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## Optimization of bio-oil yields in fast biomass pyrolysis by demineralization of low quality biomass feedstocks

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Fast pyrolysis is a feedstock-flexible thermo-chemical process that can convert low-quality lignocellulosic biomass to a liquid bio-oil fuel with high yields. However, the minerals (ash) in biomass are known to act catalytically during fast pyrolysis and shift the selectivity away from the desired bio-oil, to char and gases. An efficient strategy for minimizing char and gas formation and optimizing the bio-oil yield from ash-rich feedstocks is to remove the inorganics from the biomass prior to pyrolysis. In this work, water and acid washing were investigated as biomass pre-treatment techniques for the removal of inorganic matter from biomass and maximization of the bio-oil yields from pyrolysis. Water washing and acid washing were first carried out with a lignocellulosic feedstock from beech wood. The effect of treatment duration, temperature and acid type (acetic or nitric acid) was investigated. Optimal conditions were established and then applied for the demineralization of two wood residues (oak and pine), two agricultural residues (wheat and barley straws) and two energy crops (*Eucalyptus* and *Miscanthus*). It was found that washing biomass with acidic solutions is more efficient. For all six biomass samples, washing with water decreased the ash content in a range of 17-43% depending on the sample, whereas acidic washing led to ash removals of up to 90%. Among the two acids studied, nitric acid proved to be much more efficient than acetic acid. Concerning the different biomass types, removal of ash from the forestry residues (which have much lower ash contents to begin with) was much easier than with from the other types of biomasses. Removal of over 87% was recorded for both pine and oak after pre-treatment with nitric acid solution. On the other hand, the agricultural residues, straw from wheat and straw from barley, exhibited much lower ash removal rates. The effect of the different biomass pre-treatment methods on the removal of specific elements of the ash in relation with the type of biomass was also examined. It was found that the alkali metals, K and Na, and P are easy to remove and exhibit over 80% removal rate for any of the applied pre-treatment methods. Calcium is the element that was most affected by the treatment method and its removal increased in the order nitric acid > acetic acid > water treatment. Overall, washing biomass with 1% aq. solution of HNO<sub>3</sub> at 50°C for 2h was determined as the most effective in removing all of the abundant elements of ash from biomass. The optimal acid washing treatment was up-scaled and applied for the production of sufficient quantities of demineralized biomass samples for pyrolysis in a bench-scale fixed bed pyrolyzer in order to investigate the effect of demineralization on the yields of the pyrolysis products and their composition. De-ashing the feedstocks had a positive effect in the pyrolysis performance of all biomass types. Tests on the untreated and pretreated biomass types showed that the de-ashing helps by increasing the liquid organic yields and decreasing the coke and gas yields. Among the six feedstocks, the high ash content straws were the feedstocks that benefited the most from the pretreatment procedure, producing about 16-17 wt.% more bio-oil compared to the non-treated biomasses.

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