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.

MELT SPINNING OF SINGLE STRAND CARBON FIBRE FILAMENTS FROM ALBERTA OIL SANDS ASPHALTENES

Public Final Report

Prepared for

Alberta Innovates

Prepared by

University of Calgary

Dr. Joanna Wong, Assistant Professor

ALBERTA INNOVATES

CLEAN RESOURCES FINAL PUBLIC REPORT TEMPLATE

1. PROJECT INFORMATION:

Project Title:	**Melt spinning of single carbon fibre filaments from Alberta oil sands asphaltenes**
Alberta Innovates Project Number:	G2020000346
Submission Date:	February 16, 2021
Total Project Cost:	$62,500
Alberta Innovates Funding:	$50,000
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

This project was led by **Prof. Joanna Wong** and the **Laboratory of Engineering Materials** at the University of Calgary in collaboration with the following researchers and research groups:

- **Prof. Milana Trifkovic** and the **Trifkovic Research Group** at the University of Calgary
- **Dr. Stephan Busato**, Independent Organic Chemist
- **Prof. Philip Egberts** and the **Nanotribology Lab** at the University of Calgary

- **Prof. Paolo Ermanni** and the **Laboratory of Composite Materials and Adaptive Structures** at ETH Zurich

Our team also gratefully acknowledges the following individuals and groups for their contributions:

- **Prof. Steve Bryant** and the **Canada Research Excellence Chair in Materials Engineering for Unconventional Oil Reservoirs** at the University of Calgary for their assistance with our thermogravimetric analysis, gas chromatography mass spectrometry, and high temperature simulated distillation gas chromatography with flame ionized detection
- **Prof. Thomas Oldenburg** and the **Petroleum Research Group** at the University of Calgary for their assistance with our Fourier-transform ion cyclotron resonance mass spectrometry analysis

A. EXECUTIVE SUMMARY

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

RESPOND BELOW

The objective of Alberta Innovates' Carbon Fibre Grand Challenge (CFGC) Phase I project was to explore and test the feasibility of potential pathways for converting bitumen-derived asphaltenes contained in Alberta oil sands into high value carbon fibre materials for applications as structural reinforcements, electrodes, and filters, among others. Our team proposed and tested a method to manufacture single strand carbon fibre via melt spinning. The provided asphaltene samples from Alberta Innovates were first characterized using thermal, rheological, and molecular weight distribution analyses to gather a wide range of material data which were largely unknown prior to this project. A single nozzle melt spinner with speed-variable take up wheel was designed and built in-house. Using this apparatus, asphaltene fibres were successfully melt spun in continuous process to lengths of several meters. Stabilization and carbonization heat treatment processes were performed at temperatures up to 1000°C in a tube furnace. The fibres' morphologies were examined after melt-spinning and stabilization under optical and confocal microscopes. This project concluded that Alberta oil sands asphaltenes can be converted into carbonaceous fibres without pretreatment, but more investigations are required to determine if graphitic fibres are obtainable. In addition to the investigations on the as received asphaltenes, the team looked at compounding the asphaltenes with different commercially available polymers to increase melt strength and provide a template for the ordering of graphitic layers. Going forward, investigations are needed to relate the microstructure of the stabilized and carbonized materials to formation of graphitic layers during graphitization higher temperatures. The single filament melt-spinner must be scaled up to a multi-filament system.

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

Carbon fibres are important structural reinforcement materials used in high performance applications where high strength, high stiffness and low weight are required. Sectors where carbon fibres are commonly applied include the aerospace, automotive, robotic, and biomedical industries. According to PR Newswire, the global carbon fibre market was valued at US$ 4.7 billion in 2019 and expected to grow to $US 7.8 billion by 2029. The demand for carbon fibre is currently greater than the ability for manufacturers to produce the material which limits the use of these materials to applications which are not deterred by the price premiums.

Carbon fibres are produced through melt spinning techniques from two main precursors – polyacrylonitrile (PAN) and pitch. PAN based fibres account for over 90% of the current market share in the manufacturing of carbon fibre, however its production costs is significantly higher than that of the pitch due to the need to synthesize PAN [1]. Pitch materials also must be preprocessed into meso-phase pitch before melt-spinning to facilitate the formation of ordered graphitic layers in the produced carbon fibres. The precursor and method of production is of great importance in determining the microstructure of the carbon fibres which ultimately affects the mechanical performance of the fibres.

Carbon fibres have been produced from other sources, including lignin and coal-derived asphaltenes. However, these investigations have produced carbon fibres of lesser graphitic qualities which are not suitable for structural applications. These qualities of carbon fibres may find application as catalysts and filters where high strength and high stiffness are not required.

The use of Alberta oil sands asphaltenes as potential precursor materials for carbon fibres is an interesting proposal because asphaltenes, though currently considered a waste product, are a plentiful source of carbonaceous material which may be converted to high value products. One Albertan company is selling the asphaltene fraction at a market ‘coal’ price per ton (approximately US$40/ton), or approximately US$ 0.02/lb. The value of these asphaltenes would drastically increase if they can be upgraded to carbon fibres. Yet, at the commencement of this project little understanding of Alberta oil sands asphaltenes as they would relate to using them as precursors to carbon fibres was available.

KNOWLEDGE OR TECHNOLOGY GAPS

Alberta Innovates identified five key knowledge and technology gaps pertaining to manufacturing carbon fibre from Alberta oil sands in the Carbon Fibre Grand Challenge Program Guide. These were gaps concerning the following 1) mesophase requirement, 2) impact of sulfur and metals, 3) carbon fibre production fundamentals, 4) large-scale carbon fibre production, and 5) and economics, energy requirements, and greenhouse gas emissions [2].

This project was designed to address the primary knowledge and technology gaps associated with topic 3) - carbon fibre production fundamentals, with the specific goal of converting asphaltene into highly graphitic carbon fibre. Processing towards this goal, the project was expected to unavoidably address issues of 1) mesophase requirement and 2) impact of sulfur and materials as these issues are known to affect the quality of the carbon fibres after graphitization.

Addressing issues related to carbon fibre production fundamentals refers to identifying the processing parameters required to form fibres, which are closely tied to the properties of the precursor material. While the chemistry and physics of the carbon fibre production process are well understood for PAN and pitch, similar knowledge is lacking for Alberta oil sands asphaltenes. This project addressed the technology gap by conducting extensive material characterization studies, including thermal analysis, chemical analysis, and rheological studies which make up the bulk of the finding presented in this report. Investigations were also conducted to study the miscibility/compatibility of asphaltene with commercially available polymers which may be used as additive to strengthen the melt, increase the flexibility of the melt spun fibres, and perhaps also increase the long range order of the graphitic sheets inside the carbon fibres. With regards to the spinning process, a parametric study was conducted to study the effects of fibre pulling speed and temperature on the diameter of the melt-spun fibres.

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

This project conducted a feasibility study that investigated the suitability of Alberta oilsands asphaltenes for melt spinning. To accomplish this, the original objectives of this project were the following:

1) **To characterize the asphaltene samples with regards to their suitability for melt spinning:** The melt-spinnability of a material are most likely determined by their rheological behaviour and thermal properties, which are largely determined by molecular weight distribution and molecular structure. The purpose of characterizing the asphaltene samples was to understand the rheological and thermal properties, and their origins, to suggest a narrow range of processing parameters that would be appropriate for melt-spinning.

2) **To obtain single filament carbon fibre precursors from asphaltenes through melt spinning:** The first step in the carbon fibre making process is to impart a fibre form to the material, provided the material has sufficient melt strength to form fibres and has sufficiently long chains such that they orient along the fibre direction when subjected to the shear forces involved in melt spinning. The purpose of conductive melt spinning experiments was to test the feasibility of imparting a fibrous structure to asphaltenes, which were originally received as powder and liquid.

3) **To convert the melt spun asphaltene fibres to graphitic carbon fibres:** Graphitic carbon fibres are produced from precursor fibres through a series of stabilization, carbonization, and graphitization steps, each taking place at higher temperature. The quality of the graphitic carbon fibres, as measured by graphite fraction, is highly depending on the long-range ordering of the carbon/polymer chains in the precursor materials. The purpose of graphitizing the asphaltene fibres is to obtain a measure on the quality of the carbon fibre produced and to identify any issues that need to be addressed to improve quality, e.g. sulfur content, mesophase requirements.

4) **To determine the mechanical properties of the graphitized carbon fibres:** The mechanical properties of the graphitized carbon fibres determine the performance of these materials as potential reinforcements in structural composites, for example. The purpose of measuring the mechanical properties of the graphitized carbon fibres is to benchmark their properties against those produced by PAN and pitch. Doing so, will provide away to assess the economic potential of this technology.

UPDATES TO PROJECT OBJECTIVES

Changes to the original project objectives were made for one of two reasons: 1) limitations in existing equipment and infrastructure did not enable the objectives to be met, and 2) restrictions imposed by the global Covid-19 pandemic and the related public health mandates prevented the objectives from being be met in a timely manner.

Changes in Technical Scope due to Limitations in Equipment and Infrastructure

1) *Characterization of asphaltene molecular structure using atomic force microscopy (AFM)*. AFM was supposed to be used to image individual molecules and provide insight into the type of molecules present in the asphaltene samples, e.g. island or archipelago structures. However, the AFM equipment available at the University of Calgary does not have sufficiently high vacuum and low temperature to achieve imaging at this atomic scale. Very few AFM system in the world are

capable of this type of characterization and therefore it was not possible to complete this component of material characterization. This task was removed from the project. Some insight into the molecular structure of the asphaltenes is provided through other means such as mass spectroscopy.

2) *Graphitization of carbon fibres.* Graphitization requires extremely high temperatures (~1500-3000°C) in an inert atmosphere [4]. Despite efforts to locate a high temperature oven, none could be found in the province of Alberta. This was identified to be a serious problem for this Alberta-based initiative. Without the infrastructure to graphitize the carbon fibres, carbon fibres could only be stabilized. Objectives that depended on achieving graphitized fibres, e.g. mechanical testing of graphitic fibres, could not be met as a result.

Changes due to Reduced Operating Capacity because of COVID-19 Precautions

1) *Compounding of polymer additives into asphaltene samples*. The microcompounder that was originally intended to be used to mix the polymer additive and asphaltene samples is located in a high traffic laboratory area, which has severely restricted its occupancy in efforts to prevent the spread of the COVID-19 virus. As a result, the ability to rigorously mix the polymer additive with the asphaltenes was reduced to manual mixing. Therefore, experiments describing the miscibility of the asphaltenes may not be as accurate as if a microcompounder were to have been used. An extensive investigation of the polymer additives is highly recommended when access to the microcompounder is permitted.

2) *Confirmation of Stabilization and Carbonization by Fourier Transform Infrared Analysis (FTIR).* Due to reduced operating capacity of across university labs, FTIR analysis could not be completed on the stabilized and carbonized in time for this report.

3) *Confirmation of Stabilization and Carbonization by Elemental Analysis (EA).* Due to reduced operating capacity of across university labs, EA analysis on the stabilized and carbonized samples could not be completed in time for this report.

PERFORMANCE METRICS

As per the Performance Metrics listed in the CFGC Application Form, the project targets for this phase included two students and two publications. The former objective was completed, as more than two graduate students and research assistants across all laboratories have collaborated on this project and were able to successfully complete this study. No article has been submitted or published yet, mainly due to focusing much of the effort towards feasibility completing this project within the given timeline of six months. However, our team expects to publish the findings of this project in a scientific article in the near future.

In addition, other metrics were also listed for future phases of the project and these included future investments, filed patents, partnership agreements, new products/services, and spin-off companies. If

given the opportunity to move onto Phase II and III of the CFGC, our team is confident that all these metrics can completed upon successful delivery of the project.

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

ANALYSIS OF THE ASPHALTENE SAMPLES AND POLYMER ADDITIVES

Thermal Analysis

Thermal analysis was performed using thermogravimetric analysis (TGA) (Discovery TGA 550, TA Instruments, USA) and differential scanning calorimetry (DSC) (DSC 3, Mettler Toledo, USA). These devices were used to obtain data such as the degradation properties, thermal stability, and phase transitions of each sample tested. The provided asphaltene samples were analyzed using both these techniques, while the polymer additives were only examined under DSC analysis.

For this study, eight different polymer additives were analyzed. Some of these additives were chosen through literature based on previous successful studies with asphaltenes and others were chosen based on a presumed compatibility with the asphaltenes using their known chemical functional groups and other molecular properties.

Rheology

Rheological measurements were used to examine the flow and deformation behaviour of the asphaltene samples under shear forces. A rheometer (MCR 302, Anton Paar, Austria) was utilized in two modes: 1) rotational rheometry to measure the viscosity at different shear rates, and 2) oscillatory rheometry to measure the storage and loss moduli at varying shear strains.

Molecular Weight Distribution

A number of spectrometry analyses were conducted to examine the molecular weight distribution of each asphaltene sample. A high temperature gas chromatograph (GC-2010, Shimadzu, Japan) was used for the high temperature SimDist GC-FID analysis of the solid sample and a gas chromatograph-mass spectrometer (GCMS-QP2010, Shimadzu, Japan) was used for the GS-MS analysis on the liquid sample. The former was used to for the purpose of obtaining the distribution over a higher temperature range, as the molecules of the solid sample could not be completely observed by GC-MS. In addition to this, both samples also underwent FTICR-MS by employing a Fourier transform ion cyclotron resonance mass

spectrometer (Solarix 12 Tesla, Bruker Daltonics, USA). This analysis technique provided an ultra-high resolution of the distribution, with the added ability to identify specific molecules within the samples.

MELT SPINNING EXTRUDER

Melt spinning of the Alberta oil sands asphaltenes was done on a single filament extruder that was design and built in-house. This extruder consists of a heater block, nozzle, spool, stand, and PID controller. As shown on Figure 1, a brass heater block is mounted at the top of the stand and is powered by a cartridge heater which is controlled by the PID controller based on the readings of the thermocouple. To melt spin, the asphaltene samples are fed into a small inlet located at the top of the heater block, where it is heated to a specified temperature. Once heated, the melt is extruded out of the 1.0 mm nozzle and is converted into a single strand fibre. The fibre is then attached and wound onto the spool which is controlled by a stepper motor and set at a specified pulling speed. In utilizing this melt spinning extrusion device, pure asphaltene samples, as well as some containing polymer additives, were successfully converted to fibres.

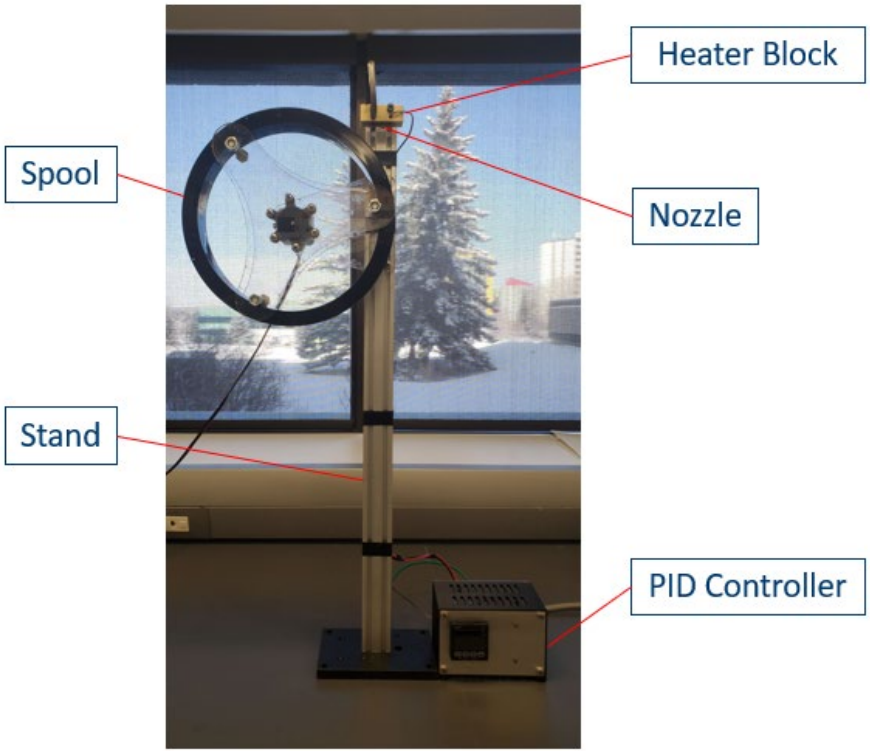

Figure 1. Photograph of the custom melt spinning extruder device.

MICROSCOPY

Imaging of the melt spun fibres were done using an optical microscope (DM6000 M, Leica, Germany) to determine microstructure, size, and other physical properties.

A confocal microscope (SP8 X, Leica Germany) was used to observe the structure and miscibility of the fibres containing polymer additives.

HEAT TREATMENT PROCESSES

After melt spinning the asphaltene samples, a series of heat treatment processes were applied to convert the asphaltene fibres into carbon fibres. Stabilization and carbonization were performed by utilizing a tube furnace coupled with a gas feedthrough system (TCVD System, Blue Waves Semiconductors, USA). Stabilization is normally performed at lower temperatures (200-400°C) in an air atmosphere, which enables oxidization and promotes cross-linking of the bonds within the fibres to make it thermally stable or thermoset [3,4,5]. Likewise, carbonization is performed at higher temperatures (800-1200°C) in an inert atmosphere to remove all non-organic elements and preserve the carbon atoms within the structure, while continuing to promote cross-linking and crystallization [3,4].

Thermal data from TGA and DSC analysis in the previous characterization stage were used as a basis to define the heat treatment processing parameters. Stabilization was performed at 250°C for 2 h at a temperature rate of 2°C/min in an ambient air atmosphere. Carbonization was performed at 1000°C for 1 h at a temperature rate of 5°C/min, with argon being supplied as the inert gas.

Optical and confocal microscopy was used to observe any microstructural changes in the melt-spun fibres caused by the heat treatment processes.

To confirm whether the fibres were stabilized and carbonized, a Fourier-transform infrared spectrometer (Cary 630, Agilent, US) and elemental analyzer (8900 ICP-QQQ, Agilent, US) have been planned. FTIR is to be used to determine if oxidation occurred within the stabilized fibre through observing any changes in the oxygen-containing groups measured in the spectrum. EA was to be used on the carbonized fibres in evaluating the changes in content of each organic element.

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

MILESTONE 1: CHARACTERIZATION OF ALBERTA OIL SANDS ASPHALTENES

The bitumen-derived asphaltenes from the Alberta oilsands were provided from Alberta Innovates' Sample Bank. Two type of asphaltene samples were included along with their respective Analytical Summary Sheet that outlined properties pertaining to its chemistry and composition. As shown on Figure 2, the asphaltenes included a powder-like solid sample denoted as S1 and a low-viscosity liquid sample denoted as L2.

Figure 2. Photographs of the asphaltene samples S1 (left) and L2 (right) provided by Alberta Innovates' Sample Bank as received.

Thermal Analysis

DSC and TGA thermal analyses were first conducted on both asphaltene samples. As shown on Figure 3, the TGA was run from 25-800°C in both nitrogen and air environments. In these experiments, mass loss as a function of temperature was measured. This provides insight into degradation temperature of these compounds. The results on Figure 3 indicated that the S1 sample started to rapidly degrade at approximately 400°C in both air and nitrogen, while the L2 sample began to exhibit significant mass lass before 75°C as shown in Figure 3. The S1 sample was shown to retain approximately 31.8% of its original mass in the inert nitrogen atmosphere. As asphaltenes generally contain heavier molecules, this indicated that the S1 sample contained a much higher asphaltene content than its L2 counterpart (which retained approximately 6.1%) by measuring the mass leftover at the end of the experiment. In oxidative air environments, the mass of both samples experienced total mass loss, indicating complete degradation occurred at high temperatures.

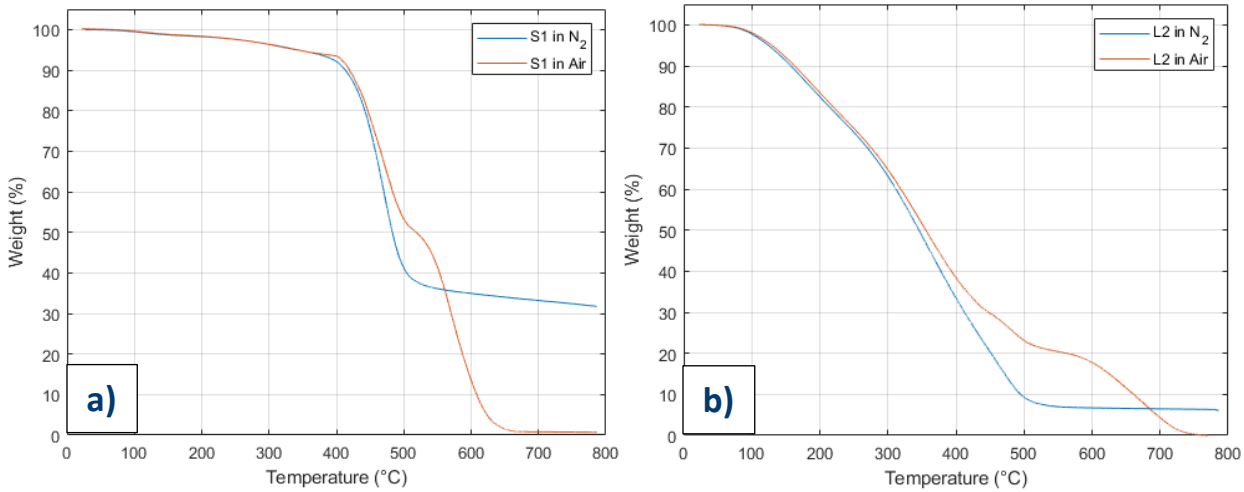

Figure 3. TGA results depicting the mass loss of samples S1 (a) and L2 (b) run from 25- 800°C in nitrogen and air environments.

The results of the DSC analyses are presented in Figure 4. As shown, both the S1 and L2 samples were cycled first from -90°C to 600°C in a nitrogen environment to observe any phase transitions or chemical reactions that may occur in this temperature range. The results were in agreement with the results from the TGA analysis, as the S1 and L2 samples showed evidence of degradation at temperature above 400°C, as indicated in the first cycle of each experiment.

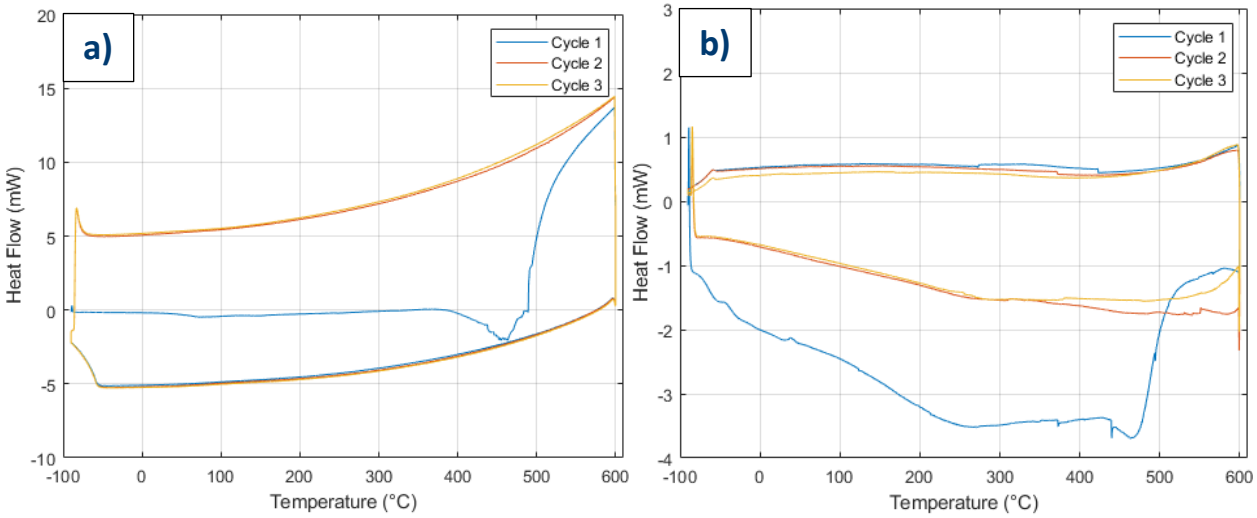

Figure 4. DSC results of samples S1 (a) and L2 (b) run from -90°C to 600°C in a nitrogen environment. Heating curves are the lower set and cooling curves are the high set of curves. Curves are to be read in a counterclockwise manner.

DSC measurements were repeated at a lower temperature range, from -90°C to 350°C, reduce the probability of degradation at high temperatures. The results are shown in Figure 5. Sample S1 seemed to have a glass transition temperature around 60°C during the first heating cycle, but location of the glass transition temperature shifts and the prominence of the step decreases with each additional heating cycle, indicating that the sample was undergoing changes during the measurement. Coking is one possibility as the sample was heated at sufficiently high temperatures for this to occur. Sample L2 behaved consistently between temperature cycles as the majority of the other molecules had already reacted or degraded at lower temperatures in the first cycle, leaving only stable compounds.

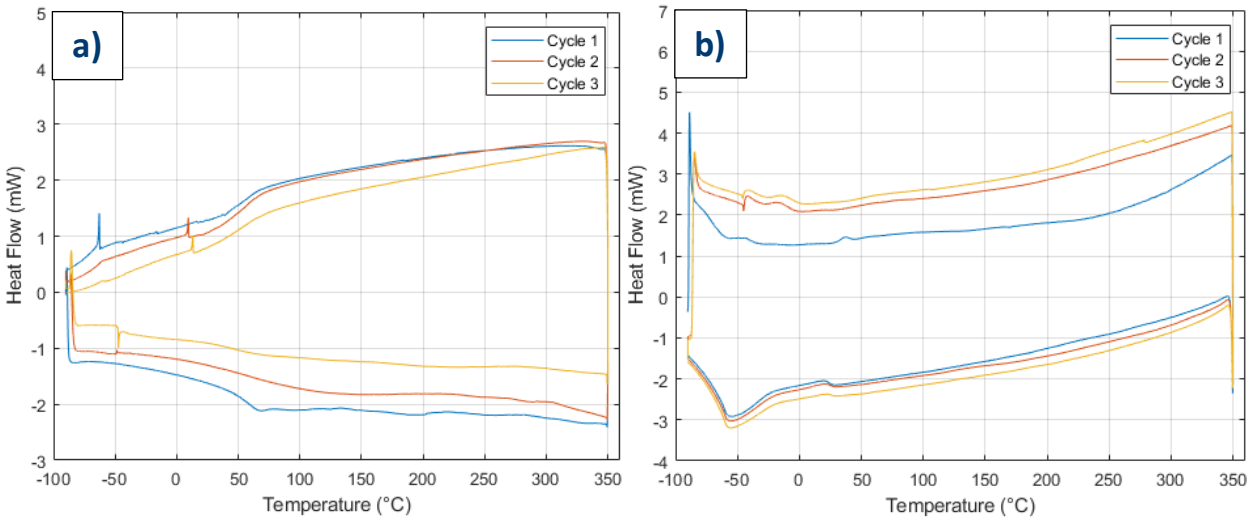

Figure 5. DSC results of samples S1 (a) and L2 (b) run from -90°C to 350°C in a nitrogen environment. Heating curves are the lower set and cooling curves are the high set of curves. Curves are to be read in a counterclockwise manner.

DSC measurements were conducted on each of the procured commercial polymers that were assessed as potential materials to be compounded with the asphaltene samples prior to melt spinning. The measured thermal properties of each polymer are tabulated on Table 1 and were used to gauge their compatibility with the Alberta oil sands asphaltenes. From the results obtained, it was determined Additive 2, Additive 3, and Additive 8 were the best options to melt spin with the asphaltenes, as they were the most thermally stable at elevated temperatures. More research is required to determine the potential chemical interactions that may occur between the functional groups of the asphaltenes and additives as they are heated to decide which is most suitable for incorporating into the melt spinning process.

Table 1. Properties of tested polymer additives obtained from their respective DSC curves.

Polymer Additive	Glass Transition Temperature (°C)	Melting Temperature (°C)
Additive 1	<100	N/A
Additive 2	<150	>300
Additive 3	>150	>300
Additive 4	<150	N/A
Additive 5	<0	<200
Additive 6	<150	N/A
Additive 7	<50	N/A
Additive 8	<100	>250

Molecular Weight Distribution Analysis

The results for the high temperature SimDist GC-FID analysis of the S1 sample using ATSM D7469 and the GC-MS analysis of the L2 sample using ASTM D2887 are presented in Figure 6. As shown, the majority of the molecules in S1 fall within the first third set (C1-C34) of the fractions. It was also observed that there is a relatively high concentration of larger molecules with high boiling points in the sample as the normalized fraction of the sample spiked within the highest temperature ranges (C98-C100). In contrast, the distribution of the L2 sample was fairly consistent throughout the temperature ranges tested. Higher concentrations appeared in the C16-C17 and C32-C33 fractions, as more of these molecules (~5% for both) were present in the sample.

FTICR-MS analysis provided more details about the nature of the compounds, including the compound class distribution and double bond equivalents. Figure 7 provides a partial dataset obtained from FTICR-MS showing the compound class distribution of both S1 and L2. These results confirm the presence of sulfur in greater concentrations in S1 than in L2. Figure 8 shows the hydrocarbon class distribution per double bond equivalent group, indicating a high concentration of unsaturated bonds as expected for the asphaltenes. Further work in interpreting the MS data is required to elucidate more information about these materials.

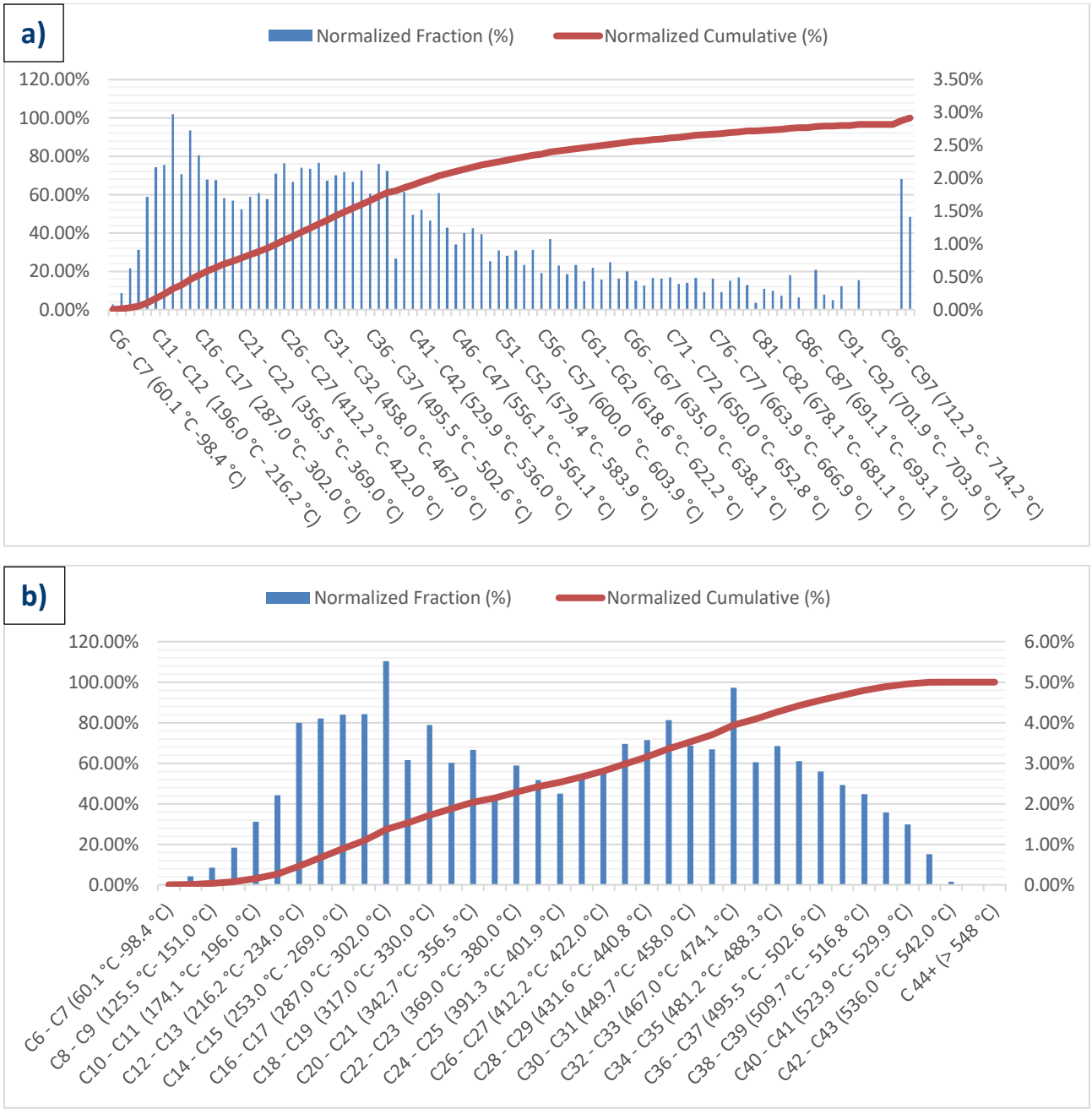

Figure 6. Distribution of molecules based on their boiling point using high temperature SimDist GC-FID on the S1 sample (a) and GCMS on the L2 sample (b).

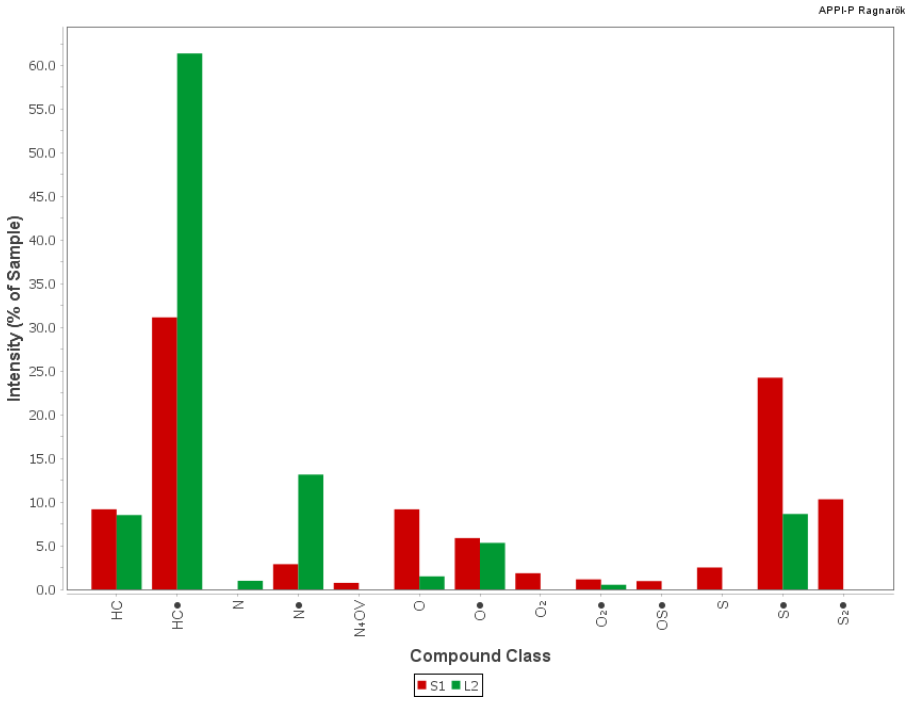

Figure 7. Distribution of compounds classes on samples S1 and L2 from FTICR-MS analysis.

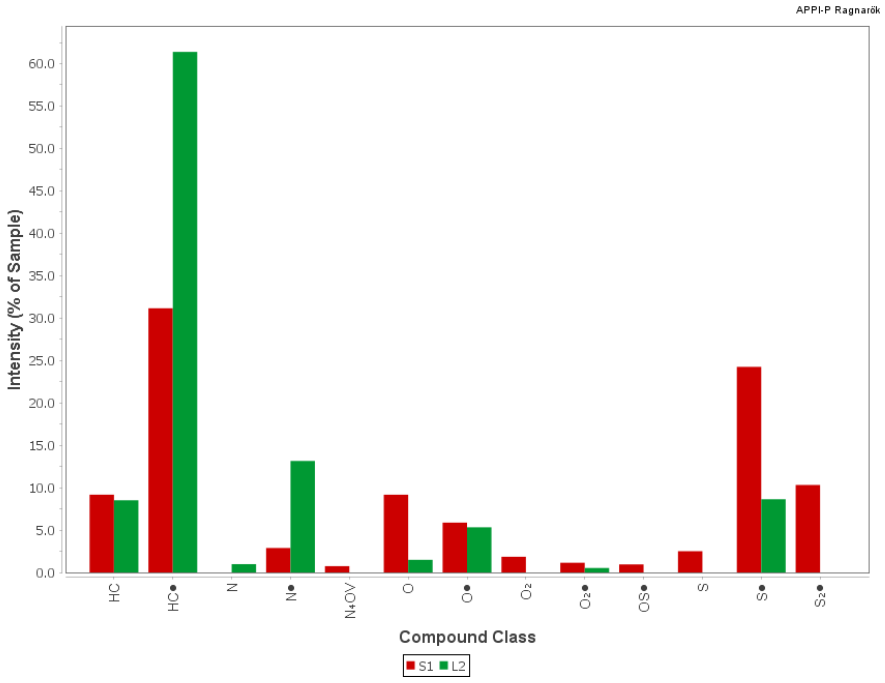

Figure 8. Hydrocarbons class distribution per DBE group from samples S1 and L2.

Hand-pulling Tests

To determine a reasonable temperature range for rheological measurements, the asphaltene samples were heated on a hotplate to various temperatures and attempts were made to draw fibres by hand using a spatula. Results of these qualitative investigations are presented in Table 2 and Table 3. It was only possible to draw fibres from S1 as the L2 samples were of too low viscosity.

Table 2. Outcomes of hand-pulling experiments for S1.

Temperature (°C)	Classification	Observations
100	Hard	Still powder; no melting observed; sticks to spatula
120	Hard	Still mostly powder; still sticks to spatula
140	Hard-Melted	Mostly powder on top; buildup of clumps on the bottom of the vial
160	Melted	Increased buildup of clumps; soft and sticky when poked
180	Melted	Increased melting; fully hard on bottom; difficult to pull
200	Melted	Increased melting; softer texture; diffcult to pull
220	Melted	Melted at bottom; still difficult to pull
240	Melted-Pullable	Melted at bottom; a little easier to pull; like taffy
260	Pullable	Less viscous; much easier to pull
280	Pullable	Less viscous; very easy to pull
300	Pullable	Less viscous; tacky; thinner fibres
320	Pullable	Very soft; less resistance/tackiness
340	Pullable	Very tacky; easy to pull
360	Pullable	Less viscous; more liquidity
380	Pullable	Less viscous; more liquidity

Table 3. Outcomes of hand-pulling experiments for L2.

Temperature (°C)	Classification	Observations
100	Liquid	less viscous, runny
120	Liquid	even less viscous; like water
140	Liquid	very thin
160	Liquid	less viscous
180	Liquid	thin; like water
200	Liquid	still thin, less viscous
220	Liquid	still runny, the same as before
240	Liquid	more runny
260	Liquid	still liquidy
280	Liquid	very liquidy
300	Liquid	same consistency
320	Liquid	still liquid
340	Liquid	even less viscous; like water
360	Liquid	smoking, less viscous
380	Liquid	very liquidy; not viscous

Rheological Analysis

The temperature ranges in which rheological studies were conducted were chosen based on the thermal analysis previously completed, as well as initial hand pulls tests conducted. Because the S1 sample showed produced fibres in the hand-pull experiments between 240-400°C, rheological tests were done on S1 at temperatures of 250°C, 325°C, and 400°C. As noted in the DSC and in the hand pulling experiments, chemical changes occurred in the samples at higher temperatures, i.e. 400°C and this was confirmed in the rheology experiments through the observations of hysteresis. To allow for the experiments to be compared, the duration of the experiments was the same for all tests. As L2 did not produced fibres at any temperatures, rheological measurements on the L2 sample were done at 25°C and 100°C.

The results for the rotational are presented on logarithmic plots in Figure 9. As shown on Figure 9, the S1 sample demonstrated a clear shear thinning behaviour at each temperature, where the viscosity decreased over an increasing shear rate. Likewise, in Figure 9, the L2 sample exhibited a similar shear thinning behaviour decreasing in viscosity at 25°C, but not at elevated temperatures where the viscosity remained relatively constant at 100°C, indicated near Newtonian fluid behaviour.

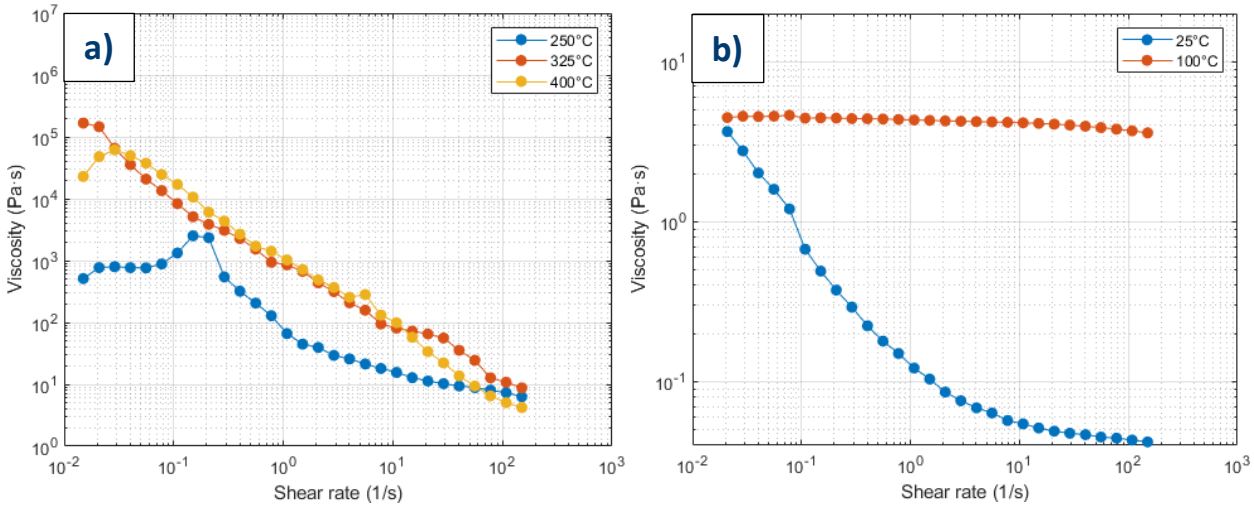

Figure 9. Plots of the rotational rheology experiments measuring viscosity of samples S1 (a) and L2 (b) over increasing shear rate.

Figure 10 provides more insight into the viscoelastic properties of the samples. The storage modulus (G') represents the elastic portion of the sample, while the loss modulus (G'') typically represents the viscous portion. Strain sweeps are powerful tool for characterizing complex fluid systems. In these measurements the frequency is fixed and the deformation or strain percent is progressively increased. Not only do these measurements identify complex fluids and soft solids as being linear (independent of strain amplitude) or non-linear viscoelastic, they also enable yield stresses to be estimated.

While viscosity of sample S1 remains similar at 325 and 400 °C, one can clearly see that G' and G'' in linear viscoelastic region (region where G' and G'' are independent of the applied strain) is higher at 325°C. Another important parameter is the critical strain, which corresponds to the crossover point between G' and G'', and is directly proportional to the material yield stress. As seen from Figure 10 a), G' and G'' in the linear viscoelastic region (region independent of the strain %) is the highest at 325 °C for sample S1. These results suggest that the optimal processing temperature for fibre spinning process is closer to 325 °C. The L2 sample on Figure 10 displayed some viscoelastic behaviour at room temperature, but not at elevated temperatures. L2 did not have sufficient melt strength for the formation of fibres.

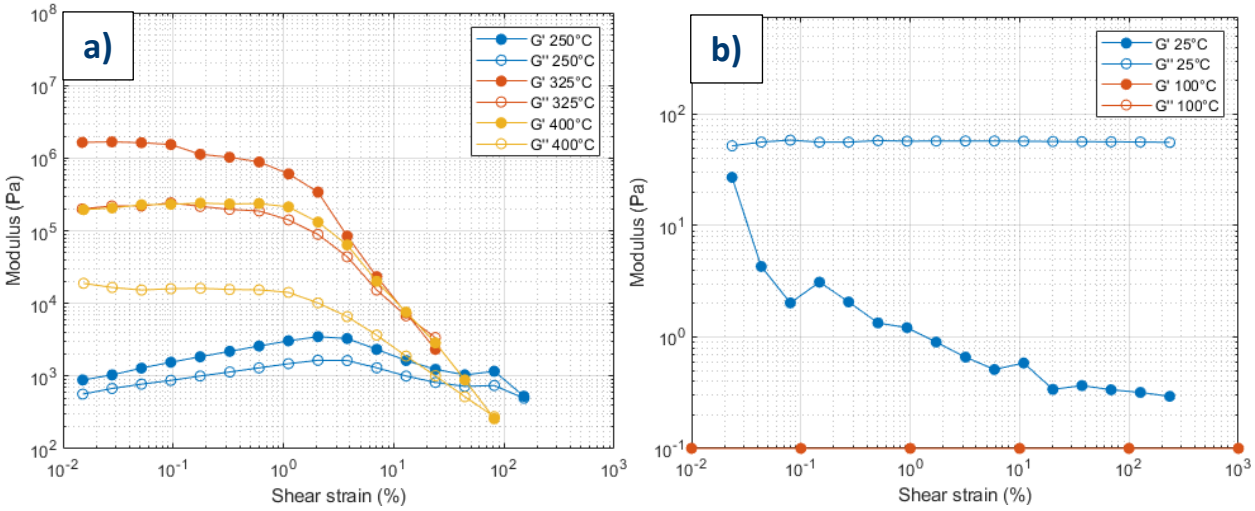

Figure 10. Plots of the oscillatory rheology experiments measuring storage (G') and loss (G'') moduli of samples S1 (a) and L2 (b) over an increasing shear strain.

The results shown here confirm that rheology-based design can be effectively implemented for screening asphaltene samples as well as finding optimal processing conditions for the fiber spinning process.

MILESTONE 2: MELT SPINNING OF ALBERTA OIL SANDS ASPHALTENES

From the data collected during characterization of the Alberta oil sands asphaltenes, it was decided that only the S1 sample was to move forward in the melt spinning process, and not the L2 sample. S1 sample demonstrated much higher potential to be successfully melt spun into fibres as it had good melt strength and was more thermal stable at elevated temperatures. The L2 sample did not have these qualities and would be too difficult to be melt spin without some form of chemical pretreatment.

A parameter study was done to determine the influence of melt temperature and drawing speed on the diameter of the melt spun fibres. Three different extrusion temperatures (280, 320, and 360°C) and

drawing speeds (6, 12, and 18 m/min) were used in different combinations for a total of nine parameter sets. The diameter of the melt spun fibres were taken from 10 different locations to gage repeatability and spread in the data. The results, presented in Table 4, were ultimately inconclusive as there were no definite trends on the fibre diameter at different processing parameters. It was presumed that the tested spool speeds may have been far too low in order to obtain any meaningful results. Therefore, the stepper motor driver on the extruder was upgraded so that even higher spooling speeds could be attained. In the future, another systematic study should be conducted to manipulate the same parameters during melt spinning at a wider processing range to more clearly observe their effects.

Table 4. Fibre diameters results of melt spinning at different processing parameters.

Processing Parameters		Diameter Measurements (µm)	
Extrusion Temperature (°C)	Spool Speed (m/min)	Average	Standard Deviation
280	6	48.08	8.56
280	12	38.16	7.22
280	18	31.69	10.89
320	6	34.83	5.49
320	12	54.85	13.66
320	18	38.42	9.44
360	6	52.31	6.88
360	12	39.15	9.53
360	18	43.76	5.85

Using the upgraded motor, the S1 sample was successfully melt spun using at a temperature of 325°C (highest viscoelastic signature in rheology tests) and a spooling speed of 25 m/min (highest speed the device could be run). As shown on Figure 11, fibres were typically melt spun from a droplet formed at the tip of the nozzle and the result produced black, hair-like asphaltene fibres that were found to be quite brittle and delicate. The melt spun asphaltene fibres were examined under an optical microscope to examine its physical properties and obtain accurate diameter measurements. An average diameter of 28.82 ± 4.58 µm was obtained and some of these images are depicted in Figure 12.

Although the faster motor achieved major improvements in fibre diameter compared the older and slower motor, the fibres were still not completely uniform throughout the process, as they ranged in diameter from 19.87-37.39 µm. This can be attributed to the fact that the flow of the melted asphaltene through the brass block and out of the nozzle was not consistent throughout the entire process. It is suggested

that adding some degree of back pressure in the system may aid in the overall extrusion process and provide more consistent results. It was also presumed that because the fibres were also initially hand-pulled before mounting to the spool, some time may have been needed to achieve a steady state process. Although the fibre diameters were measured from portions of the fibre believed to be produced under steady state conditions, it is possible that more time was needed to achieve steady state. Not achieving a steady state process would attribute to the inconsistencies in the measured fibre diameters.

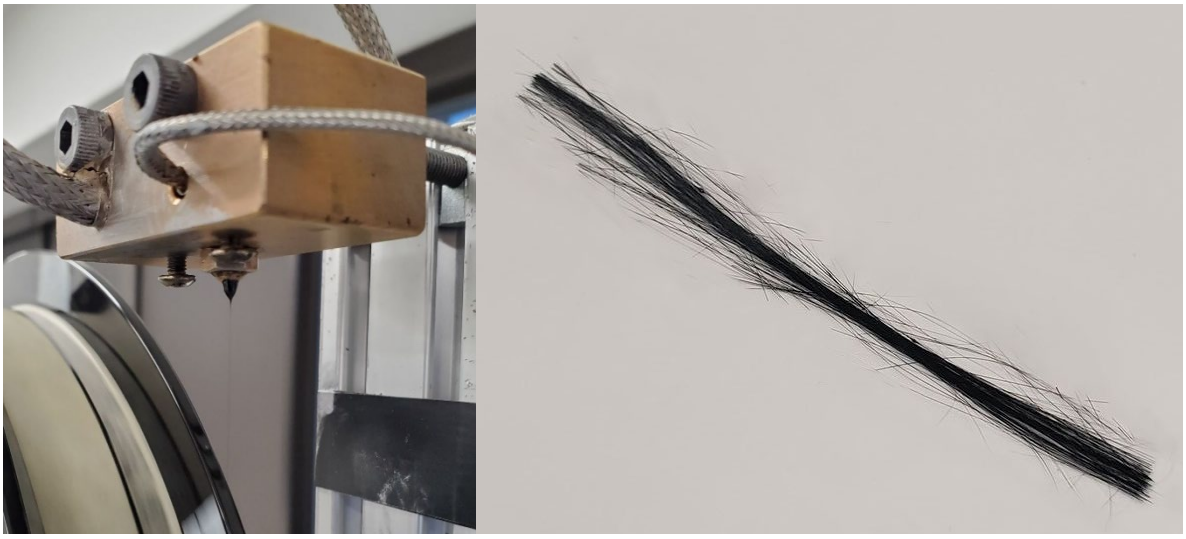

Figure 11. Melt spun asphaltene fibres produced from the custom melt spinning extruder.

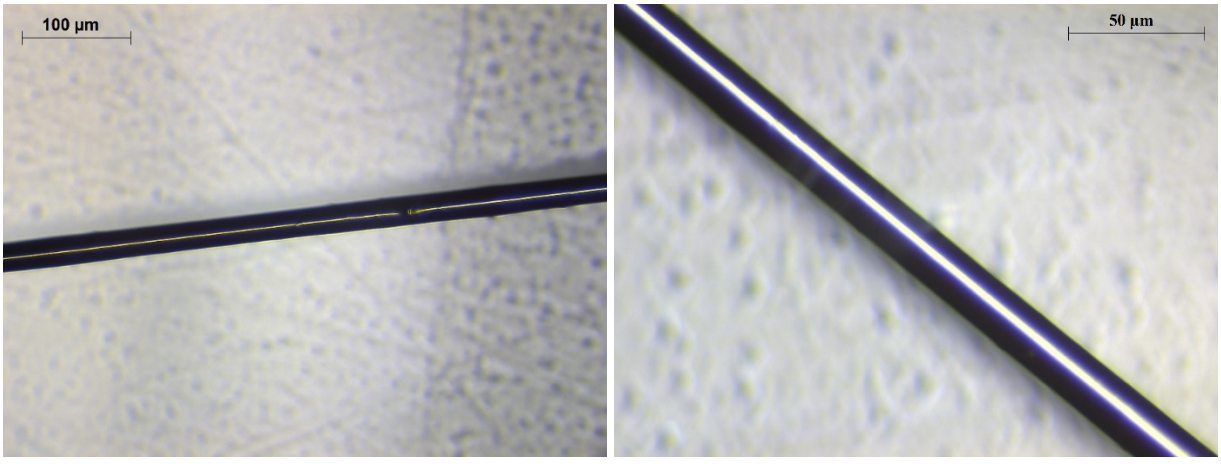

Figure 12. Optical microscopy images of a melt spun asphaltene fibre.

In some melt-spinning trials, the S1 asphaltene sample was compounded with 5 and 50 wt% Additive 3. Because the micro-compounder could not be accessed due to the limited operating capacity related to

Covid-19 precautions, the asphaltenes and additives were melted and mixed in the brass heating block of the melt-spinner. Despite the imperfect mixing method, fibres could be produced from the asphaltene-Additive 3 mixtures.

The microstructure of the resulting mixtures with additives was probed by confocal microscopy, relying on the autofluorescence properties of the asphaltenes. Figure 13 shows the example of the melt spun carbon fibre with no additives, (left), carbon fibre prepared by blending S1 sample with 5% of Additive (middle) and with 50% of Additive (right). As evident from the images, the fluorescence signal is weaker and nonfluorescing (black) regions are visible when the additive is present, most notably signified by the presence of black strip of the 50% Additive 3 sample. In addition, the diameter of the fiber is slightly higher when Additive 3 is present. This indicates poor miscibility between the Additive 3 and S1 asphaltene sample at these concentrations or these processing conditions. As the maximum occupancy in the lab where the microcompounder is located has recently increased, we will conduct a more comprehensive study to determine the most suitable additive and blending conditions, and how these factors impact crystallinity and mechanical strength of the derived carbon fibre.

These preliminary results show that monitoring the shift in the excitation/emission spectra and intensity of the sample fluorescence can serve as a quick screening tool for the suitability of the additives used in the melt spinning process prior to investing significant efforts into melt spinning and mechanical characterization of the derived carbon fibres. To the best of our knowledge, this is the first utilization of confocal microscopy to characterize microstructure of the derived carbon fibres.

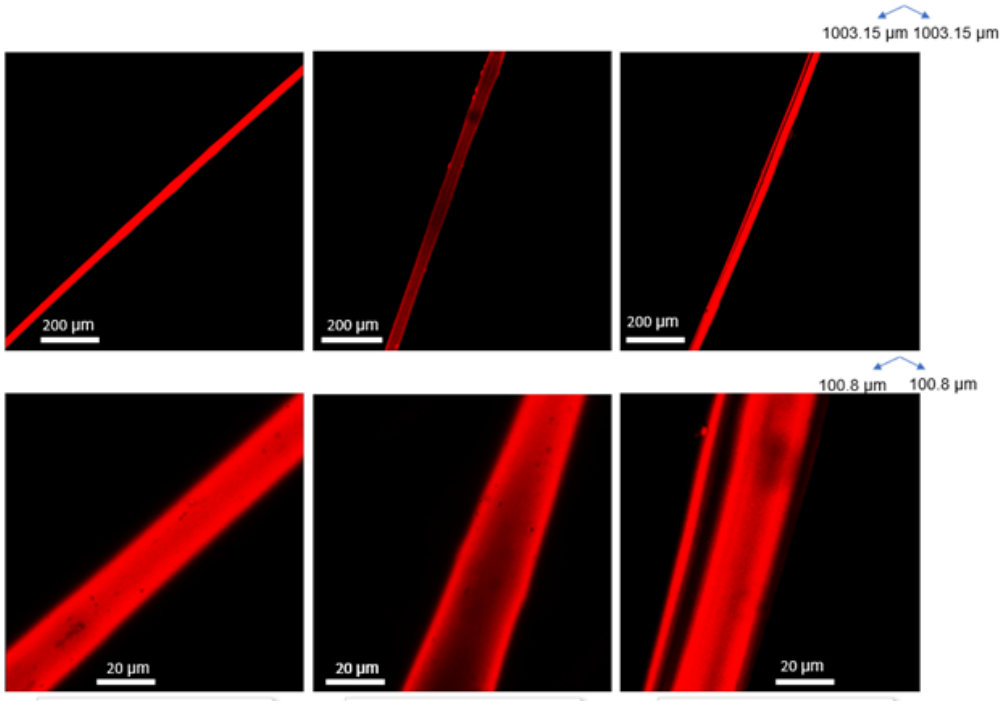

Figure 13. Confocal microscopy images of melt spun asphaltene fibres with 0 (left), 5 (middle), and 50 wt% (right) Additive 3.

MILESTONE 3: STABILIZATION AND CARBONIZATION OF MELT SPUN FIBRES

The melt spun asphaltene fibres were stabilized in a tube furnace at a temperature of 250°C for 2 hours at a ramp rate of 2°C/min in an open-air atmosphere. The fibres were then carbonized at elevated temperatures of 1000°C for 1 h at a rate of 5°C/min in argon. In both these processes, the fibres were treated in small batch quantities. Unfortunately, this resulted in some of the fibres tending to agglomerate within the tube furnace as they were heated. Regardless, both stabilized and carbonized fibres were still analyzed under an optical microscope to observe their physical properties and these images are depicted on Figure 14.

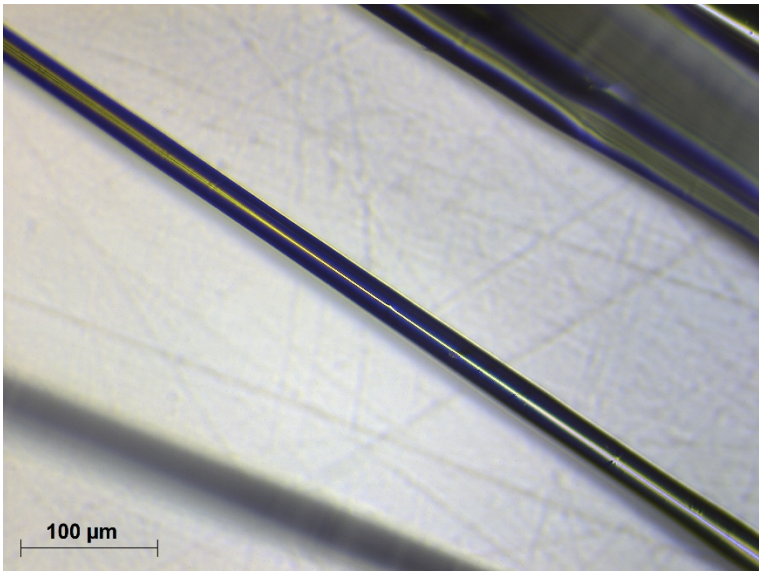

Figure 14. Optical microscopy image of a stabilized (a) and carbonized (b) asphaltene fibre.

The size of the stabilized fibres did not change much, with average diameter measuring 26.45 ± 5.39 µm. However, the stabilized fibres seemed to strengthen a bit and were less brittle compared to the melt spun fibres. The carbonized fibre are currently still being produced and analyzed in the lab. However, it is expected that carbonized fibre should be much stronger and stiff in comparison to the previous resultant fibres. All other organic elements, aside from carbon, should be removed with the fibre comprised of mostly graphitic carbon structures. It is still unknown how the presence of sulfur impacts the stabilization, carbonization, and graphitization.

To confirm if these heat-treated fibres were in fact stabilized and carbonized, FTIR and EA were planned. FTIR results are currently pending. FTIR will provide the ability to monitor the changes in any oxygen-containing groups within the stabilized fibres, assessing the extent of oxidation occurring through the generated spectra. Furthermore, EA is planned to be performed to measure the changes in organic elements (carbon, hydrogen, and nitrogen) within the fibre. The results from both these analyses will be

used to determine if any modifications to each of these processes will be necessary in order to achieve a more ordered and graphitic fibre.

4. MILESTONE 4: MECHANICAL TESTING OF ALBERTA OILSANDS ASPHALTENE-DERIVED CARBON FIBRES

Mechanical testing was not done as the asphaltene fibres could not be graphitized in this project due to the lack of an oven with sufficiently high temperature.

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

Characterization of Alberta Oil Sands Asphaltenes

In characterizing the Alberta oil sands asphaltenes provided by Alberta Innovates' Sample Bank, a large body of material data detailing specific chemical and molecular properties of each sample was successfully collected. The results gathered from the rheological, thermal, and molecular weight distribution analyses provided valuable insight on the properties contained within each sample and how they should be handled during the next step in the melt spinning process. The solid S1 sample showed excellent potential in its ability to be melt spun into fibres. It demonstrated good thermal stability at elevated temperatures (up to around 400°C) and it also displayed a high viscoelastic signature at 325°C, indicating that it was most ideal to convert these asphaltenes into fibres using these conditions. The other liquid L2 sample was deemed unable to be melt spun, as it displayed poor thermal stability and viscoelasticity at high temperatures. Through this, it was apparent that this asphaltene sample was too difficult to handle directly without a comprehensive pretreatment method in converting it into a viable precursor for melt spinning. Therefore, the S1 sample was the only asphaltene carried over to the next step in melt spinning. The data collected also provided valuable information that was used to define an acceptable processing window in the melt spinning process. The characterization methods used in this study provided a high level of insight on the properties and types of molecules prevalent within Alberta oil sands asphaltene. This information may prove useful beyond this project, as other innovation pathways for asphaltenes are continuously explored and tested.

In many studies investigating the production of pitch-based carbon fibres, a variety of different pretreatment processes are commonly used to convert the initial feedstock into a viable precursor for

melt spinning [3]. Needle coke is a high-value product that can be used for the manufacture of carbon fibre due to its high crystallinity and purity [6]. To obtain needle coke, a precursor that contains a generally low sulfur and metal content and high aromaticity is required. Therefore, in order to produce highly graphic carbon fibre used in high performance materials, it may be worthwhile to investigate methods in removing sulfur and other trace metals from the asphaltene samples. This may include using chemical or thermal pretreatments as mechanisms to reduce the amount of these impurities. In the future, more research will be conducted to explore this technology and knowledge gap further and develop methods to successfully obtain a high purity precursor viable for melt spinning.

Melt Spinning of Alberta Oil Sands Asphaltenes

The S1 sample was successfully converted into fibres using the custom melt spinning extruder without any pretreatment. From the data collected during characterization, the asphaltenes were successfully melt spun at an extrusion temperature of 325°C and a spool speed of 25 m/min. The result of this process produced a thin, black asphaltene fibre that was very delicate and brittle to the touch. Using optical microscopy, the diameter of the fibres measured 28.82 ± 4.58 μm. However, these measurements contained inconsistencies that were most likely due to the uneven flow of the asphaltenes traveling through the nozzle. A trial run of melt spinning the asphaltenes with a 5 wt% Additive 3 was also performed. No difference in the structure or composition could be observed between the pure asphaltene fibres and fibres that contained the polymer additive through confocal microscopy, indicating that the polymer may have been completely miscible in the melted asphaltenes.

During the melt spinning process, fibres were simply spun from the given asphaltenes without being pretreated in any way, using heat as the only mechanism to convert the asphaltenes into fibres. Therefore, it is unknown whether any particular formation of a mesophase was achieved. Mesophase formation is the homogenous self-assembly of planar aromatic molecules [7], and within our sample, there could have been a variation in growth of these domains as well as inconsistencies in the asphaltene molecules themselves. This is due to thermal cracking and other condensation reactions happening as the asphaltenes are heated up. In order to verify a formation of a mesophase, the use of a hot stage microscope is generally required to monitor any of these changes at elevated temperatures. Another phenomenon that is likely to occur during the melt spinning process is coking. The formation of coke is a temperature and time dependent fouling reaction. As a result, the temperature and duration of heating can lead to varying degrees of coking during the melt spinning process. According to the characterization data, coking can begin anywhere from 280-350°C. The quality of coke and its crystallinity is very much dependent on the precursor used in the melt spinning process, as mentioned in the previous section. Although these initial findings aid in the methodologies of producing a highly graphitic carbon fibre, further research is still required to understand the kinetics of coking within our process as asphaltenes are heated in the brass block.

Stabilization and Carbonization of Melt Spun Fibres

After the melt spinning process, the asphaltene fibres underwent stabilization and carbonization heat treatments. The resultant fibres were observed under both an optical and confocal microscope to observe

any physical changes in its size and microstructure. Through initial observations, the stabilized fibres appeared to strengthen a bit and became less brittle. The diameter of the stabilized fibre from optical microscopy did not change significantly, measuring 26.45 ± 5.39 µm. Carbonized fibres are still currently in the process of being heat treated in the lab, with the expected results of producing stronger and stiffer fibres.

Further FTIR and EA tests are set to be performed in order to examine any changes in the chemical structure of the stabilized and carbonized fibres, respectively. FTIR tests will verify if oxidation occurred by observing any changes in the amount of oxygen-containing groups. Likewise, EA will be used to confirm if carbonization occurred by measuring a change in the quantity of each organic element within the stabilized fibre.

Mechanical Testing of Alberta oilsands asphaltene-derived carbon fibres

Mechanical testing was not done as the asphaltene fibres could not be graphitized in this project due to the lack of an oven with sufficiently high temperature.

BROADER IMPACTS

This project addressed many fundamental questions about the material properties of Alberta oilsands asphaltene that were previously unknown. In addition to the material characterization data presented, these findings suggest that the procedures used to produce the low sulfur material L2, destroyed most of the high molecular weight molecules, rendering the material unsuitable for melt spinning without further chemical treatment.

The results of Phase I indicate that Alberta oilsands asphaltenes can be melt spun into fiber form, however more investigations are necessary to determine the quality of the melt-spun fibres and the long-range order obtainable. The conversion of Alberta oilsands asphaltenes is a topic that is worth investigating. Even if the quality of the carbon fibres that can be produced from asphaltenes is not sufficient for use in structural composites, there is a market for these materials in applications with lower mechanical demands.

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

In this phase of the project, the viability of converting bitumen-derived asphaltenes from Alberta oil sands into carbon fibre and the production fundamentals associated with this process were investigated. Initial characterization of the provided asphaltene samples offered valuable insight in understanding relevant properties of the material, as well as helping define an appropriate processing window for melt spinning. The melt spinning process was accomplished using a custom-built extruder, which successfully produced pure asphaltene fibres without the need for pretreatment. Following this, stabilization and carbonization heat treatment processes further strengthened them by providing a cross-linking mechanism for the asphaltene fibres to oxide and crystallize. Through these processes, a carbonized fibre was successfully produced from pure asphaltenes. The methods introduced in this study successfully addressed some of the knowledge and technology gaps associated with the ability of manufacturing carbon fibres through asphaltenes via melt spinning and how it compares to current traditional methods with other precursor materials.

The gaps associated with the need to generate a mesophase and the impacts of impurities were also partially investigated. Some knowledge was gained on each of their potential impact in the melt spinning process and on the resultant fibres during the treatment. More work is still required to confirm if a mesophase is being generated during melt spinning as the asphaltene is heated. In addition, methods to remove some of the metal impurities to an acceptable limit will also be investigated, as it may prevent the crystals within asphaltene fibre from becoming highly ordered during the melt spinning process.

Further research will be planned to directly address these topics in order to continually improve and optimize the quality of carbon fibre that is produced.

CLEAN ENERGY METRICS

The results of this project do not change the Clean Energy Metrics as described in the Workplan, Budget and Metric workbook. This project was one of twenty a short explorative projects to test various ideas as Alberta Innovates and its partners move towards the commercialization/implementation target.

PROGRAM SPECIFIC METRICS

In the Workplan, Budget and Metric workbook submitted in the grant proposal, this project aimed to have a carbon fibre producer participating for scale up. The results of this project have left many questions that must be addressed with regards to the process of making carbon fibres as well as the quality of the carbon fibres producible. Although, the applicant is in communication with carbon fibre producers, this technology is not yet ready for scale up.

PROJECT OUTPUTS

At the submission of this report, no publications have been produced from this study, as most of the research effort has been dedicated towards completing this project within the given timeline of six months. However, our team strongly believes that sufficient data and results have been obtained to contribute towards a scientific paper. Therefore, a journal article is planned to be drafted and submitted with the intent of eventual publication in the near future.

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

This project made advances in developing a new high-value market for Alberta oilsands asphaltenes which will eventually help diversify Alberta's energy-based economy with more emphasize on manufacturing and advanced materials development. The Alberta oilsands asphaltenes are currently being sold for US$ 40/ton, whereas non-aerospace grade structural carbon fibres are valued at US$ 21.50/kg. Therefore the economic impact of manufacturing value added materials from the asphaltenes are enormous.

ENVIRONMENTAL

This project made advances in developing a new high-value market for Alberta oilsands asphaltenes, which would otherwise be combusted for energy. The development of new lightweight reinforcement materials helps combat GHG in two obvious ways. Firstly, by redirecting carbonaceous materials to high value products, less is available to be burned as cheap energy. Secondly, the replacement of heavy materials in transportation by lightweight structural materials reduces the amount of energy required per km of travel.

SOCIAL

In developing technologies to convert Alberta oilsands asphaltenes into carbon fibres, the project is part of a network of scientists and entrepreneurs that are seeking opportunities to create value for the province. As it grows and strengthens, this network may make Alberta more attractive for new businesses and investors.

BUILDING INNOVATION CAPACITY

This project supported the training of 5 HQP in Alberta, ranging from undergraduate interns to PhD students. Due to the short duration of this project, no degree programs were completed within this project. To complete this project, HQP had to design and develop new processes and procedures. Notably, a single filament melt spinner had to be designed and produced, and new approaches for imaging fibres in the confocal microscope had to be developed. To the best of our knowledge, this is the first report of monitoring microstructural evolution of carbon fibre as additives are introduced via completely non-invasive imaging method. Both of these tasks presented interesting challenges that the HQP had to overcome.

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

Further research is certainly required to improve upon the methodologies developed in the production of carbon fibre from Alberta oil sands asphaltenes investigated in this study. One of the more significant long-term goals for this project is to upgrade and design an improved melt spinning extruder module. Currently, this device can only produce single strand fibres and in order to optimize the process in achieving Alberta Innovates' eventual goal of producing pre-commercial carbon fibre, a new extruder would be built that could produce multiple strands and be delivered at a much larger scale. Further design upgrades will also include adding some back pressure to the inlet of the extruder to attain a more

consistent fibre diameter during the melt spinning process and modifying the spooling mechanism so that the asphaltenes can by spun at greater speeds.

Improvements in the stabilization and carbonization processes will also be considered in order to prevent the fibres from agglomerating during these heat treatment processes. In the future, a systemic study will be conducted by modifying parameters such as the temperature, heating rate, and duration during each of the stabilization, carbonization, and graphitization heat treatment processes. The effects of these parameters on resulting fibres will be continuously examined and further optimized to produce a highly graphitic carbon fibre. An oven that can graphitized the carbonized fibres at much higher temperatures will also be located and incorporated into the process.

More work is also required to investigate the suitability of the current precursor material used in the melt spinning process. Part of this includes the original plan of compounding additives into the asphaltenes and examining its effects on the structure and crystallinity of the resulting carbon fibre. If the carbon fibre is found not to be of sufficient quality, more methods will be tested in order find ways of enhancing the precursor before the melt spinning process. This may involve using typical chemical or thermal pretreatment methods to increase the softening point of the precursor while still maintaining good spinnability, which is ideal when melt spinning pitch-based carbon fibre [8].

It is also unclear whether a mesophase is being generated during the melt spinning process.

At this point, the effects of mesophase formation and coking on the asphaltene fibre structure and potential carbon fibre are still largely unknown. The formation of a mesophase will be evaluated in future studies to determine if this phenomenon is occurring within the asphaltene samples as it is heated and whether is it beneficial to the production process. The impact of coking on the resultant fibres during the melt spinning process is another area of interest that will need to be further studied. As mentioned, needle coke in particular is highly desirable in the production of carbon fibre because is highly crystalline. However, it is difficult to generate, as it can only be produced from a high purity and high aromatic feedstock. Therefore, this will most likely require treating the asphaltenes by removing the impurities such as metals and sulfur. More consideration is required to determine if this is a feasible route to pursue.

The eventual goal of next phase is to further investigate all the topics and potential pathways addressed in this study on asphaltenes and establish a successful method towards the production of carbon fibre. Throughout the duration of the project, a fair amount of collaboration and discussion has been conducted with another research group, who has been comprehensively focusing and researching different methods on developing an ideal asphaltene precursor. A potential partnership between our groups is currently being discussed for Phase II of the Carbon Fibre Grand Challenge in order to combine our expertise and fully bridge the chemistry and engineering knowledge expected of teams in future stages of the project.

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 final report of this project will be made available to the public two years after the project is completed. Confidential information that may be of commercial value as intellectual property has been redacted from the final public report.

All results will be shared with Alberta Innovates in confidence. Patents may be filed to protect valuable ideas and demonstration. Once all critical findings have been patented, or if the applicants decide that no patent protection is necessary, the findings will be published as an original scientific article.

This mode of dissemination is to protect industry interest in the potential technology and enable intellectual property rights to be filed, if appropriate.

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

As part of Phase I of Alberta Innovates' Carbon Fibre Grand Challenge, our team's objective was to advance concepts and test initial pathways in the production of carbon fibre from bitumen-derived asphaltenes from Alberta oil sands for high performance structural composites. A novel melt spinning method of manufacturing single strand carbon fibres was proposed. To begin, a variety of rheological thermal, and molecular weight distribution analytical techniques were employed to characterize and gather data on the properties of the provided asphaltene samples. The solid S1 asphaltene sample demonstrated good thermal stability and viscoelasticity at elevated temperatures, while the liquid L2 asphaltene sample did not. Therefore, the pure S1 sample was the only one used in the next step of the melt spinning process. Using the results from these tests, an ideal set of processing parameters for melt spinning pure asphaltenes were defined. Asphaltene fibres were successfully extruded at a temperature of 325°C and a spool speed of 25 m/min. Following this, the fibres were stabilized at 250°C and carbonized at 1000°C in a tube furnace to promote cross-linking and crystallization. Optical and confocal microscope images were taken after each step and the diameter of each were measured to be 28.82 ± 4.58 µm and 26.45 ± 5.39 µm for the melt spun and stabilized, respectively.

Carbonized fibres were successfully produced from the pure asphaltene samples without pretreatment and valuable data was gathered at each milestone of the project. A large body of material data was obtained for each asphaltene sample provided, which in turn was used to melt spin and heat treat the produced fibres. In this way, a better understanding of the fundamentals of carbon fibre production from Alberta oil sands asphaltene was also acquired. The knowledge gained from this project serves to provide many benefits to industry in delivering an initial conceptualization of producing a high value-added product from asphaltenes. Despite all these findings, there is much research to be done in continuing to advance the methods developed in this project. The next steps will involve upscaling the melt spinning process so that it can produce multi-strands fibres while maintaining more consistency throughout its production. More work will also be conducted on improving the precursor material to ensure that a highly graphitic carbon fibre can be manufactured. All the methods developed here will be continuously studied and improved upon with plans of continuing onto Phase II of the Carbon Fibre Grand Challenge and accomplishing the goal of producing of carbon fibres from Alberta oil sands asphaltenes.

L. REFERENCES

[1] S. Ko, J. Choi, C.W. Lee, Y. Jeon, "Modified oxidative thermal treatment for the preparation of isotropic pitch towards cost-competitive carbon fiber," *J Ind Eng Chem*, vol. 54, pp. 252-261, Oct. 2017.

[2] Program Guide: Carbon Fibre Grand Challenge – Phase I - 2020, Alberta Innovates, Edmonton, Canada, 2020, pp. 12.

[3] J. Liu, X. Chen, D. Liang, Q. Xie, "Development of pitch-based carbon fibers - a review," *Energ Source Part A*, Aug. 2020.

[4] M. Inagaki, *New Carbons - Control of Structure and Functions*, 1st ed. Kidlington, UK: Elsevier Science Ltd., 2000.

[5] S. Park, *Carbon Fibers*, 2nd ed., Singapore: Springer Nature Singapore Pte Ltd., 2018.

[6] M.R. Gray, *Upgrading Oil sands Bitumen and Heavy Oil*, 1st ed. Edmonton, Canada: The University of Alberta Press, 2015.

[7] S.R. Bagheri, "Mesophase Formation in Heavy Oil," Ph.D. Thesis, Dept. Chem. Mater. Eng., Univ. of Alberta, Edmonton, Canada, 2012.

[8] F. Qin et al., "From Coal-Heavy Co-refining Residue to Asphaltene-Based Functional Carbon Materials," *ACS Sustainable Chem. Eng.*, vol. 7, issue 4, pp. 4523-4531, Jan. 2019.