Reinventing Coal: Researchers Create Novel Materials from a Declining Energy Resource

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What do carbon fiber, steel, textiles, shampoo, and laundry detergent have in common? They can all be made directly from coal or have their cost and performance improved with additives derived from coal. Innovative work at the National Energy Technology Laboratory (NETL) is attempting to expand that list to include engineered cements and plastics, water filtration devices, battery materials, 3D printing materials, and many other consumer products that are in demand in the global marketplace.

Around 2007/2008, coal production topped out at roughly 1.2 billion tons. Since then, coal production has been falling, mostly due to the attractive pricing of natural gas resources for producing electricity. According to the Annual Coal Report issued by the DOE's Energy Information Agency, maximum production was down to 0.77 billion tons in 2017.

Despite this downward trend in using coal for electricity production, coal may also find applications in markets not previously considered by the industry. In fact, coal can be used as a feedstock for manufacturing high-valued carbon products and materials and NETL is working to develop new technologies for these applications.

History with coal

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NETL has a long affinity with coal. It was established in 1910 as the Pittsburgh Experiment Station with a coal mine dug on site to support research activities. NETL offered advanced training to coal operators and miners and developed innovative coal-mining safety equipment and practices. Over the years, NETL has expanded to include new sites in Morgantown, West Virginia, and Albany, Oregon. Current research includes technologies for improving the cost and performance of: carbon capture and storage systems, gasification and combustion technologies for producing electricity, solid oxide fuel cell and turbine technologies, materials for ultrasupercritical boilers, and technologies for recovering rare earth elements from coal and its byproducts.

NETL is the U.S. Department of Energy's only national lab dedicated to fossil energy research. Its mission is to discover, integrate and mature technology solutions to enhance the nation's energy foundation and protect the environment for future generations. For more than 100 years, the organization has been building its expertise in coal, natural gas and oil technologies.

A new initiative

Nearly three years ago, NETL started developing innovative ideas for creating commercially viable technologies that use domestic coal as a manufacturing feedstock. In response, it launched its Manufacturing High-Value Carbon Products from Domestic Coal Initiative, which sets the vision and tone for research activities in this program.

NETL's Christopher Matranga, who works in the organization's Materials Engineering and Manufacturing directorate, explained the goals and opportunities that drive the initiative.

"Manufacturing high-value carbon materials from coal would create new revenue streams for the industry and establish manufacturing technologies with reduced costs and energy consumption." he said. "At NETL, we are focusing on using coal to make carbon nanomaterials, such as graphene, which can be used directly, or which can be used as an additive in composites and coatings to improve performance."

While carbon nanomaterials first made a splash in the 1980s with the discovery of the C_{60} fullerene, they have not been widely utilized since, said Matranga.

"Despite decades of promising research, carbon nanomaterials still do not enjoy widespread commercialization, in part due to their excessive cost and limited supply," he said. "These commercialization barriers partially arise from the cost of the petroleum- and natural gas-based feedstocks used, as well as the complicated vapor phase growth process commonly used to make carbon nanomaterials."

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Alternatives applications for domestic coal. Credit: National Energy Technology Laboratory (NETL)

Coal offers unique opportunities to bring down the costs of carbon nanomaterials and to increase their availability for use in innovative products. Coal is generally far cheaper per ton of carbon than the petroleum, natural gas, or graphite feedstocks used to make carbon nanomaterials. Additionally, the processes for turning coal into graphene-type nanomaterials are simple, inexpensive, and closely related to classical coal processing technologies, which suggests they are scalable. As such, a major goal of NETL's initiative is working to address cost and supply issues that prevent commercialization.

If successful, coal-based manufacturing has the potential to drive new economic opportunities for jobs, products and markets. Coal feedstocks at $30 to $60 per ton could be converted, through NETL's innovative manufacturing processes, into carbon products selling for much more. For example, carbon fiber and structural composites can cost $140,000 per ton, specialty 3D printing materials can cost $700,000 per ton, and graphene nanomaterials can cost more than $100,000,000 per ton.

"One of the really exciting aspects of this research is that coal-based manufacturing can be applied to so many products that previously were not part of the coal value chain—textiles, pigments, paints, cosmetics, specialty plastics, and more". So, the range of applications is incredibly broad," Matranga said.

Matranga and his research team have met with notable success. A big accomplishment came in the form of a tiny dot—a graphene quantum dot. Graphene quantum dots are small fluorescent nanoparticles with sheet-like structures that are one carbon atom thick and a few hundred atoms in diameter. The unique size of these materials imparts amazing optical and electronic properties to these coal-based derivatives. The chemical composition and small size of these graphene quantum dots also helps them to bond with composite materials, interact with the composite, and impart unique properties to the composite.

In the energy field, graphene quantum dots are useful in applications such as catalysis, electronics, light emitting diodes (LEDs), and sensors because of their optical and electronic properties. Graphene quantum dots absorb light of different colors, which makes

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them useful for photocatalysis. In solar cells, graphene quantum dots can be used as a photosensitizer to efficiently enhance photoelectric conversion.

At NETL, researchers have successfully processed anthracite, bituminous, and sub-bituminous coal samples from regional partners in Wyoming, Kentucky, Virginia, and Pennsylvania to manufacture small graphene quantum dots suspended in water, without the need for surfactants or other stabilizers. NETL researchers are now evaluating the use of these materials as additives for cements and plastics.

Additional processing methods developed by NETL can produce large, micron-sized graphene materials as dry, solid, powders. These forms of graphene are being investigated for use as electrode materials for batteries, water filtration materials and for chemical sensing applications.

Research at NETL is already illustrating how coal can make a difference in the price of nanomaterials.

"We started with a coal feedstock costing about one penny," Matranga explained. "With just a few hours of processing we converted this penny's worth of coal into 1 liter of graphene quantum dots in water, which has a current market value of approximately $50,000. The work shows how dramatically coal-based feedstocks will reduce manufacturing costs."

"Graphene nanomaterials are currently too expensive to use in most commercial applications," he said. "Our research is illustrating that the manufacturing costs can be brought down to levels comparable to other specialty additives used commercially. Right now, there aren't many graphene producers and only one or so doing it with coal feedstocks, so these nanomaterials will continue to be expensive until there are more manufacturers and competition in the marketplace."

Applications for cement

These graphene quantum dots have value for another specialty area for NETL researchers: wellbore cement.

"We're evaluating how coal-based additives might enhance the mechanical properties and corrosion resistance of wellbore cements for downhole applications, this approach should also work for the conventional cement and concrete used for roads and sidewalks" Matranga said.

Wellbore materials must be resistant to chemical corrosion from injected fluids, be sufficiently strong to withstand mechanical stresses associated with injection and have integrity to prevent fluids from leaking out of the well into surrounding geological formations.

"Our current investigations are using coal-derived graphene quantum dots as an additive in cement, and we find that porosity and permeability decreased, which improves corrosion resistance," Matranga said.

The team also found that the mechanical properties of the cement improve. Additional characterization is in progress, but based on these results, the team is optimistic that coal-

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derived carbon materials could provide an affordable way to improve well-bore cements critical for protecting the environment during oil and gas extraction.

Collaboration efforts

NETL is working closely with private industry to build upon its innovations. For example, in June 2018, NETL launched a partnership with Ramaco Carbon to collaborate on innovative projects that use coal as a manufacturing feedstock for high-value products. A cooperative research and development agreement (CRADA) signed June 7, 2018, enhances NETL's materials engineering and manufacturing capabilities by allowing researchers access to the coal-based manufacturing and research facilities being developed by Ramaco Carbon near Sheridan, Wyoming.

Once completed, Ramaco Carbon will operate the world's only fully integrated coal-based research, development and production facility. Ramaco areas of interest include the use of coal to create carbon-based product precursors and resins, rare earth elements from coal and coal by-products, feedstock production for carbon-based products, and production of advanced carbon materials—all areas in which NETL has extensive expertise. NETL researchers are working to establish programmatic research activities in coal-based manufacturing that will be aided by the agreement.

For more than 100 years, coal has dominated the nation's energy production, providing an affordable, reliable foundation for prosperity. Now this abundant resource is opening new doors as technology options find new applications that do not require burning this resource and generating greenhouse gas.

As research and innovation continues to drive opportunities, coal-based industries could provide a more affordable alternative to the ubiquitous petroleum-based materials that are used to make consumer products and specialty materials that are critical for the United States' energy independence and security.

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