Effect of combined hydrothermal treatment and washing on coconut fiber demineralization and pyrolysis behavior

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INTRODUCTION

The application of pyrolysis in the production of clean second-generation non-aging bio-oils and chemicals is vital in alleviating deleterious environmental impact through sustainable use, management, and disposal of agricultural waste. Raw coconut fiber (RCF) is a potassium-rich lignocellulosic biomass. Direct application of coconut fiber is hampered by inherent organics, which inevitably compromise the quality of pyrolysis oil. The presence of a high potassium concentration promotes premature charring, fragmentation reactions, low bio oil yield and aging, therefore its removal is of practical interest. Integrated hydrothermal treatment(HTT) and water washing is one of the best methods for demineralization and fuel upgrading of high moisture biomass. While demineralization via HTT is extensively investigated and reported in the literature, the effect of occurrence on demineralization is not widely reported. Upon hydrothermal treatment, the physicochemical structure of biomass evolves and alter pyrolysis behaviour. In this light, this paper investigates the effect of combined HTT and water washing on demineralization and pyrolysis behaviour.

MATERIALS AND METHODS

Hydrothermal carbonization runs were performed using a 0.5 L batch-type continuously-stirred autoclave reactor at 180, 200 and 220 °C, named HT180, HT200 and HT220, respectively. The washed hydrochars are tagged HTW180, HTW200 and HTW220. K occurrence was determined using chemical fractionation analysis and AAEM concentration was measured by an inductively coupled plasma optical emission spectrometer (ICP-OES). Ultimate, proximate analysis, XRF, N_2 Adsorption, FTIR, and Boehm titration were used for characterization of samples and their hydrochars. Activation energy was determined by the Starink, FWO and KAS methods. The mechanism was determined by the Criado method.

RESULTS AND DISCUSSION

Effect of hydrothermal treatment and washing on demineralization

Potassium in coconut fiber exists mainly in water-soluble and ion-exchange form, and only 4% is acid-soluble. Acid-soluble species are most likely potassium inclusions in precipitated calcium salts and (or) feldspars. Upon HTT organically-bound species were converted into water-soluble form by ion-exchange with organic acids, while acid-solubles remained unaffected (see figure 1a). There is a monotonic relationship between K removal and HTT temperature, only when physicochemical evolution is marginal (at temperature less than 220°C). At 220°C there is partial conversion of organically bound K and high retention of K although it has the harshest and extensive contact with acidic environment. This observation is caused by the presence of a high density of oxygenated functional groups within intraparticle porosity which reduces leaching rate

through electrostatic attraction between lone pair of electrons and cations. For the same reason, hydronium ions required for release of ion-exchangeable K, can be impeded, thus decreasing water-washing efficiency. According to the FTIR and Boehm titration, hydrochar produced at 220°C is quite distinct and confirms significant chemical transform.

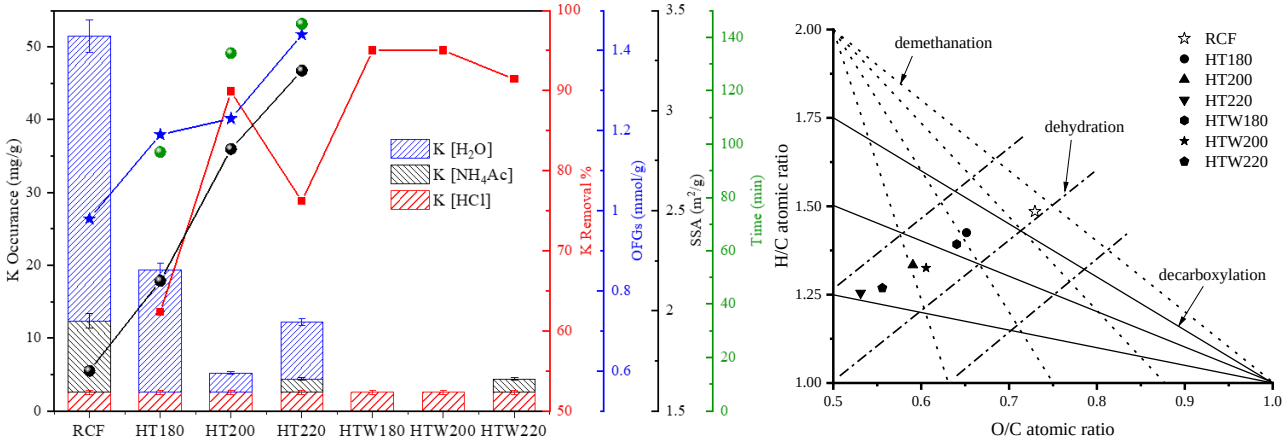

Figure 1. (a) Potassium occurrence and removal efficiency at various conditions (b) Van Krevelen diagram

The chemical transformation was effected by dehydration reaction mechanism and to a lesser extent decarboxylation as shown by the Van Krevelen diagram in the figure above. The K removal efficiency upon water washing reached 95% for HTW180 and HTW200.

Effect of hydrothermal treatment and washing on pyrolysis kinetics and mechanism.

Pyrolysis behaviour in heating range 10-50°C/min showed that pretreatment enriched cellulose such that the change in activation energy with conversion was mostly linear in the range 0.05-0.080. It was also found that pretreatment delayed charring within the same range. The Starink method was found to describe activation energy changes with the highest correlation coefficient. According to the Criado method, it was found that pyrolysis mechanism of RCF is sensitive to heating rate, while all hydrochar decomposition is independent. As hydrothermal temperature increased the mechanism became simpler, although the entirety of pyrolysis could not be described by one model. For RCF and HTW180, pyrolysis is initially described by order-based model and proceeded to diffusion reaction mechanism. Interestingly, for hydrochars produced at temperature greater than 180°C the mechanism sequence is reversed.

CONCLUSION

This study demonstrated that K removal efficiency is directly proportional to HTT temperature only when physicochemical evolution is marginal. HTT and washing could remove 95% of the K which is in water-soluble and ion exchangeable form. Kinetics showed that pretreatment enriched cellulose in resultant hydrochars. The pyrolysis reaction mechanism was simplified and reversed in sequence by the pretreatment process.

REFERENCES

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