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Research paper

Biocrude production and nutrients recovery through hydrothermal liquefaction of wastewater irrigated willow

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A B S T R A C T

Willows are increasingly used as natural filters to treat nutrient-rich wastewater. Their natural tendency to absorb minerals is exploited both for the nutrients and the metals, which are contained in the wastewater. 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 biomass is often a simple incineration for production of heat and power.

The present study proposes, alternatively, to use willow biomass, grown on wastewater irrigated fields, as feedstock for the hydrothermal liquefaction process. The thermochemical conversion route allows the valorization of the organic fraction of the biomass into a biocrude oil, and simultaneously collecting and preserving the inorganic elements in the effluent products.

The willow was converted at supercritical water conditions (400 °C) for 15 min in a micro-batch reactor (10 cm^3), and high mass yields (39.7%) of energy dense (38.6 MJ kg^{-1}) biocrude oil were obtained. It was found that most inorganics, including phosphorus (76% of total P on a mass basis), are mainly transferred to the solid products. The concentration of the elements in the solids eases their recovery and re-use for soil amendment. A different tendency was observed for potassium and sodium, which were almost exclusively collected in the aqueous phase (above 88% for both K and Na on a mass basis). Significant quantities of nitrogen and sulfur, and some metals, were transferred to the biocrude oil, however its quality resulted overall unaffected.

1. Introduction

The use of renewable energy sources for the production of fuels and chemicals is increasingly required as fossil reserves are depleting, and because of environmental concerns arising from fossil fuels usage [1]. Lignocellulosic biomasses (i.e. poplar and willow) are commonly grown in Short Rotation Coppice (SRC) as renewable carbon source to produce heat and power. In particular, willow is a fast growing plant, easily adaptable to various climates and soils, and can lead to high biomass yields per hectare of cultivation [2]. Willow plants find application also in the phytoremediation of metal polluted soils, where their natural capacity of up-taking elements through their roots is exploited for remediation of heavily contaminated lands [3–5]. Using willow as vegetation filter, for cleaning of wastewater, has been demonstrated to be a good alternative for waste management and to have an increased biomass production with no further costs for fertilizers [6]. Studies have investigated different wastewater streams: groundwater [7], municipal wastewater [8], or agricultural drainage water [9].

Every two to four years SRC willow crops are cut, and the biomass is mainly used for heat and power production. Heavy metals, absorbed by willow biomass during phytoremediation processes, are primarily recovered in the ashes after combustion [10], and some technologies have also been developed for their separation [11]; in contrast, a great portion of nitrogen and sulfur is irreversibly lost during combustion [12].

Willow biomass can also be used as lignocellulosic feedstock for biofuel production in thermochemical processes like Hydrothermal Liquefaction (HTL). HTL is a high pressure, medium temperature process, where various biomasses or organic waste sources are processed in the presence of water to produce an energy dense oily product, named biocrude, along with an aqueous phase, some solids, and gases [13]. HTL is an energy-efficient technology (85% of the energy in the feedstock is recovered in the biocrude). In continuous HTL processing, the feedstock can be efficiently converted into biocrude (45%, mass fraction of the dry ash free feedstock) [14]. In some studies, willow wood has already been investigated as a raw material for hydrothermal

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processing, for example with focus on the dissolution mechanism [15] or its application in a continuous bench scale reaction unit [16].

A new concept is proposed in this work, where the wastewater is used to grow willow trees, which are then converted by HTL to biocrude while nutrients are recovered simultaneously from the aqueous and solid by-products. Biocrude oil can be upgraded to meet drop-in fuels properties, while the nutrients could be re-utilized as fertilizers for agricultural lands.

Recycling of nutrients for cultivation of algae by recirculation of the aqueous phase produced from HTL [17,18] or hydrothermal gasification [19] of algae has been previously studied in literature. Moreover, few other studies were found on the fate of nitrogen [20] and other inorganics [21] in hydrothermal carbonization. Ekpo et al. [22] have investigated the inorganics in the solid residues and the nutrients in the water phases from hydrothermal processing of microalgae, manure and digestate at various temperatures. Lu et al. [23] have similarly looked into the inorganic content of aqueous and solid residues after HTL of human feces in subcritical water conditions. Carrier et al. [24], studied the effect of temperature on the inorganics redistribution after sub- and supercritical hydrothermal liquefaction of uncontaminated and As-contaminated fern biomass.

The aim of the present study was to understand the fate of nutrients and metals after HTL of willow, grown with wastewater, in supercritical water conditions; and ultimately to define the distribution of the inorganic elements among the different product phases from HTL, including the biocrude. Furthermore, it was investigated whether the quality of the oil was eventually affected by the presence of inorganics.

2. Materials and methods

2.1. Feedstock characterization

The raw material used in the HTL experiments is willow wood, clone variety Björn (Salix schwerinii x Salix viminalis), which has been developed in particular to get high biomass-yields and a high nutrient-uptake. The biomass was grown at Center for Recirkulering (Denmark, 55.831485, 8.635960), and it was irrigated with untreated household wastewater and sewage from local houses for two years. Two-year-old stems of fifteen-year-old roots were provided for the experiments. Stems were 25–30 cm long, with a diameter of 1–2 cm, and with bark. In order to ease the reactor loading, the willow stems including bark were chopped and further ground to sawdust with a particle size below 0.5 mm, in a cyclone mill (Foss, Cyclotec 1093). After the milling, the willow was characterized in terms of moisture content, ash content, and elemental composition, and the average results from the measurements are reported in Table 1. The moisture mass fraction of the willow sawdust was measured in a moisture analyzer (Kern, MLS) at 120 °C. The ash mass fraction was instead determined after holding pre-dried samples isothermally at 775 °C for 3 h in an electric muffle furnace (Protherm Furnaces). The TG curve of the willow biomass obtained by Thermo-Gravimetrical Analysis, confirmed both the moisture mass fraction (~5%, at 100 °C) and the ash mass fraction (< 1%, see Fig. 1).

Inductively Coupled Plasma (ICP) analysis was used to investigate the presence of nutrients and heavy metals in the willow biomass, and the average concentrations of the investigated inorganics are reported

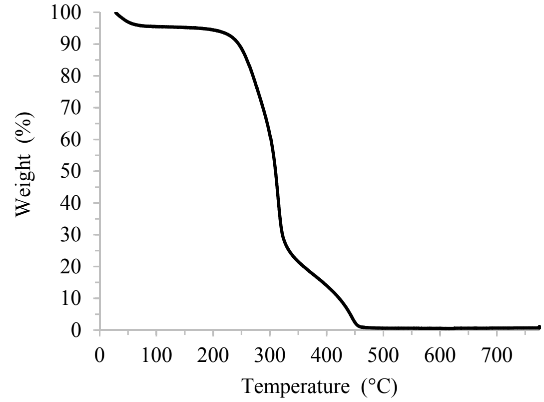

Fig. 1. Thermogravimetric curve of the willow wood.

in Table 2. Calcium and potassium are the most abundant inorganic source, while the presence of phosphorus, sulfur, magnesium, and iron is significant as well. The mass fraction of inorganics investigated by ICP sums up to 0.38%, therefore the rest of the inorganics should be attributed to the elements as aluminum, lead or nickel, which are highly abundant in wastewater [25].

2.2. Experimental procedure for HTL experiments

HTL experiments were carried out in stainless steel micro-batch reactors with 10 cm^3 volume. A total of three experiments were carried out under the same process conditions, and the average results are reported together with the standard deviations. A homogeneous slurry (7 g) was prepared by adding distilled water to the willow sawdust. The high biomass loading into the feed, corresponding to a mass fraction of 20% on a dry basis, is expected to additionally cause a relatively high biocrude yield. At the same time it will enable a smooth pumpability of the slurry when operating in a continuous system.

Potassium carbonate (K_2CO_3) was added to the feed mixture (2.5% in weight of the water-biomass mixture), as alkaline conditions promote biocrude oil production, reduce coke formation [26], and enhance the de-oxygenation of lignocellulosic biomass leading to biocrudes with lower oxygen content [27].

Reactors were sealed, purged with nitrogen to remove residual air, and then pre-pressurized to 2 MPa to push the slurry down into the reactor volume. Without pre-pressurizing, accumulation of the slurry in the upper capillary section of the reaction system [28] was observed, causing undesirable, unconverted material to appear in the products.

The biomass was converted at supercritical conditions; in this region, the thermo-physical properties of water are enhanced. The dielectric constant is significantly reduced and consequently water becomes a non-polar solvent in which organics can easily dissolve. At higher temperatures, taking advantage of the increased reaction rates, a higher degree of depolymerization can be achieved leading to biocrude oil with an improved quality (e.g. lower oxygen content, lower viscosity, higher HHV) [14,29]. Reactors were submerged in a pre-heated sand bath (Techne, SBL-2D), which provided the necessary heating to reach the reaction temperature, set to 400 °C, in about 1 min (heating

Table 1
Characterization of the willow sawdust used as the HTL feedstock material. The values measured are mass fractions.

Moisture	Ash[a]	C[a]	H[a]	N[a]	O[a b]	H/C	O/C
(%)	(%)	(%)	(%)	(%)	(%)	(−)	(−)
5.54 ± 0.42	0.70 ± 0.07	46.92 ± 0.23	6.10 ± 0.08	0.30 ± 0.11	45.98 ± 0.04	1.55	0.84

[a] Dry basis.
[b] Oxygen calculated by difference (O = 100-C-H-N-ash).