ORNL/TM-2024/3710

Coal to Carbon Fibers CRADA Final Report CRADA No. NFE-20-08273

Frederic Vautard (PI)
Aparna Annamraju
Justin Finks
Mark Arnould
Ercan Cakmak
Josh Damron
Ryan Paul
Nidia Gallego (Co-PI)
Edgar Lara-Curzio

CRADA final report for CRADA number NFE-20-08273

Approved for public release. Distribution is unlimited.

December 2024

OAK RIDGE National Laboratory

FINAL REPORT CERTIFICATION (ORNL-851)

Final Report Certification
for
CRADA Number NFE-20-08273

Between

UT-Battelle, LLC

and

Ramaco Carbon, LLC
(Participant)

Instructions: Mark the appropriate statement in 1a or 1b below with an 'IX.' Refer to the articles in the CRADA terms and conditions governing the identification and marking of Protected CRADA Information (PCI). If no PCI is identified, the report will be distributed without restriction. If PCI is identified, the report distribution will be limited in accordance with the CRADA terms and conditions governing release of data. In all cases items 2 and 3 must be true. That is, the report cannot contain Proprietary Information and a disclosure must be filed prior to release of the report.

The following certification is made for the subject final report:

1. (a) ☐ The final report contains information that qualifies as "Protected CRADA Information" (PCI). The PCI legend is printed on the report cover, and the PCI is clearly identified.

OR

(b) ■ The final report does not contain "Protected CRADA Information." The "Approved for Public Release" legend is printed on the report cover.

2. The final report does not contain Proprietary Information.

3. By the signature below, the Participant has no objection to the public distribution of the final report due to patentable information.

For the Participant:

Charles Atkins, Director of Developmen
(Name and Title)

(Signature)

November 15, 2024
(Date)

ORNL-851 (9/2007)

PRINT SAVE

ORNL/TM-2024/3710

Materials Science and Technology Division

COAL TO CARBON FIBERS
CRADA FINAL REPORT
CRADA NO. NFE-20-08273

F. Vautard, Mechanical Properties and Mechanics Group
A. Annamraju, J. Finks, R. Paul, J. Damron, Carbon and Composites Group
M. Arnould, Center for Nanophase Materials Sciences
E. Cakmak, Neutron & X-Ray Scattering & Thermophysics Group
N. Gallego, Carbon Materials Technology Group
E. Lara-Curzio, Energy Science and Technology Directorate
C. Hill, C. Atkins, Ramaco Carbon, LLC

December 2024

Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, TN 37831-6283
managed by
UT-BATTELLE LLC
for the
US DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

CONTENTS

LIST OF FIGURES

ACKNOWLEDGMENTS

This project was conducted as a Cooperative Research and Development Agreement (CRADA No. NFE-20-08273) between the US Department of Energy's Oak Ridge National Laboratory and Ramaco Carbon LLC. It was sponsored by the US Department of Energy Office of Fossil Energy and Carbon Management, through project FEAA155. The direction and support of National Energy Technology Laboratory program and project managers Joe Stoffa, Mike Fasouletos, and Mark Render is greatly appreciated.

ABSTRACT

This report documents activities carried out by Oak Ridge National Laboratory and by Ramaco Carbon LLC under CRADA project NFE-20-08273 entitled "Coal to Carbon Fibers." This project's main objective was the demonstration of commercially relevant utilization of coal as a precursor for high-value-added products, such as carbon fibers. The specific objectives included the following:

- Deploy a production platform for the conversion of coal into carbon fibers in a way that utilizes preexisting base technologies and accelerates the commercialization of coal to carbon fibers.

- Rapid deployment and utilization of versatile conversion test beds for accommodating preexisting base technologies for both the conversion of coal-to-pitch (proven donor solvent liquefaction techniques) and conversion of pitch-to-fiber (proven melt spun and melt blown techniques).

Results from the generation of an isotropic pitch from a subbituminous coal through the low severity direct coal liquefaction process are presented. Carbon fibers were produced from this isotropic pitch through melt spinning and melt blowing.

1. STATEMENT OF OBJECTIVES

Coal tar pitch supply in the United States has declined because of aging and less-competitive coking operations, new coke ovens that do not produce it, and an increased steel production using electric arc furnaces that do not consume metallurgical coke. Significant uncertainty exists for the long-term availability of coal tar pitch as a material precursor for manufacturing carbonaceous products. Therefore, creating opportunities for alternative processes that transform coal into carbon fibers and other value-added products is essential. This implies generating knowledge that will lead to scalable, efficient, cost-effective, and environmentally sustainable processes for manufacturing coal-derived carbon fibers.

To address these challenges and opportunities, Cooperative Research and Development Agreement (CRADA) NFE-20-08273 was established between Oak Ridge National Laboratory (ORNL) and Ramaco Carbon LLC. The scope of this project includes the following:

- The identification of a coal source suitable for the production of isotropic pitch precursor through the low severity direct coal liquefaction (LSDCL) process

- The manufacturing of carbon fibers from the isotropic pitch.

To achieve project objectives, the CRADA was structured into two main tasks:

Task 1. Production and characterization of coal-based isotropic pitch
Task 2. Lab-scale carbon fiber production and characterization

2. BENENFITS TO THE DOE FUNDING OFFICE'S MISSION

The objective of the Carbon Ore Processing Program within DOE's Office of Fossil Energy and Carbon Management is to repurpose domestic coal resources for high-value products, such as carbon fibers, and carbon-based products, that can be employed in clean energy technologies. Expanding innovative uses for coal and coal wastes has the potential to create local jobs and value-added economic opportunities for mining and power plant communities.

3. EXECUTIVE SUMMARY

In November of 2020, Ramaco Carbon LLC provided ORNL with approximately 4 kg of isotropic pitch produced from Powder River Basin (PRB) coal by an LSDCL process.

The isotropic pitch produced by the LSDCL process with the PRB coal had very good spinnability and an advantageous behavior for the oxidation stabilization process, as determined by thermogravimetric analysis (TGA) tests performed by ORNL. The oxygen content in the coal results in a pitch that can be more readily stabilized. Therefore, lower melting point pitches may be used, making melt-spinning or melt-blowing processing potentially easier, and the shorter stabilization process renders it more economical compared with petroleum-based pitches, pitches made from coke oven pyrolysis tars (coal tar), or some made from other types of coals. The material is attractive for high-temperature insulation and/or functional fibers such as activated carbon fibers that can be used in gas management and water purification applications. Both ORNL and Ramaco Carbon LLC performed melt blowing of the PRB coal-based isotropic pitch, and small quantities were further processed with adjusted stabilization, carbonization, and activation conditions. Values of the specific surface area of around 2,000 m^2/g, as measured by nitrogen adsorption and Brunauer–Emmett–Teller (BET) analysis, were achieved after activation processes.

4. INTRODUCTION

Ramaco Carbon LLC is developing a technology portfolio focused on coal-based product manufacturing, including carbon fiber, synthetic graphite, graphene, porous carbons, and building materials. Two projects funded by the National Energy Technology Laboratory (NETL) were completed in 2022: one with HTI/AXENS to develop an LSDCL process in a continuous pilot and the second with Terrapower to produce pyrolysis pitch from coal in supercritical CO_2. The purpose of the cooperative research and development agreement between Ramaco Carbon LLC and ORNL is to develop carbon fibers from coal products generated by the LSDCL process.

5. TECHNICAL DISCUSSION

5.1 MATERIALS AND METHODS

PRB subbituminous coal-based isotropic pitch was supplied by Ramaco Carbon LLC in granular form and used as such.

TGA was performed in high-purity nitrogen or compressed air (10 mL/min), using a TA Instruments TGA model 5500 equipped with platinum pans.

Scanning electron microscopy (SEM) imaging was performed with a field emission TESCAN MIRA3 SEM instrument.

Specific surface area of activated carbon fibers was measured by nitrogen adsorption and BET analysis using a Micromeritics TriStar II surface area analyzer. The samples were degassed for 12–14 h at 350°C in primary vacuum before testing.

5.2 PITCH PRODUCTION USING COAL LSDCL CONTINUOUS PILOT PLANT AT HTI

LSDCL continuous pilot operations using PRB coal were funded under NETL project number DE-FE-3100801. Details can be found in that project's final report, including the associated yields and properties of the pitch materials. An internal HTI report is available by request under NDA.

5.3 MELT SPINNING OF ISOTROPIC PRB COAL PITCH

In a first attempt to melt-spin the PRB coal tar pitch, a benchtop laboratory mixing extruder (LME) from Dynisco was used to produce small quantities of single fibers (Figure 1). The PRB coal isotropic pitch precursor was pulled into continuous fibers that had a shiny and smooth surface. Their diameter was large (around 50 µm). Typically, the melted pitch is not extruded with pressure; instead, it flows through the die because of a centripetal pumping effect. Therefore, the temperature of the die must be much higher than the dropping point of the pitch in order to achieve a viscosity of around 70 Pa·s that is compatible with the process. Then, the extruded pitch is pulled to a collecting drum with adjustable rotation speed. The feeding speed can be tuned by modifying the rotation speed of the cylindrical rotor. The distance between the die and the collecting drum can be controlled as well. Multiple trials involved using a larger drum to increase the pick-up speed, increasing the distance between the die and the drum, and using smaller dies (from 1/8 to 1/32 in. as the diameter). Some reduction of the diameter was noticed (from 50 µm to 35–40 µm), but this change was not enough to consider mechanical testing with single fibers. Because nonstructural applications were of interest, stabilization and carbonization of these fibers were investigated using TGA.

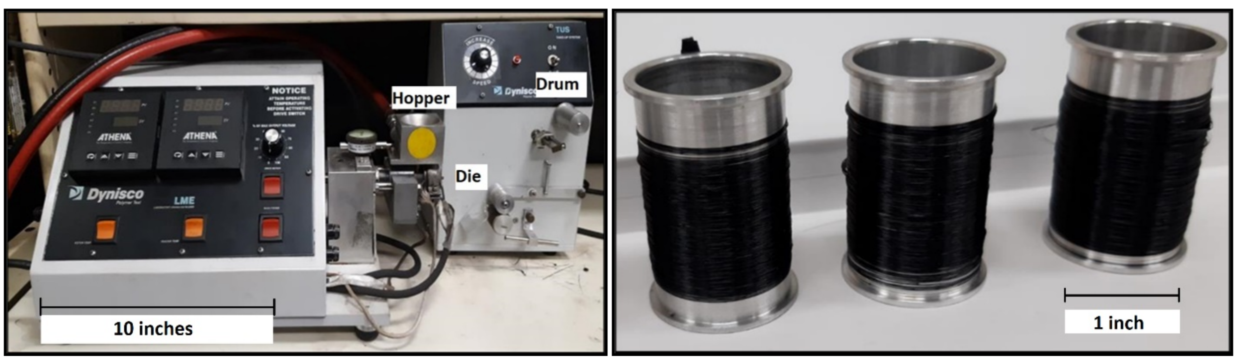

Figure 1. The laboratory mixing extruder (LME) (left) and melt spun fibers made with the PRB coal pitch precursor (right).

SEM was used to characterize a fiber mat produced by the stabilization/carbonization of the PRB coal-derived pitch fibers (Figure 2). A well-defined structure with individual filaments fused at the points of contact could be seen. The surface of the filaments was found to be porous.

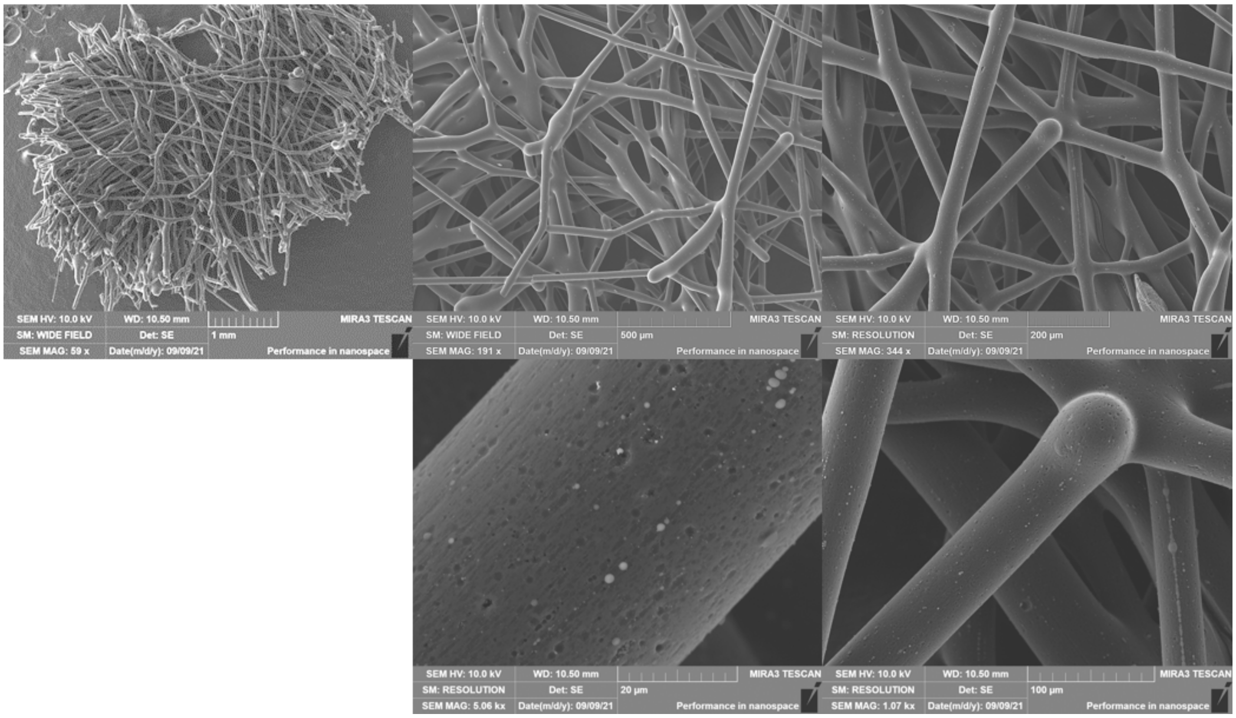

Figure 2. SEM images of the stabilized and carbonized PRB coal pitch fibers, with increasing magnification in the clockwise direction.

One very important aspect of the stabilization/carbonization studies with the PRB coal pitch is that the overall carbon yield obtained with fibers is 66%. This yield is high compared with other carbon fiber precursors (typical PAN carbon yield is 50%). The economical aspect of carbon fiber manufacturing (more precisely of carbon fiber mat at this point) is obviously in favor of this precursor. Even if individual filaments were not made, the material is suitable for the production of carbon fiber mats and carbon fiber monoliths, opening the door for many industrial applications (e.g., thermal insulation, filtration, gas adsorption). A multifilament extruder will be necessary to produce fibers with a smaller diameter (<20 μm), but the PRB coal pitch may be difficult to process because of its low softening point, because bridging in the extruder barrel is difficult to avoid.

5.4 MELT BLOWING OF ISOTROPIC PRB COAL PITCH

Melt blowing is a process well-adapted to the production of fiber mats. Furthermore, it can be easily scaled up. Therefore, melt-blown fibers were made from the PRB coal isotropic pitch with a commercial horizontal screw extruder Filabot EX6 fitted by ORNL with a customized nozzle (Figure 3). In this process, heated pitch is fed into the nozzle after it exits the extruder die. As hot air exits the nozzle, it draws the heated pitch into fibers. Optical microscopy images of two mats are displayed in Figure 4. The die temperature apparently influenced the color of the fibers, suggesting that the fiber surface may have been oxidized and that the level of oxidation was different based on the processing conditions.

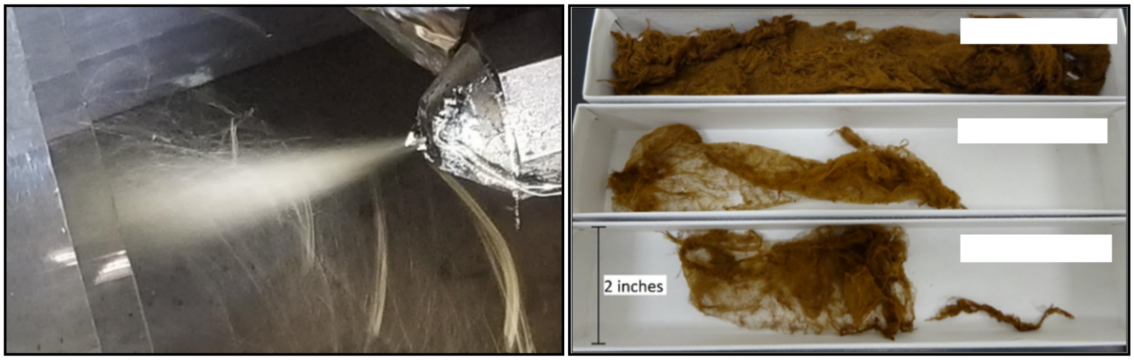

Figure 3. Processing of PRB coal pitch melt blown fibers (left) and examples of blown fiber mats (right).

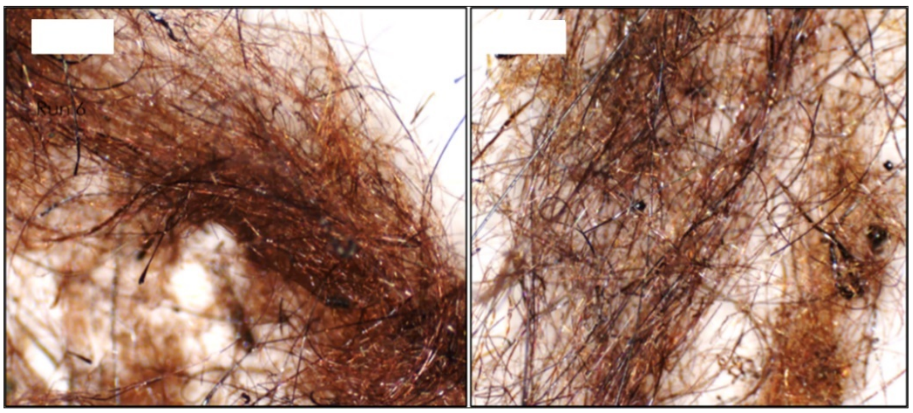

Figure 4. Optical microscopy images of blown fiber mats made with different processing conditions.

SEM images of melt-blown fibers made with three different processing conditions are shown in Figure 5. Fibers with a smooth surface were obtained. The range of fiber diameter was broad, typically between 0.5 and 10 µm.

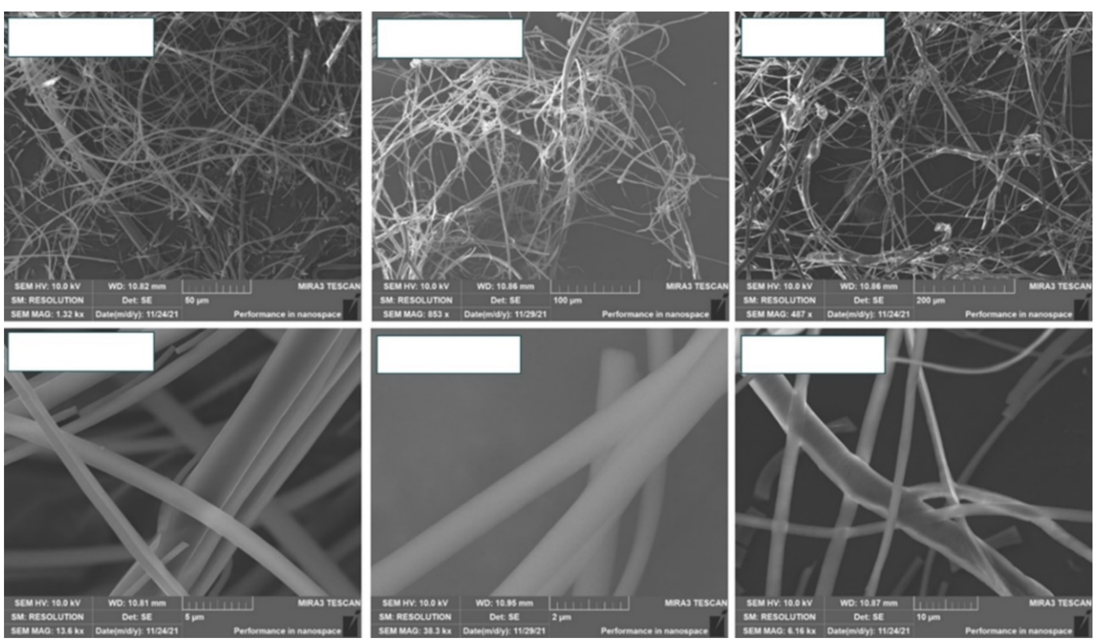

Figure 5. SEM images of melt-blown fibers made with different processing conditions.

Following the success of small-scale stabilization studies, a large amount of melt blown fibers was stabilized in a conventional forced-air oven and then carried forward for a carbonization study using TGA equipment (Figure 6). A carbon yield of 34% was obtained, which is lower as compared to the yield obtained with melt spun fibers. SEM images of carbon fibers obtained via this process are displayed in Figure 7. These fibers had a relatively smooth surface and a diameter range between 0.5 and 5 µm. Some perfectly smooth fibers were observed in certain areas, but some porous fiber surfaces were found in other areas.

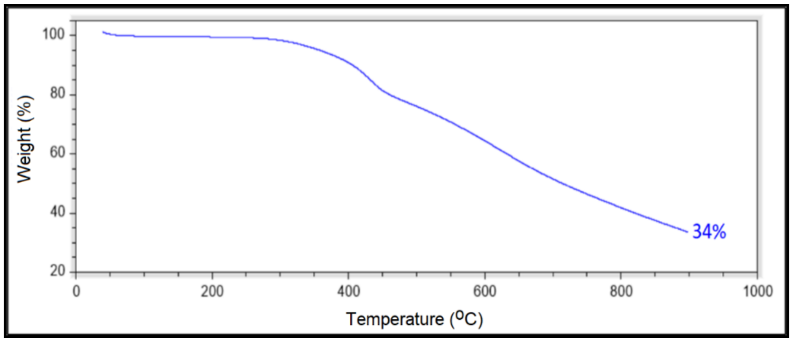

Figure 6. Carbonization of melt-blown fibers stabilized in the oven.

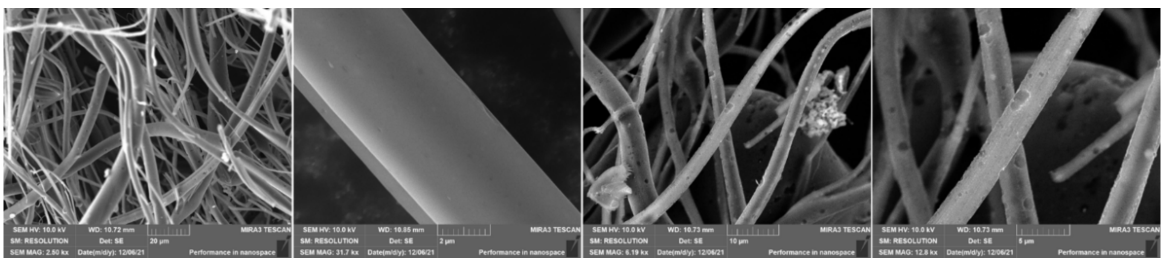

Figure 7. SEM images of PRB coal pitch melt blown fibers carbonized in the TGA equipment (corresponding to Figure 6).

The specific behavior of the PRB coal pitch fibers during stabilization (fusion at the points of contact) leads to the manufacture of a carbon-bonded carbon fiber material. This advantage is undeniable compared with the traditional process involving binders that are turned into carbon during a second carbonization step. Carbon fiber monoliths can potentially be made with one carbonization step, significantly reducing production cost and complexity. This result constitutes a significant finding from this CRADA.

Following this achievement, Ramaco Carbon LLC developed its own melt-blowing unit (Figure 8) and successfully produced pitch fiber with a diameter range of 1 to 20 µm (Figure 9).

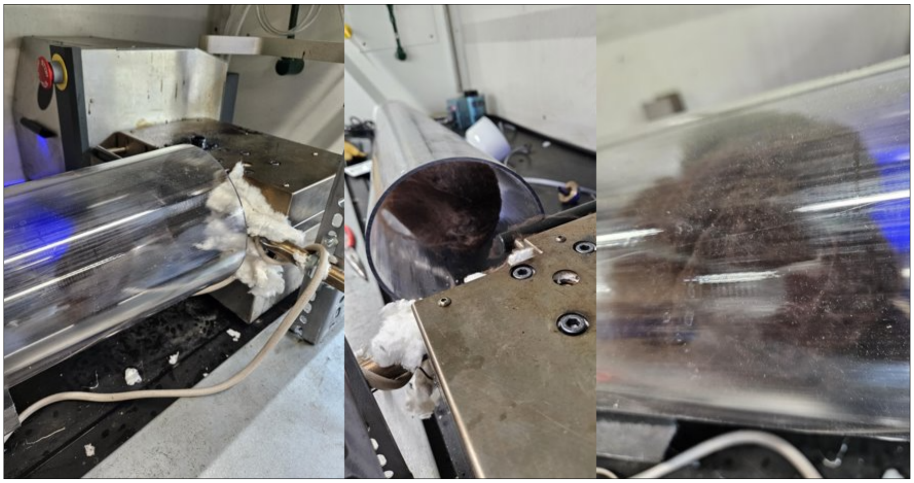

Figure 8. Production of PRB coal melt blown pitch fibers with Ramaco Carbon LLC's melt-blowing unit.

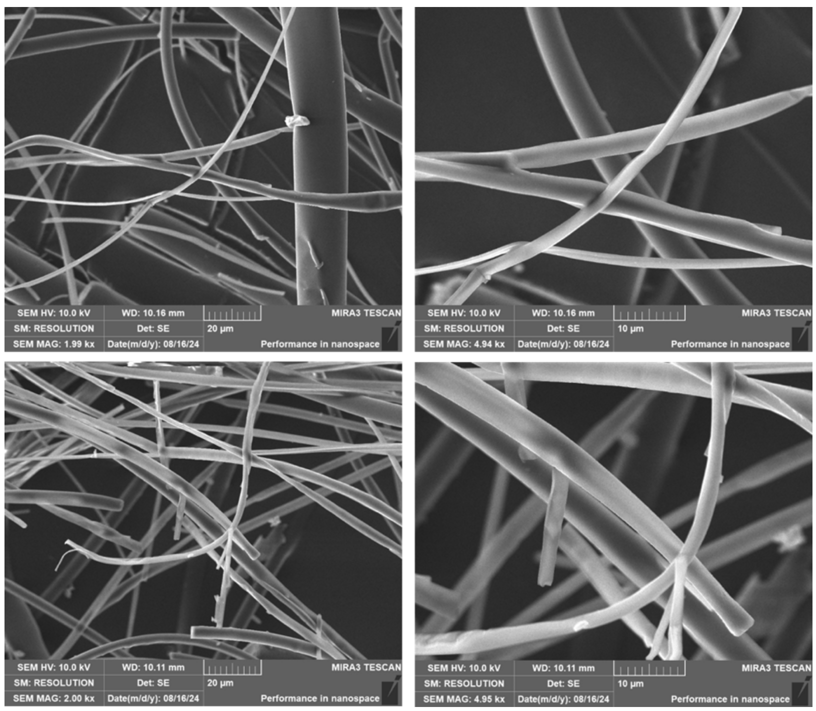

Figure 9. SEM images of PRB coal-based melt-blown fibers produced with Ramaco Carbon LLC's melt-blowing unit.

5.5 ACTIVATION OF PRB COAL PITCH MELT-BLOWN CARBON FIBER MATS

Because the carbon fiber mats obtained by the melt-blowing process are destined to be used for selected gas adsorption or liquid filtration, their surface needs to be activated in order to generate the adequate microporosity. Therefore, an activation method was investigated. First, Ramaco Carbon LLC reproduced the stabilization studies led at ORNL and produced pitch-based carbon fiber mats with a similar structure (Figure 10).

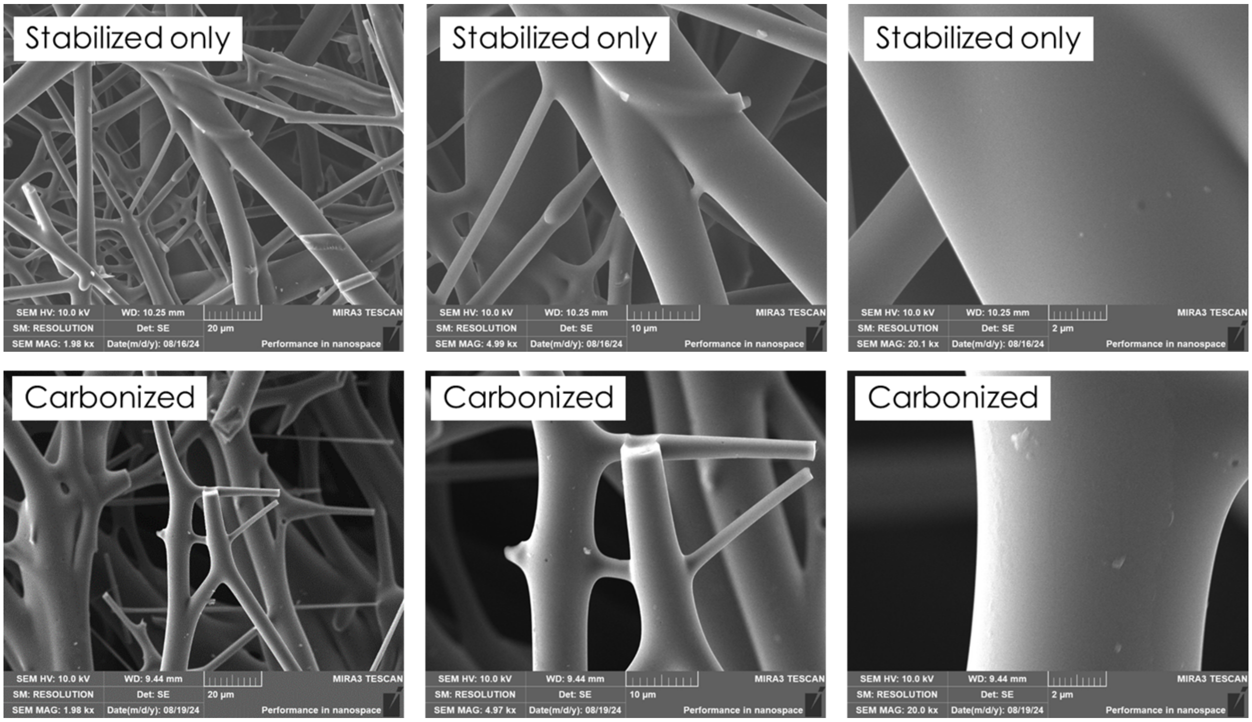

Figure 10. SEM images of melt-blown pitch fiber mats produced with Ramaco Carbon LLC's melt-blowing unit, stabilized (top) and carbonized (bottom).

Using the same tube furnace, a method of activation involving CO_2 with added moisture by bubbling in a water tank, as reported by Yue et al. [1], was investigated. Using the same activation conditions with two different samples, values of the specific surface area of around 2000 m^2/g were obtained, demonstrating that a high specific surface area can be achieved by activation of the carbon fiber mat made from PRB coal.

5.6 ELECTRICAL RESISTIVITY OF THE CARBON FIBER MATS AND JOULE EFFECT

The high value of specific surface area obtained with the activation in the mix CO_2 + H_2O enables the use of the activated carbon fiber mat as an adsorbent for gas separation, including the capture of CO_2. One of the energy-consuming steps for this application is the regeneration of the sorbent with no modification of its surface properties, so that cycles of adsorption and desorption can be run as many times as possible. Typically, heating the surface of an activated carbon material that is saturated with CO_2 to temperatures close to 100°C will desorb the CO_2 and regenerate the surface. Using the electrical resistance of the carbon fiber to reach that temperature by Joule effect seems to be an energy-efficient process [2]. This method is named electric swing adsorption. The possibility to use it for an eventual regeneration of the activated carbon fiber mat was characterized using a direct current supply and mounting the carbon fiber mat between two metallic clamps that were acting as electrodes (Figure 11).

Figure 11. The activated carbon fiber mat connected to a direct electrical current supply with metallic clamps.

Using 20 V as the voltage, a surface temperature of more than 108°C was obtained within a few seconds (as measured by an infrared camera and shown in Figure 12). Electrical swing adsorption can be used with the carbon fiber mat made with the PRB coal isotropic pitch, suggesting that activated carbon fiber mats made with the PRB coal isotropic pitch could be used as a cost-effective sorbent for CO_2 capture and could be regenerated by an energy-efficient method such as electric swing adsorption.

Figure 12. Temperature measurement of the surface of the activated carbon fiber mat by an infrared camera when heated by Joule effect using the setup displayed in Figure 11.

6. SUBJECT INVENTIONS

Two invention records were submitted in partnership with Ramaco Carbon LLC during the project:

- *Cost Effective Manufacture of Carbon Fiber Monolith from Isotropic Pitch Produced by Low Severity Direct Coal Liquefaction* which focuses on the manufacture of a carbon-bonded carbon fiber composite with one carbonization step using the specific behavior of the PRB coal-based pitch fibers during stabilization in air.

- *Cost Effective Manufacturing Process for Activated Carbon Fibers* which covers the possibility to generate an activated carbon fiber mat through a more energy and cost-efficient process as compared to the current technology.

Combined, these two processes represent a manufacturing method for activated carbon-bonded carbon fiber mats/monoliths with great savings in cost and energy as compared to the current technology.

7. COMERCIALIZATION POSSIBILITIES

Many industrial applications could benefit from a cost-effective activated carbon fiber monolith/mat. The controlled capture and release of gases, including CO_2 and volatile organic compounds, the controlled capture and release of moisture from air for indoor air conditioning are high-volume applications. A carbon fiber mat enables the use of electric swing adsorption for the regeneration of the fiber surface. Energy storage applications are another sector representing high value. A few examples include hydrogen storage and the manufacture of supercapacitors for transportation (cars, buses, trains). For these applications, intermediate values of specific surface area for the activated carbon fiber mat (several hundred square meters per gram) are appropriate.

Ramaco Carbon LLC is currently evaluating these options.

8. PLANS FOR FUTURE COLLABORATION

Ramaco Carbon LLC and ORNL are considering funding opportunities to build an at-scale prototype for controlled capture and release of CO_2, based on the activated carbon fiber mat manufacturing method developed during this project, and using electric swing adsorption for regeneration.

9. CONCLUSIONS AND PERSPECTIVES

Using the LSDCL process with PRB coal, an isotropic pitch was produced. Efforts were directed toward processing the isotropic pitch by melt spinning and melt blowing to make carbon fiber mats. The subbituminous coal pitch showed an interesting stabilization behavior: it could be stabilized despite having a low dropping point. Fusion at the points of contact between the fibers allowed the creation of structures that resembled carbon-bonded carbon fiber materials. The generation of a high specific surface area of 2,000 m^2/g by activation in a mix of CO_2 and H_2O was obtained. The carbon fiber surface was heated by Joule effect, showing that electric swing adsorption can be considered for the regeneration of the carbon fiber mat. This represents an opportunity to manufacture activated carbon fiber monoliths or activated and bonded carbon fiber mats using a simplified method that is more cost and energy efficient than the current technology. Several industrial applications, including the capture of CO_2 or volatile organic compounds from air or exhaust gas can be targeted.

10. REFERENCES

[1] Z. Yue, A. Vakili, J. Wang. 2017. “Activated carbon fibers from meltblown isotropic pitch fiber webs for vapor phase adsorption of volatile organic compounds”. *Chemical Engineering Journal* 330:183-190.

[2] R. P. P. L. Ribeiro, C. A. Grande, A. E. Rodrigues. 2014. “Electric Swing Adsorption for Gas Separation and Purification: A Review”. *Separation Science and Technology* 49: 1985–2002.