THRUST AREA: BIOCOMPOSITES

2.1 — Production of Low-cost Carbon Fiber from Heavy Fraction of Fast Pyrolysis Bio-oil

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Site: Iowa State University

Project Objectives. In this project, we propose to investigate the possibility of producing low-cost carbon fiber using the heavy fraction of bio-oil from fast pyrolysis of biomass. This provides a cost effective raw-material source for carbon fiber production. If successful, the outcome of the proposed research will provide valuable insights in producing low-cost carbon fiber from renewable resources.

Industrial Relevance, Need, and Appropriateness for the Center. Carbon fiber (CF) is a light-weight material that has superior tensile strength. Because of its unique characteristics advantages, it is popular in many applications. However, its application is currently limited because of its high production cost associated with the price of polyacrylonitrile (PAN), the main precursor of CF. Lignin extracted from biomass feedstock (pulp and cellulosic ethanol industries) could be a renewable alternative of PAN for low-cost CF. Usually this is achieved by mixing large amounts of PAN and/or plasticizer with the lignin to achieve a functional CF precursor but the result is a significantly inferior CF compared to those produced from PAN. These problems are mainly attributed to three-dimensional molecular structure of lignin, which makes it intractable in its unmodified state, and impurities carried over from lignin extraction processes.

Alternatively, fast pyrolysis, a robust and cost effective process that depolymerizes biomass in the absence of oxygen and at moderate temperatures, can be used to generate lignin-derived CF precursors. Fast pyrolysis yields a liquid mixture of sugars, acids, aldehydes, ketones, furans, aromatics, and phenolic monomers known as bio-oil that can be upgraded to biofuels and other biobased products. Bio-oil also contains 20-30 wt% of phenolic oligomers, also called pyrolytic lignin, as products of lignin depolymerization. These viscous, non-volatile molecules are difficult to upgrade to fuels and often cause problems if they are not separated from the other constituents in bio-oil prior to bio-oil upgrading. We have developed technology to separate pyrolytic lignin from other bio-oil constituents as a bio-oil heavy fraction (HF). Our work suggests that HF bio-oil has superior properties to lignin for use as a CF precursor. For example, it has a lower softening point than lignin, facilitating the spinning process of the precursor material during CF production. HF bio-oil also has higher carbon content than lignin, which could be important to improving the yield of CF. Moreover, it contains much lower metal and sulfur content than lignin, an important requirement in high quality CF production. More importantly, it may be possible to convert the phenolic oligomers in HF bio-oil into polymers with the high degree of linearity required to meet the mechanical properties of CF.
We hypothesize that using HF bio-oil as a CF precursor will produce better quality and higher yield of CF than is possible with lignin.

**Experimental Plan.**

**Task 1.** Conduct preliminary test to produce CF from existing HF bio-oil. HF bio-oil sample(s) previously produced in our lab from hardwood will be used as raw material to make CF for testing the concept.

**Task 2.** Produce HF bio-oil from different feedstock at different temperatures. Three different biomass feedstocks (for example, red oak, cornstover, switchgrass) will be selected and fast pyrolyzed in a bench scale fluidized bed, with pyrolysis temperatures of 450°C, 500°C, and 550°C, respectively. Bio-oil will be collected in 3-5 fractions maintained at different temperatures. Only the fractions containing the pyrolytic lignin will be utilized for this project. The HF bio-oil from the pertinent collected fractions of produced bio-oil will be further extracted if needed. HF bio-oil will be characterized using GPC, TGA, FTIR, NMR, CHN, Karl-fisher and ICP for overall molecular weight distribution, volatility, glass transition temperature, the extent of structural alignment, carbon content, moisture content and inorganic impurities. The existing bio-oil will be tested utilizing the same characterization protocol and compared to the newly produced oils.

**Task 3.** Produce CF from HF bio-oil and compare the qualities of final products. HF bio-oil samples will be used to produce CF. The performance of the HF bio-oil materials in the three steps of CF processing (spinning, thermostabilization and carbonization) and the qualities of final products will be compared.

**Task 4.** Modify and HF bio-oil and characterize its properties. HF bio-oil samples will be modified thermally or chemically prior to CF production and its properties will be characterized.

**Task 5.** Assess the quality of CF produced from modified HF bio-oil. The quality of CF produced from modified HF bio-oil will be assessed.

**Task 6.** Conduct techno-economic analysis to assess the cost of CF based on fast pyrolysis. Conduct an elementary techno-economic analysis based on the experimental results to determine the production cost.

**Potential risk and mitigation.** The quality of CF from HF bio-oil is unknown, and could be inferior to CF from PAN; in the case, we will mix HF bio-oil with different fractions of acrylonitrile to produce CF.

**Proposed Deliverables.** (1) Existing HF bio-oil is tested for CF production, (2) New HF Bio-oils from different types of biomass and temperatures are tested for CF production, (3) Quality of CF from different HF bio-oil is compared, (4) Structure of HF bio-oil is modified, (5) Quality of CF produced from optimized HF bio-oil is evaluated, and (6) Production cost of CF based on HF bio-oil is determined.

**Research Facilities.** The Biorenewables Research Laboratory has pyrolysis reactors that can produce fractionated bio-oil and a state-of-the-art analytical laboratory. Extruders are available in the bioplastics and biopolymers labs in the Center for Crops Utilization Research.

**Timeline and Budget.** The total proposed budget is $179,156 over three years, $59,934 in the first year. A PhD student in Mechanical Engineering will receive a ½ time appointment each year.
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