



Sandia National Laboratories



U.S. DEPARTMENT OF  
**ENERGY**

# Project Accomplishment Summary

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.



**Sandia National Laboratories**

Operated for the U.S. Department of Energy by  
**Sandia Corporation**  
Albuquerque, New Mexico

## **PROJECT ACCOMPLISHMENTS SUMMARY**

### **Cooperative Research and Development Agreement (#1640.12)**

between **Sandia National Labs** and **Goodyear Tire & Rubber Company**

Note: This Project Accomplishments Summary will serve to meet the requirements for a final abstract and final report as specified in Article XI of the CRADA.

Title: Lignin and Cellulose Functionalization to Create Advanced Filler Materials for Tire Applications

Final Abstract:

Incorporating lignin-based fillers from biomass has the potential to create a new US industry and eliminate the 3 billion pounds per year of petroleum-based carbon black fillers used today in tire manufacturing. A typical tire contains between 30-35% of carbon black, which generally improves the mechanical and electrical properties of the tire but adversely contributes to rolling resistance and decreases fuel efficiency. Sandia National Laboratories (SNL) and The Goodyear Tire & Rubber Co. (Goodyear) have collaborated to develop inexpensive, dispersible, fillers derived from the biobased material, lignin, as an alternative to carbon black to create new rubber composites. These new composites have the potential to be used in many other composite and rubber manufacturing industries. Based on our initial studies, tires fabricated with lignin are expected to have reduced rolling resistance. The Transportation Research Board estimates that 2 billion gallons of fuel (115 million tons of CO<sub>2</sub>) per year could be saved if the rolling resistance of all tires were to decrease by 10%.

Background:

Without alternatives to petroleum-based products the Energy Information Administration projects that foreign imports will increase 30% by the year 2030. To meet these challenges congress has mandated an increase in domestic renewable and alternative fuels of 35 billion gallons per year by 2017. Much of the new renewable fuels will be based on biofuels derived from lingo-cellulosic material. As a result of this increased biofuels production a large amount of lignin byproducts will potentially be available in addition to the large amount of lignin byproducts that already exist from the pulp and paper industry.

A recent study by Oak Ridge National Laboratory estimated that approximately 368 million dry tons of forest biomass (or ~30% of the total biomass) can be sustainably produced annually in the US. For many regions of the US, forest biomass represents the only biomass that can be sustainably produced in large quantities. Thus, forest biomass will be a critical part of the biomass feedstock supply. Although technical challenges exist that must be addressed before forest biomass finds utility beyond current practice, clear advantages become apparent when compared to other bio-based feedstocks. For example, wood has a high density, which significantly reduces the transportation costs, and can be harvested year round to eliminate long term storage issues. Wood is also low in ash relative to agricultural residues. Most importantly, a sustainable supply chain model has already been proven by the pulp and paper industry. For these reasons, forest biomass has a realizable advantage over agricultural residues.

The harvest of pulpwood is carried out in industrial forests using modern, certified, sustainable forestry practices to achieve maximum land utilization for both public and private use. The forest products industry is constantly developing innovative equipment for improved harvest economics and minimized environmental impact. Best Management Practices (BMP) have been established in Wisconsin, where Borregaard LignoTech currently obtains raw materials for the manufacture of sustainable lignosulfonate (chemically modified lignin) through the existing certified biomass supply chain. These practices are described in detail within the Forestland Woody Biomass Harvesting Guidelines published by the Department of Natural Resources. These guidelines are subject to continuous improvement through

periodic review and revision. This information is currently available to land managers and community developers.

Lignin is the main component of vascular plant walls providing the structure and strength of plant stems and roots. As such, it is the second most abundant organic material on earth. Lignin is commercially available through several manufacturers, including Borregaard. In most cases, the lignin is burned and used as energy within the paper mill itself. A recent study by the DOE states that lignin offers higher revenues to biorefineries through production of products, and that technology needs to be developed to realize lignin's potential.

The recent economic downturn coupled with greater access to the internet have pushed demand for newsprint to an all time low of 5 million tons per year down from 12 million tons per year a decade ago. Some forecasts for the next ten years predict an even larger decline in demand. Resources related to the year round collection of raw materials and feedstocks including wood chips suitable for the production of newsprint are already in place and potentially underutilized due to this lack of industry growth. We intend to leverage the existing feedstock collection processes of the pulp and paper industry and by BIL for the isolation and separation of lignin from cellulosic materials, which could be converted to biofuels.

An economically and environmentally sustainable biomass based replacement for petroleum-derived carbon black in tire applications may be realized through modified lignin. Over five million metric tons of carbon black are used each year as reinforcing fillers in tires. Carbon black is made through a very energy intensive spray pyrolysis of petroleum based products at temperatures reaching 1870 °C. A typical tire contains between 30-35% of carbon black which generally improves the physical properties of the rubber but adversely contributes to rolling resistance which decreases the fuel efficiency of the tire.

Numerous studies designed to use lignin as reinforcing filler in rubber compounds have been reported over the past 60 yrs. In general, it was observed that lignin displayed reinforcing properties far below those obtained with carbon black. Simply using lignin as a "drop-in" replacement for carbon black is not sufficient as negative effects are observed on properties such as tensile strength, tear resistance and abrasion resistance.

#### Description:

Lignin has great potential to replace carbon black in tire applications. Several methods were explored to functionalize lignin in order to improve dispersion within the rubber matrix and reinforce the rubber. Esterification and silylation were initially explored as potential functionalization chemistries. Esterification modified lignin was not thermally robust and did not withstand the compounding and curing temperatures required to cure the rubber. Silylation proved to be an effective method to modify and thus disperse the lignin within the rubber matrix.

Phase 1. Initial small-scale (20 g) experiments were run to determine the reinforcing power of the modified lignin. Dozens of modified lignin samples were evaluated. Those initial experiments determined that silylation was a very good method to modify and disperse the lignin within the rubber matrix. These experiments indicated that silylated lignin reinforced as well as or better than non-reinforcing grade carbon black.

Phase 2. Intermediate-scale (100g) experiments using the down selected modification chemistry identified in from phase I. The intermediate-scale experiments did not show as much promise as small-scale experiments. It was determined that the lignin was agglomerating and not dispersing well within the rubber matrix so processes were developed to decrease the average lignin particle sized from 1 um to sub 100 nm.

Phase 3. Intermediate-scale evaluation (100g) using the newly modified sub 100 nm particles did not show an improvement relative to carbon black. Several additional linkers were also evaluated to improve the final rubber properties as well.

The research resulted in one invited talk and one patent application and three technical advances.

Benefits to the Department of Energy:

Research conducted as part of this CRADA task has resulted in the development of a technology that could potentially eliminate 2 billion gallons of fuel each year by improving rolling resistance of tires improving energy efficiency.

Economic Impact:

Incorporating lignin-based fillers from biomass will create a new US industry and eliminate the 3 billion pounds per year of petroleum-based carbon black fillers used today in tire manufacturing. New energy related applications could potentially be developed as these new fillers are incorporated into tires and rubber products used in automobiles and trucks. The US Census Bureau estimates that in 2006 over 60,000 workers converted materials worth over \$10 billion into tires. In 2007, Goodyear consumed over 3 billion pounds of raw materials in the US. Approximately 70% or around 2 billion pounds were derived from petroleum sources. The major contributors to this total were synthetic rubber and carbon black. The development of bio-derived fillers in place of carbon black could assist in the conversion to bio-based alternatives and revolutionize our decades-old dependence on oil-derived raw materials. These new fillers could be applied to numerous rubber products currently used in automotive applications industry wide If the technology were fully developed and commercialized.

Project Status:

This project was terminated early.

## ADDITIONAL INFORMATION

### Laboratory/Department of Energy Facility Point of Contact for Information on Project

Shawn M. Dirk  
Sandia National Labs  
505-844-7835  
smdirk@sandia.gov

### Company Size and Points of Contact

Goodyear Tire & Rubber Company with more than 500 employees

### CRADA Intellectual Property

The intellectual property is contained in three technical advances and one patent application.

### Technology Commercialization

N/A

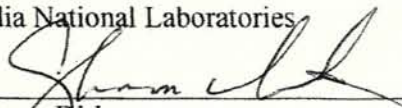
### Project Examples

N/A

**PROJECT ACCOMPLISHMENTS SUMMARY**  
**Cooperative Research and Development Agreement (SC01/01640.12)**  
**between Sandia National Laboratories and Goodyear Tire & Rubber Company**

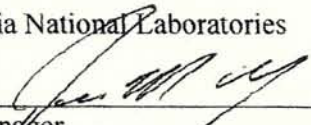
This summary has been approved for public release by Sandia and Goodyear Tire & Rubber Company

Sandia National Laboratories

By   
Shawn Dirk  
Principal Investigator

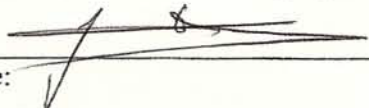
11/6/12  
Date

Sandia National Laboratories

By   
Manager  
WFO/CRADA Agreements

10-24-12  
Date

Goodyear Tire & Rubber Company

By   
Title:

11/26/12  
Date

In order to expedite the process, if we do not receive your signed reply by 12/7/2012 we will assume your concurrence for the release of this document to the public.