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Effect of mixing hydrodynamics on the particle and filtration properties of precipitated lignin

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ABSTRACT

The effects of mixing hydrodynamics on the particle and filtration properties of precipitated lignin from black liquor has been investigated. The hydrodynamics were varied in terms of turbulent shear rate and impeller flow pattern in the stirred tank. The precipitated lignin flocs were characterized in terms of particle size, size distribution, and particle shape. Our findings showed that the effect of hydrodynamics on the size and shape of primary lignin particles were negligible. However, the aggregation of primary particles into lignin flocs were affected by the hydrodynamics of the stirred tank. The size distribution and shape of the final lignin flocs could be controlled mainly through the manipulation of turbulent shear rate. Lignin flocs with higher compactness and size showed better filtration and washing properties. Optimal hydrodynamic conditions led to production of lignin with good filtration and washing properties at 1.83E + 09 m/kg specific filtration resistance, 243 kg/h m^2 lignin filtration rate, generating high purity lignin at 0.09% ash content. The reproducibility of the findings was validated using three other black liquor samples.

1. Introduction

Lignin, one of the most abundant natural polymers on earth, is currently being investigated as a feedstock for manufacture of bio-based products and chemicals. Pulp and paper industry produces around 20 million tons of lignin annually, however only 2% (1.1 million tons) of this lignin is being used for applications other than heat and power generation. The amount of lignin recovered from Kraft pulping mills are even lower, totaling to an estimated 100,000 t annually (Higson and Smith, 2011). Lignin is entrained in the residual black liquor stream of Kraft pulping mills, which is combusted to generate steam and recover pulping chemicals. The extraction of lignin from black liquor is emerging as potential lignin biorefinery pathway, including recent industrial installations. Acid precipitation is one of the most promising methods for lignin recovery from Kraft pulping mills in terms of technological maturity and economics (Benali et al., 2014; Uloth and Wearing, 1989).

A flow diagram of the acid precipitation process is given in Fig. 1. The incoming black liquor is acidified to a pH of 9 to 10 (acidification step) to precipitate lignin. Resulting lignin slurry is further agitated (ageing step) for a residence time of 30 to 90 min to complete the aggregation of lignin. The slurry is then filtered, and the cake is washed with H_2SO_4 and water to reduce the ash content (Loutfi et al., 1991; Wallmo et al., 2009; Kouisni et al., 2012).

Lignin in black liquor is a complex colloidal system. At high pH values, the phenolic and carboxyl groups of lignin molecules are dissociated, providing a negative surface charge, thus maintaining the colloidal stability. As the pH decreases, the surface charges are neutralized, destabilizing the lignin colloids, and coagulating lignin into solid macromolecule particles. The aggregation of lignin in aqueous solutions has been found to be governed by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, which describes the colloidal stability as balance between attraction and

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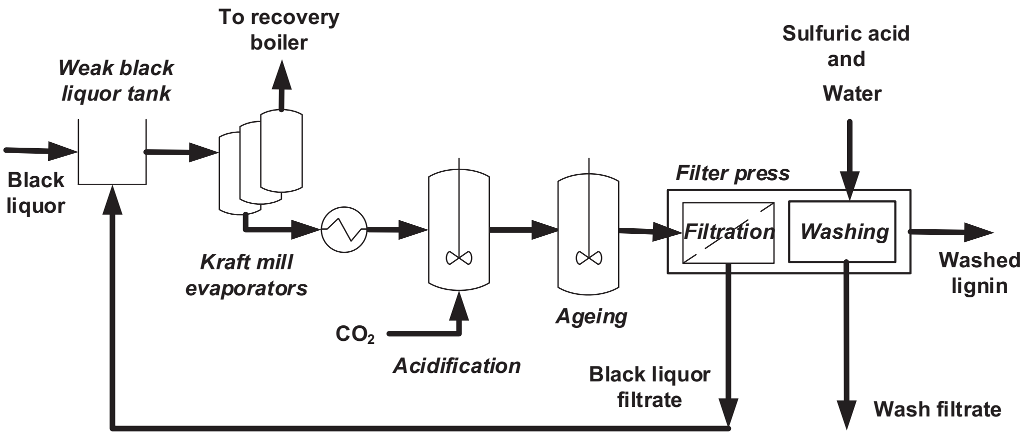

Fig. 1 – Flow diagram of the acid precipitation process.

electrostatic repulsion forces (Norgren et al., 2001; Norgren et al., 2002). As a result, the amount of lignin precipitated is mainly influenced by the solution pH, temperature and salt concentration (Norgren et al., 2001; Norgren et al., 2002). Lignin aggregation under Brownian motion, in the absence of agitation, have been reported to produce lignin particles with fractal dimensions varying from 1.9 to 2.45 and sizes in the range of 100 nm up to 1–2 μm (Norgren et al., 2002).

Although, higher yields can be obtained by adjusting the pH, temperature and black liquor solids content, the lignin precipitation process can only be conducted in a narrow range of conditions to be able to obtain filterable lignin. The precipitation pH, temperature and black liquor total solids content generally have to be in the range of 9 to 10, 60 to 80 °C and 30–40%, respectively (Loutfi et al., 1991; Ohman and Theliander, 2007; Wienhaus et al., 1990). Lignin particles produced outside these ranges have been described as very fine or soft and tacky, making filtration difficult (Loutfi et al., 1991). The changes in the particle properties arise from varying molecular surface properties of lignin as well as solution conditions. Low molecular weight lignin fractions precipitate at lower pH values, producing finer particles with less active sites for particle-particle aggregation. The temperature decreases the surface charges of lignin, providing better aggregation, however, temperatures higher than 80–85 °C produces lignin in liquid state (Loutfi et al., 1991; Norgren and Lindstrom, 2000; Zhu et al., 2014).

The reported specific filtration resistances of lignin cake were generally high, varying in the range of 1E + 10 to 1E + 12 m/kg while lowest recorded filtration resistance was around 8E + 09 m/kg for softwood black liquors (Ohman and Theliander, 2007; Wallmo et al., 2009). As a result, the filtration and washing equipment are one of the most capital intensive in acid precipitation plants due to the high filtration resistance, amount to ~30% of the total capital expenditure (Diffo, 2013; Gooding, 2012). Therefore, there are incentives in optimizing the efficiency of lignin filtration.

Although, the surface properties and the physicochemical properties of the solution tend to dominate the colloidal aggregation, the hydrodynamic conditions affect every aspect of this phenomenon including initial aggregation, growth and breakage of particles (Spicer et al., 1998; Spicer et al., 1996). The filtration and dewatering efficiencies are heavily dependent on the size, structure and distribution of the particles (Spicer et al., 1998; Jarvis et al., 2005a; Xu and Gao, 2012). The hydrodynamic flow pattern and shear rate are two main parameters that determine the hydrodynamic state of a stirred tank. The flow pattern mainly depends on the hydrodynamic design of the system including impeller type, diameter and positioning. The level of shear in the stirred tank varies from impeller zone to smallest turbulent eddy fluctuations creating a complex shear field (Paul et al., 2003; Kresta, 1998).

Despite the hydrodynamic relevance of coagulation and flocculation phenomena, the effect of hydrodynamics on lignin precipitation process has not received much attention. The published studies investigated, among other parameters, the effect of agitation rate on the filtration resistance, reporting that slower agitation speeds during the acidification and ageing steps lead to lower filtration resistance (Wallmo et al., 2009; Howell and Thring, 2000). The hydrodynamic characterization of mixing assemblies used and lignin floc properties have not been reported in these studies. Elucidating the influence of fundamental hydrodynamic parameters on the acid precipitation process is important due to two reasons. First, hydrodynamic optimization of the process could reduce the lignin separation and purification costs. Second, it provides important insights towards lignin aggregation and growth and scale-up of lignin precipitation process as well.

The goal of the present work was to investigate the effect of turbulent shear rate and hydrodynamic flow pattern on the coagulation and growth of precipitated lignin particles in black liquor. The influence of the floc properties on the filtration operation was also studied. The precipitation was carried out using two different impeller systems: Pitched blade turbine (PBT) and Maxblend^{TM} (MB) mixing assemblies. They were operated at different power levels to vary the turbulent shear rates. The lignin flocs were characterized in terms of size, shape and distribution. Filtration and washing properties of the precipitated lignin were characterized in terms of specific filtration resistance of lignin cake, washing time, and ash content of lignin. The lignin yield was also estimated. The evolution of floc size during the acid precipitation process in relation to hydrodynamic parameters was discussed. Potential scale-up parameters have been pointed out. The reproducibility of the results were confirmed using black liquor from three softwood Kraft pulping mills.

2. Materials and methods

2.1. *Experimental setup*

All the experiments were carried out in an open 2 L vessel with standard baffles (T/10). Heating was provided by a circulating hot water bath with a temperature controller connected to the