phalaris from UoT and Willow from the University of Strathclyde (UoS) were used to run experiments at different pyrolysis temperature (450-600 °C) to identify the optimal value in terms of bio-oil yield, which is set between 500 and 600 °C. Currently, the investigation on the effect of carrier gas flow rate and solid residence time is ongoing.

Finally, five kg of bio-oil have been produced using Phalaris received from UoT and delivered to CERTH for microfiltration experiments aimimg at reducing the solid content, whereas 2 kg of biochar obtained from Phalaris was delivered to UoS for agronomic experiments.

MILD combustion

Bio-gas produced through bio- or thermo-chemical conversion of biomass unquestionably occupies a relevant role in the framework of maximizing sources renewability and the storage capacity of renewable energy. However, biogases are characterized by very low heating values (LHV), due to high dilution levels in inert species. Their direct utilization in conventional systems for heat and power is not feasible as classical flame structures (premixed/not-premixed) are not sustainable. It comes that novel combustion technologies have to be resorted to. In this respect, MILD Combustion (Moderate or Intense Low oxygen Dilution (MILD) combustion, Cavaliere and de Joannon, 2004[1]) is one of the most attractive. It relies on mixtures highly diluted (close or outside flammability limits) and pre-heated through the recirculation of hot exhausted gases towards the fresh reactants.

In CERESiS, the MILD combustion concept was exploited for several biogases, characterized by very low LHVs, from pyrolysis (under different conditions) of different biomasses. Experiments were carried out in a Laboratory Unit Cyclonic burner (LUCY), conceived and designed by CNR. The basic concept of LUCY is to achieve MILD combustion conditions through a tailored cyclonic flow field, that allows for a continuous preheating and dilution of incoming reactants.

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[1] Cavaliere, A., & De Joannon, M. (2004). Mild combustion. *Progress in Energy and Combustion science*, *30*(4), 329-366

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The experimental tests were realized for biogas/air mixtures, changing the mixture equivalence ratio while valuing process stability and pollutants emissions (i.e CO, NO_x). The biogas Low Heating Values (LHV) was parametrically decreased, to define the minimum LHV still compatible with MILD combustion benefits. Analyses were started with a pyrolysis gas with a characteristic LHV=8MJ/Kg. Traditional hydrocarbons have much higher values, for instance methane LHV is equal to 55 MJ/Kg.

Results clearly indicated that the MILD combustion was feasible and stable, with CO and NO emissions well below emission limits. Further analyses have demonstrated that MILD combustion can efficiently treat bio-gases with LHV=3 MJ/Kg, if external pre-heating (easily implementable through heat recovery systems from exhausted gases) of air is applied. The overall outcome is that MILD combustion is the key technology to burn efficiently low-grade biogases with exceptional low pollutant emissions.

Cleaning technologies

A hybrid **Electrocoagulation-Electrochemical Oxidation** process has been developed and tested by the Natural Resources and Renewable Energies Lab of CPERI/CERTH which has shown great potential for the treatment of the highly saline wastewater from the SCWG process. This integrated approach combines the advantages of electrocoagulation and electrochemical oxidation to address the unique characteristics of high salinity wastewater. In the electrocoagulation stage of the hybrid process, sacrificial anodes are employed to generate metal ions in the wastewater. These metal ions undergo electrochemical reactions and form hydroxide flocs that contribute to the coagulation and precipitation of heavy metal ions. After electrocoagulation, the wastewater enters the electrochemical oxidation stage. In this phase, a suitable anode material is used to generate strong oxidizing agents such as hydroxyl radicals (•OH) or other reactive species. These oxidants have strong oxidative capabilities and can effectively degrade complex organic molecules, including organic compounds associated with heavy metals. Electrochemical oxidation contributes to the further removal and degradation of organic contaminants, increasing overall treatment efficiency and reducing the potential toxicity of heavy metals. The NRRE laboratory systematically investigated the performance of electrocoagulation flotation (ECF) and electrochemical oxidation (EO), both individually and in combination, using ECF and EO laboratory pilot units designed and constructed in-house. Experiments were conducted with simulated and real SCWG brines, to determine the near-optimal operating conditions (current density, electrolysis time, pH) for effective removal of heavy metals (lead) and organics (phenol) with minimal energy consumption. Based on the promising results and novel features of the combined ECF/EO process, the NRRE lab is continuing the research and development work in this field to further optimize the hybrid process and expand its application in pollution abatement and zero-liquid discharge of high-salinity wastewater.

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The **ceramic microfiltration (MF) membrane separation** process is systematically investigated by NRRE/CPERI/CERTH for the upgrade of the bio-oil derived from the liquid product of the FP process. Specifically, two different experimental campaigns have been performed with the aid of a fully automated laboratory pilot MF unit, designed, and constructed in-house at NRRE/CPERI/CERTH. Initially, different commercially available tubular ceramic membranes of nominal pore sizes (e.g., 0.5 to 1 μm), that are stable in a hot, pressurized bio-oil feed, were tested for the removal of undesirable heavy metal-laden char particles (less than 10 μm in size), which can be detrimental for further refining operations. Next, with the aid of ARTEMIS laboratory of CPERI/CERTH, selected ceramic membranes were modified by altering the hydrophobicity towards an effective water and solid (bio-char) particles separation. The main challenges in this investigation are a) to understand, quantify and reduce membrane fouling, and b) to deal with highly viscous liquid streams. Special attention is given to fouling analysis from longer runs of bio-oil through the membranes to determine the predominant fouling mechanisms. This will help propose measures for fouling mitigation and overall process optimization.

A hybrid **Membrane Gas Absorption (MGA)** technology has been developed and evaluated by the ARTEMIS Lab of CPERI/CERTH in order to upgrade the SCWG gas effluent, by removing H_2S and/or CO_2 from the gas mixture, and prepare it for further processing. The technology combines the advantages of conventional gas absorption with that of novel membrane technologies, providing a compact, modular, flexible and highly efficient method for gas treatment in small to medium scale, decentralized applications. The experimental results revealed that the proposed technology can effectively remove the H_2S and CO_2 from the gas stream, recovering at the same time almost 100% of the other valuable components of the gas stream (H2, CH4, CO, etc.), and reducing the installed equipment's footprint by almost an order of magnitude compared to the conventional technologies.

5 DISSEMINATION ACTIVITIES

Dissemination activities are an integral part of the CERESiS project as they ensure the visibility of the project results. It is among the project's main concerns to ensure that the generated information will reach industrial, political, and social stakeholders in an effective manner. The CERESiS dissemination strategy ensures that the key messages are sufficiently highlighted and effectively communicated towards appropriately targeted stakeholders.

In an attempt to spread the word about CERESiS to potential stakeholders and the wider audience, there is a continuous effort to communicate the latest updates, results and knowledge gained through the project's communication means (e.g., social media). Within the last year of project implementation, CERESiS partners have actively participated in

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various dissemination activities, such as conferences, events, workshops, and webinars. More specifically, CERESiS participated in 10 conferences including the EUBCE 2023, the EGU 2023, Pyroliq II, Joint Meeting of the Belgian and Italian Sections of The Combustion Institute, the 15th International Conference on Combustion Technologies for a Clean Environment, the 2nd International Conference on Sustainable Chemical & Environmental Engineering, the 38th International Conference on Geochemistry and Health, the 4th Conference on Sustainable Supply Chains (SustSC 2023), the 15th International Conference on Combustion Technologies for a Clean Environment, and the World Sustainable Energy Days (WSED-2023). Furhtremore, a webinar was organized in collaboration with the two siste projects, GOLD, and Phy2Climate, focusing on phytoremediation with energy crop for biofuel production, where CERESiS partners present the research accomplished and the latest findings. In addition, CERESiS participated ina clustering event, organized by CINEA in an attempt for CERESiS to set up collaboration and create synergies with other similar projects.

In an effort to capture the latest knowledge gained, additional scientific papers have been created and published covering the Supercritical Water Gasification experiments, by CERESiS partner KIT. Finally, during the project's 4th physical meeting at CNR, in Naples, shooting of short videos of each partner, talking about their work and contribution to the project, were scheduled, to act as an additional dissemination and communication activity. The videos can be fund in the project's website under the News and Events section, and in CERESiS YouTube channel.

Energy crops can be a suitable and effective solution for contaminated land remediation, exhibit high mass productivity and lead to sustainable biofuel production when coupled with appropriate conversion processes

For further information

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