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Cellulose-Lignin interactions during slow and fast pyrolysis

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ABSTRACT

The interactions between lignin and cellulose during the slow pyrolysis of their blends were studied by means of Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM). Fast pyrolysis was studied using Pyrolysis-Gas Chromatography/Mass Spectroscopy (Py–GC/MS). Crystalline cellulose (Avicel), amorphous cellulose, organosolv lignin, and their blends containing 20, 50, and 80 wt.% of lignin were used for the experiments. Differential thermogravimetry (DTG) revealed that the interaction between crystalline cellulose and lignin resulted in a shift toward higher decomposition temperatures, but for lignin/amorphous cellulose mixtures this effect was small. No effect of adding lignin to cellulose was observed on the yields of bio-char. Cellulose-lignin interactions during fast pyrolysis in Py–GC/MS did occur. Products from cellulose fragmentation reactions (hydroxyl-acetaldehyde and acetol) were not influenced by the presence of lignin. In general, production of lignin derived phenolics remains quite similar at 500 °C, but the yield of many methoxylated monophenols increases at 350 °C in the presence of both types of cellulose. Importantly, it was found that the presence of lignin enhanced the yield of levoglucosan, but decreased the yield of some of their dehydration products (e.g., levoglucosenone, 5-Hydrosymethylfurfural, Furfural). This result could be explained by the reduction of residence time of cellulose products in liquid intermediates, a phase where most of the dehydration reactions occur. Lignin seems to enhance micro-explosions, decreasing in this way the residence time of cellulose derived products in the liquid intermediates.

1. Introduction

Fast pyrolysis of lignocellulosic biomass is a process in which biomass is converted, in the absence of oxygen, to bio-oil, char and gas [1–3]. The main bio-polymers constituting lignocellulosic biomass are cellulose, hemicelluloses and lignin. The bio-oil obtained from these building blocks contains many different compounds like anhydrosugars (e.g., levoglucosan), mono-phenolics (e.g., guaiacols, catechols and phenols), furans (e.g., furfural, hydroxymethylfurfural) and lights (e.g., hydroxyl-acethaldehyde, acetic acid and acetol) [4,5]. The yields of these products depend on the content of cellulose, hemicellulose and lignin in the biomass. In addition, ash in biomass is known for influencing the product yields [6–8]. For example, a small amount of ash significantly reduces the yield of levoglucosan, an important platform chemical [9].

Far less information is available on possible interactions between the different biomass building blocks; cellulose, hemicellulose and lignin. This information might be important in order to optimize the pyrolysis process toward interesting chemicals such as levoglucosan. Another important factor determining the pyrolysis product distribution are the process conditions like the final pyrolysis temperature and heating rate [10]. In general, studies on interactions of the biomass building blocks might be divided into two regimes depending on their heating rate, namely slow pyrolysis and fast pyrolysis.

In many publications thermogravimetric analysis (TGA) is typically used to study reaction mechanisms with heating rates <100 °C/min (slow pyrolysis). Thermal analysis of wood shows three different degradation peaks for the three building blocks of biomass which might lead to the thought that they will react independently. Indeed, most of the literature demonstrated no or negligible interactions among the components [11–13]. Moreover, the wood behaved as a sum of its components when weight loss curves and char yields are considered. Differences in formation of single compounds due to interaction during pyrolysis were, how-

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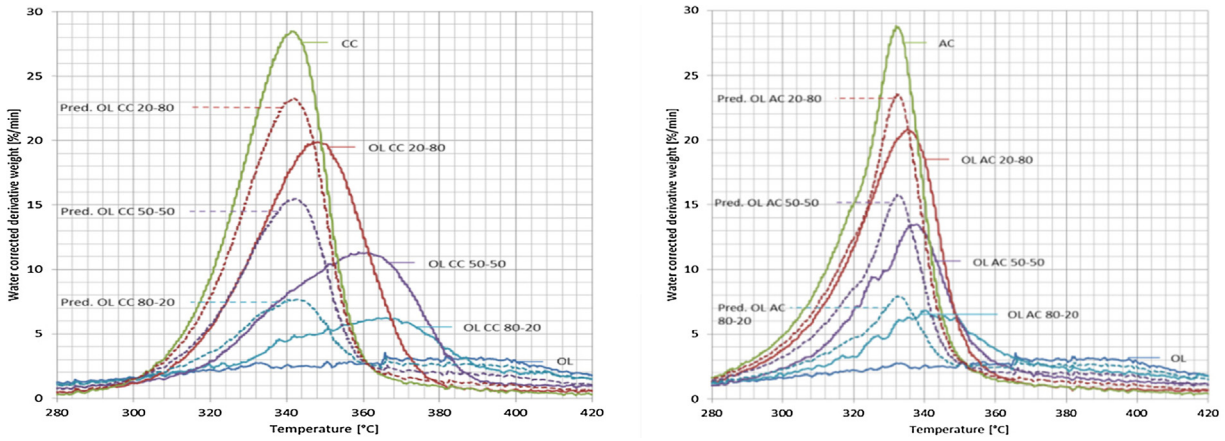

Fig. 1. DTG curves of crystalline and amorphous cellulose, organoslov lignin, and cellulose-lignin blends.

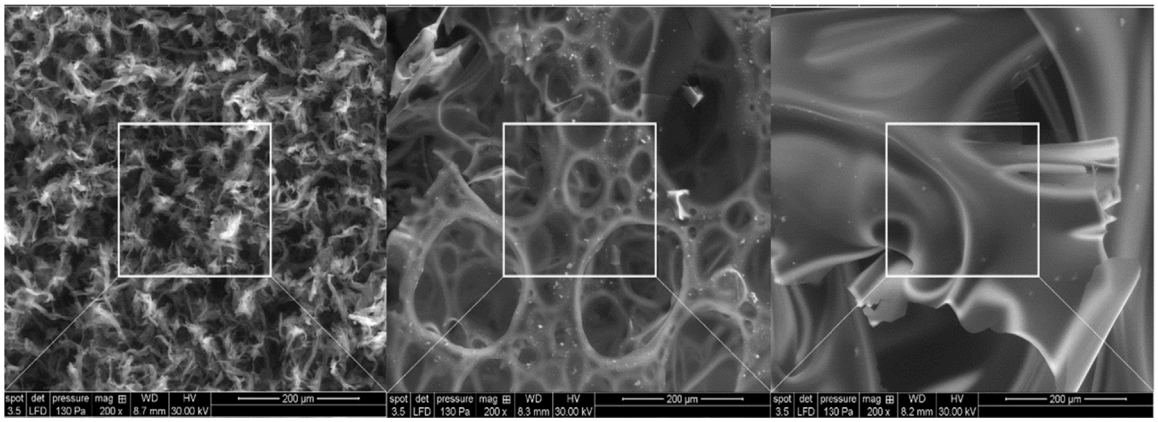

Fig. 2. SEM images of residues after the TGA experiments. Crystalline cellulose, amorphous cellulose, and organosolv lignin.

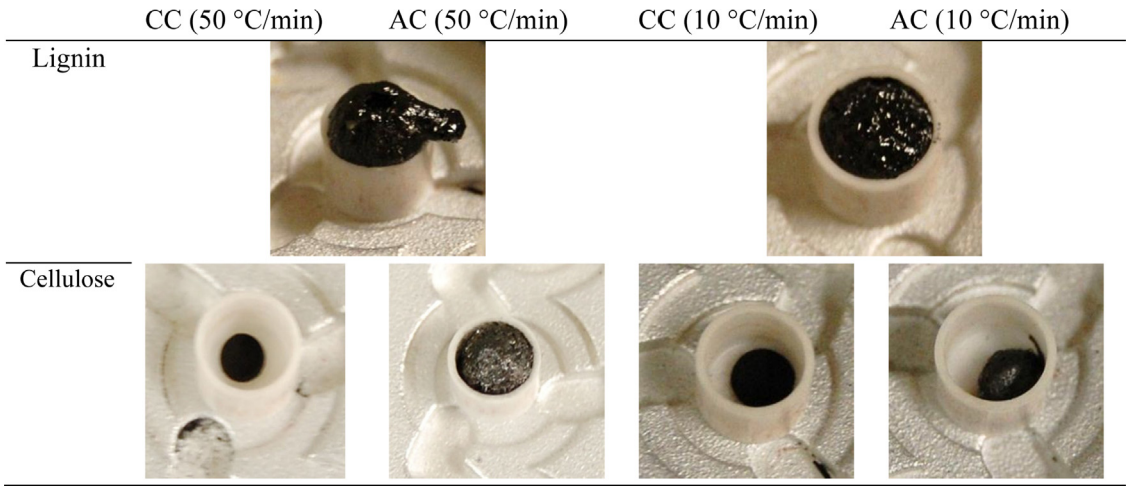

Fig. 3. SEM images of cellulose and lignin residues obtained after TGA analysis.

ever, observed when a FTIR analyzer was coupled with the TGA [14]. Fast pyrolysis of biomass and its major components is often studied using Py–GC/MS and entrained flow/fluidized bed reactors. Typical heating rates used in these studies are >100 °C/sec. Alén et al. reported minor interactions amongst the three components in comparison with the whole biomass. Their finding was only based on the observation that the same type of compound classes, produced by individual building blocks, were also present in the products of whole biomass [15]. More in-depth analysis of the interactions among components was recently performed by Wang et al. [16] Considerable interaction was observed among the components during fast pyrolysis. For example, the oil yields were considerable lower for pyrolysis of four different mixed components (hemicellulose, cellulose and lignin in certain weight ratios) compared to the calculated sum of oil of the individual components while taking into account their weight ratios in the samples.