

CATALYTIC FAST PYROLYSIS OF CITRIC ACID TREATED BIOMASS

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Catalytic fast pyrolysis (CFP) enables the production of aromatics (benzene, toluene, xylene) and olefins (C₂-C₄), from biomass pyrolysis vapours in the presence of acidic zeolites such as HZSM-5. These compounds are quite suitable to be integrated into the current fuels/chemicals production infrastructure. Unfortunately, the CFP process is characterized by low carbon yields (<15 wt.%) in the product oil, which hampers its commercial implementation [1]. It is known that the alkali and alkaline-earth metals (AAEMs) present in biomass have a negative influence on the catalytic bio-oil yield and quality [2]. Therefore, partial removal of AAEMs from biomass may be an attractive approach for increasing the carbon yields and/or the quality of the catalytic bio-oil. With respect to that, it has been shown recently that AAEMs in sugarcane bagasse (SCB) can be removed by treating the biomass with citric acid (1 h at 25 °C) without any significant biomass losses (compared to mineral acids such as HCl or H₂SO₄) [3].

To investigate the effect of AAEMs on catalytic fast pyrolysis, *in situ* catalytic fast pyrolysis experiments at 500 °C were performed in a microreactor (py-GC/MS) with untreated and citric acid (CA) treated SCB as biomass, and HZSM-5 as a catalyst. A substantial increase in the production of anhydrosugars (in particular levoglucosan) and an associated decrease in light oxygenates was observed during non-catalytic pyrolysis of CA-treated SCB compared to untreated SCB (Fig.1). However, no such differences in terms of product composition were observed during CFP of these two biomass types. This lack of difference may be caused by too short contact times of pyrolysis vapours with the catalyst in the *in situ* CFP configuration. Alternatively, the excess anhydrosugars formed during the pyrolysis of CA-treated SCB may have been converted entirely to coke instead of to aromatics. Unfortunately, the coke production could not be quantified in this setup.

To better understand the effect of AAEMs on the CFP process, *ex situ* CFP experiments with the two types of biomass, as well as *in situ* and *ex situ* CFP experiments with levoglucosan, will also be carried out in the same microreactor. The results of these additional experiments will be presented as well.

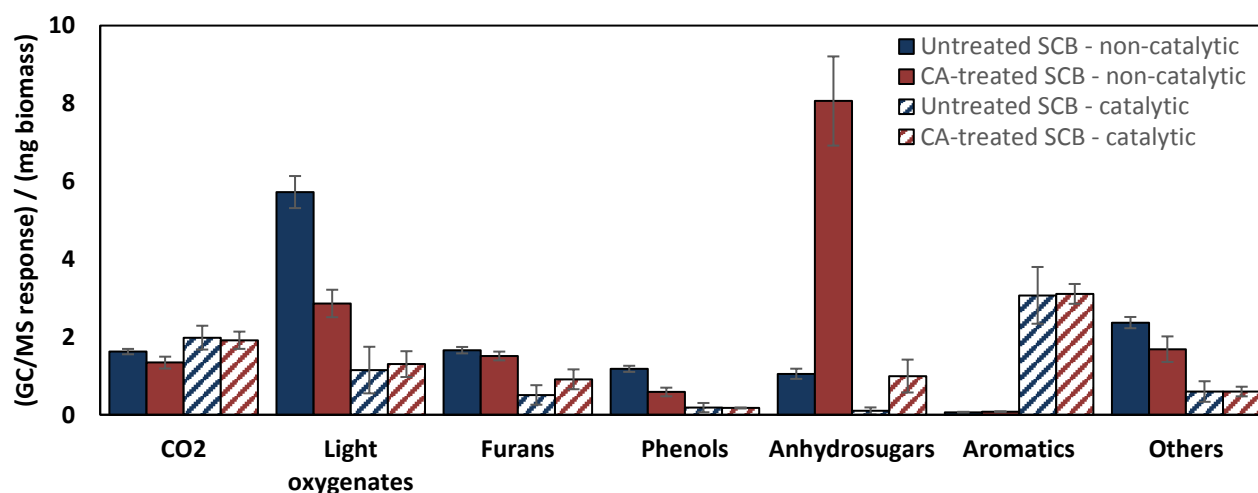


Figure 1. Comparison of catalytic and non-catalytic fast pyrolysis products (py-GC/MS detectable) derived from untreated and citric acid treated sugarcane bagasse. Non-catalytic fast pyrolysis conditions: 500°C reactor temperature, ~300 µg biomass. Catalytic pyrolysis conditions: *in-situ* catalysis, 500°C reactor temperature, mixtures of ~300 µg biomass and 1.5 mg HZSM-5 catalyst are used. Error bars represent standard deviations of triplicate experiments. Light oxygenates include carboxylic acids, aldehydes, ketones, alcohols and miscellaneous oxygenates. Aromatics include monoaromatic (BTEx) and polyaromatic (indenes, indanes, naphthalenes) hydrocarbons. Others include N-compounds, ethers and esters.

References

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