CLEAN RESOURCES FINAL REPORT PACKAGE

Project proponents are required to submit a Final Report Package, consisting of a Final Public Report and a Final Financial Report. These reports are to be provided under separate cover at the conclusion of projects for review and approval by Alberta Innovates (AI) Clean Resources Division. Proponents will use the two templates that follow to report key results and outcomes achieved during the project and financial details. The information requested in the templates should be considered the minimum necessary to meet AI reporting requirements; proponents are highly encouraged to include other information that may provide additional value, including more detailed appendices. Proponents must work with the AI Project Advisor during preparation of the Final Report Package to ensure submissions are of the highest possible quality and thus reduce the time and effort necessary to address issues that may emerge through the review and approval process.

Final Public Report

The Final Public Report shall outline what the project achieved and provide conclusions and recommendations for further research inquiry or technology development, together with an overview of the performance of the project in terms of process, output, outcomes and impact measures. The report must delineate all project knowledge and/or technology developed and must be in sufficient detail to permit readers to use or adapt the results for research and analysis purposes and to understand how conclusions were arrived at. It is incumbent upon the proponent to ensure that the Final Public Report **is free of any confidential information or intellectual property requiring protection**. The Final Public Report will be released by Alberta Innovates after the confidentiality period has expired as described in the Investment Agreement.

Final Financial Report

The Final Financial Report shall provide complete and accurate accounting of all project expenditures and contributions over the life of the project pertaining to Alberta Innovates, the proponent, and any project partners. The Final Financial Report will not be publicly released.

CLEAN RESOURCES FINAL PUBLIC REPORT TEMPLATE

1. PROJECT INFORMATION:

Project Title:	**Ultrafine Carbon Fibers by Melt Electrospinning Alberta Bitumen Asphaltenes**
Alberta Innovates Project Number:	G2020000337
Submission Date:	March 8, 2021
Total Project Cost:	$78,000
Alberta Innovates Funding:	$50,000
AI Project Advisor:	Murray Gray

2. APPLICANT INFORMATION:

Applicant (Organization):	**University of Alberta**
Address:	116 St & 85 Ave, Edmonton, AB T6G 2R3
Applicant Representative Name:	Zhi Li
Title:	Adjunct Professor
Phone Number:	780-729-0668
Email:	zhi.li@ualberta.ca

3. PROJECT PARTNERS

Please provide an acknowledgement statement for project partners, if appropriate.

RESPOND BELOW

Everest Canadian Resources is our partner in this project, who contribute in-kind contribution.

A. EXECUTIVE SUMMARY

Provide a high-level description of the project, including the objective, key results, learnings, outcomes and benefits.

RESPOND BELOW

In order to add value to Alberta's oilsands resources, the objective of this project was to use a novel technique to fabricate ultrafine fibres of diameter less than 1 micron from Alberta bitumen asphaltenes. Small diameter fibres have the potential to offer superior performance relative to the commercial fibres now on the market. The specific objectives of the project were to establish the setup to melt e-spin asphaltene fibers, then optimize operation parameters for melt e-spinning, then convert the spun asphaltene fibres to carbon fibres. The project was successful in spinning fibres in the range of 5-10 microns diameter in our lab, while a collaborating lab was able to melt e-spin fibres in the 1-2 micron size range. A novel wet-oxidation step was used to enable stabilization of the fires in air followed by carbonization. Further work is required to optimize the spinning to achieve smaller diameters and to verfy performance.

B. INTRODUCTION

Please provide a narrative introducing the project using the following sub-headings.

- **Sector introduction:** Include a high-level discussion of the sector or area that the project contributes to and provide any relevant background information or context for the project.
- **Knowledge or Technology Gaps:** Explain the knowledge or technology gap that is being addressed along with the context and scope of the technical problem.

RESPOND BELOW

- Sector introduction

The next generation CFs may come with significantly smaller diameters, as a pronounced diameter-effect has been observed on the mechanical strength of CFs (Mater. Sci. Eng. A, 1997, 2, 336). The diameter-effect can be attributed to the radial structural inhomogeneity in CFs. Raman and X-Ray diffraction (XRD) depth profiling analysis reveal the gradient distribution of graphitization degree in the

CFs, with the highest graphitic order near the surface and lowest in the core (Nat. Sci. Mater. Int., 2014, 24, 31). This radical inhomogeneity in CFs likely originates from the gradient oxygen diffusion in the thermal stabilization process of polymer fibers. Nevertheless, by reducing the diameter of CFs, improved overall graphitic order and therefore mechanical properties can be expected. CFs industry has started to fabric thinner fibers. For instance, the high-performance Toray T1000S CFs are already 28% thinner than T700S.

In collaboration with Everest Canadian Resources, we are extremely interested in asphaltene-based ultrafine carbon fibers (UF-CFs) with a diameter between 100 and 500 nanometers. Besides the diameter effect, the UF-CFs possess a substantial advantage over traditional CFs as reinforcement materials. Their 100–5,000 times smaller cross-sectional area provides tremendous refinement and improved interaction with polymer matrices, thus increasing the matrix shear strength. On carbon reinforcement materials market, UF-CFs are well-positioned to fill the gap between traditional CFs (diameter 5-7 µm, $10-30/lb) and carbon nanotubes (diameter 2-30 nm, $1,000-15,000 /lb). The small diameter of UF-CFs could also enable applications as N95 filtration materials and electrical or thermal conductive additives in energy storage and thermal management.

- Knowledge or Technology Gaps

Our group is focusing on developing carbon materials derived from various precursors, such as asphaltenes, cellulose, lignin, proteins, and polymers. Our strength lies in understanding the precursor-microstructure-performance relationship by using advanced in- and ex-situ electron and synchrotron X-ray techniques and fine-tuning the carbon structure accordingly to further improve the performance. Asphaltenes are constructed very differently at the molecular level from the two widely used CFs precursors: polyacrylonitrile (PAN) and pitch. Firstly, asphaltenes contain multi-ringed aromatic units, which greatly favor the graphitization leading to soft carbon. Our previous TEM studies confirmed that the asphaltene-derived carbon nanosheets annealed at 750℃ already develop a better-aligned lattice structure than PAN CFs carbonized at 2500℃. Secondly, asphaltene molecular are fairly small (several hundred g/mole) compared to typical PAN precursors (150,000 g/mole). Direct carbonization of asphaltenes will likely yield discrete nano graphite loosely bonded together, which significantly impairs the overall mechanical strength.

In summary, we identify the intrinsic soft carbon nature and the loose connection between nanocrystalline regions as two major challenges before realizing the full commercial value of ABA-based CFs. We are planning to address the first challenge in Phase I by improving the molecular alignment and the second one in Phase II by crosslinking asphaltenes and adding long-chain polymers. The know-how and insights gained in this project can be applied not only to UF-CFs but also to ABA-based traditional CFs.

C. PROJECT DESCRIPTION

Please provide a narrative describing the project using the following sub-headings.

- **Knowledge or Technology Description:** Include a discussion of the project objectives.
- **Updates to Project Objectives:** Describe any changes that have occurred compared to the original objectives of the project.
- **Performance Metrics:** Discuss the project specific metrics that will be used to measure the success of the project.

RESPOND BELOW

Carbon fibers (CFs) have been widely used as light-weight structure reinforcement materials due to their extraordinary strength and modulus. However, the mechanical properties of traditional CFs are approaching a plateau. In collaboration with our industrial partner, we propose to develop asphaltene-based ultrafine carbon fibers (UF-CFs), that bridges traditional CFs (diameter 5-7 µm) and carbon nanotubes (diameter 2-30 nm). The UF-CFs will be fabricated through eco-friendly melt electrospinning (e-spinning), followed by stabilization and carbonization.

Melt e-spinning has been considered as the most promising technology to produce continuous nanofibers at a large scale by avoiding the expensive solvent-removal process in conventional solution e-spinning. The tremendous elongational forces in e-spinning could significantly accelerate the molecular alignment in ABA fibers. The resulting UF-CFs are expected to possess much improved graphitic layer alignment and therefore enhanced tensile strength along the axial direction. The objectives of the project include:

1. Establish the setup to melt e-spin asphaltene fibers.
2. Optimize operation parameters to melt e-spin asphaltene fibers.
3. Develop a process to convert e-spin asphaltene fibers into ultrafine carbon fibers.

D. METHODOLOGY

Please provide a narrative describing the methodology and facilities that were used to execute and complete the project. Use subheadings as appropriate.

RESPOND BELOW

1. Preparation of asphaltene fibers

   The asphaltene fibers are processed using a home-made melt e-spinning system. Melt e-spinning has been considered as the most promising technology to produce continuous nanofibers at a large scale by avoiding the expensive solvent-removal process in conventional solution e-spinning. The tremendous elongational forces in e-spinning could significantly accelerate the molecular alignment in asphaltene fibers.

2. Pre-oxidation of asphaltene fibers

   The pre-oxidation was conducted in a tube furnace in the air flow at 250℃. To prevent the asphaltene fibers from melting, a pretreatment was performed in liquid oxidic media.

3. Carbonization of asphaltene fibers

   The carbonization was conducted in a tube furnace in Argon flow at 800 – 1,000 ℃.

E. PROJECT RESULTS

Please provide a narrative describing the key results using the project's milestones as sub-headings.

- Describe the importance of the key results.
- Include a discussion of the project specific metrics and variances between expected and actual performance.

RESPOND BELOW

1: Establish the setup to melt e-spin asphaltene fibers

We modified a standard solution e-spinning equipment to spin asphaltene melt (Figure 1a). The feed was Asphaltene Sample Bank S1 material, used as received. A heating unit was added to precisely control the temperature of asphaltene melt. The melt was forced through the spinneret by compressed argon with tunable pressure. A high voltage of 10-30 kV was applied between the spinneret and the rotating drum collector (Figure 1b). Continuous asphaltene fibers were obtained on the rotating drum as illustrated in (Figure 1c).

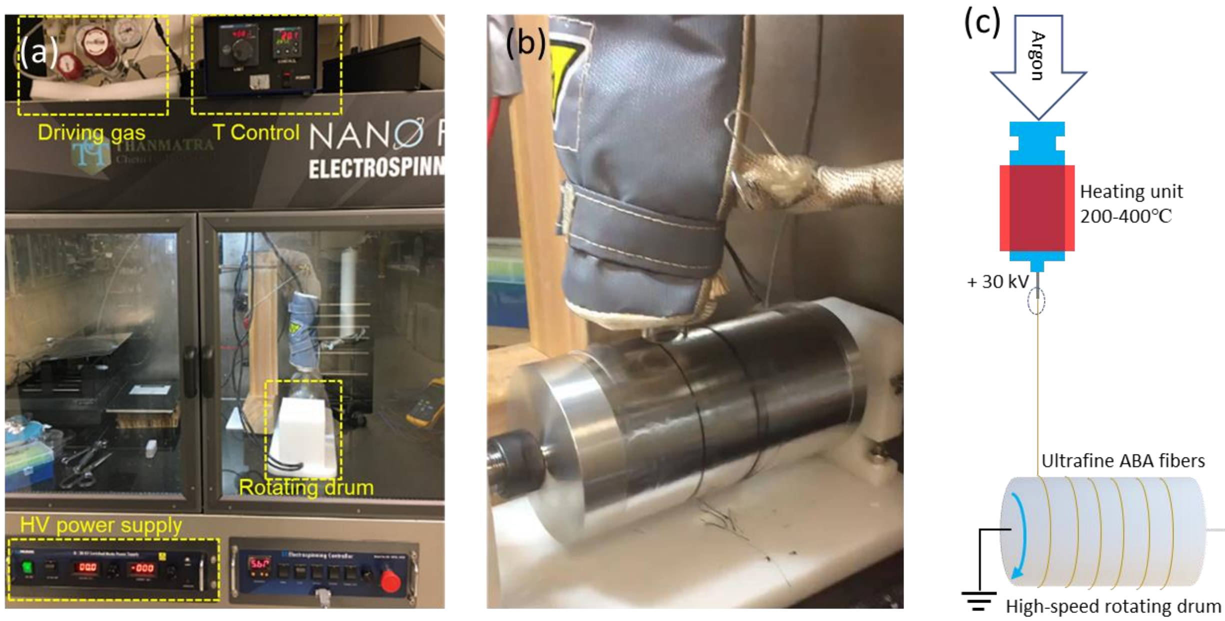

Figure 1. The pneumatic melt e-spin system composed of a temperature control unit, a compressed argon-driven spinning unit, a 30 kV high voltage unit, and a rotating drum collector.

2. Optimize operation parameters and additives to melt e-spin asphaltene fibers

After systematically optimizing the temperature, the pressure of driving gas, voltage, and rotating speed of the drum, thin asphaltene fibers were obtained on the drum (Figure 2a). As shown in Figure 2 band c, the asphaltene fibers are typically 5-10 µm in diameter. The just spun asphaltene fibers possessed excellent flexibility. When cooled to room temperature, they became more rigid which is expected given the rigid and brittle nature of asphaltene. Nevertheless, the obtained asphaltene fibers were flexible and robust enough to withstand the followed carbonization process.

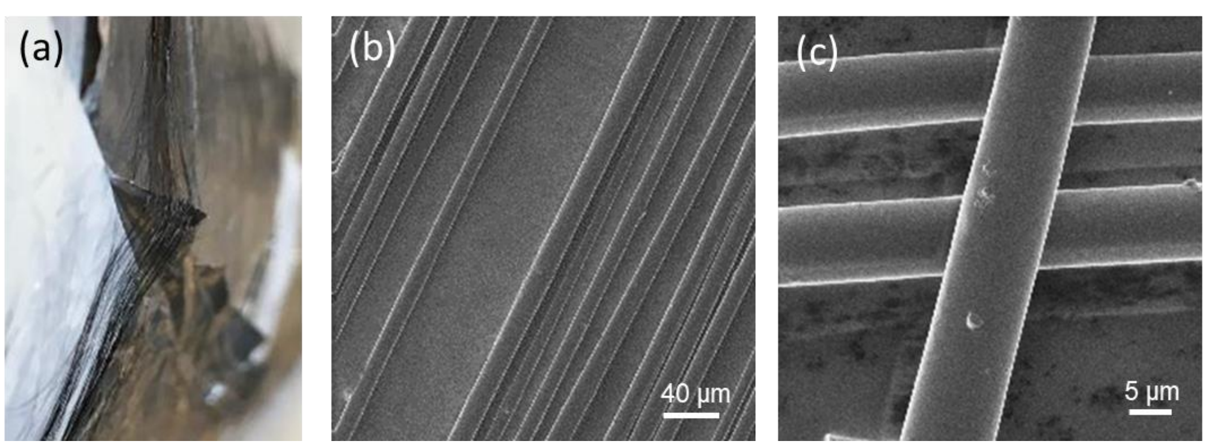

Figure 2. The asphaltene fibers produced using the pneumatic melt e-spin system.

3. Develop asphaltene-derived carbon fibers prototype

In the production of traditional carbon fibers, the polymer fibers need to be pre-oxidized in the air at 250-300 ℃. The peroxidation introduces oxygen and induces the crosslink of the polymer at the surface of fibers. The pre-oxidized surface layer prevents the polymer fibers from melting in the followed carbonized process which is typically conducted at 800 – 1,000 ℃. However, the asphaltene fibers can not withstand the typical pre-oxidation process as the actual melting point of the asphaltene sample is in the range of 130-150 ℃, much lower than the pre-oxidation temperature.

Therefore, we developed an additional pretreatment process in liquid oxidic media to generate an oxidation layer on the surface. After the pretreatment, the asphaltene fibers could withstand the followed pre-oxidation process at 250 ℃ in air and the carbonization process at 800 - 1,000 ℃. Figure 3 a and b show the resulting carbon fibers by carbonizing asphaltene fibers at 900 ℃. The average diameter of the carbon fibers is 5-10 µm. The surface of carbon fiber is very smooth. Improved flexibility was observed compared to the asphaltene fibers before carbonization.

Raman spectrum was employed to investigate the texture of carbon fibers processed at various temperatures (Figure 3c). Because of the conjugated aromatic structures, asphaltene show a similar Raman spectrum to carbon materials, with a characteristic D band at ~1350 cm^{-1} and a G band at ~1,600 cm^{-1}. But the D band is very wide. With the increase of carbonization temperature, both the D and G bands become sharper and more pronounced, indicating the increasing ordered structure in the carbon fibers.

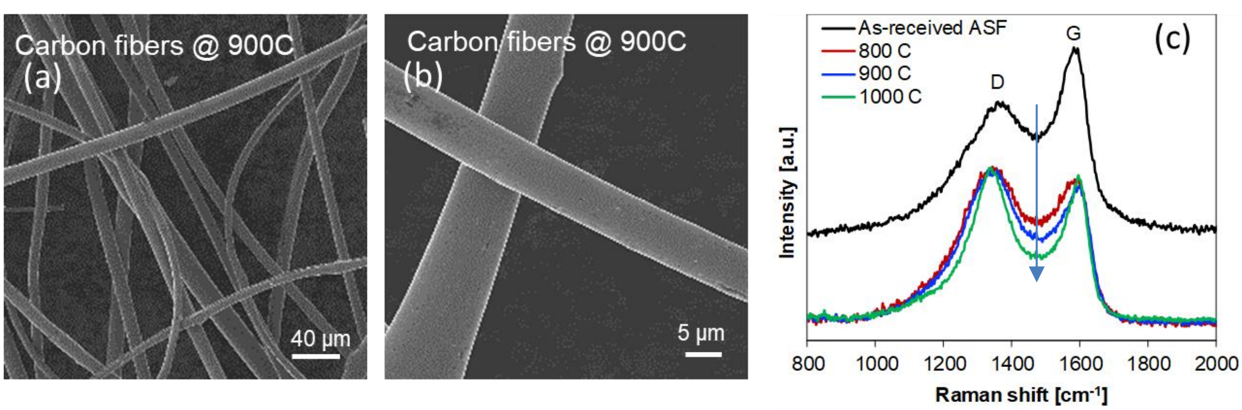

Figure 3. The carbon fibers obtained by carbonizing asphaltene fibers at 900℃ (a, b) and the Raman spectrum of carbon fibers carbonized at different temperature.

LEARNINGS DURING MILESTONE

Please discuss the key learnings obtained during this reporting period.

- Discuss the importance of the learnings for the project advancement.
- As appropriate, describe key findings and lessons learned for each task within the milestone, and the importance of those learnings towards the project advancement.

RESPOND BELOW

Melt e-spinning is an electrohydrodynamic processing technique to produce ultrafine fibers by charging and ejecting polymer melts through a spinneret under a high-voltage electric field. Unlike traditional solution e-spinning, melt e-spinning does not require an expensive scrubbing process to remove solvent vapors in fibers, which not only significantly reduces the production cost but enhances mechanical strength by avoiding the micropores induced by solvent evaporation. In this short project, we demonstrate the melt e-spinning is an effective way to make continuous and smooth carbon fibers using asphaltenes as feedstocks. We also learned two important lessons:

Firstly, the asphaltenes need to be chemically pretreated or physically separated before spinning. Asphaltenes are a mixture of aromatic compounds that are defined by solubility. In the project, we found the portion of asphaltenes starts to melt at as low as 120-140℃, while there are likely some portion (particles) stays a solid even at 250 ℃. The low melting point portion costs an additional pretreat before pre-oxidation and the high melting point portion causes blockage in the spinneret. Pretreatment is required to obtain asphaltenes with relative uniform behavior at the 200 - 250℃ range.

Secondly, the compress gas-driven spinning system is not an ideal system to continuously produce uniform asphaltene fibers. Because of the high viscosity of asphaltene melt, the pressure at the spinneret is significantly less than the pressure of driving gas. The difference is related to the volume of asphaltene melt and the self-crosslink of asphaltene at melt spinning temperature. It is difficult to maintain a constant mass flow using the pneumatic melt e-spin system. In future work, we will build a single-screw extruder-based spinning system to improve the uniformness of fibers.

F. KEY LEARNINGS

Please provide a narrative that discusses the key learnings from the project.

- Describe the project learnings and importance of those learnings within the project scope. Use milestones as headings, if appropriate.
- Discuss the broader impacts of the learnings to the industry and beyond; this may include changes to regulations, policies, and approval and permitting processes

RESPOND BELOW

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G. OUTCOMES AND IMPACTS

Please provide a narrative outlining the project's outcomes. Please use sub-headings as appropriate.

- **Project Outcomes and Impacts:** Describe how the outcomes of the project have impacted the technology or knowledge gap identified.
- **Clean Energy Metrics:** Describe how the project outcomes impact the Clean Energy Metrics as described in the *Work Plan, Budget and Metrics* workbook. Discuss any changes or updates to these metrics and the driving forces behind the change. Include any mitigation strategies that might be needed if the changes result in negative impacts.
- **Program Specific Metrics:** Describe how the project outcomes impact the Program Metrics as described in the *Work Plan, Budget and Metrics* workbook. Discuss any changes or updates to these metrics and the driving forces behind the change. Include any mitigation strategies that might be needed if the changes result in negative impacts.
- **Project Outputs:** List of all obtained patents, published books, journal articles, conference presentations, student theses, etc., based on work conducted during the project. As appropriate, include attachments.

RESPOND BELOW

The clean resource metrics stay the same as we proposed. One full-time postdoc was hired and received training through this project. We reached an agreement with Everest Canadian Resources. We are preparing one research paper based on the results of the project. Although the current technological advances in Phase I are not likely enough for applying for a patent, the findings point us in the right direction making ultrafine carbon fibers, which may result in multiple patents in future work.

The project success metrics are partially achieved. With a home-made pneumatic melt e-spin system, we fabricated carbon fiber with a diameter around 5-10 µm, which is not as thin as our targeted fibers (smaller than 2µm). We identified the uniform spinneret pressure in a pneumatic system as the key problem. We requested a collaborator who has a single-screw extruder-based e-spinning system to spin some asphaltene fibers for us. As shown in Figure 4, the average diameter of the asphaltene fibers is 1-2 µm, which meets our goal. In phase II, we will purchase or build a single- or twin-screw extruder-based e-spinning system to fabricate carbon fibers with a diameter below 1 µm.

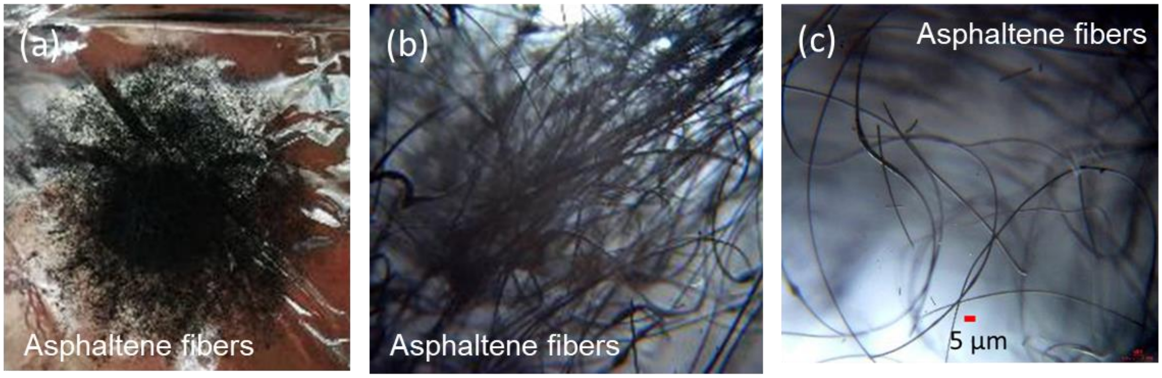

Figure 4. The ultrafine asphaltene fibers were fabricated with a single-screw extruder-based e-spinning system in our collaborator's lab.

H. BENEFITS

Please provide a narrative outline the project's benefits. Please use the subheadings of Economic, Environmental, Social and Building Innovation Capacity.

- **Economic:** Describe the project's economic benefits such as job creation, sales, improved efficiencies, development of new commercial opportunities or economic sectors, attraction of new investment, and increased exports.
- **Environmental:** Describe the project's contribution to reducing GHG emissions (direct or indirect) and improving environmental systems (atmospheric, terrestrial, aquatic, biotic, etc.) compared to the industry benchmark. Discuss benefits, impacts and/or trade-offs.
- **Social:** Describe the project's social benefits such as augmentation of recreational value, safeguarded investments, strengthened stakeholder involvement, and entrepreneurship opportunities of value for the province.
- **Building Innovation Capacity:** Describe the project's contribution to the training of highly qualified and skilled personnel (HQSP) in Alberta, their retention, and the attraction of HQSP from outside the province. Discuss the research infrastructure used or developed to complete the project.

RESPOND BELOW

The oil sands have spurred massive economic growth in Alberta. The bitumen extracted from oil sands contains up to 20% asphaltene, which makes the oil extremely heavy and viscous. The proposed work is to develop a high-value usage of asphaltene as precursors of ultrafine carbon fibers (UF-CFs) with a diameter between 100 and 500 nanometers. Besides the diameter effect, the UF-CFs possess a substantial advantage over traditional CFs as reinforcement materials. Their 100–5,000 times smaller cross-sectional area provides tremendous refinement and improved interaction with polymer matrices, thus increasing the matrix shear strength. On carbon reinforcement materials market, UF-CFs are well-positioned to fill the gap between traditional CFs (diameter 5-7 µm, $10-30/lb) and carbon nanotubes (diameter 2-30 nm, $1,000-15,000 /lb).

I. RECOMMENDATIONS AND NEXT STEPS

Please provide a narrative outlining the next steps and recommendations for further development of the technology developed or knowledge generated from this project. If appropriate, include a description of potential follow-up projects. Please consider the following in the narrative:

- Describe the long-term plan for commercialization of the technology developed or implementation of the knowledge generated.
- Based on the project learnings, describe the related actions to be undertaken over the next two years to continue advancing the innovation.
- Describe the potential partnerships being developed to advance the development and learnings from this project.

RESPOND BELOW

In the following two years, we will be actively looking for industrial partners to further develop the technology towards full commercialization. Our results in Phase I not only demonstrated the technical feasibility of making asphaltene-derived ultrafine carbon fibers using melt electrospinning technology but also pointed out two research direction in the next stage: 1) fine-tuning the structure of asphaltene to achieve uniform physical behavior at a spinning temperature of 200 – 250 ℃; 2) building a single- or twin-screw extruder-based electrospinning system able to produce 1 kg asphaltene fibers/day. In fact, melt electrospinning is a scalable process. Although a high voltage is required, the associated electricity cost is less than 1% of production cost because of the extremely low current. In China, a melt electrospinning production line is under construction to produce 1 ton/day ultrafine PAN fibers for advanced textiles.

In Phase I, we are partnered with Everest Canadian Resources. Everest Canadian Resources is satisfied with the project progress and shows interest to advance into Phase II with us. However, their business loss caused by the low oil price makes it difficult to commit cash contribution. We are actively looking for other industrial partners. If someone in Alberta Innovates' network could be potentially interested in the technology, please do not hesitate to contact us.

J. KNOWLEDGE DISSEMINATION

Please provide a narrative outlining how the knowledge gained from the project was or will be disseminated and the impact it may have on the industry.

RESPOND BELOW

The main findings in the project have been presented on the Carbon Fibre Grant Challenge workshop organized by Alberta Innovates. The presentation was attached.

K. CONCLUSIONS

Please provide a narrative outlining the project conclusions.

- Ensure this summarizes the project objective, key components, results, learnings, outcomes, benefits and next steps.

RESPOND BELOW

Melt e-spinning is an electrohydrodynamic processing technique to produce ultrafine fibers by charging and ejecting polymer melts through a spinneret under a high-voltage electric field. Unlike traditional solution e-spinning, melt e-spinning does not require an expensive scrubbing process to remove solvent vapors in fibers, which not only significantly reduces the production cost but enhances mechanical strength by avoiding the micropores induced by solvent evaporation. In this short project, we demonstrate the melt e-spinning is an effective way to make continuous and smooth carbon fibers using asphaltenes as feedstocks. Further improvements are required to achieve high-performance and ultrafine carbon fibers with a diameter smaller than 1 µm.