ALBERTA INNOVATES

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.

Energy Efficient Fabrication of Melt Spun Carbon Fibres

Public Final Report

Prepared for

Alberta Innovates

Prepared by

University of Calgary

Simon Park, Professor

ALBERTA INNOVATES

CLEAN RESOURCES FINAL PUBLIC REPORT TEMPLATE

1. PROJECT INFORMATION:

Project Title:	**Energy Efficient Fabrication of Melt Spun Carbon Fibres**
Alberta Innovates Project Number:	G2020000340
Submission Date:	Feb. 28, 2021
Total Project Cost:	$92,000
Alberta Innovates Funding:	$50,000
AI Project Advisor:	Dr. Paolo Bomben

2. APPLICANT INFORMATION:

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3. PROJECT PARTNERS

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

RESPOND BELOW

MKS has provided the in-kind ($20,000) through personnel supports (Dr. Bryan Moon and Mr. Kevin Lim) for the project.

A. EXECUTIVE SUMMARY

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

RESPOND BELOW

With an increasing trend for environmentally benign methods to use energy resources, the importance of diversifying heavy hydrocarbon usages for high valued products instead of combustion is vital for the Alberta economy. Alberta oilsands asphaltene (AOA) is typically generated as by-products from partial upgrading processes. Carbon fibre is a strong, lightweight, electrically, and thermally conductive material consisting of carbon atoms.

The objective is to produce cost-effective carbon fibre fabrications by utilizing asphaltene precursors from AOA. In this project, both melt spinning and electrospinning methods are utilized to produce fibres from different asphaltene-based precursors. Presently, pyrolysis is the most common technique to stabilize and carbonize the fibres. However, the high temperature and long stabilization and carbonization time result in significant energy consumption and GHG emissions. Polymer blended asphaltene was fabricated through the melt spinning and electrospinning methods. Each process is optimized to achieve continuous uniform fibres. The University of Calgary team has recently developed a new method for drastically reducing the stabilization and carbonization time for carbon fibre generation through the utilization of chemical oxidation and electromagnetic irradiations. This would significantly reduce costs, time and GHG generations to convert the abundant AOA into carbon fibres. By comparison, the processing time can be reduced up to 99%. Using life cycle analysis (LCA), we were also able to estimate a reduction of approximately 70% in the CO_2-equivalent emissions between our proposed process and conventional furnace methods.

The potential usages of carbon fibres generated through the proposed process include water filtration, electrodes, mechanical fillers, and sensors. This project will help diversify Alberta's income as it will provide another opportunity for using a resource that is already being extracted. The carbon fibre market is currently valued at about 5 billion USD and is expected to grow to over 13 billion USD in the next decade. By producing an asphaltene-based carbon fibre that is significantly cheaper and greener than the alternatives available, Alberta can compete on the world stage of carbon fibre production.

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:

This project contributes to Alberta's oil and gas sector by providing an opportunity to diversify Alberta's revenue streams. Due to the unstable global oil market, there is a high need to produce value-added products from Alberta hydrocarbons, and the carbon fibre market is one of the promising areas. Carbon fibre will be produced from asphaltene which is found in the heaviest component of Alberta's oil sands.

- Suitability of Asphaltene as a Carbon fibre Precursor

Most of the cost for carbon fibre is determined by precursor prices (45-50%) and equipment and energy consumption costs (20-25%). Carbon fibre is commonly produced from PAN which is quite an expensive material. It is expected that replacing conventional precursors of carbon fibre with significantly cheaper asphaltene will reduce the price of precursors by more than 90%. In addition, the advantages of asphaltene in the carbon fibre market lie in the structure of hydrocarbons as well as price competitiveness. Asphaltene is regarded as a complex mixture of high molecular weight hydrocarbons and non-hydrocarbon which can be divided into asphaltenes, resins, aromatics, and paraffin (Traxler, 1936). The materials richest in asphaltene are the most suitable for conversion to carbon fibres. However, the natural precursor contains some heteroatoms, such as nitrogen, oxygen, and sulfur. When a precursor is not transformed into a mesophase and is spun as an isotropic liquid, the resulting carbon fibres have poor mechanical properties. The impurities in asphaltene may lead to technological challenges for the application of CF generation. Therefore, there are several uncertainties and challenges associated with the production of carbon fibres from asphaltene, due to its complex constitutional nature.

Knowledge and Technology Gaps:

- Spinning of Precursor for Carbon fibre

Spinning methods of precursors for carbon fibre are divided into wet spinning, melt spinning, and electrospinning depending on the precursors and applications. Most PAN-based precursor fibres are manufactured using wet-spinning methods. However, this method not only uses a solvent but also requires a bath to remove the solvent, increasing the size and process of the facility. Presently, it is not clear which methodology is most suitable for producing carbon fibres from asphaltene precursors. In general, pitch is formed by melt spinning, which is the simplest spinning method because no solvent is used. However, melt spinning is challenging due to the brittle properties of pitch precursor. To address this problem, the pitch precursor is applied with a system that can install the nozzle of the melt spinning vertically to help the fibres fall naturally in the direction of gravity and apply tension. Tensile force applied to fibres improves the deflection of molecules, thus improving the strength of carbon fibres. Although a large portion of asphaltene is aromatic and does not require a high stretching ratio, increasing the orientation of some chains for the manufacture of high-end carbon fibres is an important step. However, asphaltene is not ductile, it requires more than a certain temperature to facilitate the movement of the chains while tension is applied to the fibres. The system for applying a certain temperature after discharge from the nozzle is a hot air blow system. Alternatively, electrospinning can be used to produce thinner fibres that are typically unaligned. The mechanical properties of electrospun fibres is often lower due to defects and poor alignment. Therefore, alternative applications and processing methods are required to address the knowledge and technology gaps.

- Oxidative Stabilization and Carbonization

Generally, asphaltene with a high degree of aromaticity is capable of forming a pitch when heated in a 250-500°C temperature range for 2-50 hours in an inert atmosphere. The oxidative stabilization temperatures above 500°C are considered undesirable due to the risk of coke formation. Conventional long heat treatment processes increase energy consumption and production cost of carbon fibre.

Moreover, the non-uniform heat treatment may break the bond of the carbon element as well as the non-carbon element bond of the fibre, and a large amount of by-products and GHG (greenhouse gas generation) such as NH_3, HCN, CO, and CO_2 may be released during the heat treatment. Therefore, in order to reduce the unit price of carbon fibre and the generation of GHG, research on the oxidative stabilization process should be conducted through intensive energy supply in a short period of time on the precursor fibres.

There are many challenges in the oxidative stabilization process. Inappropriate oxidative stabilization conditions degrade the properties of carbon fibres as it may inhibit carbonization and the formation of aligned graphitic layers. In addition, simplification of the process and reduction of GHG are separate issues. To address these problems, many researchers have studied various methods of optimizing the conditions of conventional oxide stabilization or applying microwave, UV, and gamma ray irradiation. However, the asphaltene of Alberta oil sands contains sulfur and metals, and to address these challenges, the effect of these components on carbon fibre should be further investigated. In our approach we used a combination of chemical and photoelectronic techniques as a solution for oxidative stabilization of asphaltene precursor fibres. The synergistic effects of chemical methods and photoelectronic techniques can reduce GHGs through selectively and intensively treating the precursor fibre for a short time. The installation of this technology is an efficient system that can be applied not only to the oxidation stabilization process but also to the carbonization process. The technique has such short processing times that is suitable for continuous fibre processing and can increase the carbon fibre productivity.

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

For this project, we used both melt spinning and electrospinning systems to produce carbon fibres. These are two methods of producing carbon fibres with very different properties and applications. We focused on melt spinning to achieve the strength corresponding to phase II and phase III of the Carbon fibre Grand Challenge. However, additional electrospinning was performed to expand the application areas such as filters for masks and electrodes for supercapacitors.

The pre-treatment process of asphaltene is one of the important challenges for the fibrosis of asphaltene through melt spinning. In particular, the asphaltene provided by Alberta Innovates contains approximately 28% coke. The coke should be removed for the formation of uniform fibres because it does not melt at melt spinning temperatures and affects the melting point of asphaltene. In addition, asphaltene contains more than 60% aliphatic structures. The aliphatic structures reduce the melting point of the asphaltene and improve fluidity, enabling melt spinning at low temperatures, but takes a long time during the oxidation stabilization process and reduces the mechanical strength of the carbon fibre. The aliphatic structure can be controlled by the refining process of asphaltene. The increase in aromatic structures through refinement can improve the strength of carbon fibres. The processability reduced by purifying the aliphatic structures can be improved by adding polymers. In addition, carbon nano particles can be used to reinforce the carbon fibres and improve their mechanical strength as has been demonstrated in many papers.

The main objective of our research is in the stabilization step which is often the most time-consuming step. We have proposed the goal of simplifying the pre-treatment step of the precursor, saving energy costs and reducing GHG generation during the stabilization process. Conventional oxidative stabilization is a method involves a large transfer of heat from the outside of the fibre to the inside and because the temperature inside the chamber should be uniformly formed, there is unnecessary energy loss due to a lot of heat outflow to the outside. The proposed chemical/photoelectric technology provides selective and intensive energy to precursor fibres. The purpose of the oxidative stabilization process is to allow thermoplastic fibres to form crosslinks and maintain them at high temperature during the carbonization process. This is because thermoplastic fibres melt when temperatures exceed the melting point, making it difficult for them to maintain their shapes. Thus, the chemical treatment method creates active functional groups to induce the formation of crosslinks when intensive energy through intense pulsed light (IPL) processing is provided. The IPL irradiates wavelength regions of 300 to 1050 nm, most of which corresponds to visible light. The energy of the wavelength in this region does not destroy the bonds between carbon molecules corresponding to the aromatic molecular structures and instead affects the bonds corresponding to the aliphatic molecular structures. Furthermore, the combination of IPL and ozone forms oxygen radicals, making it easier to induce molecular bonds. Furthermore, we want to compare efficiencies by applying microwave irradiation, which has been studied extensively so far, to oxidative stabilization processes and carbonization processes.

Therefore, in the stabilization step, our goal is to cross-link the precursors using IPL and microwave irradiation. To demonstrate the expected effectiveness of IPL and to correct it, a chemical method and an electromagnetic method were presented, and a preliminary test was performed. In addition, based on the results, the following research directions are presented.

Updates to Project Objectives

The overarching goal of our research is to enter the carbon fibre market using asphaltene. To gain an advantage in the price competitiveness of the carbon fibre market, the unit price of precursors and manufacturing carbon fibre with high mechanical strength will be reduced by replacing existing PAN precursors with asphaltene. The novelty of the project is the use of new methods for stabilization and carbonization techniques. The methods focus on using microwave, IPL, chemical and ozone oxidations as the primary methods.

We have proposed the development of cavitation and mechanical cracking techniques in the pretreatment process of asphaltene. However, these methods were found to be difficult to replace the conventional pretreatment methods due to the aspect of equipment setup and efficiency. Therefore, we tried the method of blending macromolecules to improve the brittle properties of asphaltene and to improve its machinability. Additive reinforcement methods were also attempted to improve the strength of the asphaltene derived from carbon fibre.

To develop alternative technologies for conventional oxidative stabilization and carbonization methods, which account for the largest proportion of carbon fibre manufacturing process time, microwave irradiation, laser, and IPL technologies were proposed. It was determined that the laser was not appropriate due to the cutting of the bonds between carbon molecules because of its strong energy. Therefore, the IPL was studied intensively, and the tests showed that IPL was an appropriate method for instantaneous high energy application to local areas. However, we found that IPL itself has limitations in inducing crosslinking of the precursor fibres. Therefore, we have proposed the combination method of chemical and electromagnetic oxidations to overcome the limitation.

The technological development of the long-term stabilization process can increase the annual production of carbon fibres and reduce manufacturing costs. Stabilization has been identified as the primary focus after consultations with industry. The stabilization technology that we present is expected to have an additional effect on reducing the occurrence of GHG in the process through local and selective processing.

Performance Metrics

As this project is part of the Carbon fibre Grand Challenge, we are measuring performance metrics based on the targets provided in Phases I – III for the challenge. In phase II of this project our metrics relate to producing a strong continuous fibre, with a target tensile strength of 3000 MPa, modulus of 250 GPa and a diameter of 7 µm using melt spinning. Our targets include a commercial cost of $8/kg, producing over 3000 tonnes of CF per year and emitting less than 20 kg CO_2/kg CF, which is the current estimate from Toray.

Using electrospinning, the performance metrics vary significantly. We are targeting a diameter of 100 nm with a BET surface area above 1000 m^2/g. We aim to produce filters that can meet the National Institute for Occupational Safety and Health (NIOSH) N-95 standards – namely airborne filtration efficiency above 95% and pressure drop below 343 Pa. We are also targeting electrical applications as an alternative application and market. A specific capacitance above 100 F/g, a power density greater than 50 W·h/kg and a discharge current density above 4 A/g. Sensitive and selective sensors may also be formed by depositing onto quartz crystal microbalances or interdigitated electrodes. We are presently targeting the detection of hydrogen at 1 ppm concentrations for sensor application. These alternative applications offer substantial alternative markets and usages for carbon fibre beyond traditional mechanical reinforcement.

Other performance metrics includes the number of papers published and the number of patents filed in relation to this project. Presently, we have submitted one provisional patent with plans for a second in 2021. After the protection of the intellectual property, the project is expected to yield approximately four academic papers. The first paper discusses the production of asphaltene-based carbon nanofibers using electrospinning and microwave-assisted stabilization and carbonization techniques. The second paper discusses melt-spinning of asphaltene fibres and subsequent optimization of chemical-based stabilization methods with IPL as an energy source. The third paper discusses electrospinning and usage of IPL to produce porous carbon nanofibers with potential applications in filtration, sensing or electronics. The final paper discusses melt spinning and carbonization techniques using a combination of microwave and IPL.

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

Asphaltene Extraction and Refining

The process of asphaltene pretreatment is mainly divided into asphaltene extraction and purification as shown in Figure 1. The asphaltene was separated from Alberta bitumen using toluene (≥99.5 purity, VWR International Ltd., UK) and n-heptane (≥99.0 purity, VWR International Ltd., UK). Firstly, toluene was stirred with bitumen in volume ratio of 5:1 at 80 °C for 1 h. Then the solution was filtered using 60 mesh filter membrane to separate the undissolved component. The filtered solution was heated at 120 °C which is over the boiling temperature of toluene to remove the solvent. The toluene-free bitumen was mixed with n-heptane at a volume ratio of 1:40 and stirred at 80 °C for 4h. Subsequently, the solution was filtered with 60 mesh filter membrane to extract the asphaltene. The solid part of asphaltene was obtained by fully evaporating the n-heptane at 100 °C. The modification of asphaltene was performed by raising the temperature up to 400 degrees C with a heating rate of 0.5 degrees C per minute under the air atmosphere and maintaining it for two hours.

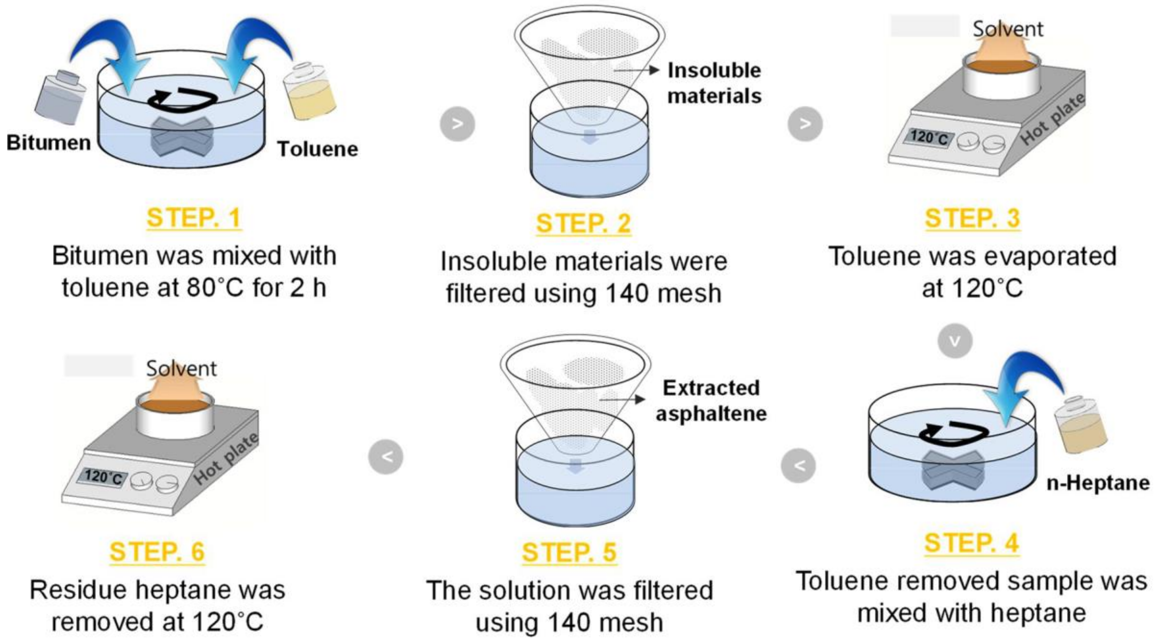
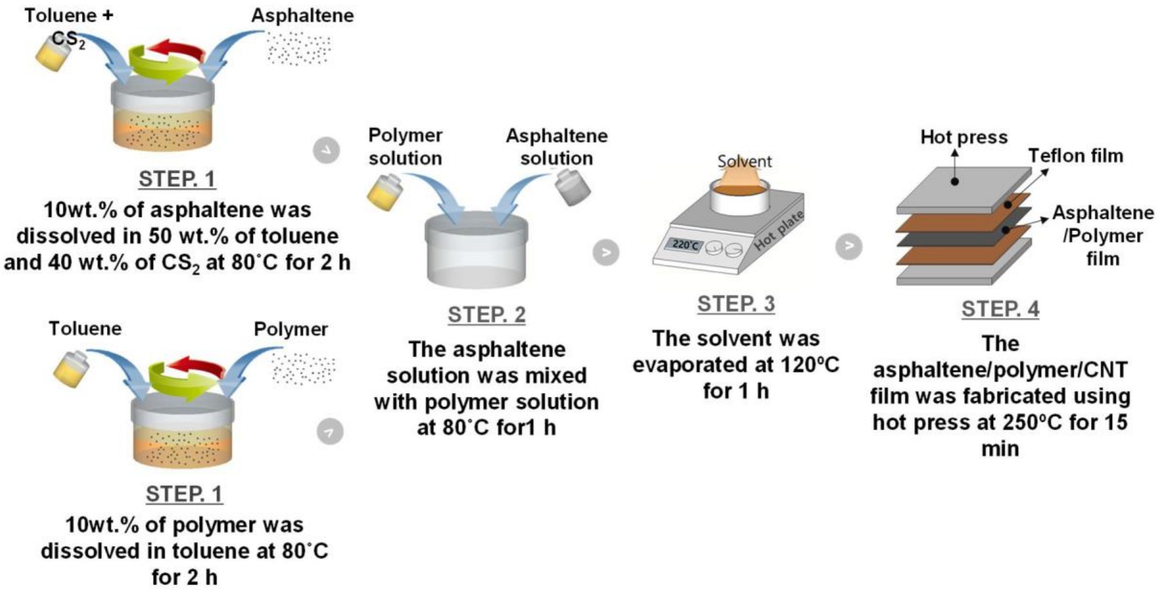


Figure 1. Schematic diagrams of process for asphaltene extraction and modification.

Precursor Film Preparation

Polymer blended asphaltene films were fabricated to check the characteristics of asphaltene and the effectiveness of polymer blending before fiberizing asphaltene. Polymer blended asphaltene films were fabricated by dissolving into solvents for uniform mixing and then evaporating the solvents as shown in Figure 2. Two types of solvents, toluene and carbon disulfide, were used because the asphaltene provided from Alberta Innovates containing approximately 27% of the toluene insoluble portion. In addition, dissolved polymers were used in solvents such as solvents used in asphaltene to prevent them from being extracted by different solvents when mixed with asphaltene solutions. The polymer blended asphaltene solution was evaporated in two stages to minimize the voids formed in the evaporation step. It was initially heated at a low temperature of 50 °C, which is enough to evaporate most of the solvent present. This is due to the high volatility and low boiling point of carbon disulfide which drag the toluene molecules away as the carbon disulfide evaporates. To remove any residual solvent, it was heat-treated to 120 °C to pass the boiling point of toluene. The polymer blended asphaltene film was separated from the Teflon mold and pressure was applied through a hot press at 200 degrees C. to form a uniform thickness.



STEP. 1 10wt.% of asphaltene was dissolved in 50 wt.% of toluene and 40 wt.% of CS_2 at 80˚C for 2 h

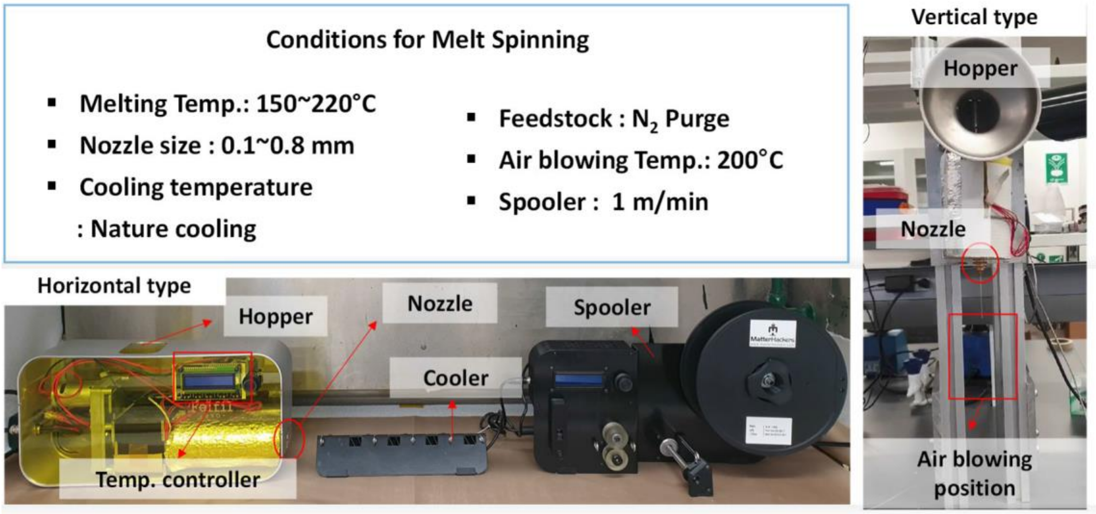
STEP. 1 10wt.% of polymer was dissolved in toluene at 80˚C for 2 h

STEP. 2 The asphaltene solution was mixed with polymer solution at 80˚C for1 h

STEP. 3 The solvent was evaporated at 120ºC for 1 h

STEP. 4 The asphaltene/polymer/CNT film was fabricated using hot press at 250ºC for 15 min

Figure 2. Fabrication process of polymer blended asphaltene film.



Conditions for Melt Spinning

- Melting Temp.: 150~220°C
- Nozzle size : 0.1~0.8 mm
- Cooling temperature : Nature cooling
- Feedstock : N_2 Purge
- Air blowing Temp.: 200°C
- Spooler : 1 m/min

Figure 3. Horizontal and vertical type of melt spinning.

Melt Spinning

One of the ways by which we created carbon fibres from asphaltene is through a process of melt spinning. We have built two types of melt-spinning systems as shown in Figure 3, which are spun horizontally and vertically, respectively. Asphaltene is mixed with a polymer and fed into a heated extruder. With this set up, a single fibre is extruded through a thin hole and collected onto a spool. The stretching of the extruded fibres allows the chains to orient themselves in the direction of the length of the fibres, and the degree of orientation determines the strength of the fibres. Hot air blowing on the extruded fibres can help it easier for the chains to orient and can have additional effects depending on the type of gas used and the temperature of the blowing. A stretching system is employed between the extruder and the spool to ensure a thin and consistent fibre is produced. Once the fibre is wound onto the spool, it results in a long strand similar to how a 3D printer filament would look. Melt spinning was performed at 200 degrees using refined asphaltene and asphaltene blended with 5 wt.% polymer and 0.5 wt.% additive.

Electrospinning

Electrospinning is another method that is used for carbon fibre production. For electrospinning, a solution is made with a solvent, asphaltene and a polymer. A syringe with this solution is placed into a syringe pump and a thin needle tip is attached to the syringe as shown in Figure 4. A high voltage power supply is attached to the needle tip, and a grounded rotating cylinder is located a few centimeters away. Once the system is turned on, the solution moves to the end of the needle tip. The high voltage overcomes surface tension and the solvent starts to evaporate and a thin strand is formed reaching out towards the grounded cylinder. By the time the fibre is at the cylinder, it is solidified and most of the solvent has evaporated. As the cylinder is spinning the fibre collects in a similar manner as on to a spool in melt spinning. In this process however, the fibres are much thinner than those produced by melt spinning and instead of one long strand being formed, electrospinning creates a fibrous mat. Some variations of this process have been investigated in the lab, including splitting up the solution stream through several needles to have a larger sized mat.

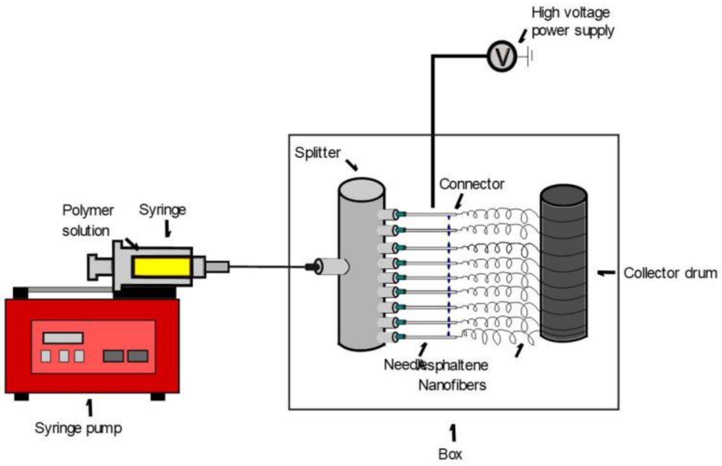


Figure 4. Schematic diagram of electrospinning setup

Oxidative Stabilization and Carbonization Methods

Several stabilization and carbonization methods are investigated in the lab as an alternative to the traditional processes done over several hours in a furnace. For comparison, the conventional method of stabilization and carbonization is first tested. This utilizes a tube furnace to heat the fibres by convection. Sufficient time is needed for heat to transfer to the inside of the fibre. The stabilization of the precursor fibres was achieved through heat treatment at 250 degrees C for 2 to 50 hours under air atmosphere.

Another experimental method is a microwave oven that can be adjusted from 100 to 1100W of power. Stabilization can be conducted at lower power settings to reduce the heating rate. Samples are placed into a small kiln and then the kiln is placed into a microwave. Stabilization can be performed without the kiln to further reduce heating rates and the maximum temperature reached. The fibres are microwaved on high power for several minutes for stabilization to occur and for a few hours for carbonization. A schematic of the microwave process is shown in Figure 5.

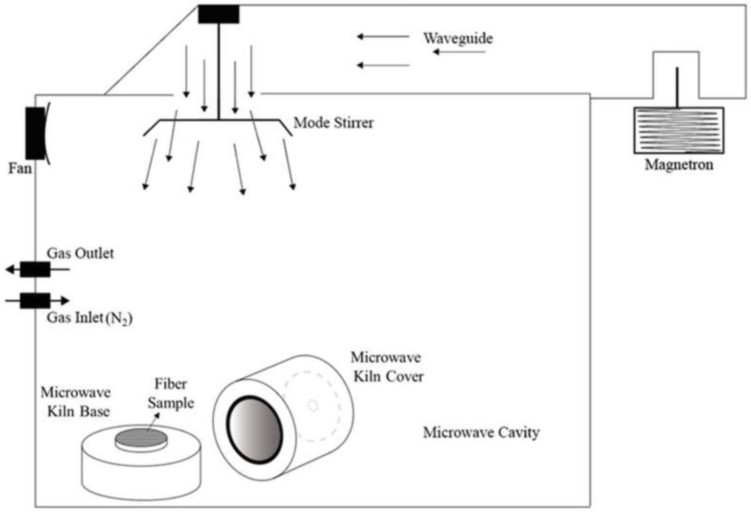


Figure 5. Schematic diagram of microwave system for stabilization and carbonization.

The other method investigated was intense pulsed light (IPL) as shown in Figure 6. The lab has capacity for two different types of IPL set ups. One is a powerful Xenon flash system, and another is a less powerful system with a flash lamp. With an IPL method stabilization is a very quick process as flashes are less than a second in length. In experiments samples are heated on a hot plate which is placed under the IPL lamp. The flash from IPL is able to break bonds at different wavelengths and produce oxygen radicals. To assist in stabilization, we add ozone and hydrogen peroxide to the system and the IPL is able to maximize radical production as shown Figure 6. Light at certain wavelengths can also create radicals on the surface of the fibre, allowing for the oxygen radicals to attach to the surface to achieve stabilization.

At higher powers, the Xenon flash system provides substantial amounts of energy that can heat the fibres above 1000 °C in fractions of a second (~6 ms). Carbonization can be possible under vacuum and/or inert gas conditions. The rapid heating and cooling result in fibres exhibiting highly brittle characteristics. The heating results in thinner fibres and the welding of the fibres do result in improved properties such as higher electrical conductivity.

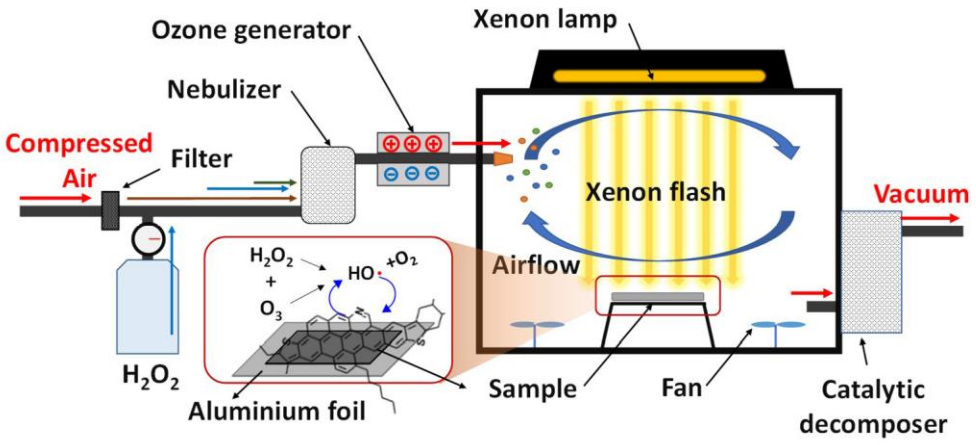


Figure 6. Schematic diagrams of H_2O_2 treatment process and ozone flash setup.

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

Asphaltene Extraction/Refining and Polymer/Additive Blending

Asphaltene consists of a multi-molecular structure of aromatics and aliphatics, which have various carbon numbers. The pre-treatment process of precursors is carried out to narrow the molecular weight distribution because volatile materials with low molecular weight interfere with uniform fibre formation. Therefore, molecular weight distribution analysis is required to predict uniformity of fibre spinning. GC-SIMDIS is useful for simplifying the distribution of molecular weight of hydrocarbon materials. GC-SIMDIS profiles for extracted asphaltene are illustrated in Figure 7 with the reference plot of a boiling point versus carbon number for n alkanes C4-C100 included. Samples were heated from 35 ◦C (hold 5 min) to 430 ◦C at a rate of 20 ◦C/min. The helium flow rate was kept constant at 10 mL/min. The resulting curves were obtained by using the algorithm defined in the ASTM D2887 method. It is first ignited by low-carbon molecules, and the higher the number of molecules, the higher the boiling point, which is detected at high temperatures.

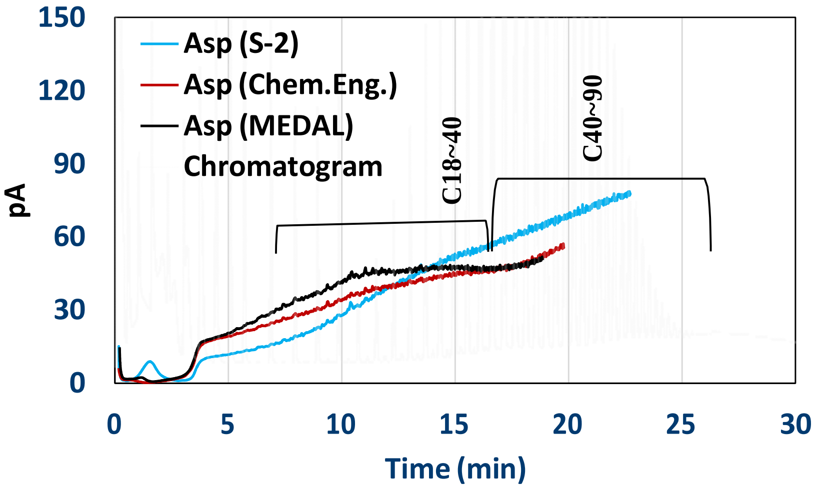
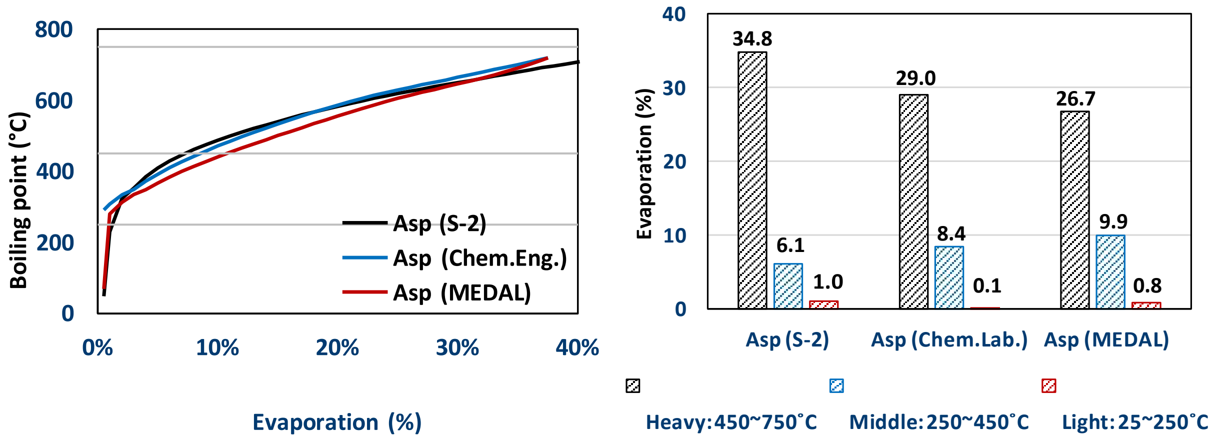


Figure 7. GC SIMDIS results and hydrocarbon number.

Figure 8 shows the fraction of the hydrocarbons by temperature interval. From approximately 300 degrees C or higher, the slope of the graph changes dramatically. At room temperature, the light hydrocarbon is shown to be between 250 and 450°C, medium and heavy hydrocarbons from 450 to 750°C. The heavy fraction of Asp (S-2) is 17–23% higher than asphaltenes extracted by solvents from bitumen obtained from Chemical Engineering and MEDAL as shown in Figure 8 (a) and (b). The higher heavy hydrocarbon content from S-2 suggests that it shows the greatest promise for producing uniform fibres.



(a) (b)

Figure 8. (a) Distribution of hydrocarbon according to temperature, and (b) hydrocarbon fractions according to boiling point.

The higher heavy content of S-2 is verified by FT-IR in Figure 9 which shows high aromatics content. Aromatic bands were observed between 720 and 870 cm^{-1} and 1600 cm^{-1}. The bands between 720 and 870 cm^{-1} corresponds to aromatic moieties in remaining solids (Ashtari, M. et al., 2016). S-2 provided by Alberta Innovates shows a smaller alkyl band compared with asphaltene by solvent extraction in the laboratory and was observed between 2800 and 3000cm^{-1}. Generally, heavy hydrocarbons have high boiling points compared with light hydrocarbons. The higher boiling point is presumably due to the ease with which temporary dipoles can be set up involving the delocalized electrons.

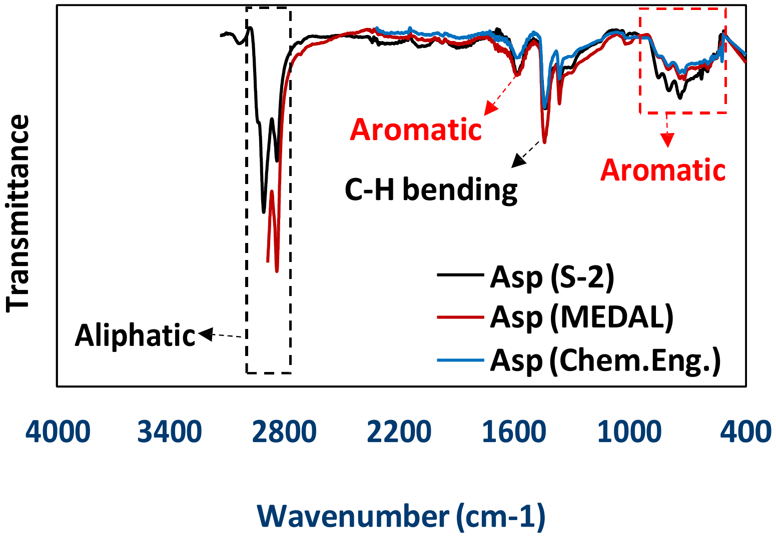


Figure 9. FTIR spectra of asphaltene precursors.

The asphaltene contains coke, toluene soluble, and heptane soluble. The asphaltene (S-2) provided by Alberta Innovates contains approximately 27% coke according to the datasheet of the sample bank. The coke blocks the nozzle during the melt spinning process and significantly increases the melting point of asphaltene and changes its thermal characteristics. Asphaltenes containing coke are not dissolved below 350 degrees C and molecules with low molecular weight are decomposed.

The heptane soluble portion, which accounts for approximately 62% of the original S-2 sample, consists of molecular structures with linear chains that have fluidity due to movement between chains. The coke consists of carbon structures, so the coke is removed and the remaining sample, which contains the toluene soluble and heptane soluble parts, has high concentrations of aliphatic structures as shown in Figure 10. Toluene soluble asphaltene, whose coke and heptane soluble parts are removed, shows the smallest aliphatic peaks. However, the large portion of heptane solubility interferes with the fibrosis of asphaltene because it does not solidify at room temperature due to its fluidity. Furthermore, a refining process is necessary because it reduces the mechanical strength of carbon fibres.

The toluene soluble part, where the coke and heptane soluble is removed, is solid at room temperature and has a melting temperature above 130 degrees C. A refined asphaltene is an appropriate form of precursor for forming fibres through a melt spinning. Therefore, the refining process of asphaltene was carried out in the same process as the extraction process of asphaltene from bitumen.

The low softening point of asphaltene is advantageous for melt spinning, but the stabilization time is longer, and the high softening point of asphaltene can reduce the stabilization time, but it requires a high melt spinning temperature. Generally, the heat treatment process of the precursor is performed to increase the temperature of the softening. The heat treatment process of purified asphaltene was carried out at 250 degrees C.

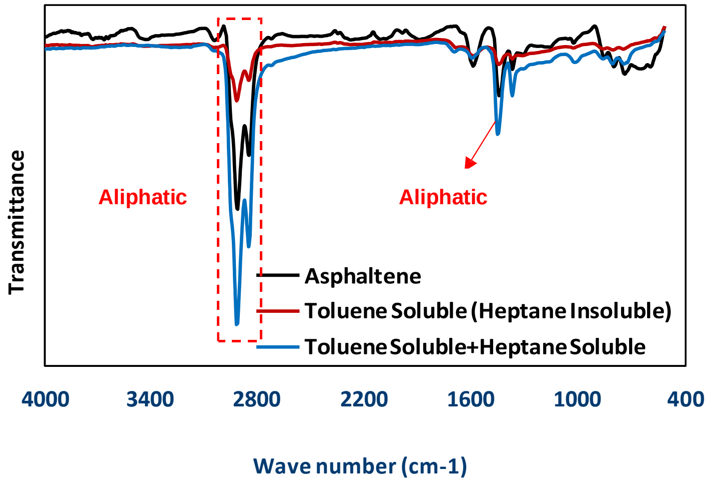


Figure 10. Aliphatic structures of asphaltene with respect to refining process.

Stabilization and Carbonization

Generally, pitch-based carbon fibres are heat treated through air blowing at 250 degrees C to increase the molecular weight of the precursor. Alternatively, in this process, steam is removed through vacuuming to remove volatile substances. Temperature and time play an important role, and it is known that the longer the treatment time at high temperatures, the more aromatics, and anisotropic pitch.

Figure 11 is provided with a commercial pitch and a mesophase pitch to compare and analyze the structure with the asphaltene used in our study. Pitch generally has peaks similar to asphaltene. However, it was found that the alkyls peak corresponding to the aliphatics at 2800 cm^{-1} was significantly lower than that of asphaltene. On the other hand, the mesophase pitch formed by heat treatment of the pitch showed a small number of peaks corresponding to alkyls, and a new peak corresponding to the aromatic C-H stretching vibration at 3040 cm^{-1}.

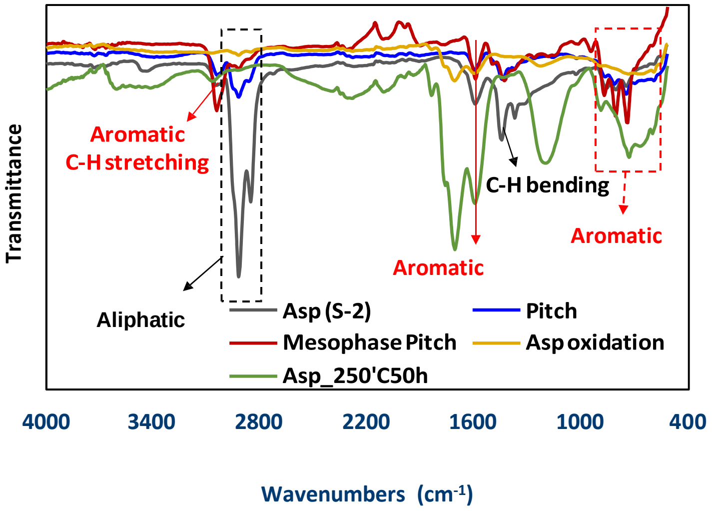


Figure 11. Molecular structures of asphaltene, oxidated asphaltene, pitch, and mesophase pitch.

As shown in Figure 11, it is difficult to form an aromatic C-H stretching bond as seen in mesophase with the simple oxidation step of asphaltene. Certain stabilization temperatures and conditions are optimized to reduce carbonization time. This heat treatment process requires high energy consumption and high unit cost of the precursor. Therefore, we blend polymers and additives to find a simple process that can replace the pre-treatment process of precursors. Polymer/additive blending asphaltene was first tested in film form to facilitate properties analysis. Polymer A used for asphaltene film making was selected as a blending polymer as it has a large number of aromatic structures and is expected to improve the strength of carbon fibres. The polymer blending asphaltene films were manufactured according to the blending ratio of asphaltene and polymer A and is shown in Figure 12. However, polymer A, which has a large amount of an aromatic structure, has a brittle characteristic in film formation. Therefore, it was considered that there was some difficulty in improving the brittle properties of asphaltene and improving the spinning performance.

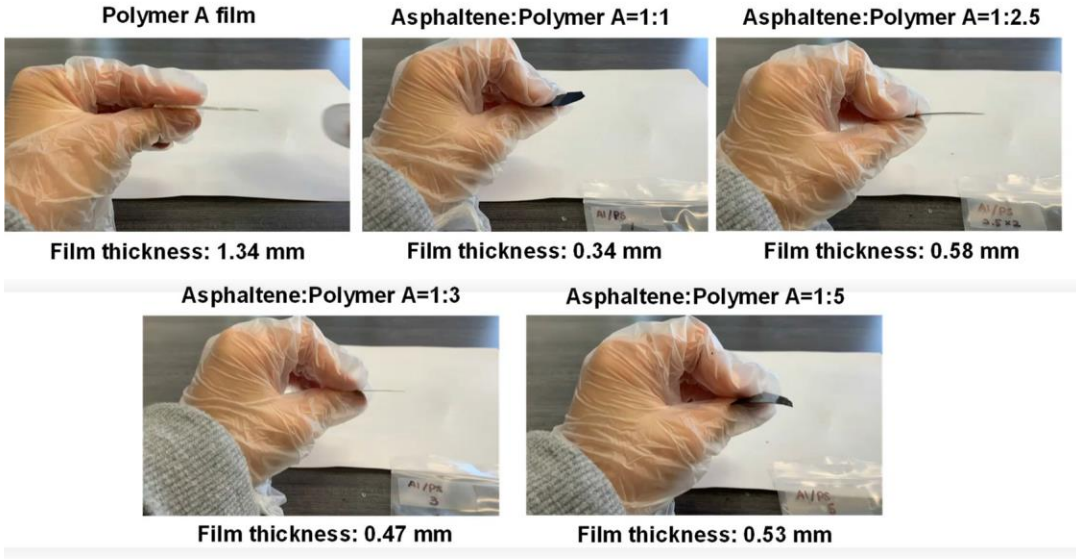


Figure 12. Film thickness and characteristics of Polymer A blending asphaltene films with respect to blending ratio.

Polymer B was chosen as another option. Polymer B contains a large number of aromatic structures similar to polymer A but consists of structures that are connected by linear chains between the aromatic structures. Linear chains are suitable for improving the brittle properties caused by the rigid structure of the aromatics. As expected, the film showed flexible properties. The films shown in Figure 13 were a mixture of asphaltene and polymer B at a ratio of 1:2, and acid-treated CNT was used as an additive. Functioned CNT by acid treatment can be more uniformly distributed within polymer and asphaltene solutions. The average thickness of the asphaltene/polymer B film is approximately 300 micrometers and 400 micrometers for the film reinforcing the CNT. For the seeding effect of CNT, we selected the 1 wt.% CNT reinforced film and used them after hot pressing at 200 degrees C to form a uniform surface.

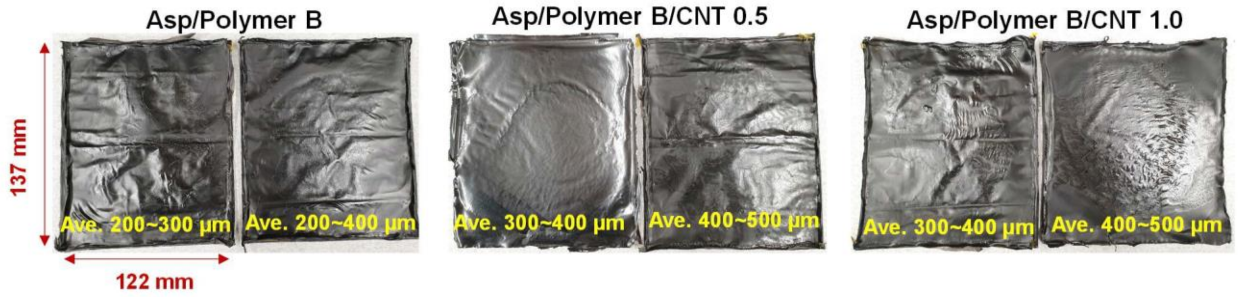


Figure 13. Pictures and thickness of Polymer B/CNT blending asphaltene films.

Preliminary Test for fibre Making

Melt Spinning

The polymer/additive blended asphaltene were attempted through a small-scale extruder held in the laboratory as shown in Figure 14. A nozzle of 0.6 mm was used for the melt spinning. The refined asphaltene and polymer/additive blended asphaltene were able to obtain precursor fibres with diameters of at least 28.38 and 8.9 micrometers, respectively. It is expected that the characteristics of polymers made it easier to stretch. In addition, precursor fibres spun from the mono-nozzle were cooled rapidly from low air temperatures, later introducing an air-blowing system to aid stretching and densification of molecular structure. We are currently setting up a roller that can be stretched more evenly. However, bubbles occurred on the surface of the precursor fibre using polymer/additive blended asphaltene, which is expected to be formed during the evaporation of the solvent after the solution blending. Therefore, the heat treatment temperature will be adjusted to remove bubbles during the solvent evaporation process.


(a) (b)

Figure 14. Melt spun precursor fibre using (a) refined asphaltene (28.38 μm) and (b) polymer/additive blended asphaltene (8.90 μm).

Electrospinning

We were provided with two types of asphalt, solid form S-2 and liquid form L-2 by Alberta Innovates. L-2 was better suited for electrospinning due to the liquid state. To achieve the desired fibre diameter and strength by electrospinning it was necessary to inject fluid at a rate of 10 mL/h using 10 nozzles, have the power supply set above 30 kV and to maintain a distance of at least 15 cm between the cylinder and the needles. After electrospinning is complete, there is no need to remove residual solvent as it evaporates during the spinning process. Melt spinning does not use solvents, and therefore there is nothing to remove once fibres are produced. Electrospinning can be used to produce fibres with diameters of 1 µm or less as shown in Figure 15. Electrospinning is conducted with the assistance of polyacrylonitrile to achieve continuous fibres. High asphaltene contents, as shown in Figure 15(b), result in welded fibres with brittle mechanical characteristics.

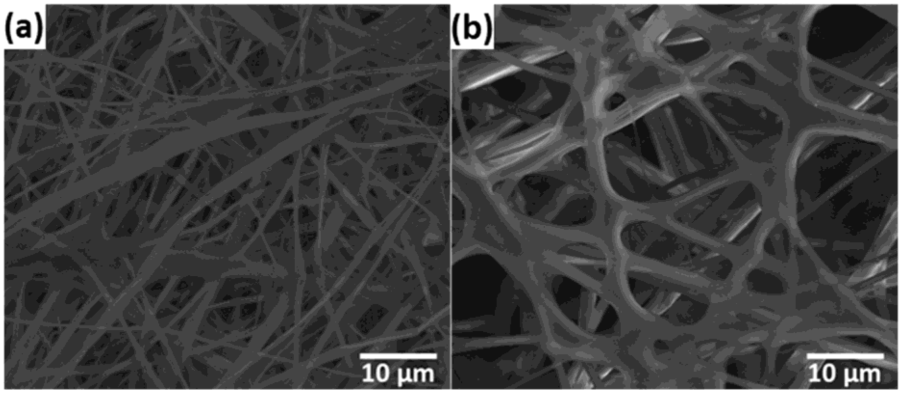


Figure 15. SEM images of asphaltene:polyacrylonitrile electrospun fibres with a ratio of (a) 1:3; (b) 2:3.

Oxidative Stabilization

IPL Irradiation using Electrospun Fibre

The use of IPL allows for the production of hollow and porous carbon fibres, as shown in Figure 16. The ultra-high surface area is especially evident after high power pulses shown in Figure 16(c) and (d) which closely resembles activated carbon fibre. The surface area is to be estimated by BET surface area in future studies. However, high energy pulses that increase the surface area can also cause fibres to agglomerate. In addition, the diameters of the fibres can clearly be reduced by increasing the pulse power. However, the agglomerations make assessing the fibre diameter difficult.

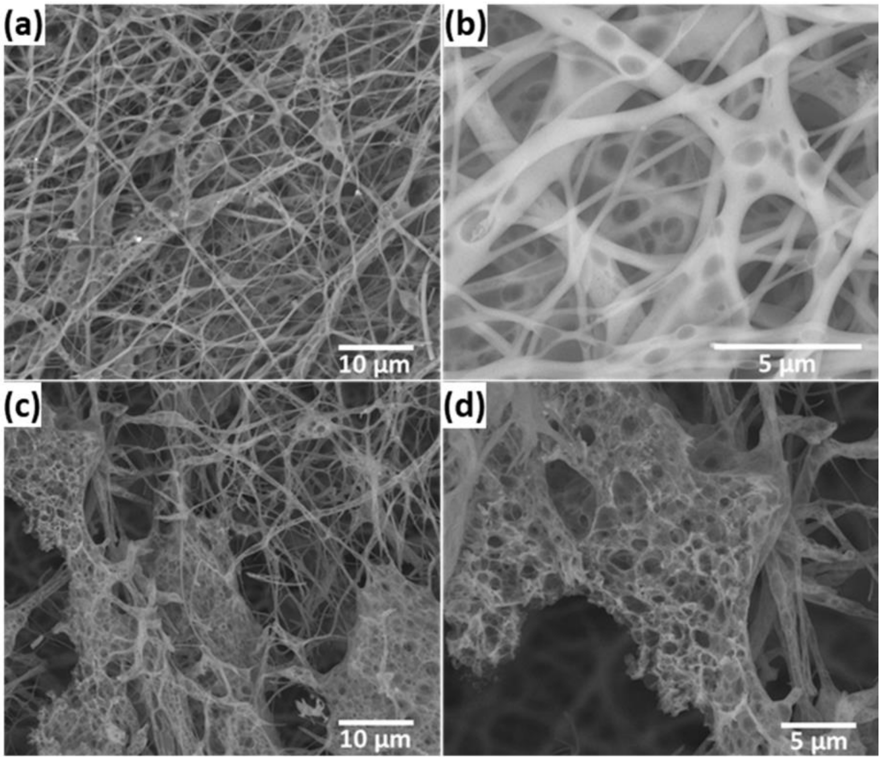


Figure 16. SEM images of asphaltene:polyacrylonitrile electrospun fibres with a ratio of 1:3 on the left (a), (c) and 2:3 on the right (b), (d). The top row (a), (b) denotes low power of 1500 V for 6 ms and the bottom row (c), (d) denotes a high power of 3000 V for 6 ms.

IPL shows promise for increasing carbon content. A single pulse is only able to raise the carbon content of the electrospun fibres up to ~65% from ~50%. This may be due to high impurities and low carbon content of the untreated L-2 asphaltene sample supplied. Further process treatments are to be explored to increase the carbon content as shown in Figure 17. Additional optimization of the number of pulses, pulse power, pulse duration and pulse frequency can help to optimize the carbon content. Reductions in the nitrogen and hydrogen content can also be observed suggesting that removal of volatiles is occurring.

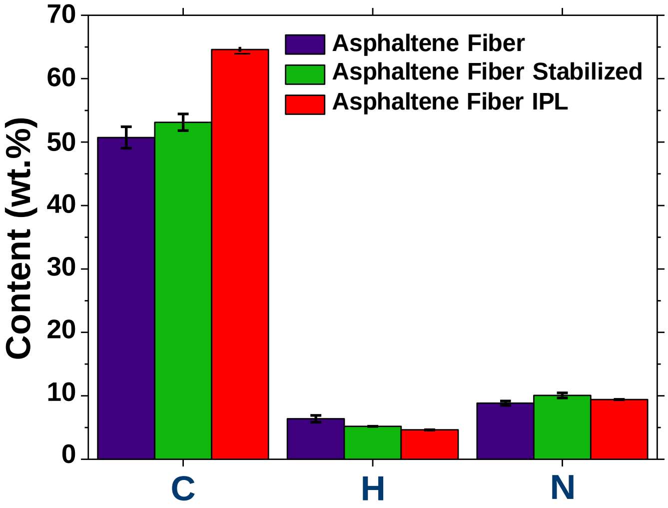
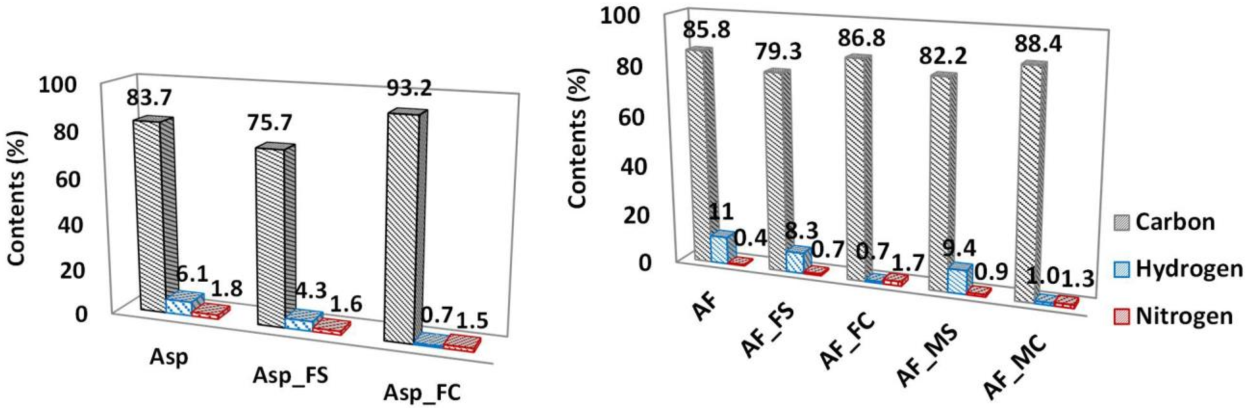


Figure 17. CHN results denoting carbon, hydrogen and nitrogen content for asphaltene fibres electrospun from L-2 provided by Alberta Innovates.

Chemical and Photoelectric Technologies

Figure 18 shows the results of CHN analysis before and after stabilization and carbonization. The hydrogen content of the precursor before stabilization indicates the spinning performance of the pitch. Rotation performance is significantly reduced when hydrogen content is reduced (Guosong Ni et al., 2019). The relative carbon content is reduced by the introduction of oxygen after the stabilization process, and the carbon content is increased back to its maximum after carbonization. As shown in Figures 18(a) and (b). Polymer B/CNT1.0 blasting asphaltene film (AF) shows the difference between carbon and hydrogen content. This is because the polymer used has both aromatic and linear chain structures. Unlike PAN precursors, asphaltene shows low initial nitrogen content and no significant change. Asphaltene showed 93.2% carbon content after heat treatment with a tube furnace. AF, on the other hand, has a relatively lower carbon content than asphaltene due to the structure of the existing polymer. However, as shown in Figure 18(b), there is no significant difference in hydrogen after the stabilization process. It is expected that there will be no significant difference in hydrogen content in the pre-processing process of the precursor. This is expected to result in good spinning performance for the asphaltene precursor mixed with polymer/CNT in spinning temperature changes. In the carbonization step, the oxygen radical mainly attacked the hydrogen atom instead of the carbon atom or the nitrogen atom, resulting in oxygen content increased and hydrogen content decreased.

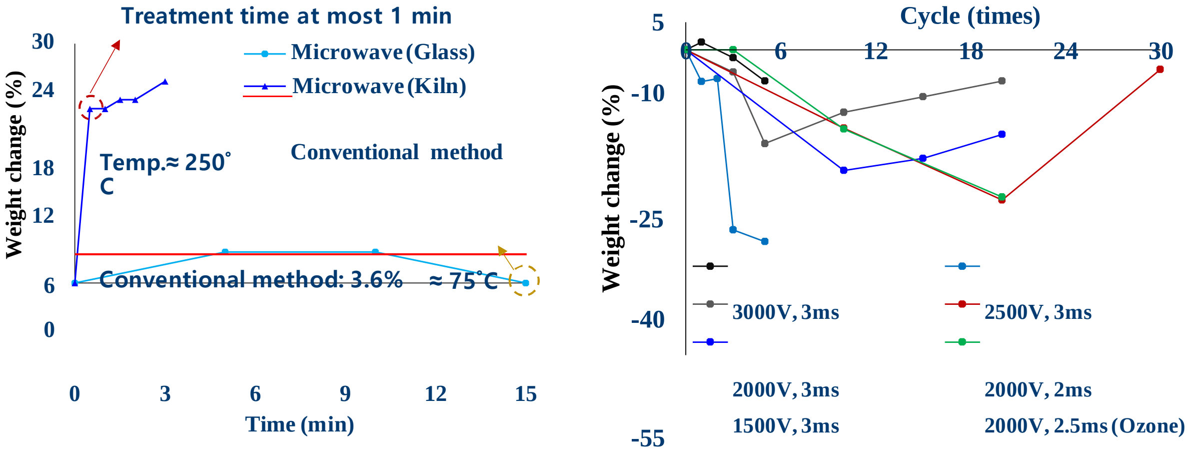


(a) (b)

Figure 18. CHN analysis for (a) asphaltene before and after stabilization and carbonization using tube furnace (conventional method), and (b) polymer/additive blending asphaltene films before and after stabilization and carbonization using tube furnace and microwave irradiation, respectively.

In this project, we proposed the development of stabilization and carbonization technologies. First, IPL and microwave irradiation were introduced for the stabilization process. As mentioned earlier, the weight of the precursor increases due to the introduction of oxygen between molecular structures during the stabilization process, and approximately 3-10% of the pitch precursors are known to be appropriate (Zhongren Yue et al., 2017). Therefore, we checked the weight change after the stabilization process of AF and analyzed the changes in the molecular structure through FTIR. Figure 19(a) shows the weight change of AF stabilized by microwave irradiation. When the sample is placed on the glass, there is a limit to the temperature increase of the precursor due to direct heating of the microwave irradiation. Therefore, the use of the kiln helped the precursor reach an appropriate stabilization and carbonization temperature.

As a result, the heat treatment method using conventional stabilization conditions increased the weight of the precursor by about 3.6%. Microwave stabilization on the glass showed similar weight changes but took more than 5 minutes. This is a significantly reduced time compared to the conventional stabilization process, which takes about 6 to 9 hours. On the other hand, microwave stabilization within the kiln took about a minute, with a weight change of about 20%. The mass increase suggests a rapid influx of oxygen atoms into the molecules of precursor, and its effectiveness will be studied. On the other hand, stabilization using IPL showed a reduction in weight. This appears to be caused by the instantaneous high energy application of microseconds, causing volatiles to be removed and thus reducing the mass of the film.



(a) (b)

Figure 19. Weight change of AFs after (a) microwave stabilization and (b) IPL stabilization.

Ozone IPL treatment methods were used to help bind oxygen atoms to molecules of the precursor. Ozone is decomposed by IPL, which provides the oxygen environment and oxygen radicals for stabilization. The tests for hydrogen peroxide and ozone IPL stabilization were also attempted. When hydrogen peroxide and ozone have been IPL-treated, hydroxyl radicals will form and bind to the surface of the precursor to aid the stabilization step.

Figure 20 shows the molecular structure of asphaltene after stabilization through ozone IPL and chemically oxidized film by hydrogen peroxide is treated with ozone IPL. As a result, the peak of the aliphatic structure of the ozone IPL stabilized sample is effectively reduced after the chemical treatment of hydrogen peroxide. However, the structure of both aromatics and aliphatic is reduced in the case of multiple treatments of ozone IPL, which is expected to have been decomposed by oxidation. Therefore, a process is needed to optimize the conditions of the hydrogen peroxide/ozone IPL stabilization process. When hydrogen peroxide reacts with ozone in a gas form, it generates oxygen and hydroxyl radicals. The oxygen environment and hydroxyl radicals will be tested as they are expected to form appropriate conditions for oxidizing the precursor.

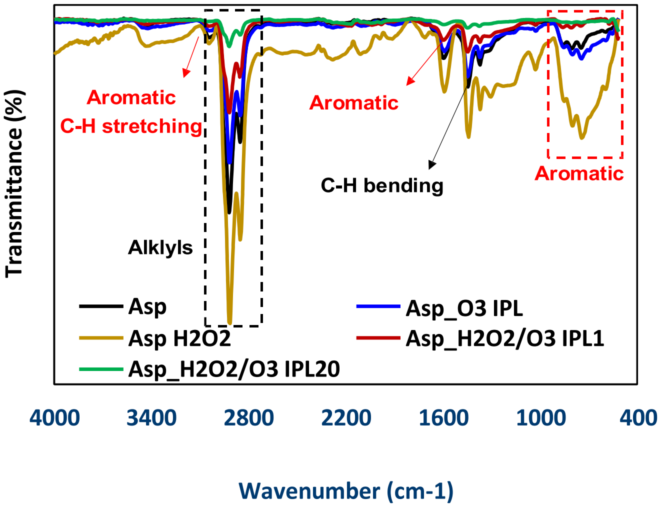


Figure 20. FTIR results of asphaltenes after chemical hydrogen peroxide treatment and IPL stabilization.

Evaluate Results Against the Desired Specifications of Alberta Innovates

Table 2. Project success metrics and targets for Phase 1

Metric	Project Target	Commercialization / Implementation Target	Comments (as needed)
Projected commercial cost	<US$12/kg	<US$8/kg	*We anticipate exceeding the minimum requirements and should achieve a lower cost.*
Greenhouse gas emissions	< 1 kg CO2/tons CF	< 1 kg CO_2/*tons CF*	*We anticipate lower GHG generation through the introduction of carbonization technology.*
Diameter	7 *μ m*	7 *μ m* (PAN/Pitch based carbon fibre)	*We anticipate exceeding the minimum requirements of fiber diameter.*
Demonstrate market potential		>3000 tonnes per year	*We anticipate production of more than 3,000 tons of carbon fiber annually.*

A lifecycle analysis showed that the processes introduced by our lab to improve stabilization and carbonization offers the biggest GHG reductions when compared to conventional methods. We found that there can be upwards of a 15 kg CO_2 /kg fibre difference in emissions between our proposed methods versus the conventional methods that use a furnace. The most recent LCA analysis looks at the overall emissions of the carbon fiber manufacturing process. This accounts for more than the projected target of 1 kg CO_2/tons CF that may be attainable if only looking at the carbonization process using IPL.

Additionally, the scaling up of a lab model may reduce CO_2 emissions even more once specialized equipment is used. As global warming becomes an increasing concern, it is important to find ways to reduce carbon dioxide emissions as much as possible. With the expectation that the carbon fibre industry will grow, it is important to understand GHG emissions and ensuring that processes are optimized to reduce harmful outputs. In addition to CO_2 emissions, we are also expecting to reduce O_3 emissions and reduce acidification in SO_2 equivalent when compared to standard methods. The reduction in emissions is primarily due to using less energy intensive processes. In addition, as asphaltene is produced within Alberta, it is expected that there will be a reduction in emissions from transportation when compared to PAN manufacturing which can stretch over several continents for production. It is expected that no additional GHG will be emitted in the oil sands as asphaltene is already being extracted. The CO_2 emissions were computed by an open LCA program using the processing conditions applied in microwave and IPL. As a result, CO_2 emissions is expected to decrease by about 50%. The reduction of GHG emissions also indicates the usage of less energy and in turn substantially lower production costs. However, conditional calculations on the lab scale have reduced the energy and time consumed by more than 90%, which is expected to be reduced below this project target of $12. Electrospun asphaltene fibers have a fiber diameter of less than 1 μm and melt-spun fibers have a minimum diameter of 9 μm. Therefore, it is expected that the diameter of the fiber after carbonization can be achieved below the project target of 7 μm (suggested in Table 2). However, the uniformity of fibers must be improved with the initial installation. Furthermore, many fibers must be spun at the same time in the future.

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

Milestone 1 –Precursor Treatment and Tests

Asphaltene consists of various molecules and has a wide molecular weight distribution. Low molecular weight components are volatile at the temperature of the next spinning step, making the morphology of the fibres uneven. Thus, pre-treatment steps are performed to narrow the distribution of molecular weights. The objective of the preprocessing step depends on the characteristics of the asphaltene. In the case of Athabasca asphaltene (S-2), it is believed that a pre-treatment step of asphaltene to eliminate coke is required. The heptane soluble portion, which has the most aliphatic structures, can be adjusted according to the melt spinning conditions and the oxidative stabilization method. In addition to heptane, other solvents such as pentane and hexane can be used to control this.

Therefore, the pretreatment processes of the precursor are recommended to produce high-quality carbon fibres with uniform and high mechanical properties. High-quality carbon fibre expands the application fields and markets of carbon fibre. The precursor pre-treatment process primarily uses heat treatment and solvents to increase the purity of the precursor and narrow the molecular weight distribution. However, the pretreatment process of asphaltene does not improve the brittle characteristics of asphaltene.

To address this, we apply the blending method of polymers/additives. This method can improve the brittle properties of the asphalt depending on the type of polymer. In this study, solvents were used for polymer/additive blending, but the use of solvents can be excluded by the introduction of tween extruders.

Milestone 2 – Melt Spinning Process of Precursor fibres

Carbon fibre requires a variety of properties such as high strength, specific surface area, and electrical conductivity, etc. depending on the application. For high-quality carbon fibres, melt spinning is appropriate to manufacture continuous fibres because the orientation of molecular structures to have high strength is important. Furthermore, the stretching of precursor fibres from the nozzle can reduce the diameter of the precursor fibres and increase the orientation of molecules. At this time, air blowing facilitates precursor fibre stretching.

On the other hand, electrospinning is a more appropriate method for manufacturing nanofiber with a high specific surface area and utilize liquid phase asphaltene precursors. High asphaltene contents result in fusing of fibres during the electrospinning process and further fusing after treatments such as IPL. The fibre diameters are substantially lower than fibre diameters for traditional carbon fibre. Therefore, we see alternative applications and markets for the fibres beyond the mechanical reinforcement applications targeted by the specifications of Alberta Innovates. However, the advantages of this method include ultra-high surface area, electrical conductivity, and filtration efficiency. These benefits make the fibres appealing for many different markets and applications that the industry currently does not maximize.

Milestone 3 - Stabilization and Carbonization for Carbon fibres/Characterization

Stabilization techniques by microwave show promising weight gains corresponding to oxygen functionalization. In addition, the oxygen bonding can be observed by FT-IR analysis. We are also learning that stabilization by IPL is not as effective as expected and additional modifications need to be made to optimize this process. The chemical stabilization process still requires optimization as the performance achieved is not consistent. Chemical treatments include the use of ozone and hydrogen peroxide. The combination technology of hydrogen peroxide and ozone IPL does not affect the binding between the carbon in the aromatic structure of the asphaltene, and oxidative stabilization can be achieved through the recombination of the aliphatic structures, and condition optimization is required for proper oxidative stabilization.

In the electrospun fibre, carbonization using microwave requires the process to be done in a kiln to show promise in producing strong D- and G-bands corresponding to good carbon structures. The process of carbonization using IPL also yields good graphitization. However, the fibres become more brittle due to the formation of pores and hollowing out of fibres. As a result, the fibres have even higher surface area. The preliminary results show promise for new ways of stabilization and carbonization. This may have substantial impacts on the industry because the reduction of the processing time, energy and GHG emissions result in substantially lower costs. The lower costs in turn may drive carbon fibre into new markets and industries that are presently limited by high costs. The ultra-low density of the fibres can substantially reduce the mass of technologies using carbon fibre reinforcement. Therefore, further GHG emissions can be reduced and help to achieve climate change policies. There is even potential to advance to more stringent climate policies if the material achieves widespread usage due to the lower costs and emissions.

Characterization aspects have been one of the key learnings. We have fine-tuned the parameters required to achieve accurate results. This includes aspects such as the vacuum pressure and working voltage for SEM as well as the substrate requirements and laser power for Raman analysis. The optimal parameters for processing of the SEM images to determine fibre diameter and porosity using image processing software ImageJ has also been learned. A Zeta optical profilometer is used to characterize the fibre diameter of melt spun fibres due to the substantially larger diameter and availability in our lab. FTIR analysis using both transmission and attenuated total reflection (ATR) mode have been successfully applied to characterize the fibres. These learnings increase the efficiency of characterization and can be applied to Phase II or other future projects. These learnings may also be applied for future collaborations. Characterization of asphaltene fibres produced by both melt spinning and electrospinning provide a strong baseline for future comparisons.

Milestone 4 – Economics and Energy Analysis

The ultimate goal of our proposed technologies is to improve energy conservation, economic value, and environmental effects. Therefore, the energy consumed, cost, and GHG generation was calculated through open LCA software. Calculation errors were minimized by bringing the assumptions applied for computation as close as possible to actual values.

Conventional oxidative stabilization and carbonization methods require temperature saturation inside the chamber using a convection method. In addition, the chamber is prone to heat outflow to the outside due to continuous carbon fibre manufacturing facilities. This means that unnecessary wasted energy consumption is high. In addition, unnecessary decomposition and reaction of molecular structures can occur during oxidative stabilization and carbonization.

However, the chemical/photoelectric techniques proposed in this work can significantly reduce unnecessary energy consumption by applying selectively intensive energy to precursor fibres in a short time. Also, as mentioned earlier, chemical/photoelectric technology can maintain the aromatic structures of asphaltene because it has less energy than the energy that can cut bonds between carbons. Unnecessary decomposition and reaction of molecular structures contribute to the reduction of GHG generation.

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 Resources Metrics:** Describe how the project outcomes impact the Clean Resources 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

Much information to fiberize asphaltene through melt spinning is unknown. In particular, the complex and diverse structures of asphalt require more information. It was also unclear whether the pretreatment process of asphaltene was a necessary process and the purpose of the preprocessing process. However, we confirm the pretreatment effect of asphaltene through our study. The structures and characteristics of asphaltene vary widely depending on the region collected, so it cannot contain everything, but it is considered appropriate information for Athabasca asphaltene.

Polymer/additive blending methods can improve the brittle properties and enhance the strength of asphaltene through small amounts of polymers and additives. Most of all, the polymers used in this study contain large quantities of aromatic structures, which can increase processability in melt spinning while minimizing the impact on the strength of carbon fibres.

Also, we can reduce the knowledge gap identified previously regarding oxidative stabilization methods. Commonly fibres are placed into a furnace for several hours to complete the stabilization process, but new methods that we have identified and researched allow for a more efficient oxidative stabilization. Furthermore, the proposed method can be applied to the carbonization process through the same facility. First, the processing facility compared to the conventional method is very simple, and the processing time is significantly reduced. As a result, the annual production of carbon fibre will increase significantly. It also consumes very little energy compared to conventional methods, has little wasted energy, and reduces the generation of GHGs. These advantages will reduce the production cost of carbon fibre derived from asphaltene and create high value-added products regardless of the fluctuation of oil prices.

Clean Resources Metrics

Table 3. Clean resources metrics of project for Phase 1

Metric	Project Target	Commercialization / Implementation Target	Comments (as needed)
$ Future Investment			Scale-up for commercialization of cavitation and mechanical shearing transformation, spinning, and carbonization system
# of Publications	1	1	Three papers will be published
# Students (Msc., PhD, Postdoc)	3	3	1 Postdoc, 2 Grads, 1 Undergrad - for Phase 1. For the commericialization phase - 2 Postdocs, 2 PhD, and 2 MSC
# Patents filed	1	3	Three patents are expected to be filed
Partnership agreements / MOUs?	0	1	Partnerships will be in infancy and further developed in the next phase of Grand Challenge.
# New products/services created	1	1	We will produce the carbon fiber derived from bitumen/asphaltene
# New Spin-Off Companies created	1	1	We anticipate one spin off arising from success in this Phase and other Grand Challenge Phases.

Table 3 shows the clean resources metrics of this project. Currently, we are trying to complete most of the project targets. Two papers are being prepared, and additional papers on changes in the mechanical strength and electrical properties of carbon fibres under oxidative safety conditions will be written. One provisional patent has been filed. Four HQSP were trained during phase 1 of the project. No new spin-off companies have been created, yet, but we anticipate them in future phases. We are progressing well towards a new product being created.

Table 4. Expected GHG generation calculated by open LCA program.

Impact category	Reference unit	Result - Microwave	Result - IPL	Result - Furnace	Difference Furnace vs IPL	Difference Furnace vs Microwave
Acidification	kg SO2 eq	5.02E-02	4.07E-02	1.22E-01	8.17E-02	7.22E-02
Eutrophication	kg N eq	1.98E-03	1.82E-03	3.16E-03	1.33E-03	1.18E-03
Freshwater ecotoxicity	CTUeco	5.92E+00	5.77E+00	7.08E+00	1.31E+00	1.16E+00
Global warming (CO2)	kg CO2 eq	8.28E+00	6.47E+00	2.19E+01	1.55E+01	1.37E+01
Human health - cancer	CTUcancer	1.24E-09	8.96E-10	3.85E-09	2.96E-09	2.61E-09
Human health - non-cancer	CTUnoncancer	3.90E-07	3.62E-07	5.99E-07	2.37E-07	2.09E-07
Human health - particulate matter	PM 2.5 eq	1.69E-03	1.25E-03	5.03E-03	3.78E-03	3.34E-03
Ozone depletion	kg CFC-11 eq	2.30E-07	2.30E-07	2.32E-07	2.46E-09	2.17E-09
Smog formation (O3)	kg O3 eq	9.78E-01	8.80E-01	1.72E+00	8.45E-01	7.47E-01

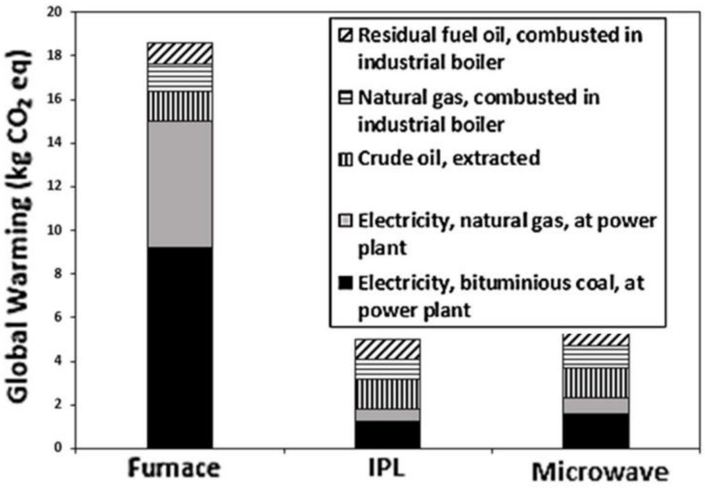


Figure 21. Global warming measured by as kg CO_2 equivalent emitted per kg of CF produced from asphaltene.

Life cycle assessment (LCA) can provide a variety of metrics to measure the environmental and clean energy improvements offered by photo-electromagnetic processing, as shown in Table 4 and Figure 21. We can see a substantial reduction in the CO_2-equivalent global warming effects and smog formation using photo- electromagnetic techniques compared to traditional furnace-based stabilization and carbonization. The potential reduction of GHG emissions from 21.9 to 6.47 kg CO_2e/kg CF is a promising result.

Program Specific Metrics

Table 5. Project program specific metrics for Phase 1.

Metric	Project Target	Commercialization / Implementation Target	Comments (as needed)
# of End Users participating	This project will partcipate Bitumen and carbon fiber experts participating.	Commercial implementation requires inspection of several pretreatment processes of bitumen.	A lab. scale system is established for performance testing.
Unique product/process	1	1	We provide unique product/process obtained from the experiments.
# commercial BBC products	1	1	We provide BBC products obtained from the experiments.

During the project in phase 1, we planned to set up the lab-scale system, develop unique technologies, and provide products obtained from experiments as shown in Table 5. We set up a vertical and horizontal melting spinning system in phase 1, and established an O3 IPL system suitable for oxidative stabilization. It also proposed chemical/photoelectromagnetic stabilization techniques that could reduce the energy and time consumption of oxidative process, and the optimization process is still required. System modifications of melt spinning are underway to improve the uniformity of asphaltene fibers formed, and asphaltene fiber can be provided.

There are several work plans that have changed in this study. The first is the pretreatment process of bitumen, which corresponds to Milestone 1. We analyze the necessity and effectiveness of pretreatment and study alternative methods to improve the brittle properties of asphaltene an improve the mechanical strength of carbon fibres through polymer/additive blending methods. Further research has also been conducted on the process of refining via asphaltene (S-2) powder, as samples have been provided from Alberta Innovates.

The second was a process that did not require the removal of the residual solvents planned for Milestone 2. The post-treatment process was carried out to remove residual solvents of refined asphaltene before melt spinning, so no process was required to remove residual solvents after melt spinning. Furthermore, to expand the application of carbon fibre, nanofiber fabrication using electrospinning was further carried out, which was not in the existing work plan.

Third, oxidative stabilization and carbonization using lasers, which were planned for Milestone 3, was not appropriate because of the decomposition of asphaltene by the strong energy of the laser. Therefore, we propose an IPL processing method with lower energy compared to laser as an alternative method. We also discovered problems with IPL and new methods developed through a combination of chemical/photoelectric techniques to address them.

Project Outputs

We have applied for a patent (US Pending 63/079,478) for oxidative stabilization technology applied with chemical/photoelectric technology. This patent contains the overall contents of asphaltene's pre-treatment, polymer/additive blending, melt spinning, electrospinning, oxidative stabilization with chemical/photoelectrics, microwave irradiation, and carbonization techniques performed in this study. Also, two papers are being prepared. The first is a paper on the study of oxidative stabilization of electronically radiated nanocarbon fibres using precursors blended with PAN and asphaltene by applying microwave irradiation and IPL. The other is a paper on oxidative stabilization that combines hydrogen peroxide and ozone IPL using melt spun asphaltene fibres.

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

By producing carbon fibre from local materials, Alberta will see an increase of available jobs associated with the project. Some jobs will be directly created in the production facility and will be associated with going through the carbon fibre process including pre-processing, spinning, stabilization and carbonization. Jobs will also be created indirectly, associated with the increase in availability of a cheaper carbon fibre product.

The cost of raw PAN material is about triple the cost of raw asphaltene. In a similar process it is estimated that melt spinning asphaltene with a polymer such as HDPE will cost USD 0.44 $/kg, while spinning PAN will cost at least USD 1.4 $/kg. fibres produced from raw asphaltene will be very competitive on the global market, as most carbon fibre is PAN based.

New stabilization and carbonization methods investigated in this project will assist in lowering the production costs of carbon fibres as they are less energy intensive and more time efficient than the standard method of using a furnace for several hours. It is estimated that performing stabilization and carbonization by microwave will need 12.2 MJ, doing the same by IPL will require 0.0126 MJ. This is in comparison to the furnace method which is approximately 105 MJ. When evaluating this energy consumption in relation to average Calgary electricity prices, a cost of 0.02 cents is determined for IPL, 22.5 cents for microwave and 192 cents for the standard furnace operation.

It is expected that carbon fibre will be exported to other provinces and countries to be used in the automotive and aviation industries. Additionally, carbon fibre may bring in new investors interested in using carbon fibre within the province for new and existing applications.

Environmental

The greatest environmental benefits of this project can be found in the new stabilization methods by microwave and IPL that we have identified. Microwave and IPL are much less energy intensive processes than the traditional method of stabilizing fibres in a furnace for several hours. Estimations for melt spinning of carbon fibre from asphaltene yields emissions of 21.9 kg CO_2-equivalent (CO_{2e})/kg carbon fibre. This corresponds well to Toray's estimate of 20 kg CO_{2e}/kg carbon fibre given the smaller scale. Based on the process utilized in the lab, it is estimated that for every kg of carbon fibre produced, stabilization by microwave will decrease CO_{2e} emissions by 13.7 kg, and likewise, IPL will decrease emissions by 15.5 kg. These stabilization methods will directly contribute to reducing GHG emissions. Additional environmental benefits include reducing O_3 production by 0.75 and 0.85 kg O_3/ kg carbon fibre through microwave and IPL respectively when compared to the furnace. If the minimum phase III targets are met of producing 10 kg of carbon fibre a day, the new stabilization and carbonization processes can result in a reduction of nearly 56 US tons of CO_2 emissions yearly compared to other methods. This project will help to improve other environmental aspects such as acidification of aquatic environments.

Social

It is expected that with a cheaper carbon fibre available, carbon fibre will be applied in various industries that were barred from utilizing the material prior due to the high costs associated with it. Local manufacturing may benefit in creating new products that require strong and lightweight materials such helmets, bikes, and vehicle parts. Moreover, the cost-effective carbon fibres can be used as fillers for concrete, ceramics, and polymers.

Building Innovation Capacity

This project will contribute to training HQSP in various parts of the manufacturing process. Initially, HQSP will be important to fine tuning and scaling up the manufacturing process. This project will provide many research opportunities to retain HQSP as it is expected that an influx of investment into carbon fibre research will occur once an affordable product is on the market. This will include working on new CF applications and optimization of CF properties. Four HQSP were trained during phase 1 of the project. Modified high efficiency melt-spinning and electrospinning apparatuses are developed to complete the project. In addition, novel IPL and microwave systems with vacuum, air, nitrogen, ozone, and hydrogen peroxide injection capabilities are also developed to complete the project.

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

The next steps include scaling up the experimental set up. Presently work is conducted on a very small scale, and in order to achieve phase II targets we will need to increase production and capabilities for stabilizing large quantities of fibre. One recommendation that will allow for scaling production, is to use a melt spinning set up with a larger extruder and a spinneret allowing to produce several strands of fibre simultaneously. Electrospinning scale-up can be achieved by introducing additional nozzles and increasing the collector size. The orientation of the molecules will play an important role in achieving the goal of carbon fibre strength in Phase 2. We have set up an air blowing system, which will make the fibre's spinning and stretching process efficient. We have ideas for the stabilization step that I learned from phase 1 that is the most important. It is a method that uses both chemical processing and electromagnetic methods at the same time. IPL facilitates the formation of hydroxyl radicals without affecting the major carbon bonds forming benzene in asphaltene, as shown in Table 1, with a wide area wavelength of 200–1200 nm. As mentioned earlier, IPL is an appealing approach to instantaneously provide large amounts of photo-electromagnetic energy. The formed hydroxyl radicals easily bond with the defects of the precursor fibres, which can be stabilized as thermosetting through crosslink bonds. Furthermore, the oxygen-enriched air atmosphere generated may form activation conditions for oxidative stabilization. We will promote cross-linking reactions in thermoplastics by forming hydroxyl radicals through hydrogen peroxide and ozone treatments combined with the energy of IPL. This method provides adequate wavelengths and energy for decomposition and recombining additional bonds without affecting the bonds between carbon. In addition, the manufacturing process of carbon fibre releases tens of thousands of fibres at once, so it must be able to handle a wide surface area at the same time. IPL is a suitable method to spread fibre and apply energy to a large area at once.

$$\mathbf{O_2 \rightarrow 2[O]}\ h\nu\ (\lambda=184.9\ \text{nm})$$

$$\mathbf{O_3 \rightarrow [O]+O_2}\ h\nu\ (\lambda=253.7\ \text{nm})$$

Table 1. Energy of wavelength and bond energy with respect to bonds (Rich M et al., 2009)

Wavelength (nm)	Energy (kJ/mol)	Bond	Bond Energy (kJ/mol)
468	256	C-C	348
365	328	C=C	607

We have begun forming a team for Phase II to ensure expertise in each relevant field. Dr. Harvey (University of Calgary) is an expert in bitumen and asphaltene. Dr. Natale (University of Calgary) is an expert on rheology, Dr. Chung (University of Alberta) is an expert on polymer, Dr. Kim (Queen's University) is working with various aerospace and automotive companies and is an expert in carbon fibre applications.

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

Knowledge dissemination is first achieved through a submitted provisional patent, US63/079,478. The provisional patent contains information on various chemical stabilization techniques; electrospinning and microwave-based carbonization; electrospinning and IPL-based carbonization; melt-spinning and microwave-based carbonization; melt-spinning and IPL-based carbonization. Each of these five topics will then be disseminated in the form of high-impact journal publications once the intellectual property (IP) is protected. Laser-based techniques and value-added applications may also warrant publications. The applications include, but are not limited to, mechanical fillers, sensors, filters, and electrodes. The research is also to be conducted with partners from Alberta Innovates, CanmetENERGY (NRCAN), companies such as MKS, Trium, Exergy, Suncor and partner institutions including the University of Alberta. The goal of the project is to use the knowledge gained from this project to commercialize the proposed technology. The commercialization is expected to have a significant impact on the industry by providing a lower-cost and more environmentally alternative to presently available carbon fibre. The cost competitiveness will also open research into new applications of carbon fibre that could sprout into new industries.

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

The project aims to synthesize continuous fibres from asphaltene and bitumen using melt-spinning or electrospinning. The process chosen depends on the precursor and desired applications. Asphaltene has a molecular structure similar to pitch in accordance with its refining process compared to pitch and mesophase pitch. When an appropriate stabilization process is applied, it is expected that the process of converting to mesophase can be shortened through polymers and additive blending.

Melt spinning enables the formation of long and strong continuous fibres using asphaltene (S-2) and polymer mixtures. Pre-treatments to isolate the asphaltene components are required. fibres with diameters ranging from 5 – 500 µm can be formed depending on the initial composition, nozzle diameter, spinning temperature and other factors. Melt spinning of commercial pitch and mesophase pitch is also tested for comparison. By comparison, electrospinning is more suitable for producing continuous fibres from the L-2 sample of asphaltene. No pre-treatment was required. The fibres had substantially lower average diameters of around 1 µm. They also exhibited fusing if the asphaltene content was too high.

Two photo-electromagnetic processes have demonstrated promise for stabilization and carbonization. Microwave is one of the most efficient ways to stabilize and carbonize in a short time. In a short period of less than a minute, the temperature increased by 250 °C and weight increased by 20 %. This corresponds to the introduction of oxygen into the molecules of the precursor. IPL is a system that can emit high energy in microseconds, and we have determined that stabilization and cross-linking of thermoplastic resins is difficult with the IPL system alone. However, IPL is a promising energy source to promote chemical reactions and bonding. To develop this, a combination of chemical and photo-electromagnetic methods will be examined, and conditional optimization must be performed. The fibres are treated using chemical treatments with ozone and hydrogen peroxide. Two different IPL systems are tested that can apply different amounts of energy and different pulse durations and frequencies. This allows both stabilization and carbonization to be conducted. Photo-electromagnetic methods were compared to conventional methods to show comparable performance.

The project demonstrates great promise in reducing the time, energy and cost of manufacturing carbon fibre. Aside from potential cost savings from asphaltene precursors, the photo-electromagnetic treatment techniques also show substantial cost and up to 70% GHG emissions reductions. The results of the project have been converted into a provisional patent and subsequent journal publications are being prepared. The results from phase I demonstrate promising new techniques for producing carbon fibre. The next step for the project is to optimize the process and narrow down potential markets. Owing to the diversity of the project team, the team also anticipates scale-up and eventual commercialization as next steps.