Structural carbon fibre from kraft lignin

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The desire to manufacture a commodity carbon fibre from lignin has resulted in the examination of several methods to separate lignins from biomass. The preferred route to carbon fibre is via melt spinning and this poses several challenges in preparing suitable lignins. It is desirable for lignins to have suitable melt flow properties for fine filament spinning, a low volatile content at potential extrusion temperatures, and as high a glass transition temperature as possible so that conversion to carbon fibre proceeds at an acceptable rate. The need for optimum rheological characteristics together with chemical and structural stability in the lignins contrast with the reactivity needed for desirable conversion kinetics[1,2]. Therefore a narrow window of opportunity potentially exists for suitable lignin preparations; however, such preparations directed towards this application are little understood.

Some lignins are prepared directly with reasonable melt properties, and these are typically manufactured using organosolv processes[3,4], but they often suffer from relatively high carbohydrate, volatile, and extractives contents which cause problems during melt spinning and conversion, particularly if the delignification level of the biomass is high. In contrast, an often reported organosolv lignin[5,6], Alcell™, has a relatively high purity and good melt properties, but conversion proceeds very slowly owing to its very low glass transition temperature. Kraft lignins on the other hand are thought to have very poor melt properties and high levels of impurities, but are able to be converted to carbon relatively quickly. Still, other lignins, typically available from biomass pretreatments (in order to bioconvert sugars), are characterized by very high levels of impurities and poor melt properties, and in many cases the impurities contribute more to product mass than the lignin.

It is clear that a wide gamut of potentially available lignins exists as a result of the processing of many differing biomasses. However, the role of lignin separation as a key process element is often overlooked. Indeed, lignins do not just appear from black liquors and so on – there is a separation process and this process must be uniquely designed to provide differing products according to their mode of use and techno-economic feasibility. In the case of kraft lignins, separation, if performed at all, usually results in materials with high ash contents and moderate carbohydrate levels, but is done in such a way for the products to be good enough for the applications in which they are intended; such as those derived for the Indulin family of products (Ingevity, USA).

Unlike most biomass pretreatments, the organosolv family of processes is typically designed to produce several relatively high purity streams, and therefore target several coproducts without significant waste[7,8]. Although there have been several organosolv processes developed over the last 50 years, only one became a commercial activity and subsequently struggled to be viable. Owing to the more recent demand for renewable fuels which is intertwined with government legislation, interest has renewed, and many proposed processes are taking form. The kraft process, however, similarly produces several products, and like organosolv, can be defined as a front end separation biorefinery. Such products include turpentines separated in the early phases of kraft cooking, and tall oils which are separated from black liquor in the recovery cycle, together with significant contributions towards biobased district heating, and substantial excess electricity sold to grid providers. However, it differs in that it has been universally adopted, deployed and characterized in its form known today for almost 80 years. It is therefore likely that the kraft process has the potential to produce the most suitable lignins for conversion to fuels, bulk chemicals, resins, thermoplastics and other materials, including carbon fibre, for the foreseeable future.

Kraft lignins are typically separated with broad molecular weight distributions, impurities, and with the potential for infusible contents and efforts to control these in a techno-economically viable way are needed, especially for use in high value products such as carbon fibres. If attractive processes can be developed for the purpose of refining black liquor, there is the potential for lignins to be produced in the same mill with properties suitable for differing products.

The GreenLight* consortium seeks to demonstrate a biobased, renewable and economically viable carbon fibre from lignin. The target is to provide a basis for the commercial production of lignin, lignin filaments, carbon fibre, and carbon fibre composites which will be demonstrated in automotive parts and exhibit a TRL of 5. GreenLight is a consortium of nine European entities, which represent the value chain from biomass to automobile integration. In order to develop lignin as a precursor for continuous filament carbon fibre, it has been identified that the most difficult boundary to success resides in melt extrusion of lignin. Indeed the main body of literature contains accounts of monofilament extrusion and perhaps up to 12 filaments, with little to no account being provided concerning continuity. Therefore for GreenLight we set out to develop a robust melt spinning platform for use up to the 1000 filament scale. In this, methodical studies were performed to examine lignin separation from differing black liquors derived from both softwood and hardwood, and to assess their viability in terms of thermal, compositional and structural properties, and then pilot scale melt spinning at the 100 filament scale.

A brief description of lignin carbon fibres together with an overview of the GreenLight consortium and some activities will be provided. One such activity will be presented in which the characteristics of some kraft lignin fractions obtained from the same Södra Mönsterås softwood kraft black liquor were recorded. The lignins were manufactured in about 10–20 kg quantities and with using several variations of the LignoBoost process to provide lignins with improved melt spinning properties. The lignins were found to be of high purity, each having low carbohydrate, extractives, and inorganic contents. Their melt properties were considered fair to very good, and all four lignins could be melt spun and converted to carbon fibre.

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References

1. Baker, D.A.; Baker, F.S.; Gallego N.C., Thermal engineering of lignin for low-cost production of carbon fiber. *Proceeding in The Fiber Society 2009 Fall Conference*, University of Georgia, Athens, GA, USA, October 27-30, **2009**
2. Baker D.A., Rials, T.G. Recent advances in carbon fiber manufacture from lignin. *J. Appl. Polym. Sci.*, **2013**, 713-728, 130
3. Aziz, S.; Sarkanen, K., Organosolv pulping—a review. *TAPPI J.*, **1989**, 72, 169-175.
4. Sun, Q.; Ratayakorn, K.; Kokouvi A. et al. A study of poplar organosolv lignin after melt rheology treatment as carbon fiber precursors. *Green Chem.*, **2016**, 18, 5015-5024
5. Pye, E. K.; Lora, J. H., The Alcell Process—a proven alternative to kraft pulping. *TAPPI J.*, **1991**, 74, 113-118
6. Kadla, J.; Kubo, S.; Venditti, R. et al. Lignin-based carbon fibers for composite fiber applications. *Carbon*, **2002**, 40, 2913-2920
7. Michels, J.; Wagemann, K., The German lignocellulose feedstock biorefinery project. *Biofuels, Bioprod. Bioref.*, **2010**, 4, 263-267
8. Bozell, J.J., Connecting Biomass and Petroleum Processing with a Chemical Bridge. *Science*, **2010**, 329, 522-523