Characterization of lignin at pre-pyrolysis temperature to investigate its melting problem

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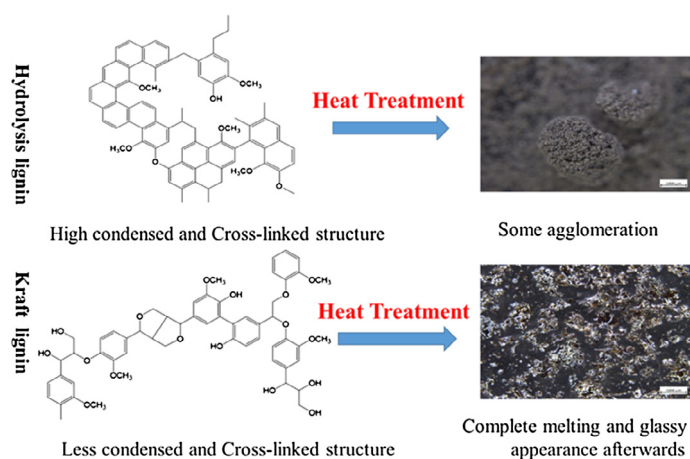[a] Department of Material Science and Engineering, KTH Royal Institute of Technology, Stockholm 114 28, Sweden
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GRAPHICAL ABSTRACT

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ABSTRACT

Technical lignin particles melt under relatively low temperature. This results in the problem in the continuous feeding and fluidization during lignin pyrolysis, which in turn limits its utilization on a large scale. In this study, two most available types of lignin have been used to investigate the lignin melting problem, which are Kraft lignin (KL) from pulping process and hydrolysis lignin (HL) from bio-ethanol production process. Elemental composition, thermal property and thermally decomposed derivatives of each sample are tested by elemental analyzer, TGA, DSC, and Py-GC/MS. Morphology, structure and crystal change before and after heat treatment are tested by microscopy, FTIR and XRD. All results suggest that lignin structure determines its melting properties. Kraft lignin from pulping process contains a less cross-linked structure. It melts under heating. On the other hand, hydrolysis lignin from hydrolysis process contains a highly crossed-linked and condensed structure. It does not melt before decomposition under heat treatment. Modifying lignin structure is suggested for the resolution of technical lignin melting problem.

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1. Introduction

Over 50 million tons of the so-called technical lignin is annually extracted from biomass as a byproduct of the pulp and paper industry. Most of the technical lignin is combusted as low-graded fuel, while only 1–2% is upgraded into bio-based products [1]. As the only renewable aromatic source in nature, lignin has a great potential for chemicals and value-add renewable biofuels [2]. Therefore, it is critical to find a sustainable and economical way to convert such lignin into biofuel and/or chemicals.

Lignin degradation has been extensively studied for decades in biological or thermochemical ways [3,4]. Fast pyrolysis is one of the most promising thermochemical conversion routines to convert lignin to bio-fuels since it is a relatively straightforward process that requires lower capital investment compared to other processes [5]. Furthermore, after in-situ or ex-situ catalytic upgradations, liquid products derived from fast pyrolysis have the potentials to be compatible with the current petroleum refinery infrastructures [6,7].

However, fast pyrolysis of technical lignin usually limits to microscale as in Py-GC/MS or small batch reactors due to the melting and subsequent agglomeration of lignin particles, which prevents continuous feeding and fluidization. Such problems heavily inhibit the utilization of technical lignin. Moreover, the inability to continuously feed technical lignin into large-scale reactors has been regarded as the primary barrier for lignin pyrolysis to fuels or chemicals [2].

Several efforts have been devoted to tackle this melting and agglomeration problem during pyrolysis process. Some comprehensive reviews are published on the topic [8,9]. The two main directions for solving this problem are either to modify the feeder and/or reactor or to pre-treat lignin. The feeder can be cooled to reduce the clogging issue [10] and a stirrer can be added to the reactor to break the agglomerated particles [11]. For the pre-treatment of lignin, mixing with clay can reduce the clogging. Pre-treatment of lignin with calcium formate [12] and calcium hydroxide [9] are also found to be effective in reducing the clogging and agglomeration during continuous pyrolysis.

Several reasons behind the melting behavior of lignin have been suggested. The international collaboration [13] stresses the importance of the cellulose content. In their work, two types of lignin have been pyrolyzed, which are lignin derived from the soda pulping process and lignin derived from the weak acid hydrolysis process. Here, the soda pulping lignin is unable to be fed into the fluidized bed reactor, but the hydrolysis lignin which contains up to 50% cellulose is possible to be fed. Zhou et al. [9] suggest that the melting and agglomeration of lignin are caused by the oxygenated functional group in the molecular structure of lignin. These functional groups include phenolic hydroxyl, aldehydes, and carboxylic groups which can easily re-polymerize to form resin-like products at a relatively low temperature during pyrolysis.

Nevertheless, the suggestions for the reasons behind melting and agglomeration of lignin described above are still insufficient. If high cellulose content can help reducing lignin melting problem, the interactions between cellulose and lignin must be clarified [13]. Moreover, the re-polymerization of phenolic hydroxyl, aldehydes and carboxylic group content only seems to be responsible for the agglomeration of lignin during thermal decomposition but not clearly related to the melting of lignin before decomposition [9]. Therefore, the investigation on the factors that cause lignin melting is essential since it can give a comprehensive understanding of the existing feeding problem and might help suggesting how to solve it.

Hydrolysis lignin which is mainly produced as residues from bio-ethanol production process is another major lignin in addition to technical lignin. It is reported that the feeding problem caused by lignin melting of hydrolysis lignin is less severe than that of lignin from pulping process [13]. However, a detailed comparison study between these two types of lignin has not been carried out. Therefore, in this study, Kraft lignin (KL) from the pulping process and hydrolysis lignin

(HL) from the bio-ethanol production process are compared to investigate the lignin melting problem. Elemental composition, thermal property and thermally decomposed derivatives of each sample are tested by elemental analyzer, TGA, DSC, and Py-GC/MS. Morphology, structure and crystal change before and after heat treatment are tested by microscopy, FTIR and XRD.

2. Materials and methods

2.1. Materials

Hydrolysis lignin (HL) was obtained a from bio-ethanol plant in Sweden in the form of solid residue. A brief description for bio-ethanol production process is as follows. The raw biomass is pretreated with diluted acid and steam to release sugar from hemicellulose. The product is then neutralized and transferred to an enzymatic hydrolysis process where yeast ferments sugar to produce ethanol. The lignin is a solid residue which is filtered out and dried after ethanol extraction is completed [14].

Kraft lignin (KL) was obtained from a mill in North Europe. It was isolated from Kraft black liquor of spruce via the LignoBoost process. A comprehensive description of LignoBoost process has been reported in the reference [15].

All sample are used after drying without sieving. Particle size distribution of two samples were measured with a Camsizer XT instrument. The results have been shown in Fig. 1. It can be seen that particle size of both two samples is fine. HL is significantly finer; however, the majority (50%) of both materials are below 40 μm.

2.2. Sample characterization

2.2.1. Elemental analysis

Proximate and ultimate analysis was provided by BELAB AB. The ash content was determined after heating to 810 °C in air. C, H, and N were determined using SS-EN ISO 16948:2015; S was determined using SS-EN ISO 16994:2016, along with moisture content using SS-EN ISO 18134-2:2017 and volatile content using SS-EN ISO 18123:2015.

2.2.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) of the two lignin samples was conducted using a NETZSCH STA 449 F3 Jupiter thermogravimetric analyzer. For both samples, around 5 mg of sample was tested under N_2 flow at a heating rate of 10 °C/min from 25 to 800 °C.

2.2.3. Differential scanning calorimetric

Differential scanning calorimetric (DSC) analysis was carried out with a METTLER TOLEDO DSC 1. Sample of about 5–10 mg was put in a standard aluminum pan which was then sealed and pierced. The tests were conducted under nitrogen atmosphere at a heating rate of 10 °C/
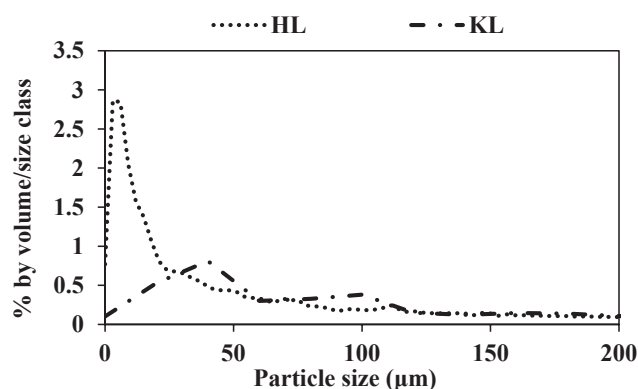

Fig. 1. Particle size distribution of HL and KL.