B. Improved Lignin Purification/Recovery Process for Carbon-Fiber Applications

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Objective

The project objective is to develop an economically-viable and technically-sound process for the purification of lignin to make it acceptable as a raw material for the manufacture of low-cost carbon fiber (CF).

Lightweighting the USA car and light-truck fleet for better fuel efficiency is a current DOE objective. The substitution of stamped steel panels and other body and interior parts with strong, yet lightweight and resilient carbon-fiber-reinforced plastic (FRP) parts can contribute significantly to this objective. Unfortunately, current processes for manufacture of CF are costly, and produce CF at well above the established target cost of under $5.00/lb needed for vehicle lightweighting.

A considerable portion of the cost of current CF is borne by the expensive synthetic polymers that are the normal raw materials. Lignin, as a byproduct of the pulp and paper industry, is an attractive alternate and potentially low-cost raw material for CF. Unfortunately, today's standard means of recovering lignin from paper-mill streams is not able to yield lignin with the levels of acceptable purity and physical properties for fast and economically-viable melt-spinning and eventual conversion to carbon fiber.

This project is tasked with developing and demonstrating at the lab-scale effective means to isolate, recover and purify pulp-mill-derived lignin with properties acceptable for its use as a raw material for CF. Initially, this effort is focused on hardwood lignin from Kraft black liquor and eventually will be extended to softwood lignin from Kraft black liquor. The purity targets that have been set for lignin by prior CF work at ORNL (see 3.A) serve as a guideline. However, we will also use a preliminary test for melt-spinnability (via a fiber-draw test) as a guideline for determining early-success potential. We will also examine other physical properties including melt index (MI) and dynamic viscosity. These physical properties are also expected to be a key to a material's ability to be processed economically into CF whose properties are acceptable for use in CF-reinforced car and truck parts.

Approach

- Evaluate the MeadWestvaco (MWV) concept of differential removal of impurities and lignin precipitation as a process route to achieving the desired level of lignin purity and properties for carbon-fiber application.

- Evaluate post-pulping processes to remove carbohydrate from lignin (using appropriate representative Kraft black liquor(s).
- Screen and determine optimal process variables for the selected process.
- Scale selected process and the optimized conditions to 300 cc and or to 1-liter batch level, or larger as appropriate, to verify process and determine overall material balance and perform preliminary assessment of adaptability to a continuous process.

Accomplishments

- Purchased MI instrument for lignin product characterization. Set up instrument and accomplished operator training and baselining with commercial polymers.
- Successfully addressed environmental, health and safety (EH&S) issues. This included standard operating procedures and safety reviews of instrumentation and autoclave equipment and approved procedures for disposal of waste and recycle materials.
- Developed approved material-handling, characterization and processing procedures.
- Developed procedures for thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) of samples to determine moisture, ash and melting-range behavior.
- Established and validated a preliminary "fiber-draw" test to assess the ability of lignin samples to be successfully melt-spun.
- Determined that existing PNNL dynamic mechanical analysis (DMA) instrumentation can adequately measure lignin sample melt viscosity under shear, another property that is deemed key to predicting its ability to be melt-spun into fiber.
- Begun combinatorial, high-throughput experiments with well-per-plate format to assess post-pulping processes. Selected several leads for further evaluation.
- Performed a preliminary evaluation of the MWV differential process for lignin clean-up.
- Performed an evaluation of % loading and methods of incorporation for one recommended type of plasticizer / rheology control agent to aid in lignin melt-spinning. Selected an appropriate loading and incorporation method. (Prior efforts by others have suggested that lignin must be plasticized in order to be effectively melt-spun.)
- Via the cooperative research and development agreement (CRADA) partner, established a technical-service type arrangement with a USA university to perform single-fiber melt-spin tests on samples that appear successful in preliminary testing.

Future Direction

- Development of technology capable of delivering hardwood lignin to the desired purity level.
- Selection of one of three best-apparent technologies for hardwood-lignin recovery and scaling these to a level suitable for validation and to provide sufficient material for single-fiber melt-spin tests at a university.
- Extension of hardwood-lignin recovery methods to the development of technology capable of delivering softwood lignin to the desired purity level.
- Selection of one of three best-apparent technologies for softwood-lignin recovery and scaling these to a level suitable for validation and to provide sufficient material for single-fiber melt-spin tests at a university.
- Delivery of 5 kilograms of the desired purified lignin for melt-spinning evaluations.

Introduction

Carbon fiber derived from lignin-based feedstock offers the potential for meeting the aggressive cost goals established by FreedomCAR for structural applications of carbon fiber. However, the critical requirement for successful development of a lignin-based carbon fiber is the ability to purify the lignin feedstock effectively so that it can be melt-spun and processed at attractive rates into a viable carbon fiber having the required physical and mechanical properties. Effective purification of lignin requires the removal of insoluble particulates, salts and undesirable carbohydrate fragments, which adversely affect the melt-spinning and overall fiber processing. In order to meet current cost targets it is essential that a practical purification process be compatible with current Kraft pulping operations as Kraft lignin is the largest practical source of lignin for the near future. It is also essential that the general lignin purification scheme be easily adaptable to both hardwood and softwood lignin. Longer term, the process must also be able to handle lignin from other renewable sources and processes other than those based on Kraft-type technology.

MWV, the project's cost-sharing CRADA partner, has developed a relatively untested and unrefined concept for lignin purification/recovery that has potential to meet the required purity levels in a cost-effective, environmentally-suitable manner. In addition, the MWV process concept is compatible with existing pulp-plant layout and function, which is a key requirement for early implementation of high-purity lignin for carbon fiber.

The most deleterious lignin components are perceived to be easily volatilized, lignin-bound carbohydrate fragments, along with inorganic salts, insoluble and non-melting materials. MWV's conceptual process is expected to remove these undesirable components very early in the lignin recovery process and also can be retrofitted into a conventional pulp mill design. Early experimental evidence suggests that this concept, although simple, is likely to be more complex and difficult to accomplish successfully than initially believed.

Approach

The overall project approach is multifold, including use of high-throughput, combinatorial methods at PNNL for fast screening and discovery. Bench-scale experiments at 300 cc to 1-liter levels to validate, verify and refine leads, found via high-throughput methods, are also planned. Scale-up to pilot-size and beyond as appropriate will also be conducted to provide confidence in the process and to provide material for single- and multiple-fiber melt-spinning evaluation and also carbonization tests. Initially, the project plan involved various tasks properly described as preparatory, including acquisitions, personnel training and items related to EH&S. This was followed by experimental recovery of lignin via various physical means and also experimental evaluations of a variety of chemical treatments. Ultrafiltration of the black liquor (BL) was also briefly examined.

Fundamentally, we are starting with lignin at the black-liquor stage, that is, when it is closest to the form in which it is first removed from the wood. Prior CF development work with lignin has used material that had already been recovered, isolated, subjected to some degree of purification and dried. Since lignin can have significant reactivity before and during drying, we think that beginning at the BL stage allows us to intercept lignin and process it more effectively before undesirable and irreversible changes take place.

Results

Early accomplishments include the acquisition, set-up, personnel training, a safety review and standard operating procedures (SOP) approvals of a Tinius-Olsen Melt Index testing machine. We have evaluated and validated this instrument with several commercial polymers with known ability to be melt-spun and blown into films.

We have also set-up and validated a preliminary test to very simply evaluate a new material's potential ability for melt-spinning. This preliminary test, known as the "fiber-draw" test is modeled closely after a test designed and successfully used by some staff at Clemson University for determining if a given sample is likely to be suitable for melt-spinning. The "fiber-draw" test apparatus is contained inside a N-filled glove box as lignin is often perceived to be reactive with air. The test is quite simple in concept. A sample is placed in a small aluminum pan on a hot plate whose surface temperature may be accurately controlled and changed. As the sample temperature is raised by increasing the hot plate's surface temperature, a visual indication of possible melting or softening can be observed. When melting or softening behavior is seen, a sharp-pointed pin is touched to the sample and slowly removed. If a long, uniform, thin fiber can be drawn from the sample as the pin is removed while the sample transitions through a melting or softening stage, then the sample is considered to have good potential for melt-spinning. Figure 1 shows the "fiber draw" behavior of M-50 pitch, a material known to have good melt-spinning behavior. Note the relatively nice looking long fibers drawn from the melted pitch contained in the pan.

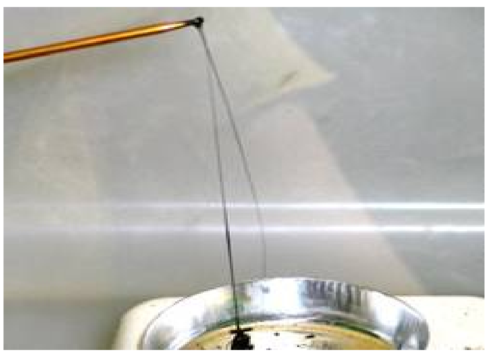

Figure 1. M-50 Pitch fiber-draw test.

Other early activities included staff training on a TGA-DSC apparatus used to determine melting points or melting ranges and also weight loss vs. temperature in inert or air atmosphere.

Experimental work for recovering lignin from hardwood BL is using a commercial BL obtained from the MWV Kraft pulp mill in Charleston SC. We found that most particulate matter and the tall oils could be removed in a single centrifuging step after appropriate pH adjustments. The liquid remaining after this treatment contained about 14% lignin along with dissolved inorganic salts and other organics. Simple precipitation of this lignin followed by washing to remove the inorganic salts and soluble organics followed by vacuum drying, did not yield a particularly good fiber draw test (see Figure 2). The "clumps" and "nodules" on the drawn fibers are indicative of poor melt-spin behavior and are consistent with earlier work which established the need to plasticize the lignin prior to melt-spinning, regardless of its purity.

Figure 2. Precipitated lignin.

Figure 3. Pc-1369 lignin.

As a comparison, Figure 3 shows the fiber-draw test result with unprocessed PC-1369 which is a commercial grade of hardwood lignin shown in past ORNL studies not to be suitable for melt-spinning. The PC-1369 and also the lignins shown in Figures 2 and 4 contain the preferred plasticizer/rheology control agent; but, note the very severe degree of clumping and poor fiber formation in Figure 3 which suggests quite poor melt-spin behavior for PC-1369.

However, Figure 4 shows a fiber-draw test that appears positive for a lignin sample that was obtained from high-throughput screens to evaluate various other BL pretreatments before precipitation, washing and vacuum drying. An approach such as this in combination with a suitable plasticizer is expected to ultimately produce the desired result, an easily melt-spinnable, lignin-based precursor to carbon fiber.

These results appear to be worth following up. Thus, a series of follow-up tests are planned for next quarter at both the 20 mls combi level and at a larger bench-scale. Note that high-throughput combinatorial screens are performed in the PNNL combi system using a 6-well plate. The capacity of each well is about 20 mls. Only a few grams of lignin can be recovered from these screens, about enough to do only TGA-DSC and a fiber draw test.

Figure 4. Fiber draw-test Experimental combi lignin.

Conclusions

Initial experimental results suggest that the conceptual MWV differential recovery / purification process may require a more complex approach than originally anticipated.

PNNL combinatorial studies and corresponding fiber-draw tests have suggested post-pulping process modifications that may provide alternatives that have promise for leading to a lignin product acceptable for melt-spinning. These require further evaluation. They also probably can be integrated into a typical Kraft pulp mill. This and several related methods are presently slated for further evaluation and scale-up to bench-level in the next two quarters at both combi and larger-scale levels.

Presentations/Publications/Patents

None in FY 2006.