EFFECT OF BIOMASS ORIGINATED ASH IN CATALYTIC FAST PYROLYSIS OF BIOMASS

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Fast pyrolysis is an attractive single-step process for solid biomass conversion to an intermediate liquid energy carrier, suitable for further production of liquid fuels [1]. It includes the rapid thermal decomposition of lignocellulosic material in absence of oxygen, followed by quick condensation of the vapours produced initially. The condensed liquid is a mixture of numerous organic molecules with water, together often called pyrolysis oil or bio-oil. Crude bio-oil has a heating value roughly equal to that of the biomass, which is almost half the heating value of fossil fuel oil [2]. To improve the quality of crude bio-oil in relation to biofuel applications, and to reduce the upgrading costs, biomass fast pyrolysis can be carried out in the presence of suitable catalysts. Catalysis, either by adding catalyst particles to the reactor (in situ) or by secondary conversion in the vapour phase (ex situ), is applied for the removal of oxygen and the catalytic cracking of high molecular weight compounds in the pyrolysis vapours.

All biomass feedstocks contain various amounts (depending on their type) of inorganic ash-forming mineral nutrients in the form of cations which are bound onto the organic matrix of biomass. These indigenous and catalytically active minerals such as alkali and alkaline earth metals (AAEM species, e.g. Ca, K, Mg, Na) within biomass structure are known to catalyse cracking and several thermolysis reactions in gas phase which remould the chemical composition of resulting bio-oil and pyrolysis product distribution [3].

The primary goal of this work was to investigate the effect of alkali and alkaline earth metals in the form of pine wood ash on the fast pyrolysis product yields (e.g. organics, water, carbonaceous solids and non-condensable gases), non-condensable gas compositions, bio-oil compositions and the elemental distribution over various pyrolysis products and to gain an insight of the underlying mechanisms. A known amount of pine wood originated ash, ca. 3 wt.% relative to the amount of biomass fed and ca. 0.002 wt.% relative to the amount of bed material (pure sand in case of non-catalytic and a catalyst-sand blend in case of in situ catalytic fast pyrolysis experiments), was added within the process. Moreover, the in situ catalytic fast pyrolysis results obtained from the eight times reacted/regenerated catalyst (a commercial, spray dried heterogeneous ZSM-5 based FCC catalyst) were also compared with the ash-added in situ catalytic experiments in order to understand whether catalyst deactivation resulting from sequential reaction/regeneration cycles was due to thermo-mechanical, chemical and structural changes or because of the

presence of the biomass originated ash. Experiments were performed in a newly designed laboratory scale mechanical agitated bed reactor at a fixed fast pyrolysis reaction temperature of 500 °C.

In case of non-catalytic experiments, biomass originated ash catalyzed the reactions that led to the formation of non-condensable gases, coke and acids (specifically acetic acid) while the yields of the organic phase of the bio-oil, sugars (specifically levoglucosan) ketones and phenols decreased. The presence of ash in in situ catalytic pyrolysis of pine wood favored the production of non-condensable gases (specifically CO, CO_2 and CH_4), sugars and acids while the yields of the organic and water phases of the bio-oil, coke, and phenols decreased. The results revealed that even very small amount of biomass originated ash present in the pyrolysis process were sufficient to change the resulting pyrolysis speciation and the catalyst deactivation was not only related to the presence of ash but also to the thermo-mechanical, chemical and/or physical changes (e.g. poisoning, fouling, and attrition) occurring within the catalyst during the reaction/regeneration cycles.

References

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