DOE Lignin to Carbon Fiber Workshop

Detroit, MI

Presented by:

Mark Downing
Bioenergy Program
Environmental Sciences Division

Oak Ridge National Laboratory

June 4, 2013

Substantive importance discussions

- **What are the larger substantive issues?**
- **What are the questions we need to be asking?**
- **What is the State of Technology?**
- **What is currently researchable?**
- **What is deployable? At what scale? With what quality?**

Substantive importance discussions

- **What are our capabilities?**
  - **Carbon Fiber (materials) State of Technology**
- **What are our processing capabilities? At what scale?**
  - **Carbon Fiber Technology Facility (CFTF)**
- **What are our analytical capabilities?**
  - **Manufacturing Demonstration Facility (MDF)**
- **What about precursor sources?**
  - **Bioenergy Science Centers (BESC)**
- **What are our partnership possibilities?**
  - **Carbon Fiber Technology Consortium (CFTC)**

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Key Policy Driver: Renewable Fuel Standard Program

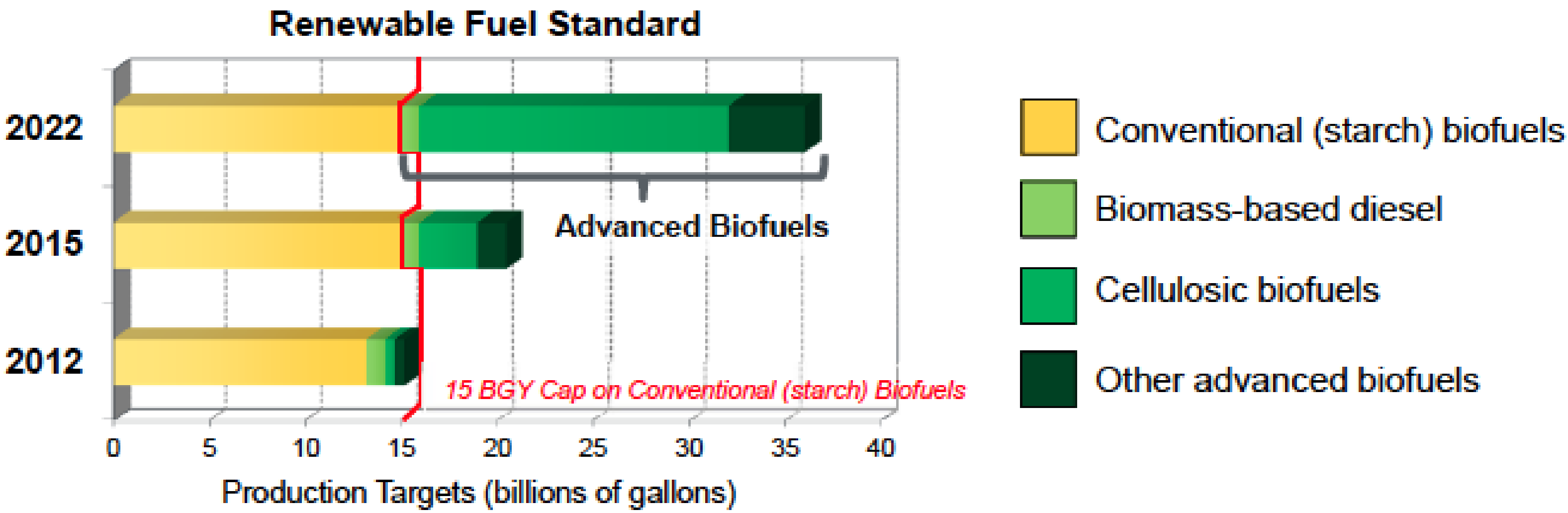
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

The Energy Independence and Security Act (EISA) of 2007 sets aggressive goals:

- Move renewable fuels into the marketplace
- Reduce the nation's dependence on foreign sources of energy
- Reduce GHG emissions from the transportation sector.

EISA established production volumes for the Renewable Fuel Standard Program (RFS), increasing the supply of renewable fuels to 36 billion gallons by 2022.

The U.S. Department of Energy's (DOE) Biomass Program focuses on developing advanced biofuels to help meet the RFS goals.



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Overall picture:
Biomass for fuels and bioproducts

Cellulose and hemicellulose

Chemical building blocks: Plastics, industrial additives, biomedical applications

Biofuels

BESC
BioEnergy Science Center

Lignin

Up to 50% reduction in finished carbon fiber production cost

Melt spinner

Carbon fiber production line

Conversion cost: 50% of conventional

Robotic preforming

Lignin and innovative processing: ~50% less than PAN and conventional processing

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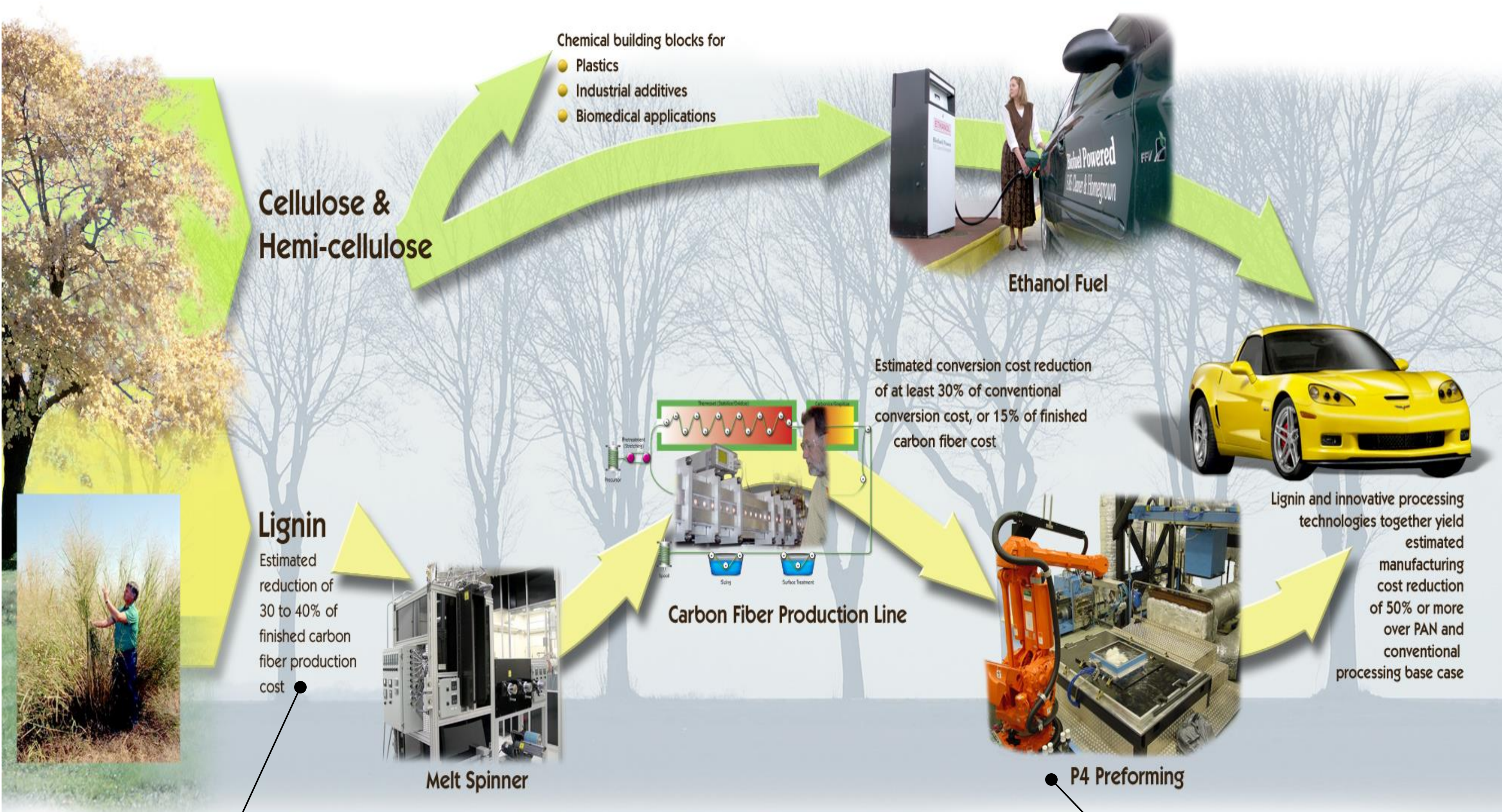
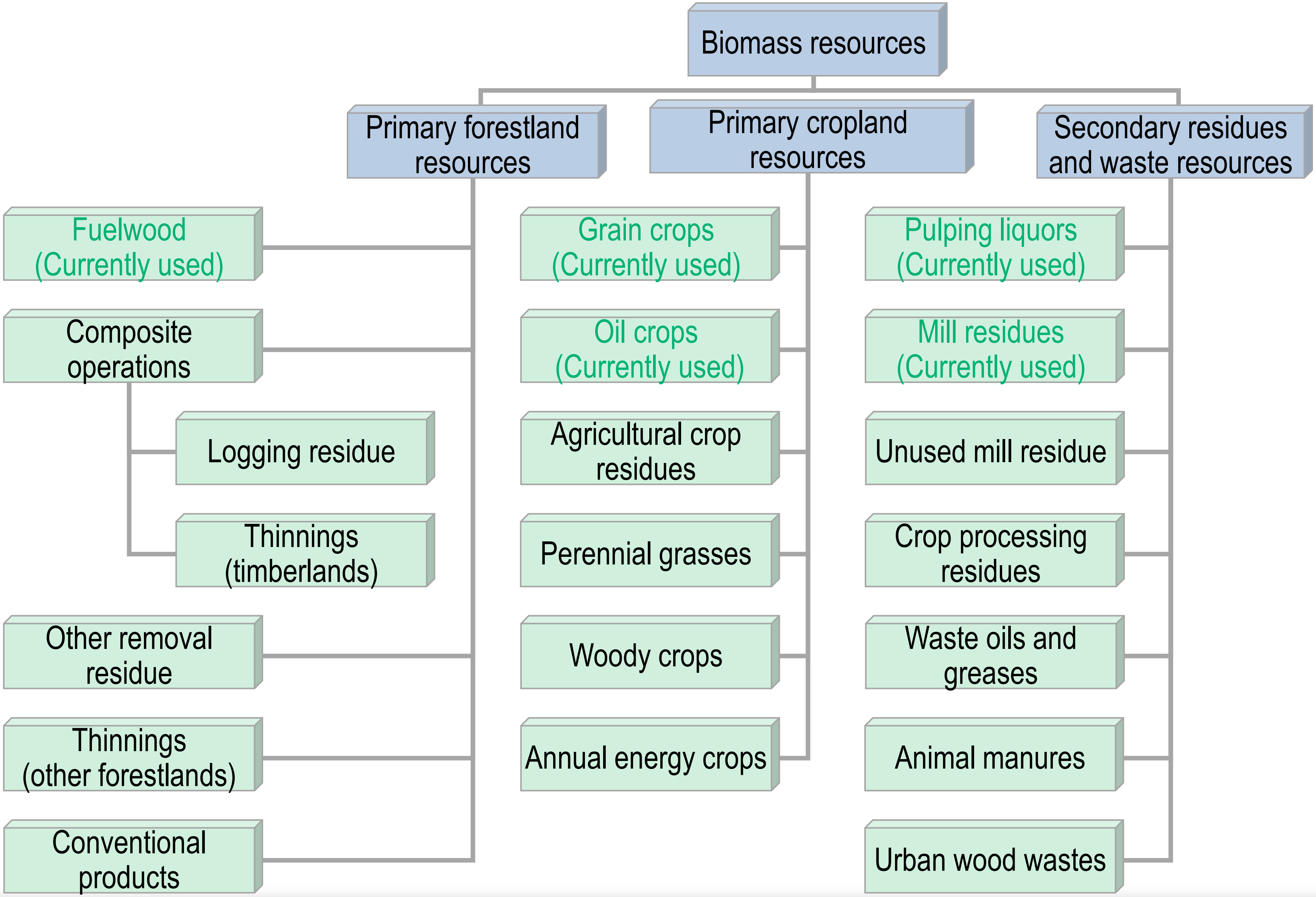
Biofuel and Lightweight Materials from Renewable Resources



30% to 60%

Robotic preforming

Biomass feedstocks for energy



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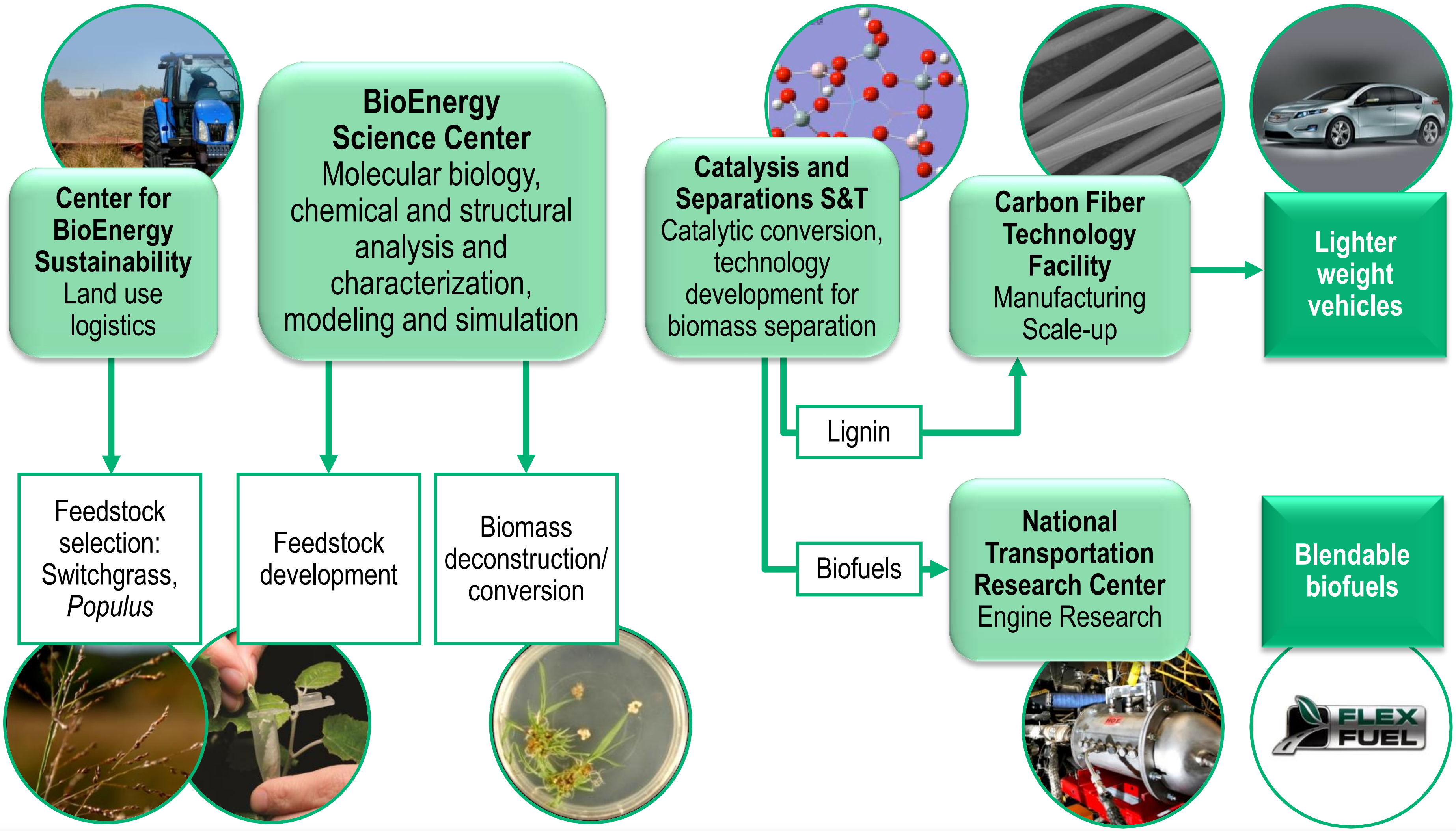
Bioscience and biotechnology spans resource to end use

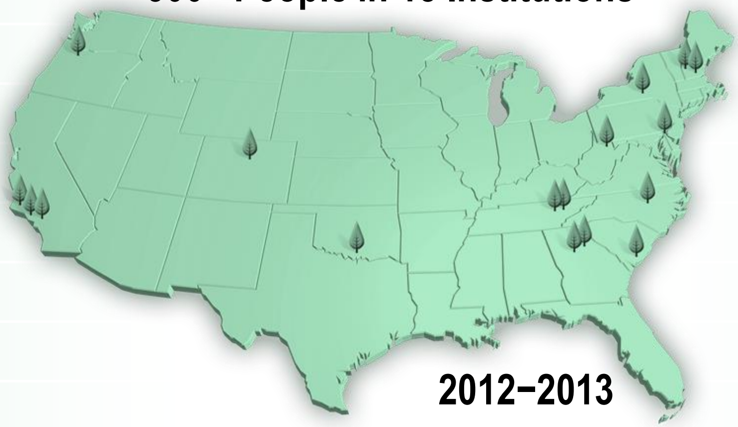


BioEnergy Science Center

A multi-institutional, DOE-funded center performing basic and applied science dedicated to improving yields of biofuels from cellulosic biomass

- Oak Ridge National Laboratory
- University of Georgia
- University of Tennessee
- Dartmouth College
- Georgia Institute of Technology
- West Virginia University
- ArborGen, LLC
- Ceres, Incorporated
- Mascoma Corporation

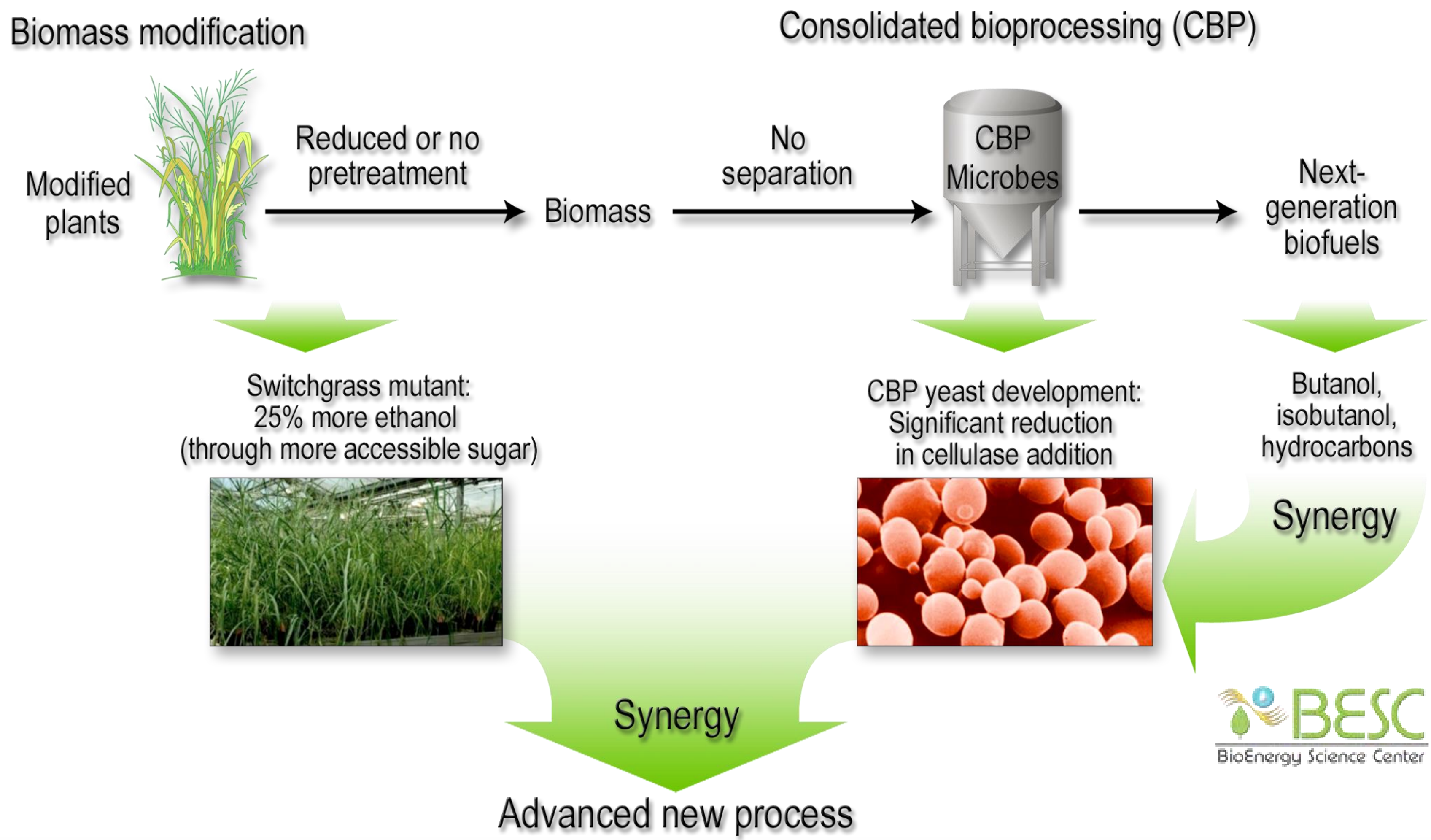
300+ People in 18 Institutions



2012−2013

- Samuel Roberts Noble Foundation
- National Renewable Energy Laboratory
- Cornell University
- University of California—Riverside
- North Carolina State University
- University of California—Los Angeles
- DuPont
- GreenWood Resources
- University of North Texas

Consolidated bioprocessing (CBP) will revolutionize how biomass is processed and converted



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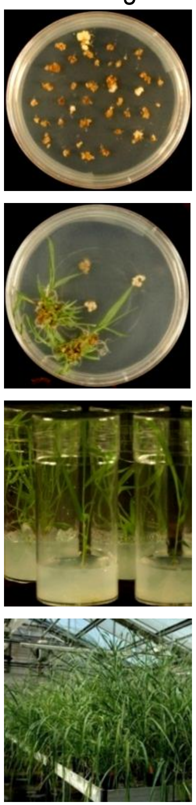
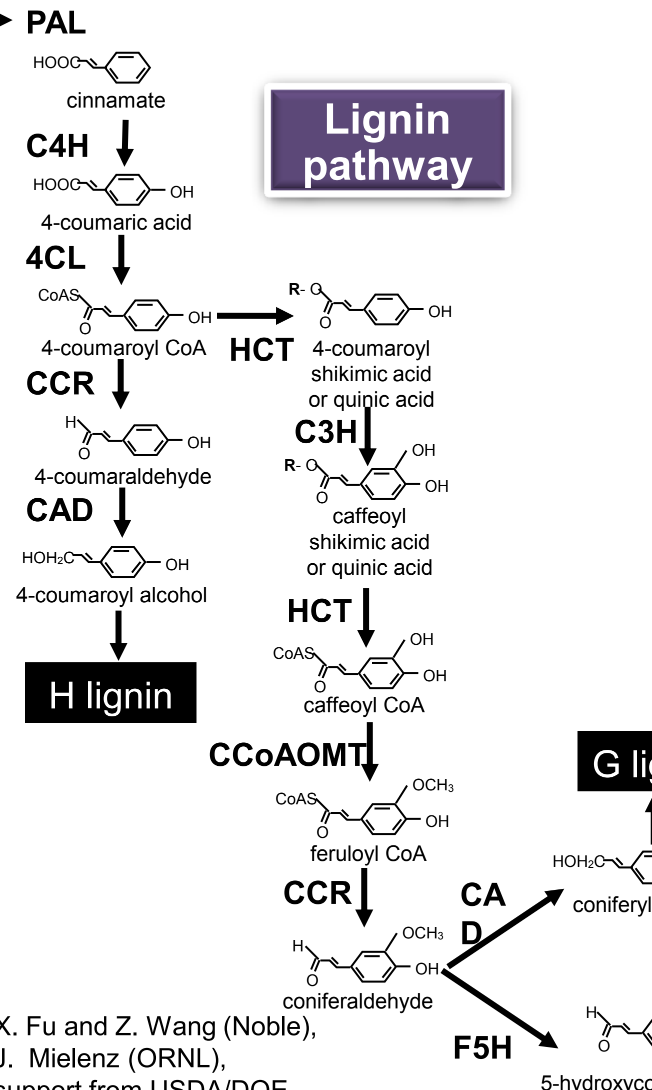
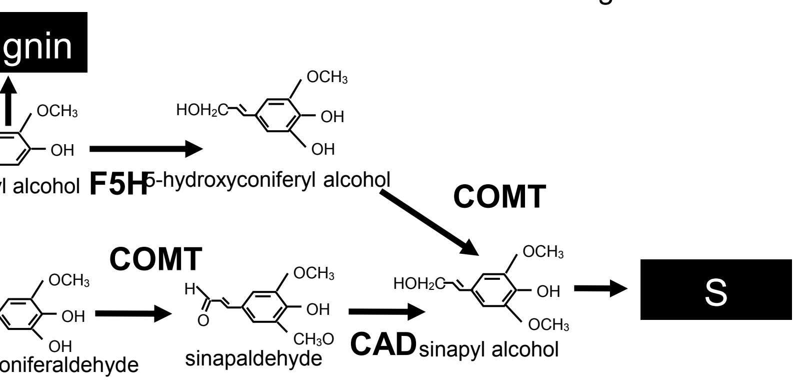
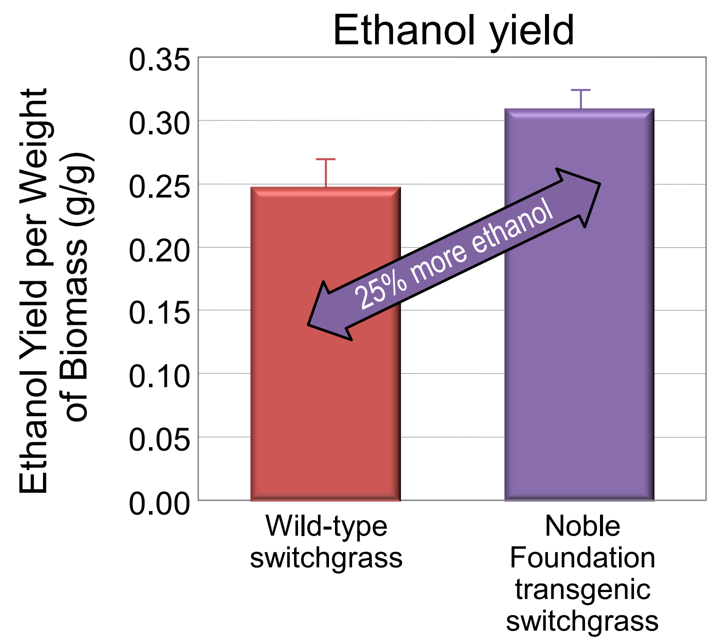
Genetic block in lignin biosynthesis in switchgrass increases biofuel yields

Agrobacterium-mediated transformation of switchgrass









THE SAMUEL ROBERTS NOBLE FOUNDATION

X. Fu and Z. Wang (Noble),
J. Mielenz (ORNL),
support from USDA/DOE

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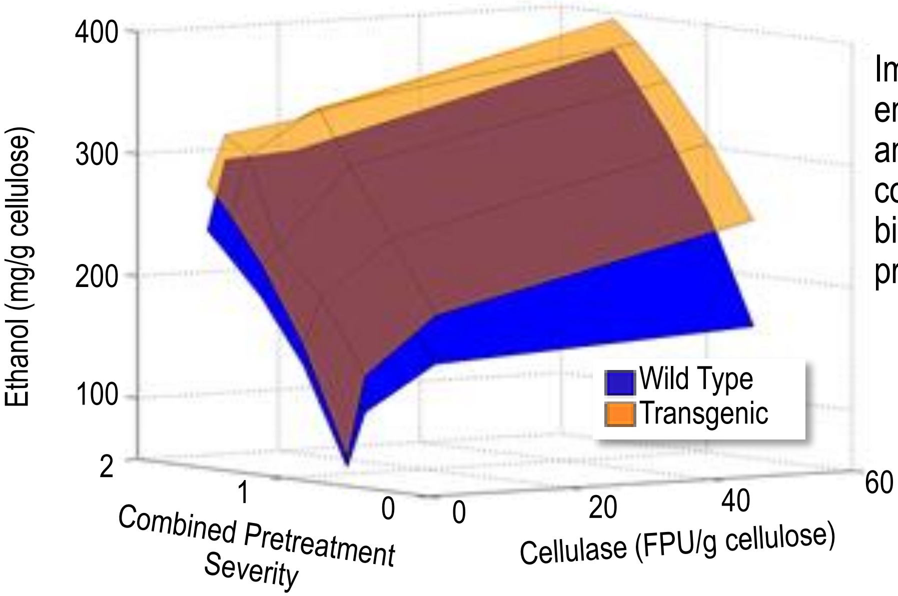
Genetic manipulation of lignin improves biofuel production from switchgrass

- Down-regulation of a single gene reduces recalcitrance with no apparent growth defects and leads to:
  - Increase in ethanol production by over one-third
  - Reduction in needed severity of pre-treatment
  - Evidence that biofuel processing costs can be reduced by at least 20% with 300−400% lower enzyme costs

Wild-type (L) and 3 transgenic switchgrass plants (R)



Impact of enzyme levels and pretreatment conditions on biofuel production

Fu *et al. PNAS*, 2011

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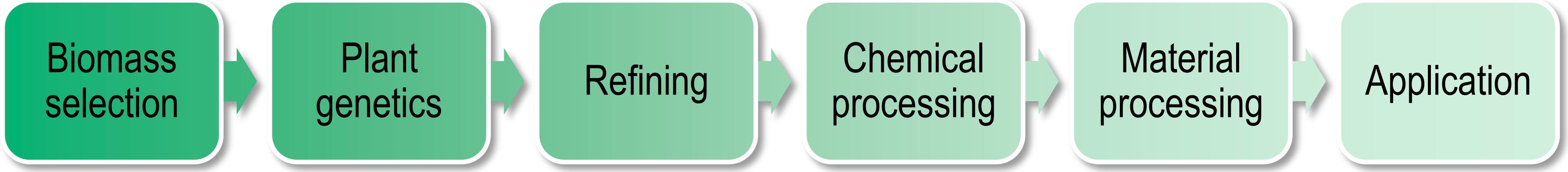
Lignin: A renewable low-cost feedstock

- Characteristics
  - Can be derived from trees (20−30% lignin) and other biomass
  - Currently a by-product of pulping and biorefineries
  - Readily available non-petroleum-based CF precursor
  - Potentially lowest cost precursor



The case for lignin

- Abundant: 40M tpy can be extracted from Kraft mills with no adverse effect on mill balance
  (source: Peter Axegard, Innventia)
- Inexpensive: \$0.03−\$0.08/lb fuel value
- Procured sustainably
- Renewable and carbon rich
- Domestic
- Rural jobs
- Enhances biorefinery economics

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Potential lignin-derived products

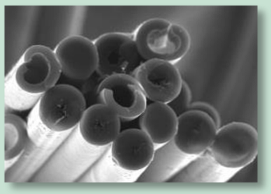
Product	Current technology status	Market risk	Challenges	Market volume
Hydrocarbon and aromatic chemicals				
Benzene/toluene/xylene	Partially developed	Low	Catalytic challenges: Selective dehydroxylation, demethoxylation and dealkylation	High
Phenol/substituted phenols	Partially developed	Low	-do- and Secondary derivatization of BTX chemicals	High
Aromatic polyols	Emerging	?	-do-	?
Biphenyls	Emerging	?	-do-	Moderate
Cyclohexane	Emerging	Low	-do-	High
Aromatic monomers	Emerging	?	Selective hydrogenolysis	?
Oxidized products (vanillin/DMSO)	Developed	High	Biocatalytic route for selective oxidation	Low
C1-C7 gases and mixed liquid fuels	Emerging	Low	Catalyst life, reduce process steps, process scale-up	High
Macromolecules and their derivatives				
Carbon fiber	Partially developed	Moderate	Economic challenges: Isolation of lignin, spinning rate, carbon yield, varied lignin sources	High
Polymer extender	Partially developed	Moderate	Modification of lignin to compatibilize with polymer matrices, color of lignin-extended product	Moderate
Thermosets	Emerging	Moderate	Molecular weight and viscosity control of the product, varied lignin sources	?
Formaldehyde free adhesives	Partially developed	Moderate	Consistency of lignin to ensure constant cure rate	High
Syngas products				
Methanol/dimethyl ether	Developed	Low	Technological challenges: Economic syngas purification, process scale-up	High
Ethanol/mixed alcohols	Emerging	Moderate	Economic syngas purification, catalyst and process improvement to produce 2-C alcohols, process scale-up	High

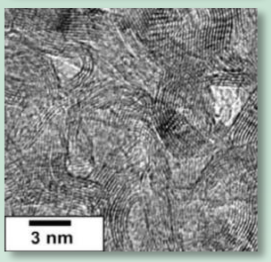
Source: Holladay et al., Top Value-Added Chemicals from Biomass, PNNL-16983, October 2007

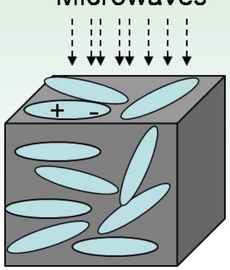
Current carbon fiber technology:
From lab discovery to commercialization

DOE Office of Science

- Precursor chemistry and microstructure
- Process science: Microwaves create internal heating through material dipole vibrations







Fiber processing

DOE EERE

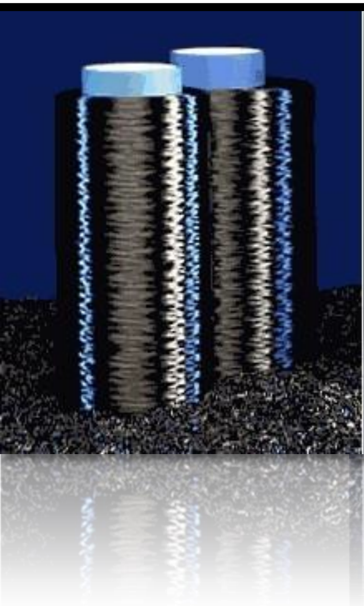
- Melt spinning increases throughput with less energy and solvent
- Microwave/plasma-based conversion processes reduce residence time and energy demand

Industry partnerships

- CFTF: 25 ton/year pilot line facility
- Large IP portfolio available for licensing
- Developing key partnerships in multiple industries

Carbon fiber product forms

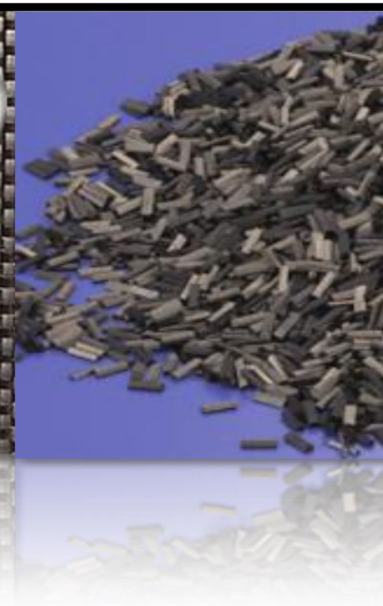
Continuous fibers



Unidirectional tapes and prepregs

Woven fabrics and prepregs

Chopped or milled fibers



Non-wovens

Source: Chris Red, “2012 Global Market for Carbon Fiber Composites,” Carbon Fibers 2012

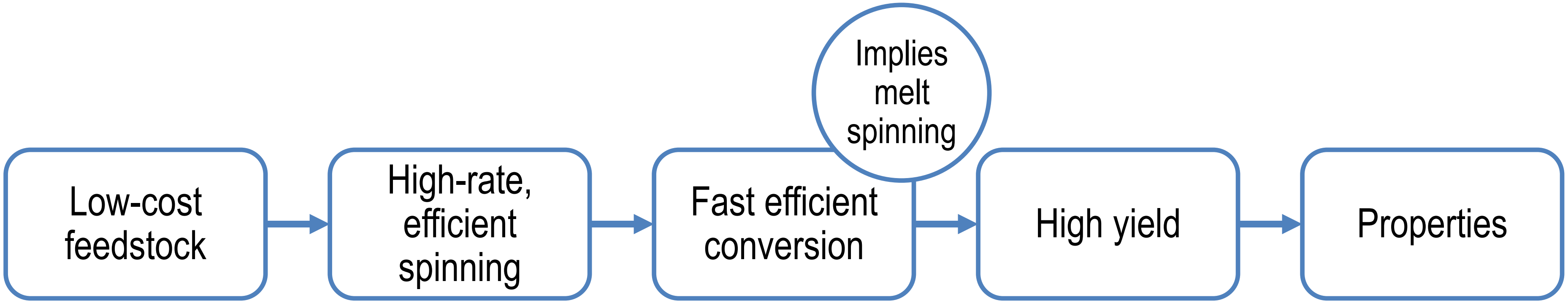
Carbon fiber research priorities: Alternative precursors

Petroleum-based polyacrylonitrile (PAN)	Textile PAN and polyolefin-based precursors	Lignin: A sustainable resource material
• Most common precursor • Cost fluctuates with crude oil prices	• Lower cost • Petroleum-based	• Commonly derived from wood via Kraft pulping • By-product of cellulosic ethanol production: Supply will increase as biorefineries are built • Cost is largely independent of oil prices

Today, almost half of carbon fiber manufacturing costs are associated with precursors

Keys to maximizing lignin carbon fiber value

- Tendencies:
  - Hardwood lignin melt spins well and stabilizes slowly
  - Softwood lignin stabilizes well but doesn’t readily melt spin
  - High purity is needed for melt spinning



Scalable achievement of fast conversion, high-rate spinning, and high yield has proven to be very elusive

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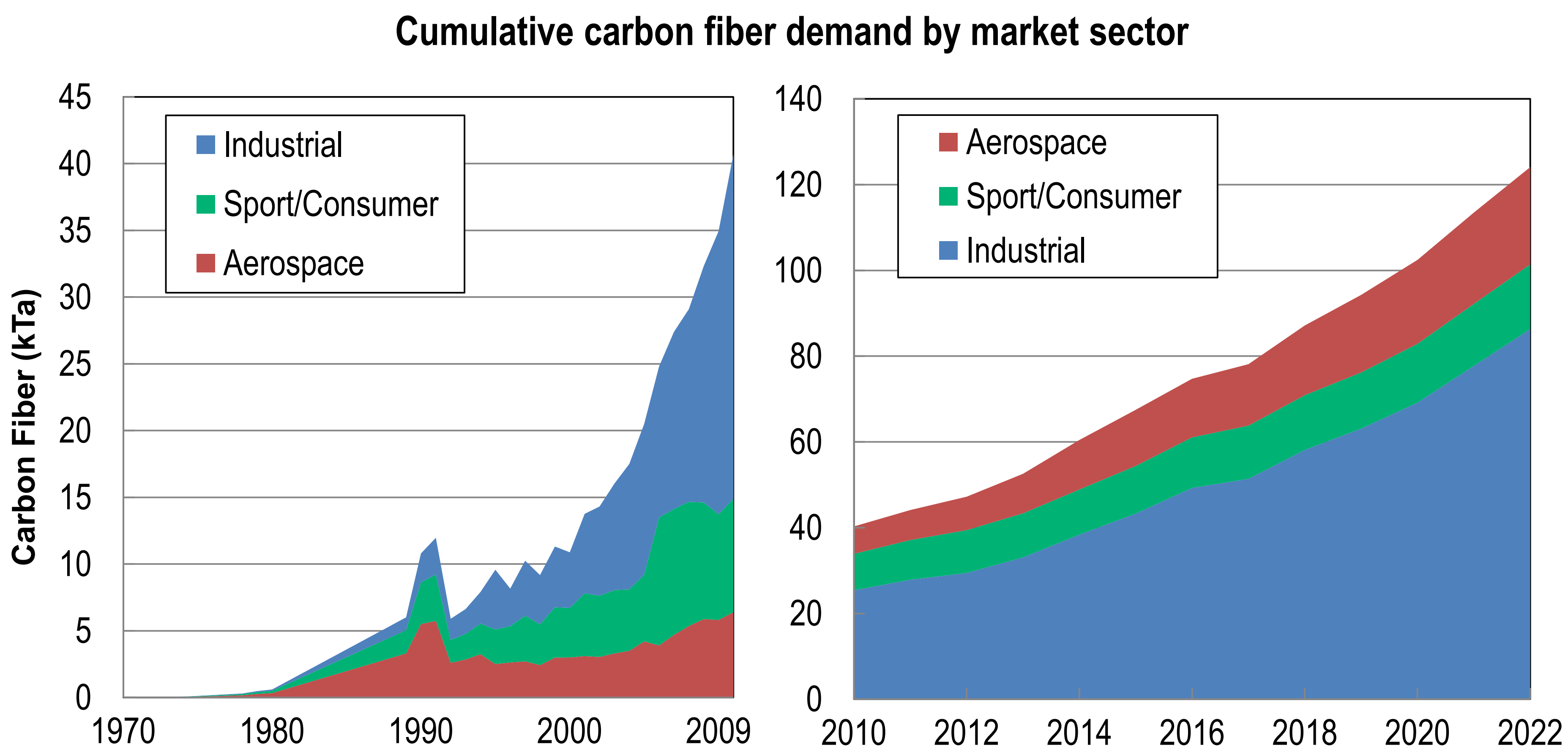
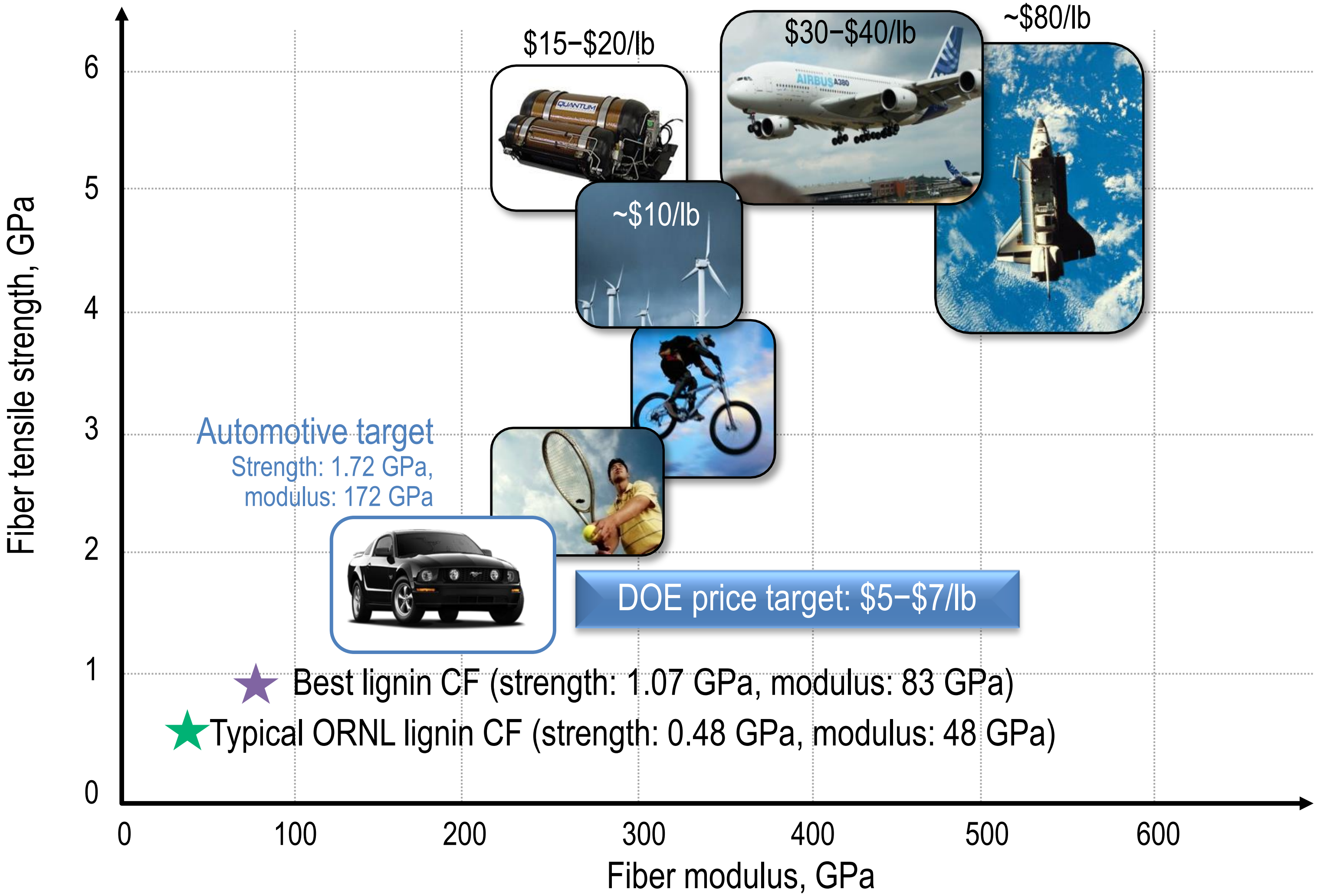
Carbon fiber market

Automotive, wind energy, pressure vessels, oil and gas, and all other high-volume energy applications of carbon fiber composites are in the "industrial" market sector



Source: Chris Red, "2012 Global Market for Carbon Fiber Composites," Carbon Fibers 2012

Costs and properties of structural carbon fibers

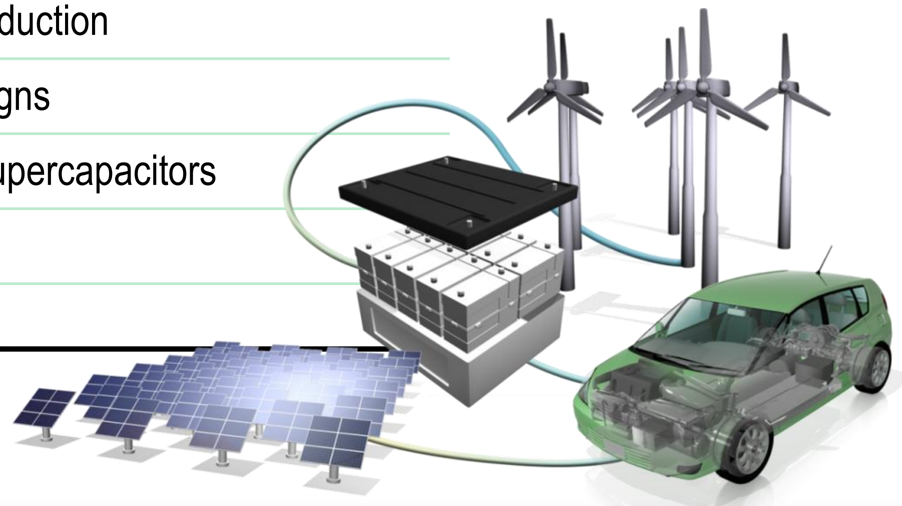


Other potential markets for low-cost carbon fiber

Civil infrastructure	Rapid repair and installation, time and cost savings
Biomass materials	Alternative revenue, waste minimization
Nontraditional energy	Geothermal, solar, and ocean
Non-aerospace defense	Light weight, higher mobility
Aerospace	Secondary structures
Power transmission	Less bulky structures, zero CLTE
Oil and gas	Offshore structural components
Vehicle technologies	Necessary for >50% mass reduction
Wind energy	Needed for longer blade designs
Energy storage	Flywheels, Li-ion batteries, supercapacitors
Electronics	Light weight, EMI shielding
Pressurized gas storage	High specific strength

Common issues

- Fiber cost
- Fiber availability
- Design methods
- Manufacturing methods
- Product forms



Potential automotive market is huge for low-cost carbon fiber

Carbon fiber potential in 2017 at 50% of current price

Global automotive production by car type	Expected vehicle production	Expected use of CF in cars	Demand for CF at 50% of current price (pounds)	Market for CF at 50% of current price ($M)
Super cars	6,000	100%	1.3 million	$7M
Super luxury cars	600,000	10%	101.2 million	$506M
Luxury cars	4 million			
Other/regular cars	92 million	1%	202.4 million	$1,012M
Total	**97 million**		**305 million**	**$1,525M**

3× current global CF demand for **all applications**;
10B lb potential automotive demand at full market penetration

Source: Lucintel, ACMA Composites 2012

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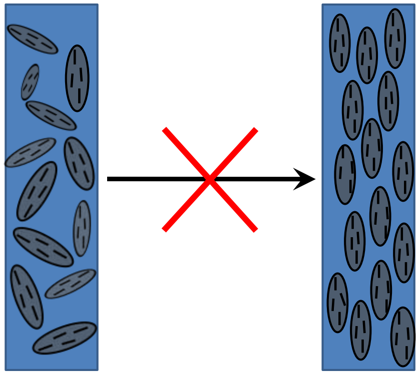
State of structural lignin carbon fiber technology

- Mechanical properties:
  - Best strength and modulus to date ~ 155 ksi / 12 Msi (with softwood)
  - Typical strength and modulus ~ 70 ksi / 7 Msi
- Multi-filament tows not despoolable
- Single filaments that are moderately stretchable have been produced
- Lignin carbon fiber filaments exhibit evolving graphitic that is isotropic
  - Aligned crystallite morphology has not been reported
- Earliest development work dates to 1960s; DOE funding initiated in late 1990s

Multi-filament lignin tows

Lignin does not readily produce structural fibers



Filament crystallite orientation

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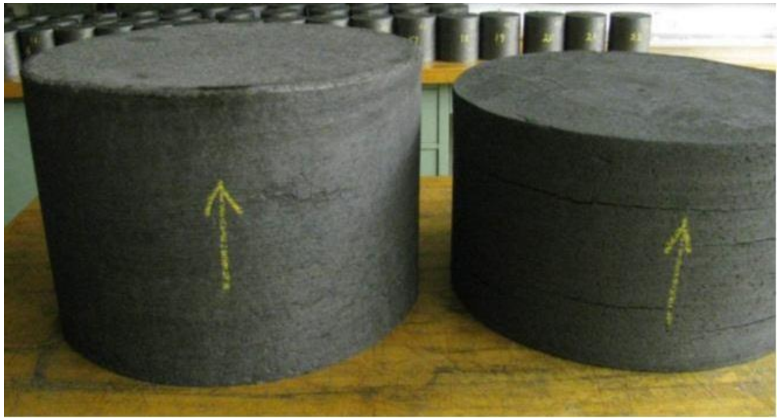
Lignin-based carbon fiber (LCF) meets performance requirements for high-temperature thermal insulation



18 in. diameter lignin GRI™ prototypes

Various GRI™ products machined into shapes

GRAFTech International | Redefining limits

Figures courtesy GrafTech

Other potential functional applications: Batteries, capacitors, sorbents (filtration, natural gas storage), fireproof fabrics

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Keys to structural properties: Possible solutions to the problem

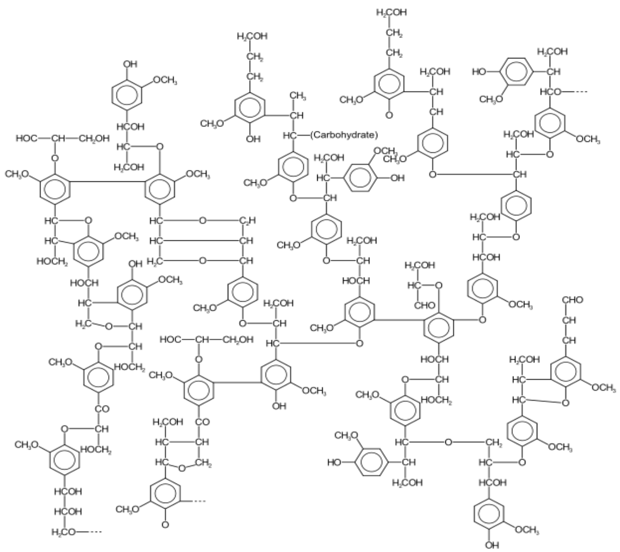
Feedstock selectivity

- Identify preferred lignin characteristics (currently not well understood)
- Select and/or genetically engineer plants that produce lignin with preferred characteristics
- Mill selectivity
- Selective isolation/extraction/purification processes
- Molecular weight control (fractionation)

Chemistry is the "master key" to structural properties

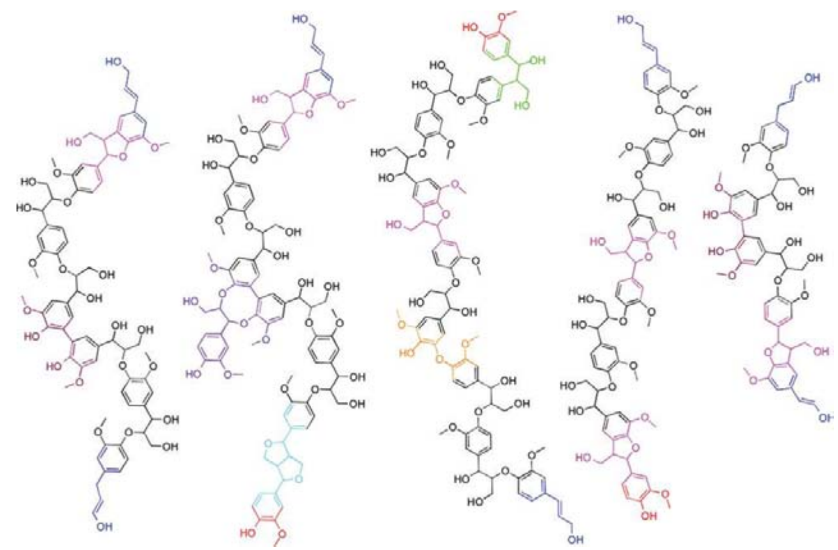
Extensive chemical characterization is needed				
Blending	Doping	Derivatization	Modification	Cracking

PAN based precursor is not 100% PAN



Accepted hyperbranched structure of lignin

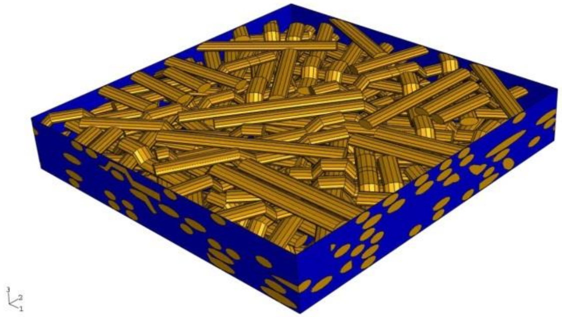
Lignin structure is a matter of debate



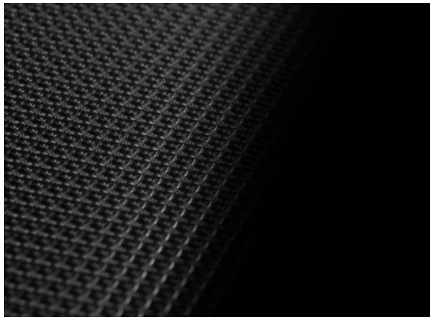
Recently proposed linear structure of lignin (Crestini et al., *Biomacromolecules* 2011)

What is a composite?

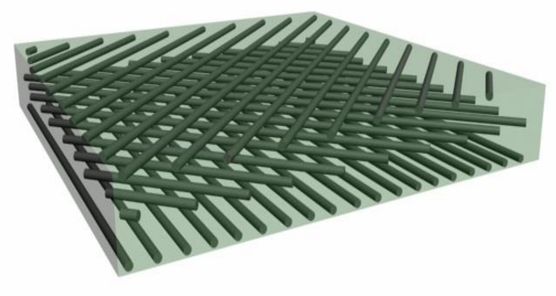
- Combination of 2 or more constituent materials, each retaining its distinct phase, working together to deliver properties that cannot be achieved by either alone
- Common examples:
  - Paper (cellulose fibers in a binder)
  - Concrete (steel rods reinforcing cement matrix)
  - Particle board (wood chips reinforcing polymeric matrix)
  - Trees (cellulosic reinforcement in lignin matrix)



Chopped fiber,
random composite
(courtesy Rutgers University)

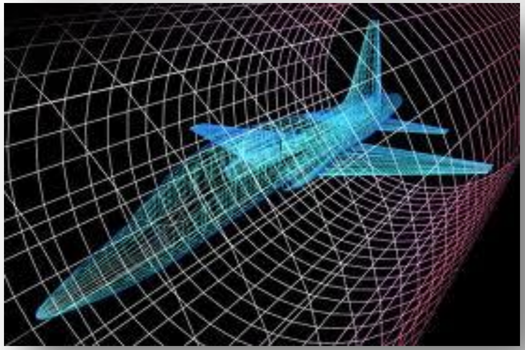


Woven carbon fabric



Continuous fiber composite with unidirectional lamina

Manufacturing Matters



U.S. Manufacturing Sector

- Contributes about 12% of gross domestic product (GDP)
- Directly employs ~12 million people
- Accounts for 60% of U.S. engineering and science jobs
- Supplies about 57% of U.S. exports
- Produces nearly 20% of the world's manufacturing output

Manufacturing is the most diverse end-use sector— in terms of energy services required, sources of energy used, technologies needed, and product output.

We are focusing ORNL resources to support manufacturing initiative

- Manufacturing and materials R&D to:
  - Reduce the energy intensity of U.S. industry
  - Support development of new products
  - Strengthen our nation's competitiveness and economic vitality
- Leveraging ORNL's distinctive core capabilities
  - Neutron scattering
  - High-performance computing
  - Advanced materials
  - Advanced characterization

***MDF*: a multidisciplinary DOE-funded facility dedicated to enabling demonstration of next-generation materials and manufacturing technologies for advancing the US industrial economy**

www.ornl.gov/manufacturing

ORNL has exceptional resources for materials and manufacturing R&D

National user facilities	Specialized capabilities	Secure work space
• Building Technologies Research and Integration Center • Center for Nanophase Materials Sciences • High Flux Isotope Reactor • High Temperature Materials Laboratory • National Center for Computational Sciences • National Transportation Research Center • Spallation Neutron Source	• Carbon Fiber Technology Center • Center for Advanced Thin-film Systems • Materials Processing • Metrology • Robotics and Energetic Systems • Sensors and Signals Research • Thin Film Deposition and Analytical Facility	• Multiprogram Research Facility

End-to-end research at a single site to reduce costs, accelerate innovation, and maximize capital investment culminating in prototypes

MDF – integration of cutting-edge manufacturing technologies

Additive Manufacturing

- Metal Powder Bed Consolidation
- Direct Metal Deposition
- Polymer Extrusion
- Ultrasonic Consolidation

Carbon Fiber

- Precursor to Filament
- Filament to Carbon Fiber
- Carbon Fiber to Composite Material

Advanced Materials & Processing

- Lightweight Metals
- Roll-to-Roll
- Low-Temperature
- Transient Field

Automation & Controls

- Modeling & Simulation
- Sensing, Tracking & Measurement
- Communicating Wirelessly
- Systems Engineering

Manufacturing Demonstration Facility

Market

Technology Impacts:

- Market Driven Adoption of New Materials and Processes
- Transformational & Cross-Cutting for Next-Generation Products

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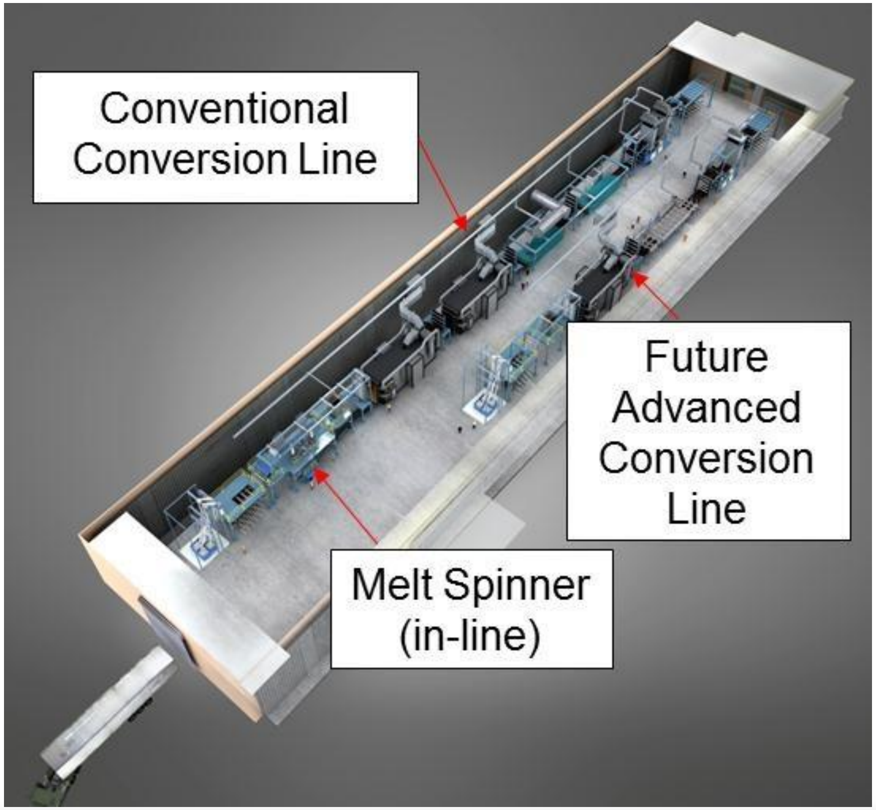
Carbon Fiber Technology Center (CFTF) Delivers Unmatched Flexibility

- Highly instrumented, highly flexible conventional carbon fiber line for "any precursor in any format"
- Melt-spun fiber line to produce precursor fibers
- Provisions for additional future equipment
- Produce up to 25 tonnes/year of carbon fibers
- Demonstrate technology scalability
- Train and educate workers
- Work in partnerships with industry



Facility and equipment perspective

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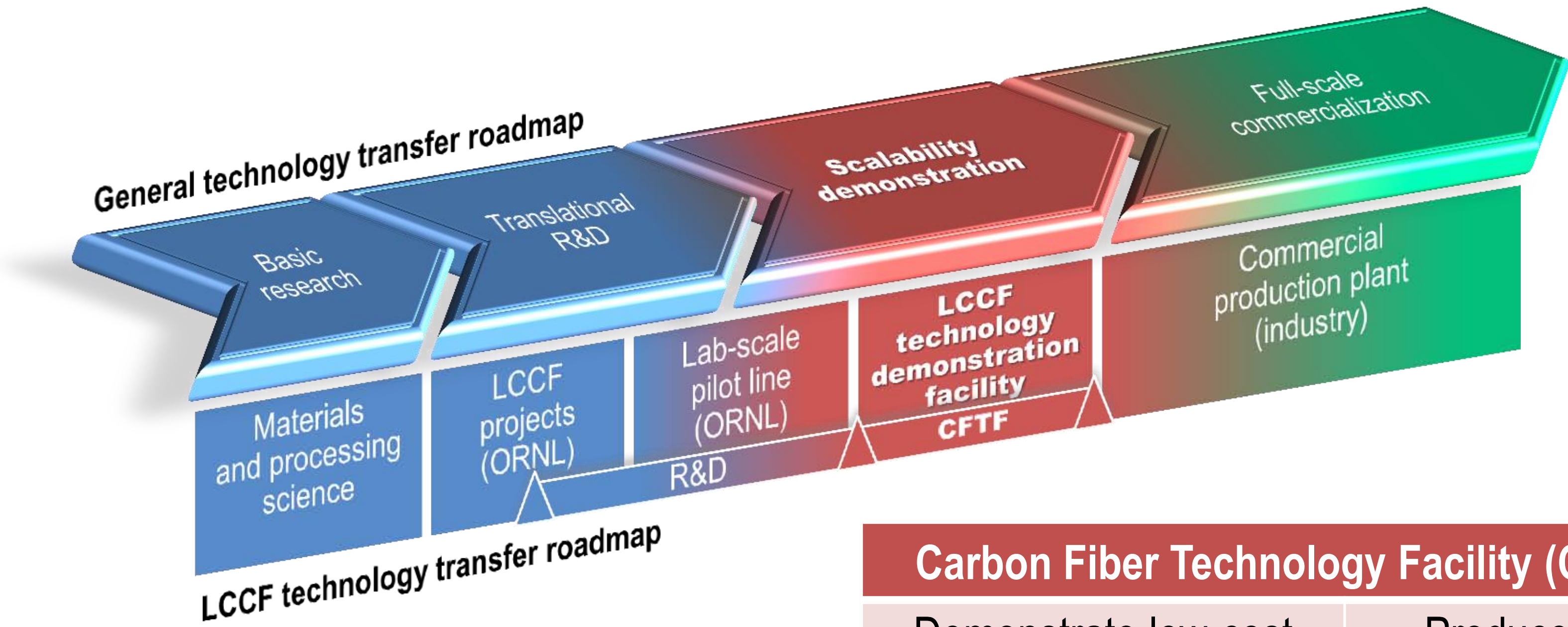
Building a bridge from R&D to deployment and commercialization



Carbon Fiber Technology Facility (CFTF) roles	
Demonstrate low-cost carbon fiber (LCCF) technology scalability with the last scaling step before full-scale commercial production	Produce quantities of LCCF needed for large-scale material and process evaluations and prototyping

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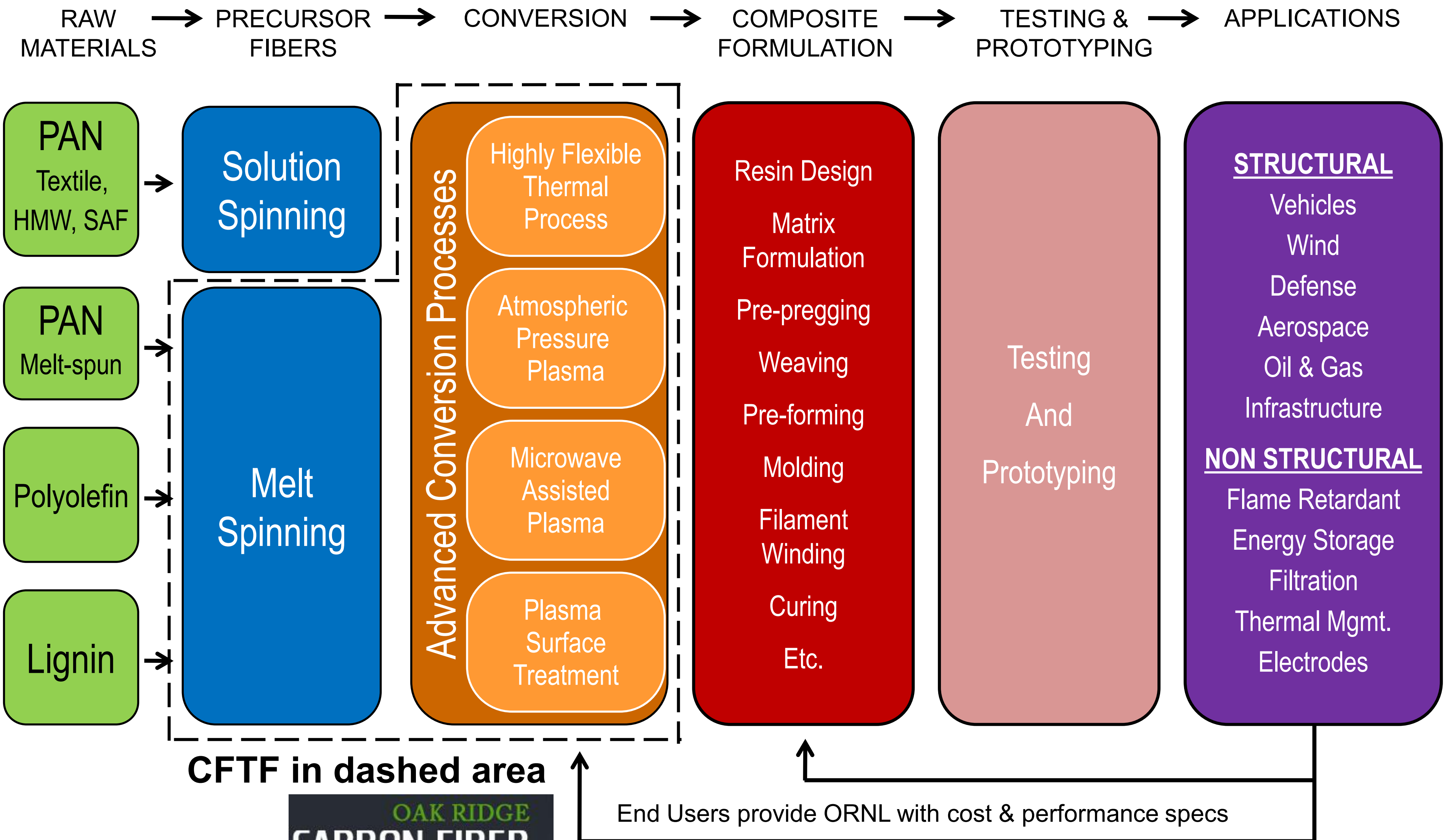
CFTF Engages the Entire Composites Value Chain



OAK RIDGE CARBON FIBER COMPOSITES CONSORTIUM

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Collaboration in Workforce Training

Roane State Community College
AMTEC — A vision for the future — Roane State Community College Advanced Materials Training and Education Center

ORISE — Oak Ridge Institute for Science and Education
ORAU — Oak Ridge Associated Universities

Oak Ridge National Laboratory — Managed by UT-Battelle for the Department of Energy
Carbon Fiber Technology Facility

Pool of Candidates

- DOL grant funded
- Located at ORNL
- Industry focused training
- For qualified unemployed or under-employed

Technician Internship Program

- High-quality STEM learning experience
- Collaboration with researchers in field of interest
- Growth of S&T talent
- Hands-on experience on complex CF line
- Learn S&T underpinning ORNL research
- Develop skills directly transferrable to industry

Longer term Vision:

(i) Develop workforce training system for future carbon fiber manufacturing partners

(ii) Develop internship and other training programs from high school through university graduate level

Photo courtesy of Michael Patrick & Knoxville News-Sentinel

Oak Ridge Carbon Fiber Composites Consortium

Our Mission

To accelerate the development and deployment of new lower cost carbon fiber composite materials, creating a new generation of strong, light-weight materials to enhance America's economic competitiveness.

Established July, 2011

Value proposition

- Serves as a platform for industry to develop a pre-competitive technology roadmap to accelerate the development and deployment of strong, light-weight materials
- Enables industry to collaborate across the value chain to develop new precursors, explore new conversion technologies, and create new applications for low-cost carbon fiber composites

Oak Ridge Carbon Fiber Composites

Consortium

Currently at 50 Members and continuing to grow!

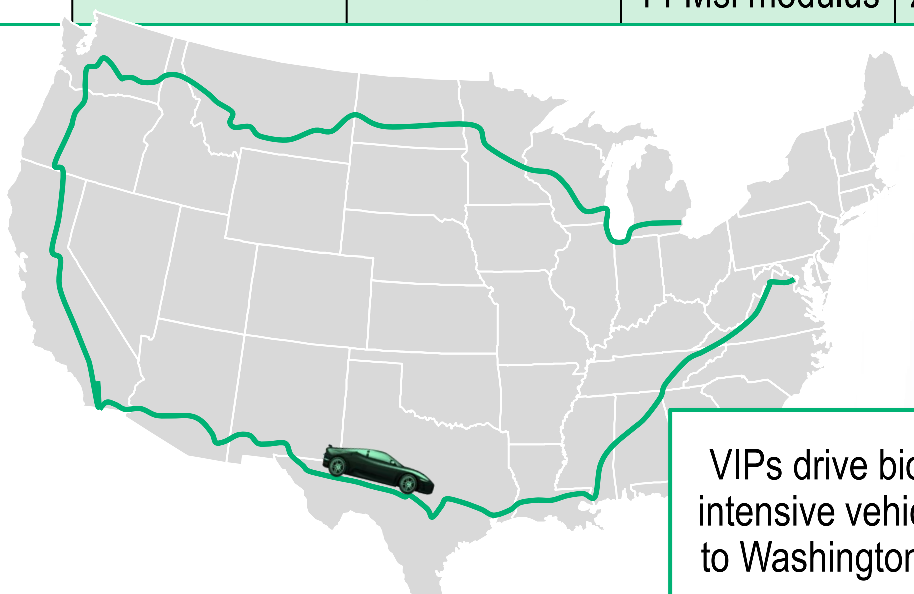
- 3M Company
- ABC Group Sales & Engineering
- Advanced Composites Group
- Alpha Industries
- Ashland
- ATK Launch Systems
- Barge Waggoner
- BASF Corporation
- Chomarat NA, LLC
- CIMV
- Composite Applications Group
- Continental Structural Plastics
- Cytec Carbon Fibers
- Domtar
- Dow Chemical Company
- DowAksa
- Despatch Industries
- Faurecia
- Fibria
- Ford Motor Company
- General Electric
- Georgia-Pacific
- Global Composites Solutions
- Graftech International
- Hanwha Azdel
- Harper International
- Hills, Inc.
- Innovation Valley Inc.
- Innventia
- INOAC USA
- Lignol Innovations
- Materials & Chemistry Laboratory
- Metalsa Structural Products
- Metso Power
- NovusFolium
- Plasan Carbon Composites
- Renmatix
- Sabic Innovative Plastics
- SGL Carbon Fibers
- Sodra
- Southern University
- SSOE Group
- Steelcase
- TennEra
- Toho Tenax America
- United Technologies Research Center
- USEC
- UT-Battelle
- Virdia, Inc.
- Volkswagen Group of America

Grand vision

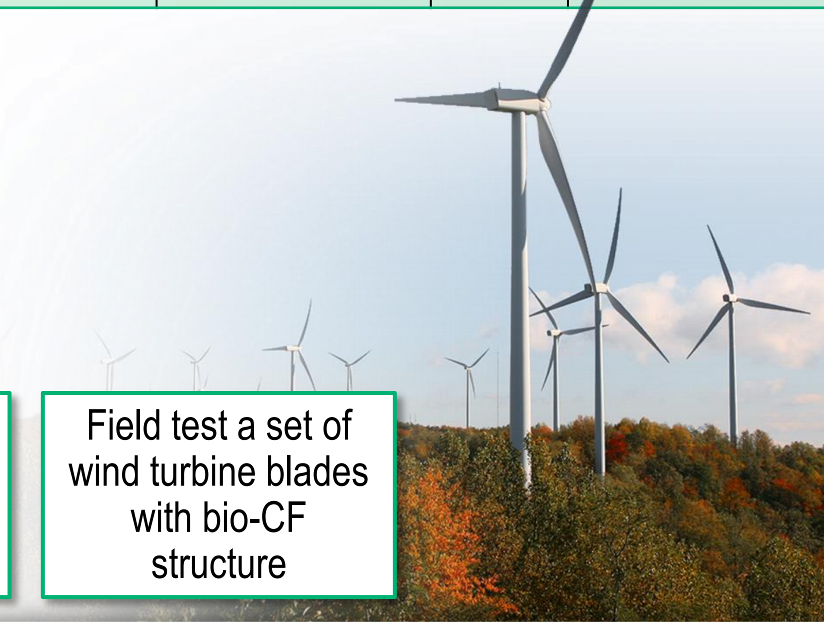
2014	2015	2016	2017	2018	2019	2020
Extensive characterization					10 tons of structural bio-CF produced	**The vision is realized**
	Biomass engineering and extensive chemistry					
		Process and property optimization				
			Bio-CF production and component/system prototyping			

Milestones

			Raw materials: Tensile properties				
	Papers in high-impact journals	Prototype suppliers selected	1% strain 14 Msi modulus	1% strain 22 Msi modulus	1% strain 32 Msi modulus	Bio-CF pro-duced	10 tons of vehicles and blades



VIPs drive bio-CF intensive vehicle(s) to Washington, DC



Field test a set of wind turbine blades with bio-CF structure