Enhancing the feasibility of sustainable biofuel production: The role of inorganic content and potential removal strategies from fast pyrolysis bio-oil based on residues

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Abstract

Biofuels made from residual non-edible biomass, like agricultural and forestry residues, are crucial for the transition to a biobased circular economy. These biofuels reduce dependence on non-renewable resources, emit less greenhouse gases than fossil fuels and subsequently contribute to meeting the climate goals set by the Paris Agreement. Additionally, they reduce byproducts by valorizing materials that would otherwise be used as lower value product such as heat. Fast pyrolysis, which is a process at elevated temperatures in the absence of oxygen, converts solid biomass residues into a liquid within seconds. The liquid has a chemical structure that makes it a potential resource to be further upgraded into a biofuel. Due to the high water and oxygen content of the pyrolysis oil, as well as its high acidity, a catalytic process for removing oxygen with hydrogen can be used. However, the presence of inorganic elements poses a risk of deactivating these catalysts during the upgrading process. This limits the use of some biomass resources which naturally contain a low but varying concentration of alkali and alkali earth metals, transition metals and non-metals. The focus of this licentiate thesis is the inorganic content of fast pyrolysis bio-oil produced from residual, non-edible biomass. In the first study, removal of inorganic elements from pyrolysis oil was studied using sorbent materials. The process removed 85-98 % of phosphorus (P), calcium (Ca), iron (Fe), potassium (K), and magnesium (Mg) at 30 °C, ambient pressure and 4 h residence time. It was found that Lewis acid sites on aluminum oxide material is likely key in the removal of P, while strong Brønsted acid sites on an acidic zeolite and strongly acidic ion-exchange resins are vital for the adsorption of Ca, Fe, K, and Mg. However, the inorganic elements in pyrolysis oil are not only in ionic forms. The organic content in the oil was studied before and after the sorbent removal using 2D gas chromatography, and showed negligible effects on contents of alcohols, phenols, acids, furans, sugars, and ketones/aldehydes, likely due to the mild conditions used. In the second study, water extraction of pyrolysis oil was examined to study the distribution and solubility of the inorganic elements and their forms present in pyrolysis oil. It was found that K and Mg were to a greater extent present in a water-soluble form, compared to Ca, Fe, and P, which to a greater extent were suggested to be part of ash particles or possibly soluble in the organic fraction. This effect was more pronounced when investigating a pyrolysis oil with higher inorganic content. During the water extraction, the mass yield of carbon was 50 % indicating a significant amount in the feed oil is polar. Using 31P nuclear magnetic resonance analysis, it was shown that it consisted to a large part of aliphatic hydroxyls.

The removal of the inorganic content from fast pyrolysis oil is crucial for the development of cost-efficient production of biofuels. By increasing the available biomass feedstocks there is a potential of increasing its cost-competitiveness to fossil fuels, which is especially important for parts of the transport sector for which electrification is impractical. The utilization of all sources that can contribute to sustainable advanced biofuels represents a significant step towards our common goal of transitioning to a fossil-free economy and climate change mitigation.

Keywords: Advanced biofuels, inorganic content, removal, adsorption, liquid extraction, pyrolysis oil