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.

Process Development for Transforming Alberta's Asphaltenes into High-value Carbon Fibers

Public Final Report

Prepared for

Alberta Innovates

Prepared by

University of Calgary

Md. Golam Kibria, Assistant Professor

CLEAN RESOURCES FINAL PUBLIC REPORT TEMPLATE

1. PROJECT INFORMATION:

Project Title:	**Process Development for Transforming Alberta's Asphaltenes into High-value Carbon Fibers**
Alberta Innovates Project Number:	G2020000352
Submission Date:	March 02, 2021
Total Project Cost:	$100 K
Alberta Innovates Funding:	$50 K
AI Project Advisor:	Paolo Bomben

2. APPLICANT INFORMATION:

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3. PROJECT PARTNERS

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

RESPOND BELOW

A. EXECUTIVE SUMMARY

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

RESPOND BELOW

Asphaltenes, the heaviest component (15-20% by weight) in bitumen, is a low-value/waste by-product in crude oil refineries. Asphaltenes hold great promise to serve as a cheap feedstock for a wide variety of non-combustible, high-value products with diverse applications. Recent market assessments identified carbon fibers as one of the most attractive products due to its high demand for numerous and large-volume market applications including automotive, aerospace, and construction industries. Conversion of asphaltenes to carbon fibers can potentially offer six-fold increase in value-proposition for a barrel of oil, leading to a $120 billion future market opportunity in Alberta. Unfortunately, little to no work has been done focusing on the potential of asphaltenes to produce commercially compliant carbon fibers. Since asphaltenes consist of adequate aromatic rings and high carbon content, they are excellent precursors for manufacturing high performance carbon fibers to revitalize the incumbent polyacrylonitrile (PAN) based fiber industry. The integration of low-value Alberta oil sands Asphaltenes (AOA) can drastically decrease the costs of carbon fiber production, thus providing an alternate solution to expensive PAN-based fibers.

In Phase-I of Carbon Fiber Grand Challenge (CFGC), we first received two different AOA samples from the suppliers. At first, our objective was to thoroughly conduct their physicochemical characterizations via multiple state-of-the-art characterization techniques to understand if they meet the requirements for producing high performance carbon fibers. Surprisingly, distinct differences in the physicochemical properties of the two types of AOAs, which had possibly gone through different extraction processes, were observed. The second objective of this project was to design and demonstrate the efficacy of various pre-treatment processes to tune the physicochemical properties of these as-received AOAs. Appropriate pre-treatment techniques (e.g., thermal treatment, solvent extraction) with respect to the current properties of AOAs were developed and optimized. Next, we focused on the third objective of the project in which three principle steps in the carbon fiber production route were studied: melt spinning, oxidative stabilization and carbonization. Investigations on the temperature dependent rheological behavior and parameters for continuous melt extrusion (e.g., dye-swell effects, filament formation, etc.) of as-received and pre-treated AOAs were carried out. Through these rheological studies, the primary challenges (e.g., identifying an ideal viscosity range at high melt-spinning temperatures) associated with melt spinnability of AOAs were identified and optimized for continuous extrusion. We successfully demonstrated spinnable (melt spinning temperature > 230 °C) green fibers with diameters in the range of 10-500 µm. Later on some of the key challenges associated with oxidative stabilization of the melt-spun green fibers, including fiber degradation at elevated temperatures as well as long stabilization period, were revealed. Based on this first-hand understanding, single-step and multi-step stabilization processes were developed that led to successful stabilization of green fibers with diameters in the range of 40-200 µm. Subsequently, carbonization of stabilized fibers were performed and surface morphologies, cross-sectional microstructures and mechanical properties of those carbon fibers (10-200 µm) were studied in detail. Our findings based on the key learnings from this project would open multiple doors to effective utilization of AOAs for developing high performance carbon fibers for large scale applications in different sectors. As a result, we expect an exponential growth in both the industrial diversity and economy of Alberta.

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:

In this era of declining crude oil reserves in the world, Alberta serves as the third largest producer of crude oils and bitumen. With around 180 billion barrels of bitumen reserves present in Alberta, an appreciable amount of asphaltenes (low value components) within these bitumen samples are highly carbonaceous. As such, Alberta oil sands Asphaltenes (AOA) can be transformed into value added products like carbon fibers, eventually acting as an alternative solution to the expensive polyacrylonitrile (PAN) based carbon fiber industry. Carbon fibers exhibit impressive mechanical properties (e.g., five times stronger and lighter than steel) and offer great promise as an ideal manufacturing material for various purposes.

The current carbon fiber industry is approximately worth $5 billion with an expected rise to $13 billion by 2029. This is an excellent opportunity for AOAs to blend within the market as AOA feedstock could cut down the precursor cost by ~90% relative to PAN based feedstock. The production cost could reduce from ~$10/lb. (for PAN based carbon fibers) to ~$5/lb. if AOAs are utilized as carbon fiber precursors causing an overall increase in demand for carbon fibers in automotive, aerospace, and construction industries. Specifically, inexpensive and high strength carbon fibers from AOAs can be effectively utilized as structural materials, such as in the production of lightweight vehicles with increased performance (~35% fuel efficiency) and larger wind turbines with longer blades for clean energy harvesting. Moreover, other potential applications of AOA derived carbon fibers in the field of polymer composites, carbonaceous materials, structural materials (e.g., 3D printed complex structures, etc.) and super capacitors have not been explored so far. Likewise, extensive physicochemical characterization of AOAs are yet to be investigated to reveal the key challenges and opportunity areas. Most of the studies over the past decade focused on the development of value added products originating from coal/petroleum asphaltenes in China, Japan, and South America. Thus it is of high relevance to first understand the physical and chemical properties of AOAs for transforming them into value added carbon fibers. Current literature shows incorporation of carbon fibers in structural materials, such as concrete and composite materials, could drastically enhance their physical and mechanical properties. Therefore a clear pathway of producing high value carbon fibers from AOA feedstock need to be carefully elucidated.

Besides the above-mentioned applications, valorization of AOAs to carbon fibers can open up new possibilities for structural engineering applications. Thanks to the high degree of control and flexibility in designing high-resolution complex architectures, additive manufacturing (AM) techniques, also commonly known as 3D printing, have recently been at the technological forefront for realizing structural materials. Tailoring the rheological properties of AOAs and employing extrusion based 3D printing techniques, 3D carbonaceous structures with complex architectures can be rapidly built that can find potential applications as catalyst support, gas adsorption, casting mold, nuclear reactors, heating elements, lab crucibles, seals and many more. Furthermore, the AOA derived printed construct can be infused in various matrices i.e. polymers, cement etc. to develop composites with superior mechanical properties (e.g. damage-tolerance/delaying, impact and/or vibration resistance etc.).

Knowledge or Technology Gaps:

Asphaltenes fall under the category of petroleum pitch molecules with only a handful of applications (e.g. reservoir characterization, enhanced interfacial stability, etc.) in the field of oil and gas engineering. However, the process of transforming them into structural materials like carbon fibers still remains challenging. Specific attention is required to first understand the chemical (e.g., aromaticity, chemical structure, double bond equivalency, etc.) and physical (e.g., rheological, structural, softening point, thermal stability, etc.) properties of AOAs that are currently missing in literature. The fundamentals of their physicochemical characteristics are extremely important to evaluate and explore the feasibility of their use, particularly in carbon fiber production. As the extraction technologies directly impact the chemical and physical properties of AOAs, extensive studies are necessary to bridge the gap between them. Typically, AOAs also contain high sulfur and trace amounts of heavy metals. The effects of these impurities on the synthesis and mechanical properties of carbon fibers are still inconclusive. Even though the extrusion of fibrous or polymeric materials is well known and advanced, melt extrusion of AOAs to form fibrous filaments have remained challenging because of limited studies available in literature. In addition to that, comprehensive studies on the oxidative stabilization of AOA-based green fibers with careful consideration of economic feasibility and environmental benefits are also missing in the literature. Efficient optimization of physicochemical properties (specifically for AOAs) affecting carbon fiber formation, such as mesophase content, softening point and aromaticity, is lacking in the literature and need to be addressed in detail. For example, the relationship between mesophase content and mechanical properties of carbonized fibers is essential to investigate for the development of high strength carbon fibers from AOAs. Thus, is it important to understand these key parameters that govern all the steps in carbon fiber production and tailor them towards appropriate processing of AOAs with respect to their physicochemical properties.

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

Knowledge or Technology Description:

The objective of this project was to develop an economically and environmentally viable process that would enable valorization of AOAs - the organic molecules found in bitumen - into high-value carbon-fibers to create alternatives to PAN and pitch-based carbon-fiber technologies. This project has significant potential for profitable collaborations with oil sands industries in Canada and beyond. The process consists of some sub-technologies such as purification, pre-processing for spinnability, spinning optimization, stabilization and post processing. Each sub-process was optimized specifically for AOAs with an eye to achieve the targeted technical specifications of carbon fiber. The technology aims to minimize the energy expenditure and global carbon footprint in a cradle-to-grave model along with cost optimization at each step. The quality of carbon fibers produced in this process will be competitive to the commercial PAN and pitch-based carbon fibers in the market.

To summarize, the five primary objectives in this project are as follows:

1. To identify the knowledge gaps in asphaltenes derived carbon fiber production and evaluate the key challenges in carbon fiber processing from AOAs via extensive literature review.
2. To perform extensive chemical and physical characterizations (e.g., FTIR, FTICR-MS, XPS, CHNS, shear rheology, mesophase formation, TGA, ^{13}C NMR, etc.) on AOAs to understand their physicochemical properties suitable for spinnable pitch formation.
3. To develop pre-treatment techniques for AOAs combined with physicochemical characterizations to increase softening point, mesophase content and aromaticity while reducing the molecular weight (MW) distribution in order to improve spinnability of the pitch samples.
4. To optimize the spinning parameters (e.g., spinning temperature, shear rate, winding speed, etc.) and stabilization routes (e.g., single step, multi-step, etc.) of non-treated and pre-treated AOAs for continuous extrusion and successful carbonization, respectively.
5. To develop AOA based ink formulations with optimum rheology that enables high-resolution 3D printing of complex architected structures of tunable geometries.

Updates to Project Objectives:

Apart from pursuing the key and overarching objectives towards developing carbon fiber production, we have explored (with permission from Program Manager) additive manufacturing approaches to reveal the feasibility of AOAs in structural engineering. The target was to transform AOAs to complex architected structures of tunable geometries as a means of value addition to AOAs. We explored such parallel approaches with an end goal of rapidly developing 3D carbonaceous structures of complex architectures as well as multifunctional composites. Furthermore, direct-ink-writing, being an extrusion based 3D printing technology, has allowed us to bolster our understanding of rheological behavior of AOAs and facilitated in optimizing various physicochemical properties (e.g., flowability, viscosity, solubility, etc.) that can influence the extrusion of this material. Thus the learnings from this approach have greatly benefited us in our primary goal of developing carbon fibers.

Performance Metrics:

The project success would be recognized by meeting the following performance metrics as described earlier in the project proposal:

1. Understanding the structural/physicochemical properties and chemical compositions of asphaltenes/AOAs via extensive literature review and their influence on the spinnability of green fibers.
2. Designing effective pre-treatment strategies (e.g., physical, chemical, etc.) to optimize mesophase content and eventually control metal/sulfur impurities, average MW and MW distribution.
3. Optimizing the aromaticity and softening point if needed to or above ~40% and ~180 °C, respectively, for high temperature extrusion and efficient oxidative stabilization
4. Optimizing melt-spinning parameters (spinning rate, temperature, winding rate, etc.) for continuous extrusion of green fibers
5. Formulating a 3D printing ink for suitable extrusion to form stable complex architectures

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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

The following list describes the methodology and facilities used to complete and meet the specific objectives proposed in this project:

1. **Rheological measurements:** The rheological behavior of the raw and pre-treated AOAs at different temperatures were studied using Anton Paar MultiDrive MCR 702 rheometer with a parallel plate assembly. The sample was loaded first, heated to a certain temperature, and then the plate gap was adjusted to 1 mm with trimming before applying the shear. The test was performed under nitrogen to avoid any reaction/degradation in the samples.
2. **Softening point measurements:** To understand a suitable temperature range for extrusion of AOAs, softening point measurement was carried out using a standard ball and ring apparatus (ASTM D36). The set up consists of two horizontal holders containing AOAs (each supporting a steel ball) immersed in a water bath. Then the water bath containing these two holders was heated at a controlled rate using a temperature regulator. The softening point was measured as the mean of the temperatures at which the sample in these two holders softened enough to allow each ball (covered in AOAs) to drop and fall a distance of 25 mm within the water. For samples with softening points higher than 100 °C, shear viscosities measured through rheological characterizations were used to estimate the softening points.
3. **Fourier-Transform Infrared Spectroscopy (FTIR)**: To study the chemical structure of the raw, pre-treated and stabilized AOAs or green/stabilized fibers, solid state Fourier-transform infrared spectroscopy (FTIR) characterization was employed using PerkinElmer Spotlight 400N FT-NIR Imaging system (ATR sampling) with a wavelength range of 400-4000 cm^{-1} at room temperature.
4. **Thermogravimetric Analysis (TGA)**: Thermal stabilities of the raw, pre-treated, extruded and stabilized AOAs/fibers were investigated with TA Instruments Q50 thermogravimetric analysis (TGA) Analyzer in the range of 20 - 800 °C. The analysis was performed in air and nitrogen to have more insights about the thermal stability of these materials in different conditions. This measurement is helpful to identify if the AOAs and green/stabilized fibers are thermally stable enough to undergo extrusion, stabilization and carbonization steps at different temperatures above 200 °C.
5. **Elemental Analysis**: The concentrations of carbon, hydrogen, and nitrogen in the raw and pre-treated AOAs were measured with combustion elemental analysis (CHN analysis) using a PerkinElmer 2400 CHN analyzer.
6. **Cross-polarized Light Microscopy:** To quantify the mesophase content in raw and pre-treated AOAs, cross polarized light microscopy was performed using an Olympus BX-51P polarizing microscope. Thin films of different AOA samples were prepared in coverslip chambers by heating in an inert environment at high temperatures of ~350 °C for 2 hours. Cross-polarized images were captured from multiple areas and an average was reported for the mesophase content. Image analysis was performed using ImageJ and the mesophase content was calculated according to ASTM D4616-95.
7. **Melt Flow Index and Melt Spinning Apparatus:** To understand the effect of spinning parameters on the extrusion of raw and pre-treated AOA samples, melt flow index (Galaxy V Capillary Rheometer 8052 by Kayeness Inc.) and conventional melt spinning apparatus were used. In the melt flow index, AOA samples were loaded in the hot furnace of desired spinning temperature

first. Then the samples were mechanically sheared within a shear rate of 0.1-1 s^{-1}. The extruded filaments were collected through a 200 µm spinneret and carefully winded in an automatic winder. On the other hand, green fibers in the melt spinner were produced using a single hole spinneret (diameter= 150 µm, L/D=5) at a winding rate of ~230 m/min.

8. **Thermal Treatment:** Thermal treatment is a common approach for asphaltene based precursors such as AOAs to remove low MW components, narrow down the MW distribution, or increase softening point. Different procedures were designed to study the effect of thermal treatments on the physical and chemical properties of AOA samples. The as-received AOAs were fed into a 100 mL Parr batch reactor that is equipped with a heating oven and connected to a temperature control loop. The sample was continuously stirred at 300 rpm upon heating at a specific temperature and was cooled under nitrogen within a certain period of time.
9. **Oxidative Stabilization/Carbonization:** The stabilization and carbonization on the extruded green fibers were carried out in a Carbolite Gero EHA 12/600B tube furnace. The stabilization and carbonization steps were performed under air and nitrogen, respectively.
10. **Fourier Transform Ion Cyclotron Resonance Mass Spectroscopy (FTICR-MS):** To measure the concentration of different compound classes, average MW, and MW distribution within the AOAs, a 12T Bruker SolariX mass spectrometer coupled with different ionization modes was employed. Two different ionization modes were exploited: atmospheric pressure photoionization in positive-ion mode (APPI-P) and electrospray ionization in negative-ion mode (ESI-N). For APPI-P analysis, sample stock solutions were diluted in toluene and infused into the ionization source (a krypton lamp at 10.6 eV) using a syringe pump at a certain flow rate. The transfer capillary temperature was set to 400 °C whereas the nebulizer pressure was 1.5 bar. For ESI-N analysis, sample stock solutions were diluted in toluene and methanol of equimolar ratio followed by doping with 2% ammonium hydroxide. The ESI-N parameters include controlled flow rate of 200 µL/h, capillary voltage of 4 kV and nebulizer pressure of 1 bar. The instrument was calibrated beforehand using a known reference sample.
11. **X-ray Photoelectron Spectroscopy (XPS):** The surface elemental compositions, chemical states of components were analyzed by X-ray photoelectron spectroscopy (PHI Quantera II with monochromated Al Kα at 1486.6 and 26 eV pass energy). 50 W, 15 kV and 200 µm diameter X-rays were shot on the sample. The XPS survey scan spectra in the 1100–0 eV binding energy range were recorded in 0.5 eV steps with a pass energy of 140 eV. High resolution spectra were recorded in 0.1 eV steps with a pass energy of 26 eV.
12. **Nuclear Magnetic Resonance (NMR):** Solid state ^{13}C MAS NMR spectra were obtained on a Bruker Avance III, two channel spectrometer with a 4.7 T magnet (50.3 MHz ^{13}C). Samples were spun in a 4 mm outer diameter zirconia rotor barrel with a Kel-F [poly (chlorotrifluoroethylene)] rotor cap. Direct ^{13}C pulse MAS spectra were acquired using standard Bruker pulse programs modified to incorporate a fixed waiting period before each experiment in a series of repetitive experiments (i.e., with different relaxation delays: 10 s, 30 s, 90 s, 180 s). Direct ^{13}C pulse spectra were obtained with 12 kHz MAS and a spectral width of 50000 Hz (994 ppm), which results in any spinning

sidebands at multiples of ±238 ppm from a center band. Experiments used a 2.5 μs, 90° ^{13}C pulse, and a short Hahn echo33 (total duration = 8 μs) immediately preceded FID acquisition.

13. **Scanning Electron Microscopy (SEM):** Surface morphology, size and cross-sections of extruded, stabilized, and carbonized fibers were studied by a field emission SEM (FEI Quanta 250 FEG) equipped with a Bruker QUANTAX energy-dispersive X-ray spectroscopy (EDS) system.
14. **3D Printing:** For direct ink writing, a high-resolution 3D printer (Hyrel Engine HR) was utilized to print the AOA-based ink. The cold flow syringe head (SDS-60 Extruder) was used to extrude the ink at room temperature. The ink was loaded in a 60 mL Luer-lock syringe and vibrated to make sure that the bubble was removed. Smooth-flow tapered tips (Nordson EFD) was used to resist clogging and printing discontinuity during the dispensing of the ink. The ink was printed on wax paper to prevent the adhesion of asphaltene structure and build plate and facilitate detaching the printed object from the build plate. The slic3r software was used to generate the G-code script based on the geometry and other parameters like extrusion width, printing speed, and layer height to determine the print path. Printed parts were cured at room temperature for four days with intermittent water spray.
15. **Mechanical Testing:** For tensile testing experiments, an ARES G2 rheometer was used. The fibers were first glued at both ends to laser cut paper strips with a rectangular cut in the center of length 20 mm before mounting them in the tensile tester. Once each end of the fiber is fastened to the grips, the small paper strips on both sides of the fiber are cut before running the experiment. Diameter of the fractured fiber was determined by optical microscopy to calculate the cross-sectional area of the fractured surface allowing conversion from measured force to calculated stress values. To investigate the reduced elastic modulus of the carbonized fibers, Nano indentation experiments were performed using a Hysitron TI980 Triboindenter. The fiber samples were prepared by adhering them to metal magnetic discs using a thin layer of glue. Experiments of varied indentation depths (e.g., 40 nm, 100 nm, etc.) were performed for better accuracy of the results.

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

Importance of key results:

The importance of the key results and their subsequent discussions are provided as follows:

1. **Literature review on asphaltene properties and physicochemical characterization of AOAs:**

Upon extensive literature review, we understand that asphaltenes are complex aromatic macromolecules which are naturally abundant in crude oil, residues of petroleum, and coal processing. The chemical compositions of asphaltenes vary based on their origins and extraction techniques. Petroleum based asphaltenes usually have a high sulfur content (~7-8%) relative to coal asphaltenes that are mostly present in the form of thiophenes, sulfides, and sulfoxides. At the same time, petroleum asphaltenes also contain higher amounts of aromatic carbons (~40-50%) with greater alignments than coal asphaltenes which makes them promising candidates for high strength carbon fibers and graphitic materials. It is important to note that petroleum asphaltenes also contain longer alkyl side chains representing methyl, methylene, methine and ethyl groups that are likely to oxidize and form strong cross-linked networks. Even though asphaltenes are chemically distinct because of their functional groups (polar/non-polar groups depicting acidic/basic properties), their macromolecular structures can only be classified under two models: island model (single aromatic core) and archipelago model (multiple aromatic cores). From these two structures, the archipelago structure is found to be more effective as a precursor for carbon fiber production due to high double bond equivalent (DBE) and greater aromaticity. Moreover, these structural and functional features are directly dependent on the MW of asphaltenes. This means archipelago asphaltenes with higher DBE and aromaticity are expected to have a higher MW with a narrower MW distribution. This would consequently result in higher softening points with greater thermal stability. Although plenty of work has already addressed the characterization of coal and petroleum based asphaltenes of different origins, no work has been done so far focusing on the potential of AOAs in the process of carbon fiber manufacturing. With sufficient amounts of asphaltenes present in Alberta, it is crucial to have a solid understanding of their physicochemical properties (e.g. aromaticity, MW distribution, mesophase, thermal stability, etc.) with detailed analysis of their spinnability (e.g. viscoelasticity, flow properties, etc.) and purification techniques to bridge the gaps in literature.

In this project, we worked with two types of AOA samples and would be referred to as sample 1 and sample 2 from now on. As received and pre-treated AOAs have been extensively characterized to identify their physicochemical properties (shear viscosity, aromaticity, softening point, mesophase content, thermal stability, carbon content, etc.) required for carbon fiber production stages. The as received samples were found to have different concentrations of asphaltenes, such as pentane and heptane insoluble asphaltenes. Sample 1 contained a higher amount of asphaltenes (also higher aromaticity) than sample 2 with similar carbon content (~78-80%). Both of these AOA samples are viscoelastic in nature because of the long alkyl chains present in them interconnected through multiple domains of polyaromatic hydrocarbons (PAH). The presence of larger amounts of low MW alkyl groups in sample 2 have been confirmed through both FTIR and FTICR-MS relative to sample 1. The presence of low MW components in both the samples confirms their spinnability, but at different temperatures because of distinct softening points. Since sample 2 has a very low softening point of <100 °C, green fibers spun from this batch would be extremely difficult to stabilize at higher temperatures (above 200 °C). From TGA results (in N_2) we understood that sample 2 starts degrading ~80-120 °C along with sharp clear peaks around the temperature range of 100 °C-400 °C (on DTG profile). Moreover, sample 2 contains only less than 30% pentane insoluble asphaltenes (not suitable for a strong graphitic material because of low expected carbon yield) with a low aromaticity index (<30%) measured through solid state ^{13}C NMR. In addition to these, mesophase content for sample 2 was at least one order of magnitude lower than what is reported in literature for PAN based fibers with appreciable mechanical properties (~GPa for tensile strength and modulus). Even though sample 2 was thermally unstable to withstand melt spinning above 200 °C, rheological measurements were carried out to highlight a suitable temperature range. Since sample 2 has a low softening point (~25-60 °C), it can be melt-extruded within a temperature range of ~30°C-70°C, where it exhibits extrusion favorable viscosities (~1-20 Pa.s). Eventually our extensive analysis categorized sample 2 as a poor candidate for AOA based carbon fibers. On the other hand, sample 1 had a high softening point in the range of ~150 °C-200 °C with a mesophase content over ~20%. Furthermore, rheological measurements on sample 1 explain how it exhibits favorable melt spinning shear viscosities within a temperature range of ~50 °C-80 °C above its softening point. The aromaticity through solid state ^{13}C NMR of sample 1 was calculated to be >35% and was confirmed with multiple longer delay times (e.g., 90 s, 180 s, etc.) to verify the complete relaxation of all the aromatic and aliphatic domains. Since sample 1 has a higher softening point and asphaltene content compared to sample 2, we realize this sample can be independently used for melt extrusion. From now on, we would refer to pre-treated sample 1 as PT sample 1 and pre-treated sample 2 as PT sample 2 for convenience.

2. Design of pre-treatment/purification processes:

Two different pre-treatment processes (thermal treatment and solvent extraction) were designed in order to increase the asphaltene/carbon content, aromaticity factor, mesophase content, softening point and thermal stability of AOAs. Extensive physicochemical characterizations were carried out on the pre-treated samples to study the effects of pre-treatment techniques on carbon/sulfur content, aromaticity, mesophase content, average MW/MW distribution, thermal stability and softening point through FTICR-MS, CHN, XPS, cross-polarized microscopy, ^{13}C NMR and TGA analysis. For sample 1 we employed thermal treatment under both N_2 and air. These approaches were chosen to optimize the ordering and alignment of anisotropic domains while carefully monitoring the change in shear viscosities. Thermal treatments (above 200 °C) such as heating under N_2 or air, are expected to significantly increase the softening point, average MW and aromaticity index of sample 1. Moreover, they are also expected to induce thermal cracking (weak bond cleavage) leading to changes in chemical structures (e.g., free radical formation) thus enabling some thermal polymerization. We noticed significant increases in carbon content (>80%), mesophase content (~45-50%), aromaticity (>40%), softening point and average MW in PT sample 1. These pre-treatment techniques were also successful in decreasing the overall sulfur content (<2.5%) of sample 1. However, we observed significant deteriorations in the sample's viscoelastic properties due to extensive cracking of short alkyl chains and low MW components.

For sample 2 we decided to perform a physical pre-treatment (solvent extraction) to increase the asphaltene content. Extracting the asphaltenes from sample 2 via solvent extraction has demonstrated significant increases in softening point and average MW. Even though it can be an expensive process on a larger scale, the asphaltene yield of this solvent extraction was ~98-100% as we were able to recover all the pentane insoluble asphaltenes. However, the sulfur content in sample 2 remained unchanged after solvent extraction. This is mainly because solvent extraction is a physical separation method and does not provide the energy needed to split and degrade the sulfur compounds. Nonetheless, solvent extraction serves as an effective process that can easily increase the anisotropic mesophase domains within the AOAs leading to higher aromaticity (>40%) as well. This could be possible due to the extracted AOAs having higher anisotropic content leading to an overall higher mesophase content in sample 2 without any applied shear or heat. As the softening point increased fourfold (after solvent extract), the sample was predicted to be extrudable at temperatures within a range of ~170-250 °C and was justified through rheological measurements. Since solvent extraction was mostly a physical separation technique, this process did not promote any chemical changes within the AOAs unlike thermal treatment.

3. Melt spinning of raw and pre-treated AOAs for carbon fiber production:

The extrusion of a material is directly dependent on its rheological properties (e.g., polymeric or viscoelastic behavior) that dictate if the material is able to expand or elongate. Importantly, shear viscosity also plays a major role to define whether the sample is extrudable or not. Unfortunately the thermally treated samples were not continuously extrudable and this would be our subject of interest in Phase-II of CFGC. Processes like thermal treatment under air or N_2 are difficult to optimize in terms of time and temperature and the optimization parameters vary from one material to another. That is why, optimizing both temperature and time is extremely important to induce minimum cross-linking besides optimizing the removal of low MW components. Thus finding an ideal point where the material forms weaker bonds and retains its spinnability can be extremely challenging. However, both sample 1 and PT sample 2 could be sheared and extruded at different temperatures. Sample 1 and PT sample 2 were melt spun continuously above a temperature of ~180 °C when they both exhibited Newtonian shear viscosities in the range of 1-20 Pa.s under low shear rates of ~0.1-1 s^{-1}. It is important to verify that the sample viscosity falls within the above mentioned range to avoid any damage to the plunger/extruder. It is noteworthy to mention that we were able to continuously spin green fibers, through both melt flow index and melt spinner, of various diameters (10 μm-300 μm). The green fibers (both thin and thick fibers) were found to be brittle and need to be handled with extra care. The following figure shows optical microscopy and SEM images of some green fibers produced from both sample 1 and PT sample 2 with different diameters:

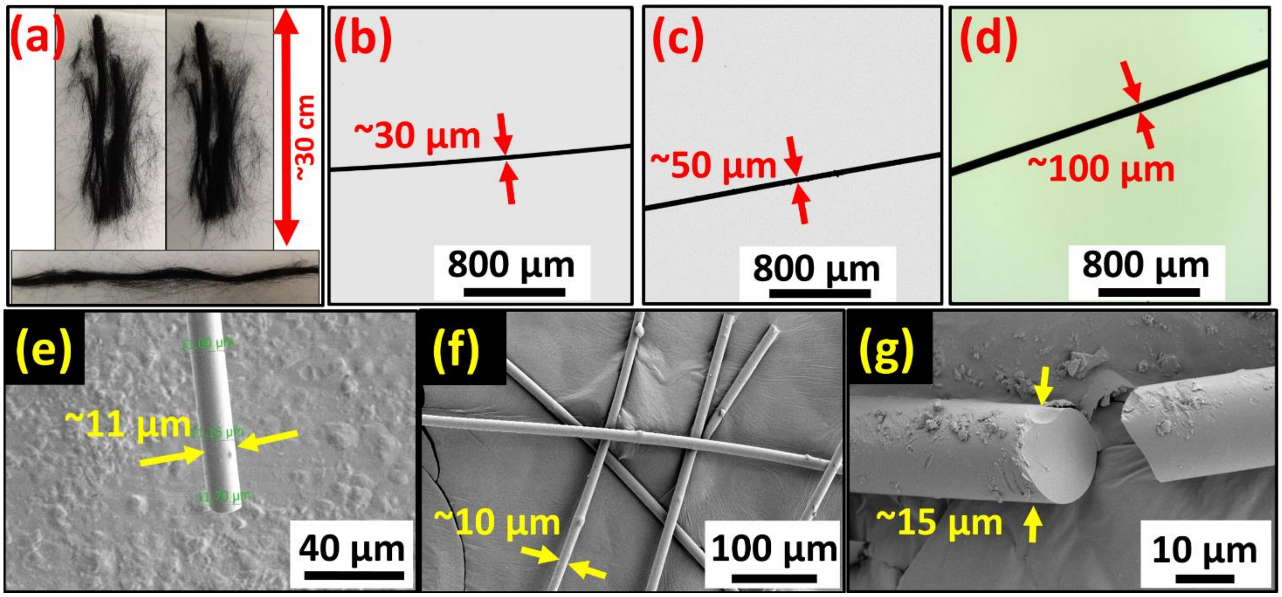

Figure 1. (a) Batches of continuously spun green fibers from sample 1 with diameters of ~10-50 µm; Bright field optical microscopy images of green fibers of various diameters: (b) 30 µm from PT sample 2, (c) 50 µm from sample 1, (d) 100 µm from sample 2; SEM images of small diameter green fibers from sample 1: (e) 11 µm, (f) 10 µm, (g) 15 µm.

4. Oxidative stabilization and carbonization of green fibers:

Green fibers from sample 1 and PT sample 2 were stabilized through oxygen-mediated cross-linking under various temperatures and time periods. It is crucial to understand that these asphaltene precursors are extremely heterogeneous in nature, therefore, we have developed single-step and multi-step stabilization processes in the temperature range of 200 °C-400 °C for effective thermosetting of green fibers. Initial O_2 diffusion begins at the fiber's surface as it continues radially towards the core. Initial cross-linking at lower temperatures is crucial to make sure that the fibers are thermally stable enough to sustain stronger oxidation at higher temperatures. The formation of cross-linked networks (these strong oxidized networks) were verified using FTIR and XPS analysis on green and stabilized fibers for comparison. Upon successful stabilization, the fibers were carbonized at different temperatures (e.g. 600 °C-1000 °C) to remove all the heteroatoms and eventually form tightly interlocked chains of carbon networks. To confirm this effect, extensive XPS analysis was performed. The effects of single-step and multi-step carbonization (with various soaking times) were carefully studied based on the cross-sectional layout of the carbon fibers. The following figure includes SEM images of different cross-sections (e.g., hollow, solid, porous) of stabilized and carbonized fibers prepared from AOAs:

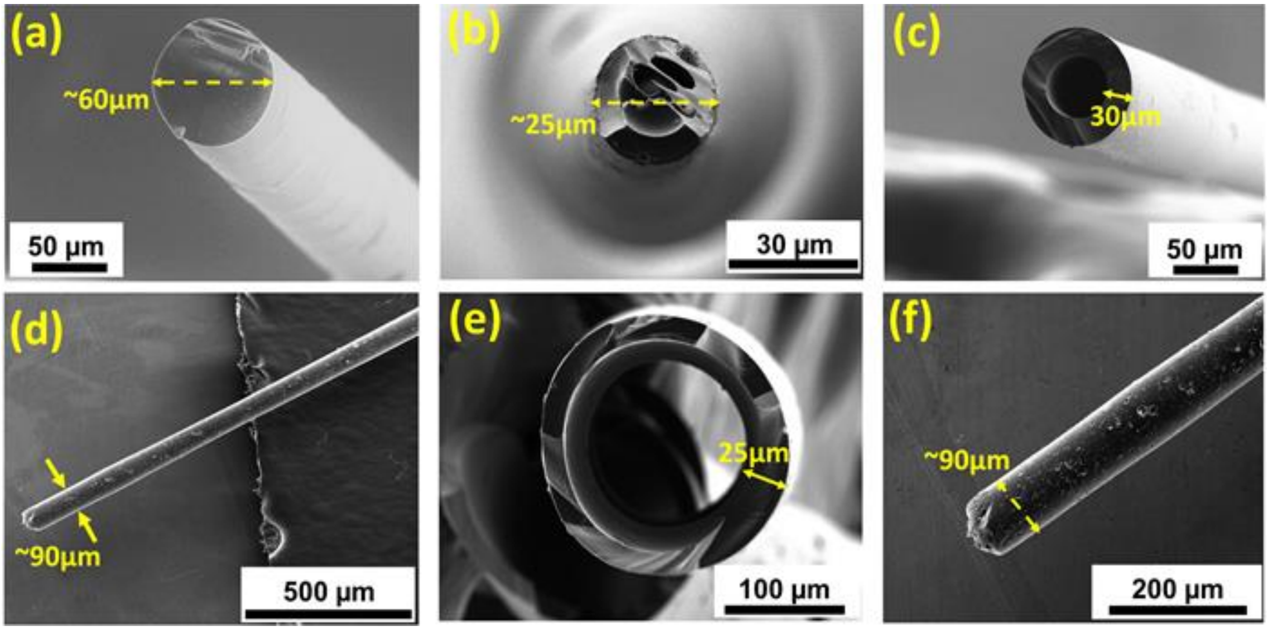

Figure 2. Scanning electron microscopy (SEM) images of stabilized (a) and carbonized (b-f) carbon fibers from AOAs (sample 1 and PT sample 2).

The carbonized fibers were later tested for their mechanical performance using a tensile tester and Nano indenter. The carbon fibers showed an average tensile strength of ~36 MPa ± 9 MPa with an average reduced elastic modulus of ~8 GPa ± 2 GPa. Both the tensile strength and elastic modulus values, if compared to PAN based fibers, are off by two orders and one order of magnitude, respectively mainly because of low mesophase content (<50%) in the untreated AOA samples. Elaborate studies on how impurities, fiber diameter, aromaticity and stabilization mechanisms generate stress and affect fiber mechanical properties would be prioritized in the next phase along with optimizations. Thus we expect greater mechanical properties upon careful melt-spinning and optimization of pre-treated AOAs in Phase-II of CFGC. The following illustration explains how the flexibility and mechanical properties of the carbon fibers improved after stabilization and carbonization:

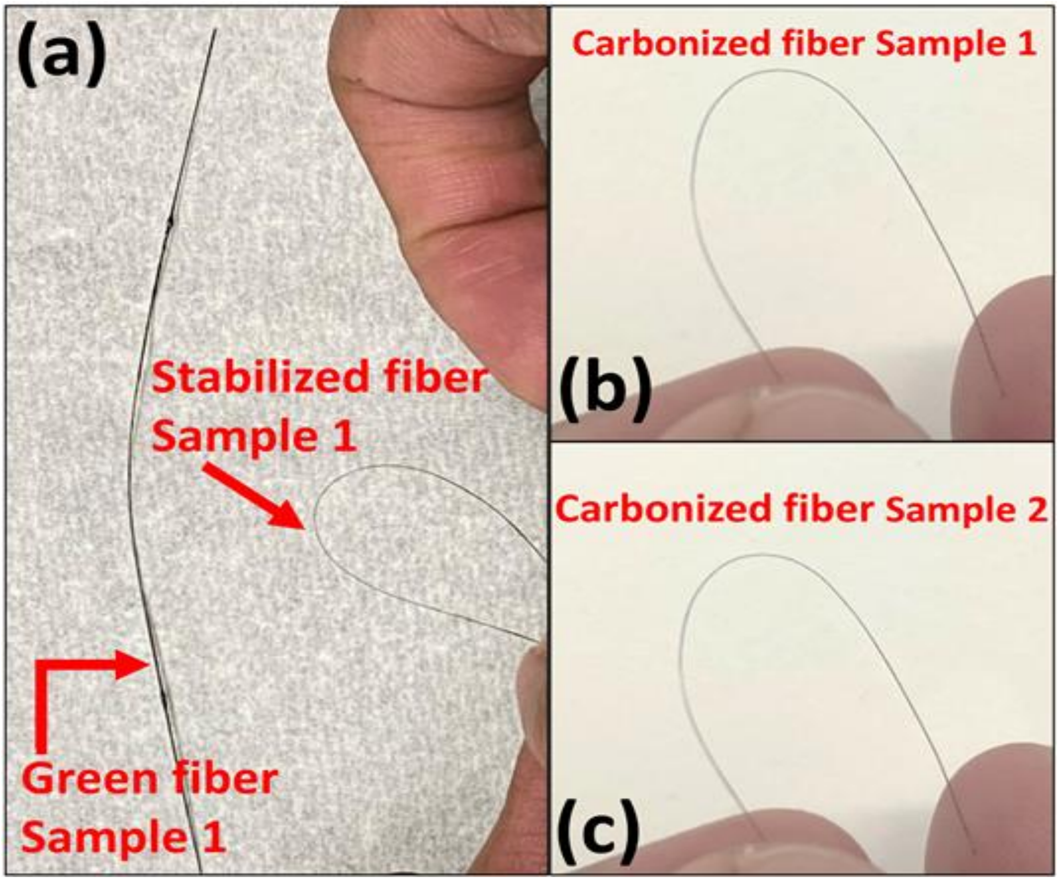

Figure 3. Differences in carbon fiber flexibility after single-step and multi-step stabilization and carbonization: (a) brittle green fiber from sample 1 and stronger stabilized fiber from sample 1; (b) carbonized fiber from sample 1; (c) carbonized fiber from PT sample 2.

5. Direct ink writing of AOAs to develop 3D printed complex architectures with tunable geometries:

For 3D printing, two types of asphaltene based inks were developed. One was modified with nanoscale additives (nanoclay), while the second approach includes mixing asphaltene with an epoxy polymer. Both approaches enabled 3D printing of complex architectures with tunable geometry. The developed inks have satisfied the essential rheological properties, such as shear thinning, and rapid gel strength required for high resolution printing of any structures. The modified rheology facilitates ink extrusion even from a micro-nozzle (~400 µm) in ambient conditions conserving the filamentary shape. A series of cellular complex architected structures with a variety of patterns e.g., rectangular, 2D honeycomb, 3D honeycomb, square honeycomb and porous structures have been printed, which were later heated at high temperatures (~200 °C) to get rid of the modifiers. Depending on the post-processing temperatures, structures with tunable flexibility/stability could be realized.

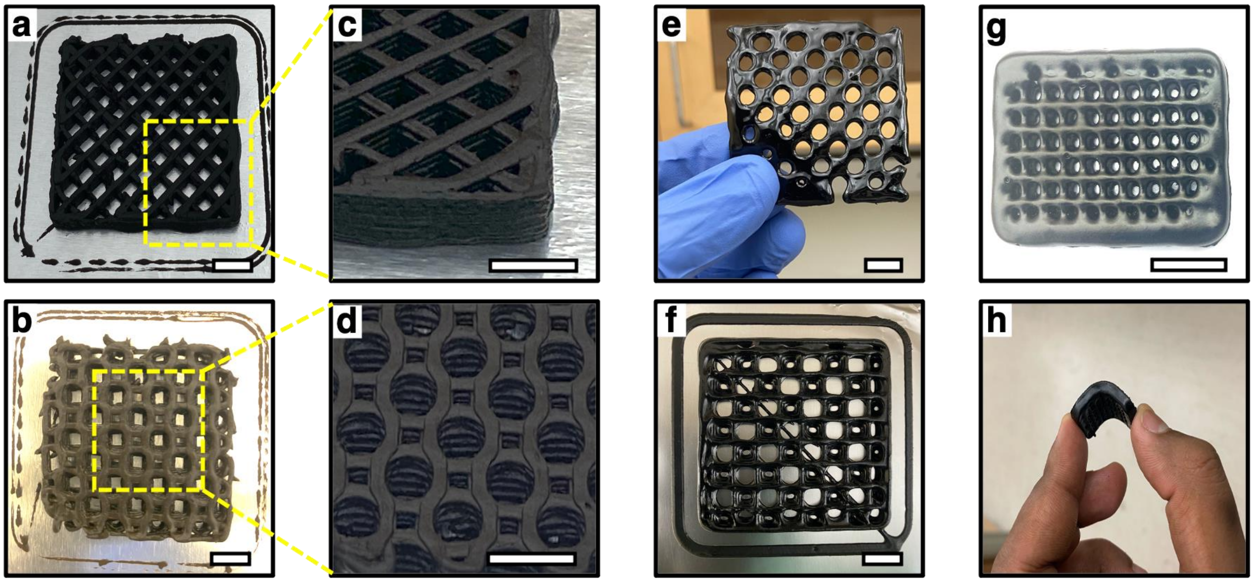

Figure 4. 3D printed structures from sample 1 following approach 1 (a-e) (a) rectilinear structure, (b) 3D honeycomb structure, (c) zoomed in image of (a), (d) zoomed in image of (b), (e) flexible porous structure, following approach 2 (f-h) (f) square honeycomb, (g) porous structure (h) flexed form of the structure shown in (g). Scale bar corresponds to 1 cm.

Variances between expected and actual performance:

The following list describes the metrics that have been considered as the standard to meet the objectives of this project and how the variances are for each of them in terms of expected and actual performance:

1. **Understand the structural/physiochemical properties and chemical compositions of asphaltenes via extensive literature review and their influence on the spinnability of green fibers:** From literature review, we expected to understand the fundamental physicochemical properties of asphaltenes needed for smooth extrusion of green fibers with enhanced thermal stabilities to undergo effective stabilization and carbonization. After our extensive research, we were able to accumulate all the resources from literature (e.g., characterization techniques, suitable experimental parameters, target properties, etc.) to move forward with our characterizations and observed no variances between expected and actual outcomes.
2. **Design effective pre-treatment strategies (e.g., physical, chemical, etc.) to enhance mesophase formation and eventually reduce metal/sulfur impurities, average MW and MW distribution:** Through pre-treatment techniques, the mesophase content of sample 1 and sample 2 were expected to increase by ~80-100%. This target was achieved for both sample 1 and sample 2. In fact, the mesophase content increase in PT sample 2 was more than 100% thus proving the effectiveness of our designed pre-treatment techniques. The results were verified through cross-polarized light microscopy and compared with bright field microscopy to recognize the differences in terms of mesophase sphere formations. Our pre-treatment strategies also narrowed down the

MW distribution for both the samples (as measured through FTICR-MS) with a calculated increase of up to ~15% in average MW. We predicted a decrease in the sulfur concentration by at least 20% for sample 1 and did not expect any sulfur content change for sample 2. Through XPS analysis we were able to conclude a decrease of ~21% in sulfur content for sample 1 whereas no change in sulfur content was reported for sample 2 after pre-treatment. So our final results met the expectations because of significant rise in anisotropic mesophase content and substantial decrease of sulfur impurities.

3. **Increase the aromaticity and softening point if needed to or above ~40% and ~180 °C, respectively for higher temperature extrusion and efficient oxidative stabilization:** Since sample 1 and sample 2 had aromaticity of ~20-40%, the goal was to increase their aromatic content by ~40-50% for development of carbonized fibers with higher microstructural alignment and robust mechanical properties. After controlled thermal treatments under N_2 and air, aromaticity index for sample 1 increased by ~20-30% whereas for PT sample 2 the increase in aromaticity was ~40-50%. Interestingly, this increase in aromaticity index (measured via solid state ^{13}C NMR) was two times higher via solvent extraction relative to thermal treatment. Thus solvent extraction was as effective as thermal treatment in generating more aromatic molecules. In addition to that, the softening points of sample 1 and sample 2 were expected to rise above ~170 °C-200 °C. Thermal cracking under nitrogen and air produced mesophase pitch from sample 1 with a softening point around ~250 °C- 350 °C. For sample 2, solvent extraction increased the softening point from below 50 °C to ~180 °C with clear appearance of more mesophase spheres. These changes in softening points were confirmed by rheology studies, melt extrusion (extrudable only >250 °C or more) and TGA analysis. Thus, the actual metrics are the same as the expected ones and were successfully achieved with no variance.

4. **Optimize spinning parameters (spinning rate, temperature, etc.) for continuous extrusion of green fibers:**

   Continuous spinning of green fibers at a rate of ~236 m/min were produced with spinning temperatures above 220 °C within a shear rate of 0.1-1 s^{-1} from both sample 1 and PT sample 2. This continuous extrusion was possible in both the melt flow index and melt spinning apparatus with spinnerets of size ~100-200 µm and L/D ~2-5. These results exactly match with our initial predictions and we report no variance between our expected and actual results.

5. **Formulate a 3D printing ink exhibiting shear thinning behavior for suitable extrusion with a high enough storage modulus to retain its filamentary shape after extrusion and build stable complex architectures:**

   In order to achieve the essential rheological properties required of the asphaltene slurry, a number of polymeric and nanoscale additives were included in the ink. The ink was formulated using an appropriate ratio of each of the components, which introduced shear-thinning behavior suitable for extrusion through the nozzle. The engineered ink, upon extrusion, was able to retain its filamentary shape. Leveraging such appropriate rheological behavior of our developed ink, complex architectures were constructed.

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

Project learnings and importance:

Through this project we first explored the physicochemical properties of AOAs and their efficiency on green fiber extrusion. Then we looked into possible pre-treatment routes appropriate for these AOAs to reduce the impurity and enhance some of their physicochemical and thermal properties that are needed for continuous extrusion and stabilization. Finally, we investigated the effects of single-step and multi-step stabilization/carbonization processes on the carbon fiber microstructure. The following list describes specific milestones, what we learn from them, and their importance in the project scope:

1. **Softening point:** We learned that untreated AOAs have low softening points (below 180 °C) in both sample 1 and sample 2 because of low aromaticity (≤40%) and high aliphatic content. Since a high softening point represents a higher thermal stability, we have successfully increased the softening point above 200 °C through optimized pre-treatments. This is an important parameter to control as oxidative stabilization is directly dependent on softening point and thermal stability. Higher softening point allows to perform thermal oxidation at elevated temperatures and reduce the stabilization time. Subsequently, this helps to reduce the required energy and time for the stabilization process. Hence achieving a high softening point falls under the scope of this project.
2. **Average MW:** We learned that both sample 1 and sample 2 containing AOAs have broad MW distributions due to high content of aliphatic side chains. However, sample 2 contains a higher amount of alkyl side groups than sample 1 (H/C ratio and DBE parameters measured through FTICR-MS), which makes it more promising for melt spinning. However, sample 2 was not a feasible material to extrude at low temperatures because of its low softening point (~40°C) and poor thermal stability. Therefore, it is crucial to understand the optimum region where MW distribution is narrow and the AOAs exhibit favorable viscosities. For both the samples, we employed different pre-treatment strategies (physical separation and chemical modifications) to increase the average MW (up to ~12% quantified using FTICR-MS characterization) while narrowing down the MW distribution. This is a critical parameter to control because a large reduction in MW distribution might disrupt the extrusion properties of the sample. Hence monitoring the change in MW distribution of AOAs falls under the scope of this project. Table 1

describes how different physical and chemical pre-treatment techniques can change the average MW of both sample 1 and sample 2:

Table 1. Effects of different pre-treatment techniques on the average MW of sample 1 and sample 2

Sample Name/Pre-treatment type	% increase in average MW
PT Sample 1(chemical)	~12%
PT Sample 2 (physical)	~2%

3. **Mesophase content:** One of the most important properties desired within AOAs is the presence of high anisotropic content (~50-60% ideally according to literature) that contribute to a liquid crystalline behavior for production of carbon fibers with enhanced mechanical properties. We learned that thermal treatments at high temperatures (>300 °C) for a long period of time (~2-7 hours) can remove low MW components, induce initial cross-linking, and narrow down the MW distribution. Such processes can increase the mesophase content to an extent that low MW components like naphthenic groups could be completely broken down, thus destroying the sample's spinnability. This is a very important parameter to control as the final mechanical properties strongly depend on the macromolecular alignment and mesophase content. For such reasons, optimizing and achieving an ideal mesophase content falls under the scope of this project. Table 2 shows percent increase in mesophase content after pre-treatment and extrusion under shear for both the samples:

Table 2. Percent increase in mesophase content after pre-treatment and melt extrusion under shear of Sample 1 and Sample 2

Sample Name	Mesophase after pre-treatment	Mesophase after extrusion with shear
Sample 1	~80%	~38%
Sample 2	~135%	~190%

4. **Oxidative stabilization:** Upon extrusion of green fibers from pre-treated and untreated AOA precursors, we found out that the green fibers are extremely brittle and difficult to handle, similar to isotropic pitch based fibers. However, vigorous study of single-step and multi-step stabilization methods have generated dense cross-linked oxidized networks (validated through FTIR, XPS) within the stabilized fibers. The presence of these oxidized functional groups reduces the brittleness and improves the overall mechanical performance (e.g., bending, compression, etc.) of carbonized fibers. Moreover, the overall sulfur content (initially present as thiophenes, sulfides and sulfoxides) has decreased by ~15-40% as a result of extensive oxidation. Oxidative

stabilization of green fibers is one of the most challenging as well as energy intensive (typically contributes to ~30% of the overall process energy) steps in carbon fiber production and therefore optimizing it to meet the requirements of mechanically strong carbon fibers from AOAs falls directly under the scope of this project. Table 3 shows the percent increase/decrease in carbon, oxygen, nitrogen and sulfur content via XPS analysis after stabilization:

Table 3. XPS results depicting % change in C, N, O and S contents in oxidized fibers from Sample 1 and Sample 2

Sample Name	C	N	O	S
Sample 1 stabilized fiber	-4.78%	-20%	74%	-17%
Sample 2 stabilized fiber	-2.5%	-96%	457%	-35%

5. **Cross-sectional structure and surface morphology:** Once the stabilized fibers were successfully carbonized, the goal was to understand their surface morphologies and cross-sectional microstructures. Interestingly we learned that larger fibers (~60-100 µm) have hollow cores (~30 µm) with solid sheath of up to ~30 µm whereas thinner fibers (~20-30 µm) have solid cores. The formation of hollow fibers is a result of weak cross-linked domains in the cores that are not thermally stable to withstand high carbonization temperatures (600 °C, 800 °C, etc.). Therefore, stabilizing fibers with diameters larger than 60 µm is extremely difficult as O_2 diffuses slowly from the surface towards the core. Such oxidation reactions are temperature dependent (rate determining step) and we learned that most of the stronger hydrogen bonds and cross-linked structures are formed within a temperature range of ~250 °C-300 °C. In addition to that, carbonization at 800 °C or higher has demonstrated some abrasions or defects on the carbon fiber surface that are not observed in carbonized fibers at 600 °C. This was another important learning because the presence of some impurities (e.g., solid insoluble nanoparticles) or isolated sulfur content could be responsible for such abrasions or defects only at high temperatures. Since reducing impurities and sulfur content was one of the objectives in the main proposal, it is significant to understand the effects of stabilization and carbonization on the final carbon fiber microstructure.
6. **3D printing:** The rheology of asphaltene can be modified via nanoscale additives and/or using polymers for constructing complex architectures via extrusion based 3D printing technology. Therefore, this waste product holds great promise for additive manufacturing of structural and functional materials.

Broader impacts of learnings to the industry and beyond:

The current carbon fiber industry is heavily dependent on PAN based carbon fibers with no knowledge about the potential of AOAs to serve as precursors for carbon fibers. This project allowed us to understand the physicochemical and rheological properties of AOAs that are important for large scale melt spinning setups. For example, through rheological measurements we learned that AOAs have Newtonian shear viscosities at lower shear rates with some shear thinning at higher shear rates similar to PAN or lignin solutions. Such investigations could help understand the spinning characteristics of AOA based green fibers on a larger industrial scale for continuous production. Moreover our findings (pre-treatment strategies) could help the carbon fiber industry to understand how to generate and identify high mesophase content in AOAs, which is directly proportional to higher graphitic content and better thermal stability. Since PAN based fibers do not have an ordered stacking arrangement of parallel plate like molecules, it is important for the industry to understand the mechanism of mesophase formation via different pre-treatment techniques for commercialization purposes. Similarly, it is crucial to understand how the softening point and thermal stability of AOA based carbon fibers change with respect to certain modifications like pre-treatments, oxidation, air blowing and incorporation of plasticizers/elastomers for improving any necessary large scale processes. Additionally, the mechanism of temperature-mediated oxygen diffusion through asphaltene structures and its impact on oxidized structures are completely unknown. Therefore, our findings through extensive stabilization studies would be valuable in understanding how oxidized functional groups and cross-linkages within complex asphaltene architectures at different temperatures are formed. These types of findings could open multiple doors to solving long-term challenges of catalyzing oxygen diffusion rate through radial structures of varying thicknesses with potential oxidizing agents. It is important to address this issue as stabilization takes up almost 30-40% of the cost in producing carbon fibers because of slow oxygen diffusion. Therefore, our learnings that help address how to enhance O_2 diffusion to generate higher amounts of oxy-radicals, is key to understanding and optimizing the economic and energy feasibility of carbon fiber production. Mesophase content, aromaticity index and stabilization/carbonization profiles directly alter the transverse microstructures (e.g., radial, onion, random, flat, folded, etc.) of carbonized fibers and are desired for applications in the development of high compressive strength materials with high buckling resistance. Thus, AOA based carbon fibers would not only serve as an alternate candidate in the carbon fiber industry, but would also have significant impacts in thermal management applications (e.g., reducing thermal gradients), concrete and polymer composites (e.g., increased toughness), high temperature filters and biomedical fields (e.g., highly selective absorption characteristics). While carbon fibers are widely used in fabricating carbon fiber reinforced composites, our additive manufacturing based approach demonstrates that the 3D printed structures can also be used to develop architected composites along with topological structures. We envisage that composite industries would find such innovations of carbonaceous materials and composites intriguing for structural applications.

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

Project outcomes and impacts:

The technology to commercially produce, optimize and apply AOA based carbon fibers directly into market products is still in its infancy and distant from commercialization. Therefore our comprehensive study would act as a stepping stone to identify the challenges in extrusion (shear rheology), stabilization (optimum temperature, time and rate for effective oxidation/cross-linking) and carbonization (temperature and time) steps to develop AOA based carbon fibers. In addition to that, our understanding of how mesophase content and sulfur/impurities change upon specific pre-treatment or purification processes can add value to the initial extraction technology as AOAs are usually contaminated. The results and outcomes through our investigations would help suppliers to modify their extraction technologies in a way to meet the standards of large scale processing of carbon fibers from AOAs. For example, improved feedstock containing higher asphaltene/carbon content in both sample 1 and sample 2 would be helpful to cut down the processing costs in purification and pre-treatment. In this way the feedstock can be utilized directly for melt spinning without the need for excessive filters, vacuum treatments or time consuming solvent extraction. Improved quality of the asphaltene feedstock would increase the demand for bitumen for processing of high value materials in different sectors leading to overall increase in employment both in the raw material and manufacturing zones. In addition to that, our investigations would also bridge the gap in current literature in terms of AOA based value added products (e.g. carbon fibers, carbon composites, graphene based smart materials, etc.) while filling in the voids and need for their extensive characterizations.

Clean Energy Metrics:

(i) **Number of jobs created from project:** This project has allowed us to hire two research assistants who were directly involved in the project. We plan to install a carbon fiber melt spinning facility here at the University of Calgary in Phase-II of CFGC to proceed with our innovation. This fiber spinning facility would create at least 2-5 new jobs (technicians, operators, researchers, etc.) for continuous operation, maintenance and support.

(ii) **Number of publications:** From the outcomes of this project we plan to publish two peer-reviewed articles in established journals focusing on the field of energy, sustainability and fiber science.

(iii) **Number of students:** This project brought together two research assistants, three post-doctoral scholars and one graduate student to accomplish the project deliverables from two universities.

(iv) **Number of patents filed:** We are in the process of filing one patent with Innovate Calgary based on the outcome of this project. We are anticipating one potential IP generation from Rice University as well.

(v) **Partnerships/Agreements:** The outcomes of this project has allowed us to collaborate and form partners with two specialized fiber processing organizations.

(vi) **New products/services created:** The outcomes of this project would help facilitate the development of a fiber spinning facility here at the University of Calgary and eventually boost employment and service to other departments and organizations.

(vii) **New spin-off companies:** Through the outcomes of this project we anticipate the formation of at least one startup company in the near future.

Program Specific Metrics:

1. **Unique product/process:** As we stated in our proposal earlier, we anticipated the development of at least one unique process through this project. Surprisingly, we achieved great success in developing two unique pathways to generate value added products from AOAs: carbon fibers and carbonaceous complex structures via direct ink writing. Eventually, we see enormous potential for these two innovative processes to commercialize and generate market value in the next two years or so.
2. **Number of commercial BBC products:** Although we did not expect any development of commercial BBC products, we expect at least one product to be available by the end of Phase-II for commercialization.

Project Outputs:

From the work conducted through this project, we expect the filing of a patent to acknowledge and announce our findings within the scientific and commercial industry. We also plan to publish at least two scientific articles in high-impact relevant journals and participate in multiple scientific conferences within the fiber science community.

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

Economic:

One of the major outcomes of this project is the possibility to install a carbon fiber spinning facility here in Alberta. This facility can individually support the growth in employment by appointing multiple technicians, operators and researchers for timely management and troubleshooting of the facility. Steady production of carbon fibers for commercialization purposes could generate royalties, taxes and other revenues to scale up the profit margin. The project has infinite potential in commercial utilization of AOA based carbon fibers both in Alberta and worldwide. For example, carbon fibers show excellent corrosion resistance and strength to weight characteristics because of which they could potentially replace 10% of steel uses in the transportation and construction sectors. Other economic sectors that could benefit from proper utilization of AOA based carbon fibers include the automotive/aerospace industry (e.g., lightweight vehicles/aircrafts), concrete industry (e.g. structural materials with carbon fiber reinforced cement) and wood industry (e.g. carbon fiber-wood composites for interior/exterior reinforcement). Once fibers with optimum mechanical properties are prepared, their increased demand on a global scale would initiate partnership with multinational companies. Such consequences would increase the demand for Alberta bitumen (from ~7k barrels per day to ~29k barrels per day by 2030) and could lead to a six-fold increase in value for a barrel of oil. This could escalate the export of AOAs all across the world and enhance this $72 billion industry even further. Increased consumption of end products made from AOA based carbon fibers would stimulate potential investors to invest here in Alberta and diversify the economy to greater extents. As a result, highly skilled employment opportunities would be created not only in the oil sands industry but also in its supply and end product sectors. This would also help to protect Alberta's oil sands industry from potential declines in demand of fossil fuels and minimize Alberta's dependency on inter provincial and international pipeline capacities.

Environmental:

Through this project we see infinite potential in utilizing waste plastics (e.g. PET) as incorporating agents within AOAs for high quality carbon fibers with impressive mechanical properties. This could reduce plastic pollution within the environment and preserve the marine population and control climate change. Introducing waste plastics within AOAs can increase their softening points significantly via energy effective processes at low temperatures with higher yield, thus reducing greenhouse gas (GHG) emissions. Moreover, carbon fibers produced from AOAs as a result of this project could be invested in wind turbines with longer blades. As a result, clean energy production from atmospheric air could be elevated and generate electricity in comparison to commercial short blade turbines. Furthermore, carbon fibers produced from AOAs could act as an effective precursor to manufacture and assemble light weight vehicles and aircrafts with an expected fuel efficiency of at least 30% or more with superior performance. Such applications would initiate clean energy production with reduced pollution. To interpret the effects of our technology on global GHG emissions, current literature specifies a cradle to grave approach to study the total life cycle assessment for carbon fibers. The study shows once AOA based carbon fibers are incorporated in lightweight aircrafts, a 20% reduction in fuselage weight cuts down CO_2 emissions of ~1400 tons over a life cycle of 10 years per ton of carbon fibers used. Similarly, lightweight automobiles assembled using AOA based carbon fibers would result in a 30% reduction in vehicle body weight that would likely reduce CO_2 emissions by ~50 tons over a life cycle of 10 years per ton of carbon fibers used. Further opportunities like proper utilization of readily available clean hydropower to run the fiber production unit could also significantly reduce GHG emissions. By the start of Phase-II we would be carefully considering the recycling options of these AOA based carbon fibers. Since they do not readily degrade, end of life solutions like incineration and gasification and their environmental effects would be clearly highlighted.

Social:

The production of low-cost carbon fibers from AOAs would drastically impact the social advantages within the Albertan communities. Light weight vehicles and recreation rides are attractive consumers of AOA based carbon fibers, thus boosting the opportunities of social gathering and economic activities. Once commercialized, startup companies would provide entrepreneurship opportunities besides increased interests of potential stakeholders. Because of light weight and strong mechanical properties, carbon fibers from AOAs could also be utilized in the defense and sport industry for protective gears and smart apparels.

Building Innovation Capacity:

Through the completion of this project, multiple HQPs like technicians, post-doctoral scholars and research assistants were trained in different instrumentation techniques essential for pre-treatment, extrusion, stabilization and carbonization of carbon fibers from AOAs. These HQPs gained valuable skills and knowledge through this project and applied them wisely to enhance the performance and meet the objectives of this project. This project resulted in employment increase within the fiber science sector, hence increasing the possibility of generating revenue very soon. HQPs from outside of Alberta (Rice University, Cornell University, Oak Ridge National Laboratory, etc.) who are experts in fiber science and technology have also shown high interests to further collaborate and help develop the technology even further. The overall research infrastructure includes accurate utilization of customized melt extruders, tube/muffle furnaces for stabilization/carbonization, pressurized vessels/reactors for effective pre-treatment and customized vacuum technologies.

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

Long-term Plan for Commercialization:

The insights and knowledge gained while working on AOA samples under Phase-I of CFGC project would enable us to further develop the technology in Phase-II of CFGC. During the course of Phase-I, we had opportunities to engage in discussions with multiple stakeholders to initiate a ***Carbon Fiber Research Hub (CFRH)*** at University of Calgary with support from the university, industry, provincial and federal government. The aim of CFRH would be to bring together experts from suppliers, academic, industry and carbon fiber producers to work on valorizing AOAs to high-value products that would diversify Alberta's economy. The long term plan is to develop a scalable, economically feasible and environmentally compelling process for commercialization in partnership with suppliers, academic/industry experts and carbon fiber producers.

Project Learnings and Next Steps:

In Phase-II, we would explore opportunities to work directly with the suppliers to better comprehend their extraction technologies, and find ways to improve the overall process efficiency both from economic and environmental aspects. We aim to further explore other energy efficient processes like plasma assisted oxidation and UV stabilization routes and compare them with traditional methods in terms of energy cost, production rate, fiber mechanical properties etc. We aim to establish fully-equipped lab-scale and commercial scale facilities to accelerate the development of the technology. Some of these facilities include pressurized vessels, multiple soaking chambers and reactors, stabilization, carbonization and graphitization ovens alongside lab-scale melt spinning facilities that are essential for continuous production of AOA derived carbon fibers.

Potential Partnerships:

We are in discussions for potential collaboration with leadership teams of commercial-scale melt-spinning facilities, including Oak Ridge National Laboratory (ORNL). The innovation would be continued to put to work on a commercial platform in the next two years to understand how the process yield (e.g. carbon content, fiber yield, etc.) varies between a lab scale production and a commercial setting. Mechanical properties of AOA based carbon fibers would be tested vigorously and compared with PAN based fibers in order to provide an alternate solution to the fiber market. Testing of mechanical properties would be carried out both in our research facilities as well as in the industry production hubs for higher accuracy. We expect direct partnerships with other research and industry officials in the beginning of CFGC Phase-II and optimize the innovation to meet the standards of applied consumers. We plan to establish the technology locally here in Alberta along with multiple investors, advisors and partners on an international platform.

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 specific findings of this project would be shared with potential large scale manufacturing and supplying companies in Alberta and different parts of the world (North America, Asia, Europe, etc.) to take this innovation another step forward. Knowledge dissemination of key findings would help suppliers to optimize their extraction techniques to meet the specific demands of the manufacturers and reduce the cost of pre-processing. This direct integration of suppliers and manufacturers within the project scope can drastically increase the efficiency of the process and help utilize the resources with the highest yield. For example, understanding the effects of metals and sulfur content on the final microstructural and mechanical properties of the fibers would be important for suppliers while tailoring their extraction methods. Other properties like mesophase content and aromaticity are also highly desired in the raw feedstock and if can be controlled from the suppliers side would greatly benefit the manufacturers. This is because modifying a single step in the extraction process could be less costly and more energy efficient than running a thermal reactor for ~5-6 hours under continuous stirring. Filling such gaps in technology could also increase employment and eventually lead to higher profits once the carbon fibers are commercially distributed. Moreover, installment of large scale instrumentation for commercial production of carbon fibers would increase recruitment of subsidiary manufacturing companies for day to day maintenance and troubleshooting. These would accelerate the job market in Alberta and lead to greater economic benefits. In addition to that, we plan to publish scientific articles in high impact journals and present our findings in relevant scientific symposiums/conferences to clearly highlight the novelty and importance of our innovation. Thus proper dissemination of the knowledge would have tremendous positive impacts on the industry to commercialize the innovation for the benefit of the Albertan economy.

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

In this project, we investigated the physicochemical characteristics of two different samples of AOAs and their importance in the process of developing high-value carbon fibers. We designed and implemented pre-treatment strategies to understand how changes in mesophase content, MW distribution, aromaticity, softening point and rheology can improve the spinning, stabilization and carbonization of AOA based carbon fibers. Interestingly we discover that sample 1 has an appreciable amount of mesophase and suitable softening point with ample amount of elastomers/plasticizers for continuous extrusion of green fibers unlike the sample 2. Although sample 1 had clear advantage over sample 2, solvent extraction on sample 2 allowed us to achieve a higher mesophase content while increasing the softening point above 150 °C for continuous extrusion. Therefore, green fibers of size ~10-500 µm were successfully extruded from both sample 1 and PT sample 2. Even though higher softening points, aromaticity, mesophase content and average MWs were achieved through pre-treatments, AOAs with poor rheological properties were also produced in some cases that were not suitable for continuous extrusion. Careful studies on how integrating different elastomers/plasticizers can impact the flow properties and extrusion of these treated samples were also investigated.

The continuously extruded green fibers were stabilized and carbonized to understand the challenges associated with oxygen cross-linking as well as cross-sectional microstructure evolution of carbonized fibers via FTIR, XPS and TGA. Specifically for stabilizing AOA based green fibers, we detected the essential need of multiple temperatures (e.g., 200 °C-400 °C) and soaking times (e.g., 10-30 minutes) to form strong oxidized cross-linked networks. Carbon fibers with different cross-sectional microstructures (e.g., solid, hollow, porous, etc.) were fabricated from AOAs with average tensile strength of ~36 MPa and average elastic modulus of ~8 GPa. The obtained mechanical properties are after minimal optimization and are expected to improve further upon better control of the process parameters. Greater optimization of process parameters such as heteroatom content, infusion of particulate matter during melt spinning, reduced diameter, hollow cores and mesophase content could boost the fiber mechanical performance and would be actively examined in Phase-II. During the course of this project, we identified multiple challenges in the pre-treatment, extrusion, stabilization and carbonization routes. For instance, increased viscosities of AOAs during pre-treatments, continuous spinning of thin fibers (~10-50 µm), fiber deformation at high stabilization temperatures, energy optimization during stabilization and slow oxygen diffusion along the fiber cross-section. Strategies on how to enhance melt-spinning and stabilization of green fibers (e.g., single-step and multi-step stabilization, optimum temperature and winding rate for melt-extrusion, etc.) were clearly presented with room for more improvement in the near future.

In Phase-II of CFGC, the effects of infusible solid particles, metals and sulfur content on the spinning, stabilization, carbonization and mechanical properties of carbonized fibers would also be extensively studied. Important parameters like optimum temperature and time for pre-treatment processes would be explicitly studied and melt extrusion of pre-treated AOAs with higher mesophase content would be prioritized. Further studies for Phase-II include effects of various green fiber diameters and mesophase content on stabilization, carbonization and mechanical properties of carbon fibers. The outcomes of this project would help facilitate the growth of carbon fiber manufacturing here in Alberta for commercial applications in multiple corporations worldwide. The province would be highly benefited from the creation of new jobs and build potential partnerships with other fiber science institutes outside of Alberta to reduce economic dependency on crude oil. Development of efficient pathways to commercialize and shape the process to a larger scale in conjunction with industry partners would also be covered in Phase-II of CFGC.