Studies on Oxidative Degradation of Biomass in Alkaline Water

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ABSTRACT

The energy crisis caused by the depletion of fossil fuels is globally recognized as a serious threat to humanity in the near future. Moving away from fossil fuels in favor of reliance on renewable sources is an inevitable trend in development. Among renewable resources, lignocellulosic biomass is the most abundant renewable organic resource on the earth which has been used as an alternative to fossil fuels for the extensive production of sustainable fuels, chemicals, materials, and biological products. Global researchers have devoted their great efforts to develop effective technologies for biomass conversion in the past decades, the economic transformation and utilization of biomass is restricted by the efficiency and selectivity due to the complexity and resistance structure. High lignin content biomass has stronger resistance than low lignin content biomass. A pretreatment process to reduce its recalcitrance or to fractionate lignocellulose into its main components that improves the conversion efficiency is considered to be the foundation step for the establishment of an economical and sustainable lignocellulosic biorefinery. Alkaline wet oxidation, which allows milder conditions than thermochemical conversion and higher efficiency than bioconversion, is a popular technology to treat biomass for delignification and has been widely used in commercial paper and pulp processes. However, there are still problems such as severe loss of carbohydrates, unclear mechanism of biomass degradation, and the use of expensive or toxic reagents.

A main focus of the present study is the alkaline wet oxidation of biomass under mild conditions using the green oxidant O_2 to achieve deep delignification and thus recover cellulose residue. We achieved deep delignification (96%) of a kind of high lignin content woody biomass, Japanese cedar, using NaOH solution and pressurized O_2 under mild conditions (90 ℃). Chemical mechanisms were explored via investigating the degradation

of carbohydrates and establishing the removal relationship between lignin and carbohydrates. Polysaccharides (hemicellulose) were directly decomposed into small molecules without forming monosaccharides. Delignification consists of three stages (early, mid, and late stages) and the late-stage (removal rate >65%) requires cellulose decomposition for making the lignin accessible to oxidizing agents. Secondary reactions of products dissolved in liquid have a detrimental effect on delignification. Repeated short-time oxidation with renewal of alkaline water suppressed the lignin condensation enhancing the delignification. It is very difficult, even impossible, to analyze the primary reaction using a batch reactor, due to the inevitable secondary reactions of the dissolved products in the aqueous phase. A newly developed flow-through fixed-bed reactor (percolator) was thus employed for the primary extraction. Quantitative kinetic analysis revealed that the cedar consisted of three kinetic components (C1, C2, and C3) that underwent extraction in parallel following first-order kinetics with different rate constants. C1 was converted most rapidly by non-oxidative reactions such as alkali-catalyzed hydrolysis, while C2 by oxidative degradation. C3 was the most refractory component, consisting mainly of glucan and very minimally of the lignin and hemicellulose. Although the hemicellulose was converted into organic acids, it is more valuable if it can be recovered as monosaccharides or oligosaccharides. Hydrothermal treatment and alkaline wet oxidation were combined to recover hemicellulose as oligosaccharides and then to deeply delignify under mild conditions. Most hemicellulose in cedar was recovered as mannose-oligosaccharides with molecular weight (200-10000 Da) by hydrothermal

extraction using H_2O at 180 ℃. In the subsequent alkaline wet oxidation, the comparison between NaOH and Na_2CO_3 revealed that Na_2CO_3 was more favorable for the oxidative depolymerization of lignin and removed 98.9% lignin at 120 ℃ recovering a high-cellulose residue (98.8%). As a typical herbaceous and agricultural waste, rice husk was also treated with hydrothermal treatment and alkaline wet oxidation to prepare high-purity pulp. High-purity cellulose fibers (98.1%) were obtained in a high yield (>83 wt%) by using Na_2CO_3 solution and O_2 at 120 ℃ for 120 min. The Na_2CO_3 solution maintained a good delignification effect (84%) even after being reused four times.