Hydrothermal Processing for Biomass Conversion from Wetland Engineered Wastewater Treatment Systems [Willow-*Salix viminalis*].

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Introduction and study objectives

Evaporative willows-based systems are increasingly being used in wetland-engineered systems to treat nutrient-rich wastewater due to their natural capacity to translocate minerals and metals contained in the wastewater. Studies have confirmed that the nutrients supplied by the influent wastewater are effectively translocated and are accreted in the willows as biomass (i.e., the composition of the wastewater corresponds to the willows' nutrient requirements). Willow systems are mostly designed to treat all the influent water through evapotranspiration, so there is no outflow from the system. Additionally, there are also willow systems that combine percolation with evapotranspiration or that are designed as flow-through systems that produce some outflow, which is used for the recovery of resources, such as nutrients and reclaimed water for irrigation.

This application allows addressing environmental concerns related to wastewater management and, at the same time, achieving higher biomass yields. However, the end-use of this lignocellulosic biomass is often simple incineration for the production of heat and power. In contrast, producing platform chemicals from lignocellulosic biomass using hydrothermal processes has grown into a central point of interest due to the limited availability fossil resources coupled to reduce the carbon footprint of such products. Platform chemicals have a key role in a bioeconomy, which aims to replace fossil carbon sources with biomass. For instance, Furfurals are special bio-based platform chemicals because they have a wide range of application and can be produced exclusively by thermochemical conversion routes. The most important members of furfurals are 5-Hydroxymethylfurfural (HMF) and furfural. Furfural is derived from pentoses (which can be obtained from hemicelluloses). Recent studies confirmed that the HMF formation comes mainly from the dehydration of C6-sugars (hexoses and their polymers, which also includes cellulose) in the furanose form.

Therefore, as an alternative to the simple incineration of the willow-system biomass, the present on-going project aims to study the biomass, grown on wastewater irrigated willow fields (*Salix viminalis)*, as the feedstock of a hydrothermal process to study the yields of platform chemicals and the production of HTC-Hydrochar (i.e., low-temperature hydrothermal carbonization).

Methodology

This project has two objectives, the first aims to gain a better understanding of the yields and factors affecting the generation of platform chemicals (i.e., 5-hydroxymethylfurfural, furfural, acetic acid, formic acid and levulinic acid) under subcritical water conditions (SCW; below the water critical point 374 °C and 25 MPa). Secondly, the project aims to study the effects of low-temperature hydrothermal carbonization (HTC). Our experimental design focuses on the willow-biomass-derived HTC-carbon material. Hydrochar is our desired product in the HTC process with an estimated mass yield of about 40–70%. Hydrochar, resulting from the carbonization of willows might have the potential to be used as an adsorbent in environmental remediation applications, a novel carbon material, a storable solid fuel for energy generation (via co-combustion or use in carbon fuel cells), and possibly as a soil amendment. The concept of biochar (terminology commonly used to denote char application in soils) as an approach to carbon sequestration, as well as increasing soil fertility, raising agricultural productivity, and reducing pressure on forests, has received increasing attention over the past few years.

The experimental design will firstly determine the composition of cellulose, hemicellulose, and lignin content in the willow-biomass (extractives of hexoses, pentoses, and lignin - NREL/TP-510-42618). The project will use Swagelok-batch reactors to react water with the biomass (*Salix viminalis*). The reaction without catalyst (170 °C to 275 °C and 0 to 30 min reaction time) will take place in an OMEGA FSB-3 fluidised sand bath via a steel chain linked to the reactor with a carabiner. A thermocouple inside the reactor will monitor the temperature inside the reactor. HPLC and GC-MS will be used for the analytics. In the solid fraction Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) will be used to measure nutrients and heavy metals like Pb, Cd, Cr, Cu, Zn, As, Ni, Ag. Analysis of the high calorific values of the Hydrochar will also be performed.

Results and conclusions

The end-use of the lignocellulosic biomass produced in willow systems is often simple incineration for the production of heat and power. To diversify the uses and to identify potential and limitations with innovative developments in hydrothermal processing, fundamental research to study the reactions of willow (*Salix viminalis)*, under subcritical conditions is necessary for determining comparative data among different lignocellulosic biomasses and treatment conditions.

Currently, we are performing the willow characterization and yield determinations that will be presented at SuWaNu Europe – International Conference. We aim to present the hydrothermal processing as an innovative technology to close the loop between water reuse but also to use the biomass produced in wetland-engineered systems.