ALBERTA INNOVATES

1.1: 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.

ALBERTA INNOVATES

CLEAN RESOURCES FINAL PUBLIC REPORT TEMPLATE

PROJECT INFORMATION:

Project Title:	**Carbon fibre production using Alberta oilsands asphaltenes**
Alberta Innovates Project Number:	G2020000338 (202010058)
Submission Date:	March 15, 2021
Total Project Cost:	$119,600.00
Alberta Innovates Funding:	$50,000.00
AI Project Advisor:	Shunlan Liu

APPLICANT INFORMATION:

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PROJECT PARTNERS

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

RESPOND BELOW

The main project partner for this project is Alberta Innovates, and we appreciate for their supports.

A. EXECUTIVE SUMMARY

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

RESPOND BELOW

AOA asphaltene feedstock from Alberta sample bank has been characterized by CHNS elemental analysis, TGA-MS-FTIR, ATR-FTIR and SEM. Additional processing with toluene/pentane-methodology has been conducted for removal of maltenes and insoluble mineral residues. The CHNS results were used as a reference point to compare the AOA, the green fibre and the CF. We could track the nitrogen and sulfur contents in each step to find the effect on forming green fibre. The amount of nitrogen and sulfur did not have big effect on green fibre, and currently the effect on CF synthesis is unknow. TGA-MS-FTIR results also have shown the H2S and SOx formation around 500^{o}C under nitrogen. This information can be used in the future to optimize the CF synthesis to find the effect of sulfur contents in the green fibre.

The asphaltenes and purified asphaltenes have been successfully electrospun into asphaltene green fibres from small size to large size sample matt (30 x 20 cm) from different solvents at optimized conditions. However, we learned that the resulting asphaltene green fibres are very brittle, even after thermal treatment and stabilization up to 400 ^{o}C in air for many hours, the asphaltene fibres can be survived but they are crosslinked and fused together by sections and still lack of flexibility, preventing from additional thermal treatments towards stand-alone carbon fibres.

Hence, chemical modification to the AOA asphaltene feedstock becomes essential. Our chemical modification strategies and composition to the AOA asphaltenes have proved the outcome of homogenous sample systems that have been successfully spun into asphaltene green fibres by electrospinning as well as wet-spinning from small size to large size of samples. The feasibility for scale-up production has been evidenced through wet-spinning process that is more adaptable for industrialization. Furthermore, the resulting fibres have been thermally treated up to 400 ^{o}C in air for many hours and demonstrated certain flexibility by stretching and bending tests.

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

Alberta oilsands asphaltenes (AOA) contain numerous known polycyclic aromatic components with variable structures and many unknown components that have not yet been identified structurally. From previous studies by NRC, we have observed that AOA has ~8 wt% sulphur, ~2 wt% nitrogen and variable levels of metals, depending on what process technologies the AOA are obtained from.

We address three main opportunities in this project. The first is the purification of AOA feedstock. The second is the modification and optimization of purified AOA to produce a dope that is spinnable and transformable to CF, a critical step for CF manufacturing. The third is the implementation of an electrospinning method at a lab-scale using the AOA-derived dope as an entrant for CF production.

To produce either general-purpose (isotropic structure) or high-performing (anisotropic structure) CF, knowledge/technology gaps related to the mesophase requirement and the impact of sulphur, nitrogen and metals must be assessed. To investigate these gaps, we investigated both (i) thermochemical treatment to form AOA-based precursors and (ii) cross-linking of polyaromatic and heterocyclic compounds within AOA. In two studies [1-2] where it was attempted to make CF from asphaltene, both used heat treatment and/or cross-linking. The effects of sulphur, nitrogen and metals are currently unknown. For example, sulphur in AOA may generate defects in CF during the carbonization, however, few reports [3-4] suggest that sulphur is a catalyst for the growth of CF/carbon materials in the vapour phase using H_2S. Nitrogen is key for cyclization at the stabilization stage and polycyclic condensation through denitrogenation at high temperature in CF formation from polyacrylonitrile (PAN) fibres [5].

Chemical treatment of AOA is a significant challenge because not all components in asphaltene have characteristics similar or close to those of one-dimensional, infinitely-connected graphitic structures found in preform PAN fibres after stabilization/oxidization stage [5]. Cross-linking among graphitic structures is a pre-requisite for carbonization at high temperature to create CF. Direct carbonization of AOA can only lead to the formation of small domain graphene and graphite crystallites, which are too small to produce useful fibres. Few reports [6-8] considered chemical reactions to connect components similar to those in AOA, and this will be applied here.

Production fundamentals for AOA-based CF might be similar to those of pitch-based CF because of their similar origin, however, this remains to be validated [5]. Here, we focused on determining and optimizing the stabilization/carbonization conditions via parametric studies, including thermal treatments, and ratio of drawing and winding steps, for fabricating isotropic/anisotropic CF.

NRC not only has capacity for the scale-up of CF production but also has key international collaborations with the United States, South Korea, Germany and China that may be leveraged to establish global partnerships for large-scale AOA-based CF production and world-wide distributions.

[1] J. Eng'd. Fibers Fabrics 6:2 (2011) [2] ACS Sust. Chem. Eng. 7:4523−4531 (2019) [3] Adv. Funct. Mater. 19:1193–1199 (2009) [4] Carbon 32:569-576 (1994) [5] DOI: 10.1007/978-94-017-9478-7_2 [6] J. Energy Chem. 34:186-207 (2019) [7] JACS 142:4162-4172 (2020) [8] JACS, 142:3696-3700 (2020)

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

Technology Description

The scope of the project is to develop key technologies to convert Alberta oilsands asphaltenes (AOA) to carbon fibre (CF) and its commercial production. The project has three main tasks to address technological gaps. Milestone 1 will address the purification of AOA. Milestone 2 is the preparation of AOA-based precursors by chemical modification of the purified AOA from milestone 1. Milestone 3 is to investigate the spinnability of modified AOA-based precursor, its conversion into CF and the potential of large scale manufacturing.

The success of the technologies from this project will transform the wasted asphaltenes from the Alberta oilsands to carbon fibre as an economic product. This will inspire the Alberta oilsands companies and carbon fibre manufacturers for creating a reliable and low-cost CF production with additional values to the Canadian oilsands industry.

The key goals of the project are utilizing the wasted asphaltene produced from oilsands bitumen production processes and add value by transforming it into a feedstock for commercial CF fabrication. The following summarizes the three key goals in the milestones planned for this project.

- Establish a full characterization protocol of the asphaltenes provided by the program office and protocols for additional purification as needed.
- Developing spinnable AOA-based precursors which can be converted into CF
- Establish AOA-based fibre spinning protocols and demonstrate carbonized AOA-based fibre samples (CF) with certain flexibility and strength.

Updates to Project Objectives

The project objectives have remained the same. We have executed all the milestone described in the project except high temperature carbonization.

Performance Metrics

Table 1 is the performance metrics provided in the application for this project. We have provided the metrics so they match with the milestone provided in the application form and also to test the feasibility of the AOA for CF production. The targeted metrics have been all achieved except high temperature carbonization that has not been performed yet due to the time limitation.

The first metric is the fabrication of AOA asphaltene green fibres using the feedstock as received. The success of the metrics has been evaluated by the electro-spinning and wet-spinning process. The objective intends to find out whether the CF fabrication is achievable without using any modification to the AOA. The results have been shown in the project result section and the conclusion has been drawn.

The second metric is characterization of the AOA to understand the impurities and also find out any changes after the modification for CF precursors. The success of the metrics is evaluated by providing series of characterization performed to the AOA and also CF precursors. The results are provided in the project result section and discussed for more details.

The third metric is the chemical modification of the as-received and purified asphaltenes to trigger chemical reactions and assembly amongst asphaltene components with additives by initiating radical chemistry for large segment formation with homogeneity and spinnability. The success of this metrics is demonstrated with the experimental results from the modification of the AOA. The results are shown in project result section.

Fourth metric is thermal treatment that is part of the ongoing chemical modification reaction for aromatic cyclization and condensation as well as part of green fibre stabilization/oxidation for further carbonization processes to study and optimize the CF manufacturing. The success of the metric is evaluated by detailed thermal characterization of the AOA and CF precursors. The results are shown in the project result section.

The last metric is the carbon fibre demonstration, where the green fibres from as-received asphaltenes and chemical modified asphaltenes have demonstrated through electrospinning and wet-spinning processes. Their flexibility and mechanical strength have been visually tested. The carbonization of these asphaltene fibres have not been performed due to the time limitation. The results are also shown in the project result section.

Table 1 Project performance metrics

Metric	Project Target	Target
Fabrication of carbon fibre	*Validate the initial feasibility to fabricate AOA-green fibres using an electrospinning process in Phase 1.* *Validate the initial feasibility to fabricate AOA-green fibres using a wet-spinning process in Phase 1.*	*Achieved* *Achieved*
Impurity content tracking (e.g. Sulfur)	*To understand the mechanism of the reactions on the stabilization and carbonization process using AOA-based carbon fibres.*	*Achieved*
Chemical modification of the AOA asphaltenes	*Visual assessment of viscosity changes before and after modification*	*Achieved*
	Develop of homogenous and spinnable sample system *Discovery of proper solvent system*	*Achieved* *Achieved*
Thermal treatments	*Thermal treatment/stabilization of AOA green fibres in air up to 400 ^{o}C*	*Achieved*
Carbon fiber demonstration	*The spun AOA green fiber precursor oxidization/stabilization.* *Further carbonization beyond the above temperature.* *Characterize the mechanical property of the obtained carbon fibers and their morphology through electron microscope.*	*Achieved* *Not performed yet* *Not performed yet*

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

MATERIALS

Asphaltene preparation

Alberta oilsands asphaltenes (AOA) were supplied by InnoTech Alberta. As-received asphaltenes (S1) were treated using toluene/water interfacial separation to obtain ashes-free asphaltenes (S1-T/W-1), followed by the purification for the removal of maltenes by Energy, Mining, and Environment Research Centre of

National Research Council Canada (NRC) to obtain purified asphaltenes (S1-pent-1). Toluene (99.5%) and xylenes (99.9%) were purchased from EMD Chemicals (USA) and Fisher Scientific (USA), respectively.

Commercial polyacrylonitrile (PAN, Mw: 150,000) was purchased from Sigma-Aldrich and used as received. Acrylonitrile (>99%, Merck, Germany) containing 35-45 ppm monomethyl ether hydroquinone inhibitor was purchased from Aldrich and used as received. All other chemicals used in this project were purchased from Aldrich and VMR and used as received.

Asphaltene purification

Quantitative pentane-induced asphaltene precipitation is used to separate Maltenes. Asphaltene is dissolved in toluene and heated to 60 ^{o}C. Pentane is added slowly (1 drip per second) to the asphaltene solvent for precipitation. Vacuum filtration is used to separate asphaltene precipitate. Asphaltene are further purified by removing fine solids. Precipitated asphaltene is dissolved in toluene and centrifuged. The supernatant is collected and dried. The solid is washed with water and toluene

Modification of asphaltene

The as-received AOA S1 and purified S1-pent-1 were dissolved in their favorable major solvent and mixed with an unfavorable minor solvent that is more favorable for PAN in its solubility. To the reddish asphaltene solution system, acrylonitrile and a catalyst were added at room temperature, then the reaction mixture was maintained between 50 -65 ^{o}C for 24 hrs, and then the temperature was raised stepwise to their boiling point for an additional period time from 5hrs to 10 hrs. Afterward, in one scenario, incorporation of commercial PAN in solution by slowly adding, in another scenario, No commercial PAN incorporation to the reaction mixture. The resulting reaction mixture was concentrated by evaporating solvents under well magnetically mixing for preventing dry/solid sample out of the mixture. Finally, a concentrated solution or a homogeneous slurry was obtained and ready for fibre spinning process.

More details have been described in our submitted invention Form-1 (NRC-2021-100) in process for an US provisional patent application.

Equipment

Electrospinning

The electrospinning setup consists of a syringe pump (KD scientific, power input: 0.25 A, 250 V), a syringe with a metallic spinneret, a rotating collector, and a high voltage power supply. The syringe was mounted on the syringe pump to control the infusion rate and it was connected to a positive terminal of the high voltage power supply through the stainless-steel spinneret (18 Gauge) with an internal diameter of 0.84 mm. The rotating drum connected to the negative terminal of the power supplier was wrapped by a piece of aluminum foil for collecting fibre mats. The conditions of the electrospinning process are discussed in the project result section.

Wet-spinning

The wet-spinning setup consists of a syringe pump, a plastic syringe with a metallic spinneret (22G3/4, internal diameter of 0.7 mm), and a coagulation bath with double layered coagulants. The syringe was

mounted on the syringe pump vertically on an adjustable stage. The spinneret tip was immersed below the coagulant surface.

MATERIAL CHARACTERIZATION

TGA-MS-FTIR

Thermogravimetric analysis (TGA) was performed on the ashphaltenes as received (S1) and then on the processed ashphaltenes by toluene/water interfacial separation (S1-T/W-1) and by pentane induced precipitation (S1-pent-1) in order to gather information on the changes in sample composition due to processing of the ashphaltenes. A series of experiments were conducted in nitrogen purge with a constant heating rate of 5°C/min up to 800°C followed by a 15 min isotherm after which, the purge gas was switched to air for full oxidation of the material. The same experiments were also acquired while monitoring the evolved decomposition gases by both mass spectrometry and FTIR detection in an attempt to gain a better understanding of the released degradation species such as sulfur for example. The mass spectrometer was set to record the intensities of m/e from 10 to 100 over 50 seconds time periods while the FTIR recorded spectra (4000-600cm-1) over 4 seconds time periods. A final series of TGA experiments were conducted in air purge at a constant heating rate of 5°C/min up to 600°C.

The instruments used were: TGA model Q5000 IR from TA Instruments, MS model Thermostar from Pfeiffer Vacuum, FTIR model Nicolet 6700 from Thermo Scientific equipped with a TGA accessory.

CHNS

The Vario EL cube has an autosampler and ball valve that inputs the sample capsule into the combustion chamber. Helium is then purged through the system to remove any air. Oxygen is then flushed into the system (the sample size determines the amount of time it is purged) to initiate combustion and reduction. Once combustion and reduction is complete, Helium is purged through the system to allow the resulting Carbon dioxide, water, Nitrogen, and Sulfur dioxide to enter their respective adsorption columns and each adsorption column is purged separately to determine the actual concentrations using the thermal conductivity detector. The concentrations are determined using an internal calibration that is corrected by using a calibration standard (most commonly Sulfanilamide) for a daily factor drift correction.

SEM

Scanning electron microscope (SEM, SU3500, HITACHI) was used for investigating electrospun fibre product for their morphology, geometry and fibrous structures instantly while optimizing spinning conditions for success. The sample was either stickered on a piece of carbon tape or remained on the aluminum foil for SEM analysis. The voltage at 15 kV and sample distance about 6 mm are proper conditions for most of our samples tested.

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

PURIFICATION OF AOA FEEDSTOCK

S1 was purified as explained before in section D to see the effect of maltene on CF precursor formation and CF property. The results summarized in Table 2 were identical with the data provided from Alberta Innovates for this sample.

Table 2 – Purification results of the as received sample

Contents	Weight (%)
Asphaltene	77.0
Maltene	22.1
Solids	0.9

CHARACTERIZATION OF THE ASPHALTENE

TGA-MS-FTIR

TGA in Nitrogen purge

Thermogravimetric analysis (TGA) was performed on the asphaltenes as received (S1) and then on the processed asphaltenes by toluene/water interfacial separation (S1-T/W-1) and by pentane induced precipitation (S1-pent-1). Each sample was run in triplicates; the overlapping curves showed good reproducibility which denoted homogeneity in the samples. The first set of experiments was run in nitrogen atmosphere at a heating rate of 5°C /min up to 800°C. The purge gas was then switched to air for a full oxidation of the remaining char. The resulting TGA curves are showed in Figure 1.

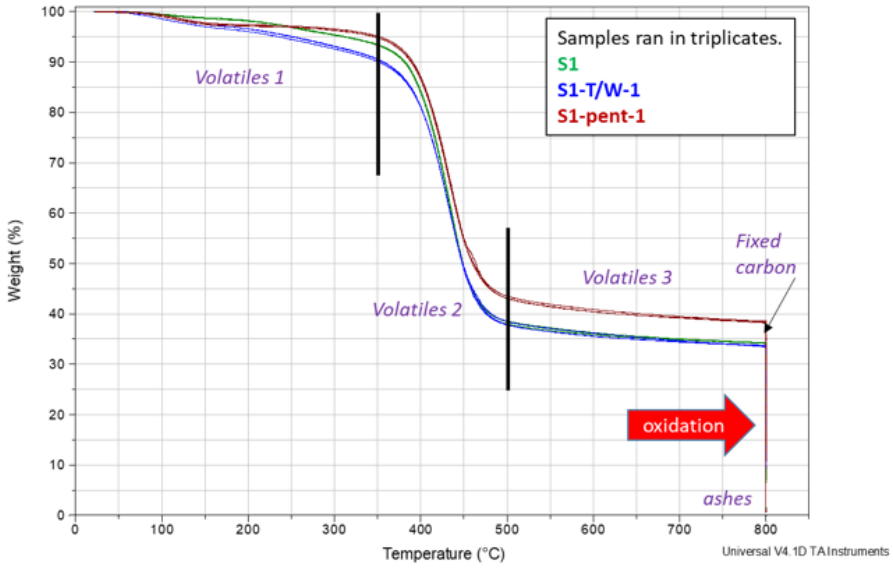

Figure 1. TGA curves for the asphaltenes as received (S1) and the processed asphaltenes (S1-T/W-1 and S1-pent-1) acquired using the following TGA procedure: 1- Isothermal at room temperature for 30 mins, 2- Ramp 5 °C/min to 800°C, 3- Isothermal for 15 mins, 4- Switch purge gas to air, 5- Isothermal 30 mins.

It was decided to divide and report (Table 3) the released volatiles into three weight loss categories along with the weight loss resulting from the oxidation stage and finally the weight of residual ashes.

Table 3. Weight loss obtained from TGA on asphaltenes as received (S1) and the processed asphaltenes (S1-T/W-1 and S1-pent-1) for different temperature ranges, oxidation and the weight resulting from the residual ashes.

	20°C to 350°C		350°C to 500°C		500°C to 800°C		20°C to 800°C		oxidation		residue	
	volatiles 1		*volatiles 2*		*volatiles 3*		*all volatiles*		*fixed carbon*		*ashes*	
sample	weight loss (%)	± STDdev (%)	weight loss (%)	± STDdev (%)	weight loss (%)	± STDdev (%)	weight loss (%)	± STDdev (%)	weight loss (%)	± STDdev (%)	weight (%)	± STDdev (%)
S1	6.6	0.1	55.0	0.4	4.5	0.4	66.2	0.1	32.5	0.1	1.0	0.1
S1-T/W-1	9.6	0.2	52.3	0.3	5.1	0.7	67.0	0.4	32.1	0.4	0.36	0.09
S1-pent-1	5.1	0.2	51.7	0.4	5.4	0.3	62.1	0.2	37.1	0.3	0.33	0.05

The curves and weight losses reported in Figure 1 and Table 3 were split in 3 sections identified as volatiles 1,2 and 3. The temperature range from room temperature to 350°C, volatiles 1, is attributed to low boiling point hydrocarbons. The main weight loss caused the release of volatiles, categorized as volatiles 2, and attributed to the decomposition of the weaker bonds holding the components of asphaltenes which are not part of the main aromatic systems. The weight loss which occurred at high temperatures (500 to 800°C) is likely the result of more bond cleavage resulting in re-arrangements in the aromatic core. The weight loss resulting from the oxidation step, at 800°C, revealed the percent of fixed carbon (solid carbon residue) remaining after volatiles were expelled and finally, the residual ash content.

The comparison of the TGA results for Table 1 reveals some of the differences between the raw asphaltenes as received and the processed ones. The toluene/water interfacial separation was done in order to remove some of the solids content from the asphaltenes and the results show a decrease from 1.0 to 0.36%. The pentane induced precipitation sample also had low solids content at 0.33% but also had more fixed carbon at 37.1% compared to 32% for S1 and S1-T/W-1 hence an increase in the more aromatic core structures and a decrease in the lower molecular weight species such as maltenes. It is clear from the volatiles 1 weight loss that toluene washed sample S1-T/W-1 had toluene trapped in the asphaltenes after the treatment. In fact, further TGA experiments coupled with mass spectrometry detection of the evolved gases confirmed the detection of toluene in both the processed sampled; it is worth mentioning that, adjustments to account for the trapped toluene would not affect the above conclusions. Finally, it can be visually observed from the curves of Figure X that the purified (S1-pent-1) sample clearly contains less of the lower temperature volatiles 1 and 2 (RT to 500°C) and more of the fixed carbon content; this is re-enforcing the above affirmation that pentane purification resulted in low molecular weight species removal while concentrating thermally stable, high molecular weight aromatic species.

TGA-MS-FTIR in Nitrogen purge

TGA with coupled FTIR and MS detection of the evolved gases was also executed on S1, S1-T/W-1 and S1-pent-1. The FTIR detection was not sensitive enough and also not selective enough to extract relevant information. On the other hand, it was possible with mass spectrometry to monitor the release of sulfur species which is of interest to this project since sulfur may have undesirable effects on carbon fiber. We were able to monitor fragments related to the release of H_2S, SO_2 and SO. Unfortunately, the nature of the asphaltenes molecules and their thermal degradation products had severe effects on the qualitative and quantitative test results. It was found, in nitrogen atmosphere, that large fragment molecules would condense in the TGA furnace and then undergo slow degradation; this rendered sulfur species monitoring unpractical since the signal detection could not be directly linked to real time sample degradation. In addition, the large fragments contaminated the MS system which had detrimental quantitative effects.

Figure 2 shows the detection of H_2S, which is associated with organic sulfur release such as saturated hydrocarbon fragments, and the detection of SO (fragment of SO_2) which is also associated with organic sulfur in the presence of oxygen atoms but is mainly associated with degradation of aromatic sulfur species. As mentioned above, the MS curves suffer from both the qualitative and quantitative perspective due to the nature of the ashphaltene degradation products but it was decided, nevertheless, to show the curve results.

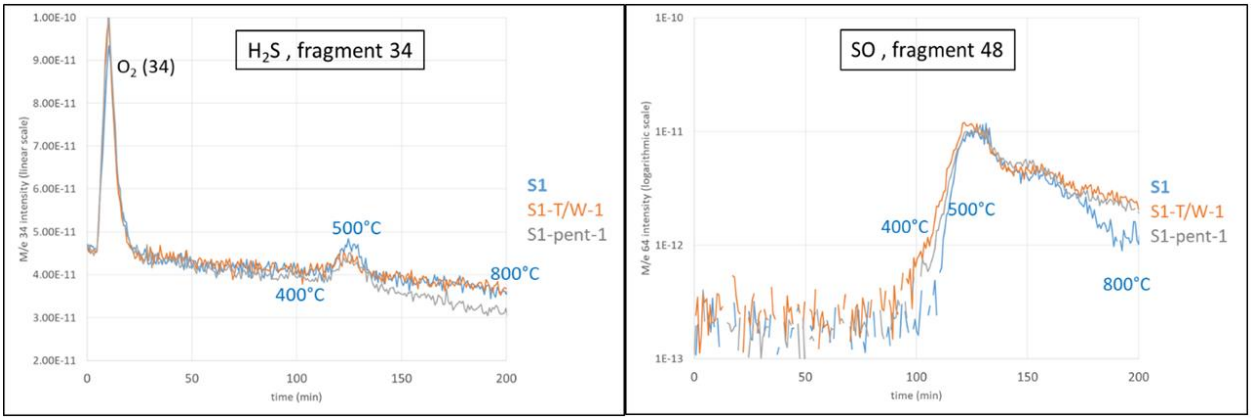

Figure 2. Evolution of sulfur species from the TGA as detected by mass spectrometry as a function of time and temperature in nitrogen purge: H2S fragment of mass 34 on the left and SO fragment of mass 48 on the right.

The tail end of the curves from 500 to 800°C (Figure 2, right) was a result of sulfur species condensed in the TGA furnace and slowly degrading as the temperature increased. The same tests done in air purge showed a single SO peak from 400 to 600°C with no tail end; a clear indication that under oxidizing conditions, large ashphaltene fragments undergo fast degradation rather than collecting in cold spots of the furnace.

TGA in Air purge

The TGA experiments ran in air for the same S1 and processed S1 samples are displayed in Figure 3. The TGA curves in air show the same first stage of degradation between 375 and 470°C as seen in nitrogen and resulting from decomposition of the weaker bonds holding the components of asphaltenes which are not part of the main aromatic systems. Temperature, more than the nature of the purge gas, is therefore causing bond cleavage. On the other hand, the presence of oxygen has a dramatic impact on the destruction of the aromatic core as opposed to the previous nitrogen purged experiments where a stabilization of the char's weight loss was observed. The second stage of degradation in air showed a faster rate of weight loss than the first stage, as revealed by the steeper slope in the 470 to 500°C range. It is worth mentioning that the samples had a tendency to generate bubbles in air near the degradation temperature (375°C); the bubbles interfered with the purge gas flow resulting in an unstable balance hence irregular curves around 375-400°C.

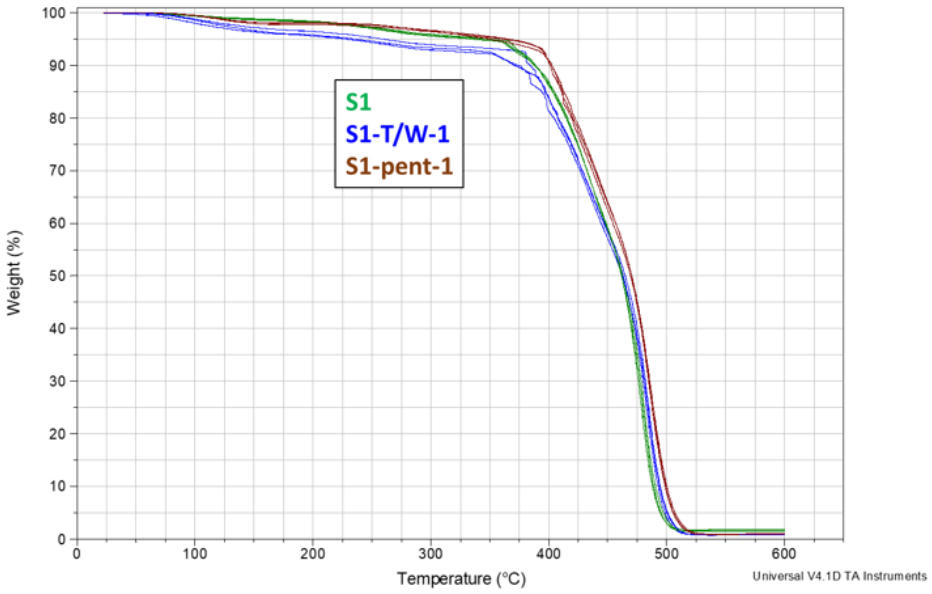

Figure 3. TGA curves for the asphaltenes as received (S1) and the processed asphaltenes (S1-T/W-1 and S1-pent-1) acquired using the following TGA procedure: 1- Isothermal at room temperature for 30 mins, 2- Ramp 5 °C/min to 600°C, 3- Isothermal for 15 mins.

CHNS

Figure 4 shows the result of CHNS analysis of the asphaltene samples. When the as-received sample (S1) was compared with processed asphaltene (S1-T/W and S1-pent), weight percent of the nitrogen was decreasing from 2.3 to 1.1 wt%. However, the sulfur amount increased from 7.8 to 8.3 wt%. S1-fiber (Tol) and S1-fibre (Xyl) samples are green fibres from S1 sample dissolved in toluene and xylene respectively. During spinning process we could observe the reduction of nitrogen and increase in carbon. S1-pent-3 (1) and S1-pent-3 (2) were collected during the preparation of S1-pent-3 fibers. S1-pent-3 (1) was those failed to be collected on the rotating drum and it was collected from the spinneret/the sample travelling from the spinneret to the collector. S1-pent-3 (2) is the fibre that was on the rotating collector. CF-13, CF-21, are CF-22 fibre samples are the green fibres from modified S1. CF-13 was mixed with commercial polyacrylonitrile (PAN) during the modification. The result also indicates the obvious increase of nitrogen. The solvent used in the chemical modification contains nitrogen, which likely participates in the reactions. CF-21 and CF-22 were modifies using pyridine and xylene as solvents, respectably, without using commercial PAN. Two solvents were used to test the effect of nitrogen in the solvent. No obvious change in the nitrogen was observed between CF-21 and 22, however, slight change in sulfur was observed, 7.8 and 8.2 wt% for CF-21 and 22 respectively.

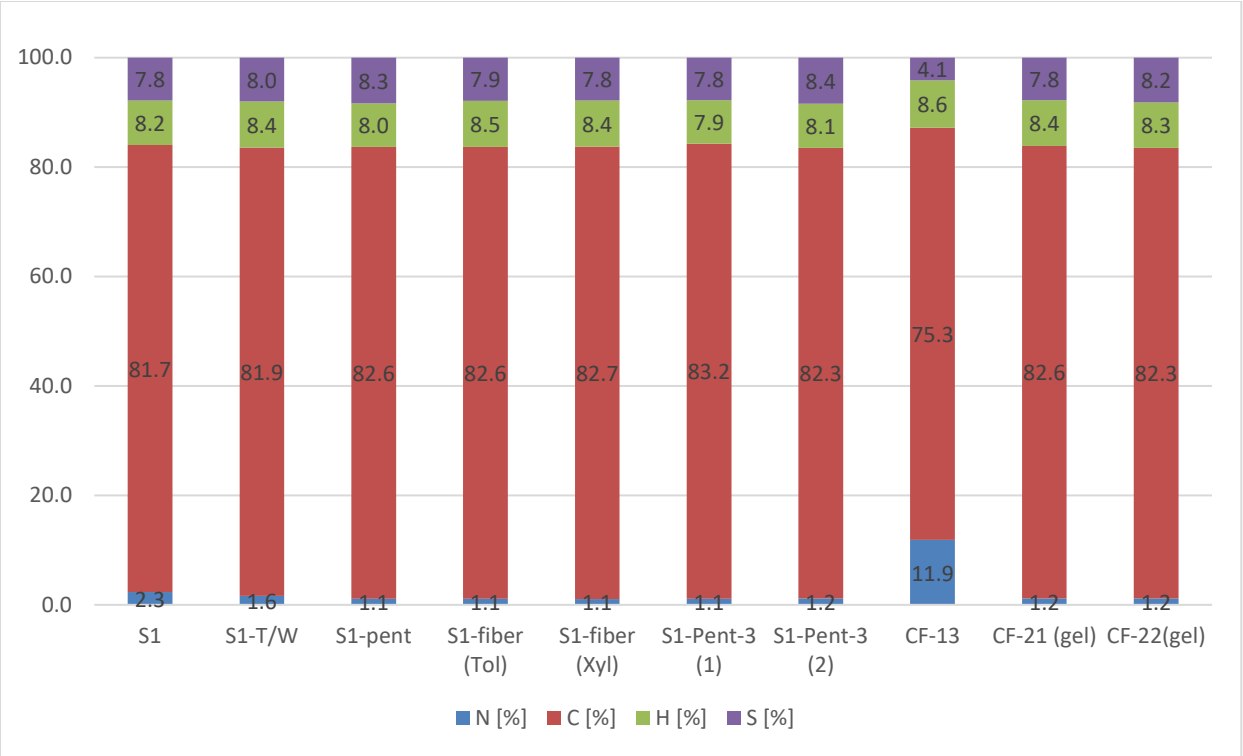

Figure 4 CHNS of asphaltenes and CF feedstocks

Preparation of AOA–based carbon fibre precursor (AOA-based green fibres)

Non-modified AOA-based green fibres using as-received asphaltene (S1) and its pentane-precipitated purified asphaltene (S1-pent-1)

(1) Protocol establishment of AOA-based green fibres from as-received S1 in toluene by electrospinning

Electro-spinnability of as-received asphaltenes (S1) in toluene was investigated. S1 is very soluble in toluene. Proper solution concentration of S1 and electrospinning parameters (feeding rate, working voltage, spinning distance and rotation speed of drum collector) have been optimized, and the final protocol of green fibre formation from S1 in toluene has been achieved.

Our study revealed that the solution concentration at 50 wt% gives the best quality and highly aligned S1-green fibres with the electrospinning conditions at the electric field of 60 kV/m, the feeding rate of 5 µL/min and the rotation velocity of drum collector at 280 rpm, as shown in Figure 5(a) and scaled sample shown in Figure 5(b), (c) and (d).

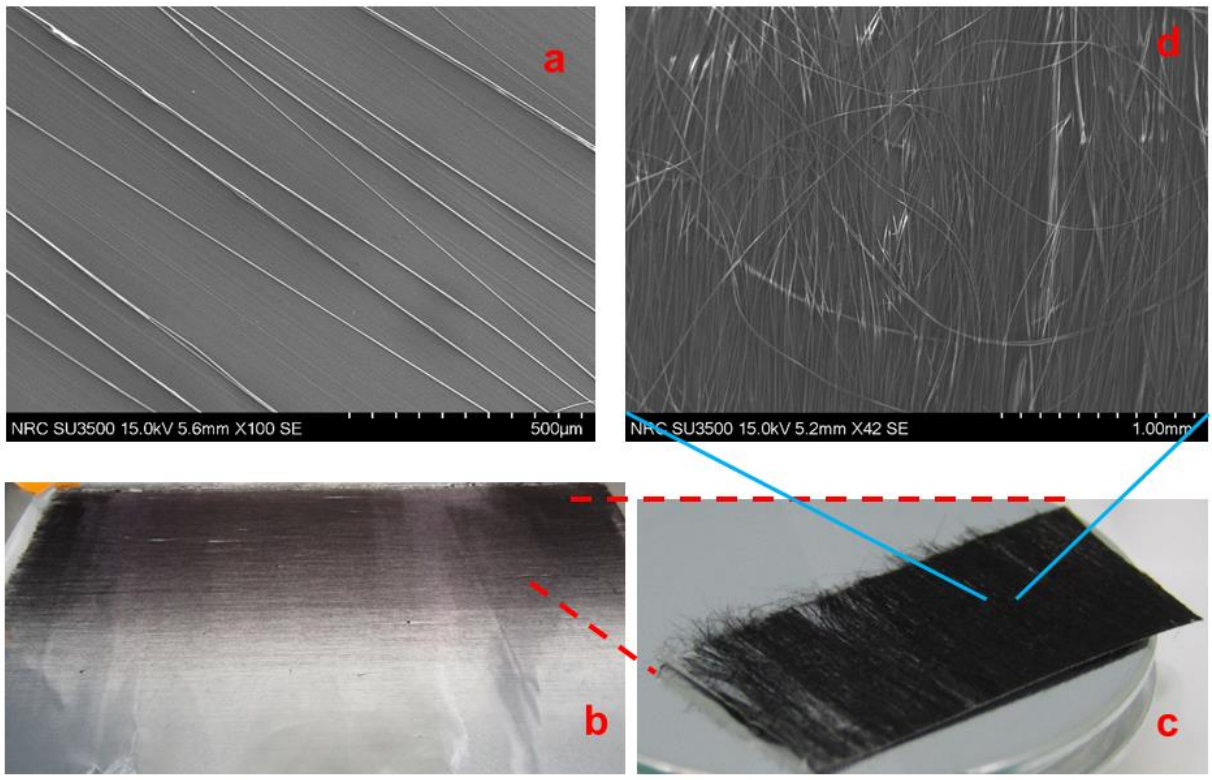

Figure 5 S1-green fibres electrospun from toluene solution at 50 wt% with electrospinning conditions: electric field 60 kV/m, feeding rate 3 µL, drum speed 280 rpm

Other cases have been studied as well. The solution concentration of S1 in toluene at 60 wt% is not practically operational for electrospinning process, lower than 50 wt%, the resulting spun product is either short fibres, mixture of short fibres and droplets or completely droplets as illustrated with their SEM images in Figure 6. These results are correlated with the report by Natarajan [1], indicating that sufficient solution concentration needs for enough aggregation to mimic high molecular domain as required in the electrospinning process [2].

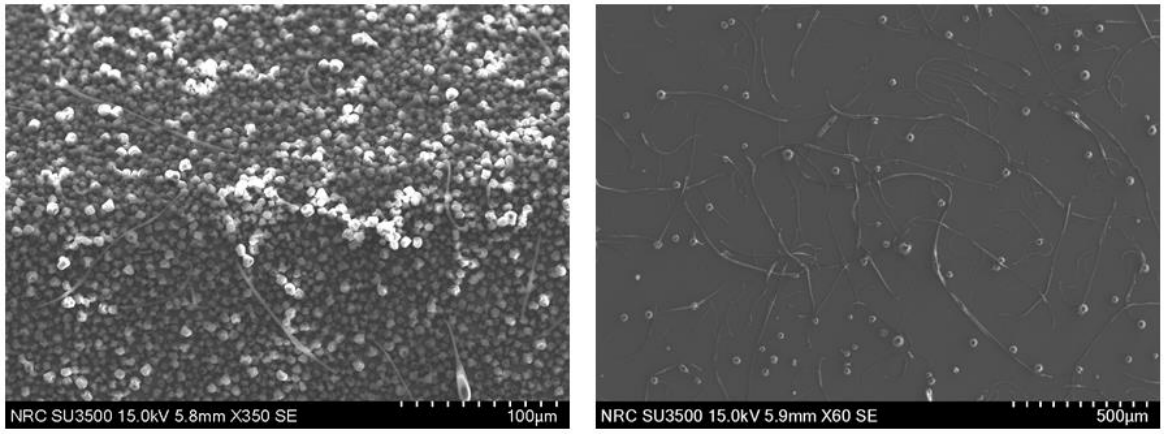

Figure 6 SEM images of electrospun S1 from toluene: left side 30 wt% and right side 40 wt%

The drum speed was also optimized at given feeding rate and electric field, we found that the 50 wt% solution of S1 gives fully aligned fibre mats at relatively low drum speed of 280 rpm in comparison with the literature report for other type of polymeric material such as polyvinylidene fluoride fibres that get aligned at 2500 rpm [3]. The reason of the high alignment at such low drum speed is unclear yet and further study is expected.

We have clearly observed that the obtained individual fibres are extremely brittle, they are quickly broken and chopped into small pieces under the microscopic electrobeam focus if one fibre has a space underneath by another crossover fibre as shown in Figure 7.

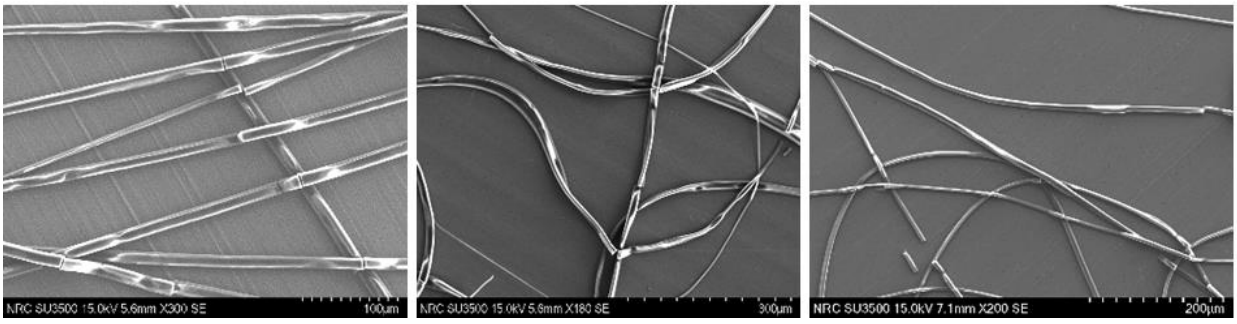

Figure 7 SEM images of individual S1-green fibres and their brittleness under electromicroscopic beam focus

It is in the hope that thermal treatment of S1-green fibres in air can stabilize and oxidize the fibres and hence improve their mechanical strength. During the thermal treatment from low temperature starting 150 ^{o}C up to 400 ^{o}C as shown in Figure 8 monitored by SEM analysis at each temperature step, we found that below 150 ^{o}C the fibre morphology has no change. Once the temperature reached to 200 ^{o}C, the fibres start to fuse and crosslink each other. At 250 ^{o}C, the fibres seem to reach to the most of crosslink, and thereafter, with the temperature further increase, the crosslink seems not to get any worse with extended exposure duration, and the fibres can still survive at 400 ^{o}C with nitrogen flow to avoid violent oxidation, indicating that after 300 ^{o}C in air for a long hours period, the fibres might be stabilized and oxidized at least on their surface.

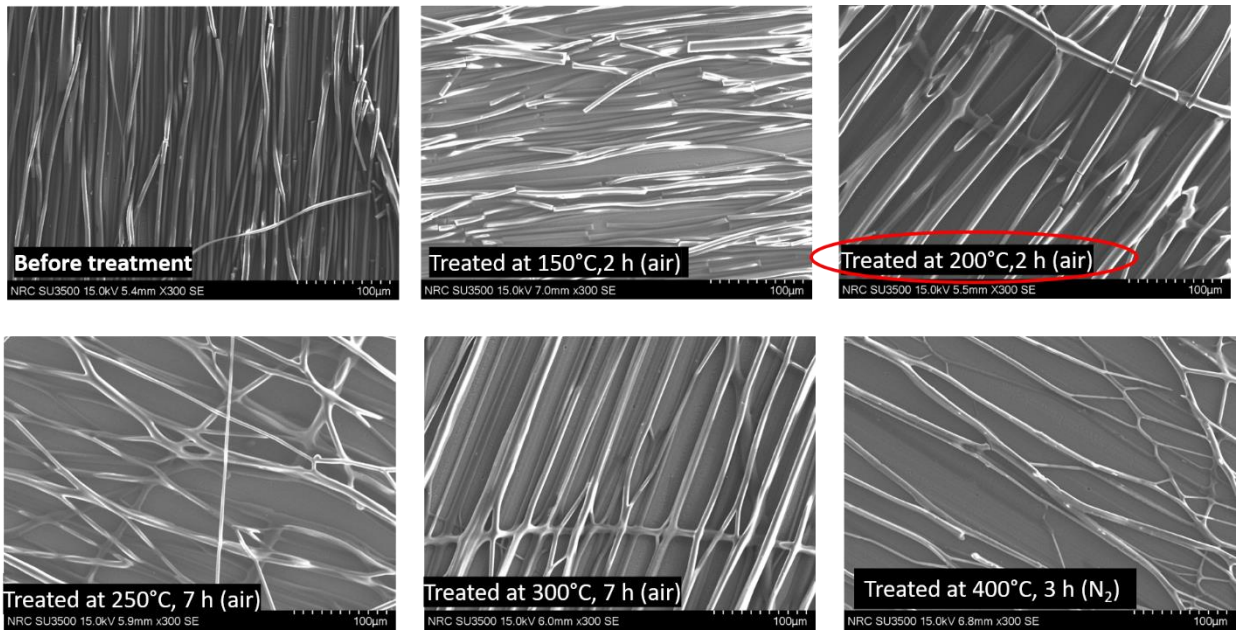

Figure 8 SEM images of thermally treated S1-green fibre mats resulted from elevated temperature and monitored at selected temperature steps

The fast evaporation of toluene solvent causes an issue for continuing spinning for scaling up sample and results in the quick-dried-out solution at the apex of the spinneret and getting clogging quickly shown in Figure 9. An alternative solvent with less volatility but a good solvent for AOA such as xylene has been selected for next trial.

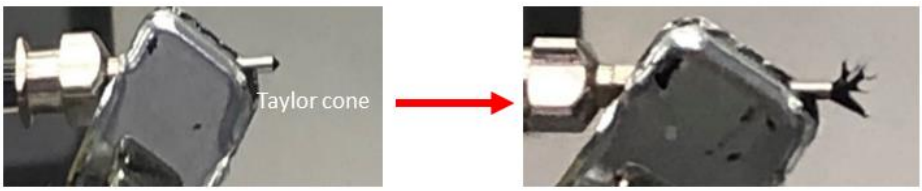

Figure 9 The clogging of the spinneret from normal Taylor cone to the dried sample clogging

(2) Protocol establishment of AOA-based green fibres from as-received S1 in xylene by electrospinning

Based on the knowledge we learned from the S1-toluene protocol above and the challenge issue, we took the advantage of the solution concentration at 50 wt% as a start point to prepare a solution of S1 in xylene for electrospinning. Xylenes having similar properties to toluene but a higher boiling point and less volatility should give a longer spinning duration. S1-green fibres were produced as shown in Figure 10, using the same spinning parameters as in the S1-toluene protocol above.

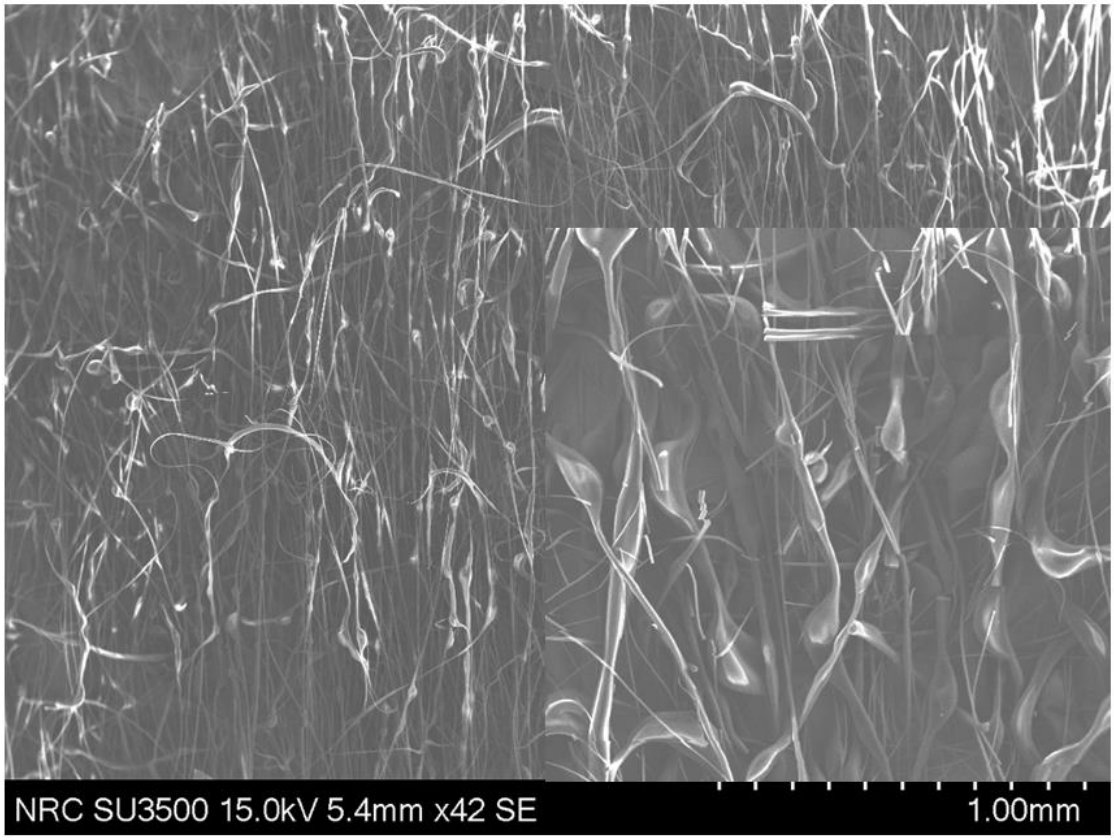

Figure 10 SEM images of S1-green fibres from 50 wt% xylene solution with the same electrospinning conditions: electric field 60 kV/m, feeding rate of 5 µL/min and drum collector speed 280 rpm. Inset: enlarged morphology with "snack-swallow-frag" phenomena

However, as seen from Figure 10, the S1-green fibres from xylene solution in the exact same conditions are not smooth and uniform, and a "snake-swallow-frag" phenomenon has been observed as shown in the inset in Figure 10. We believe that this may result from the slower evaporation of xylene than toluene during the travel of fibres from the spinneret to the drum collector, causing wet-fibres locally re-aggregates. Hence, different electrospinning parameters have been tuned in order to improve the quality of fibre morphology while the solution concentration of S1 in xylene remains unchanged. Finally, a new protocol is established for the production of S1-green fibres: electric field 60 kV/m, feeding rate 3 µL/min and drum speed 520 rpm.

With this protocol, S1-green fibres from xylene with as good quality as the S1-fibres from S1-toluene have been successfully produced as well as scaled-up sample (~30 x20 cm) as demonstrated in Figure 11. The difference is that the spinning duration has been much improved due to less volatile of xylene than toluene. This optimized protocol has much improved the spinneret clogging and eliminated the "snack-swallow-frag" phenomenon to the resulting fibres, and will be an establishment as a standard reference protocol for future AOA and modified AOA sample processing toward green fibre production.

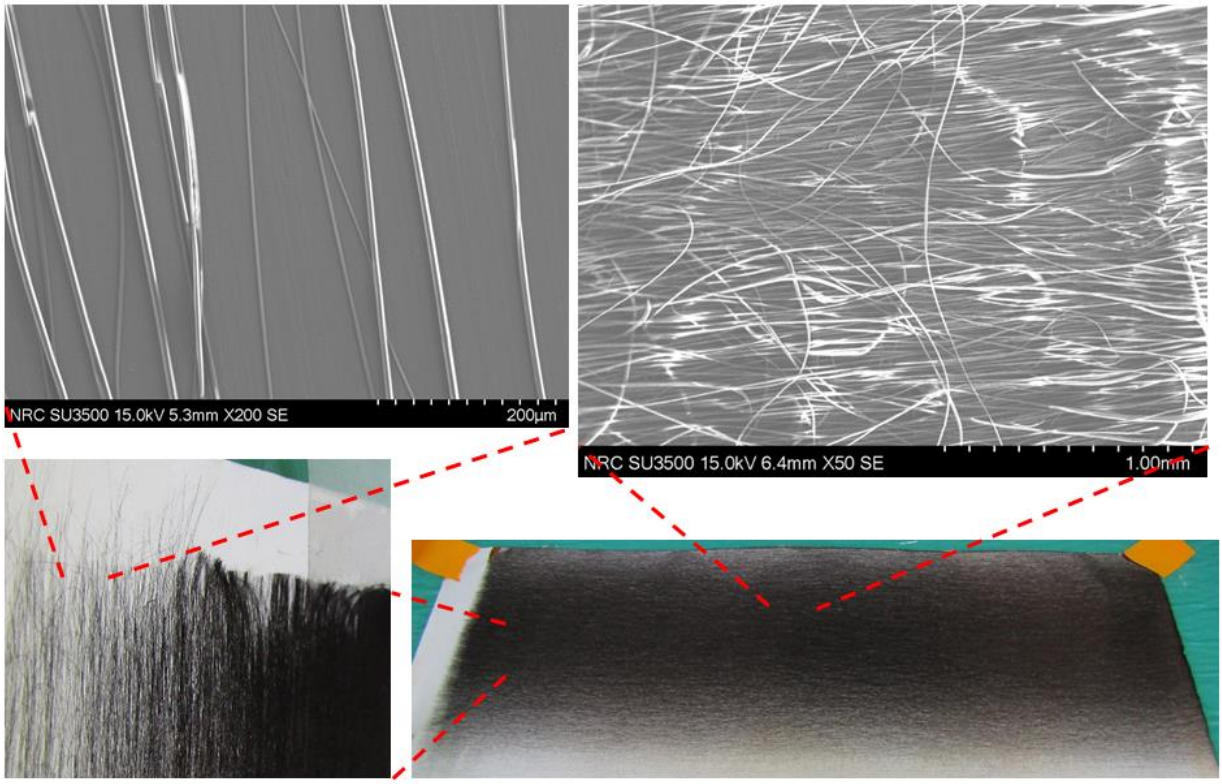

Figure 11 SEM images and digital photos of a scaled-up S1-green fibre mat from xylene solution at 50 wt% concentration and electrospinning condition: electric field 60 kV/m, feeding rate 3 µL/min and drum speed 520 rpm

Again the same as the S1-green fibres from toluene solution, the S1-green fibres from xylene are extremely brittle as well. Figure 12 showed the broken and chopped fibres and fibre mat under SEM electronic beam focus.

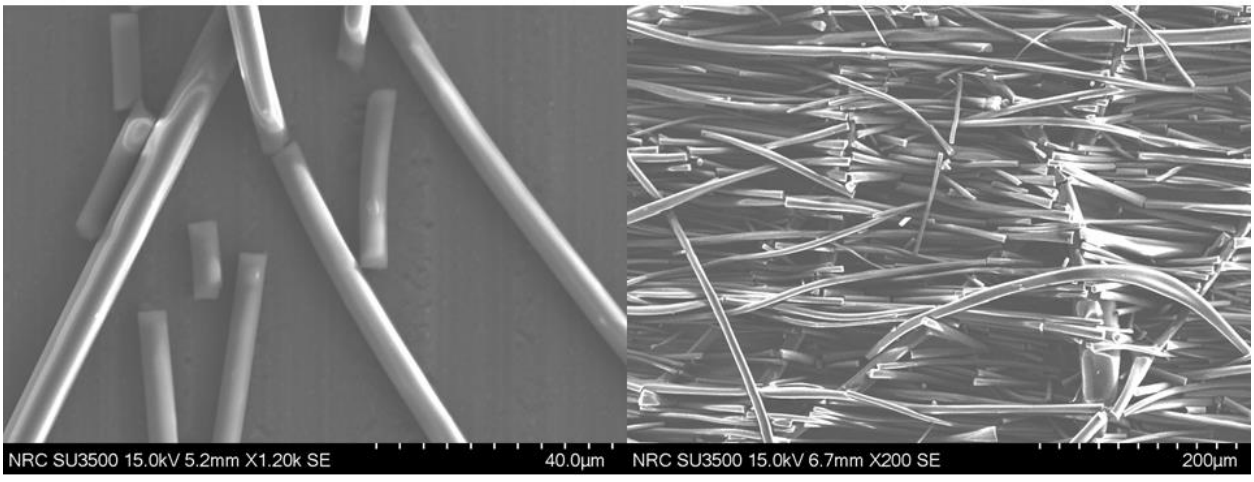

Figure 12 SEM images of S1-green fibres from xylene with extreme brittleness

Further thermal treatment was also conducted for the obtained fibres from xylene solution after dry at 100 °C overnight. They have similar temperature profile as the S1-green fibres from toluene solution.

Before the temperature at 150 °C, the individual fibres are standing alone each other, while once the temperature reaches at 200 °C, the individual fibres start to fuse together and crosslink each other. As shown in Figure 13, by the temperature reaches to 300 °C, the crosslink degree seems to be stabilized and no longer developed any further or get worse. Such crosslinked fibre mat can still withstand at 400 °C in nitrogen atmosphere for a few hours without changing its crosslinked structures and fibre morphology. Additional notes have been taken that many tiny and crosslink fibres between big fibres are more stronger than big fibres as seen clearly in the inset high magnified SEM images, and the crosslinked fibre mat overall has much less break sections than the fibre mat before crosslink under SEM electronic beam focus.

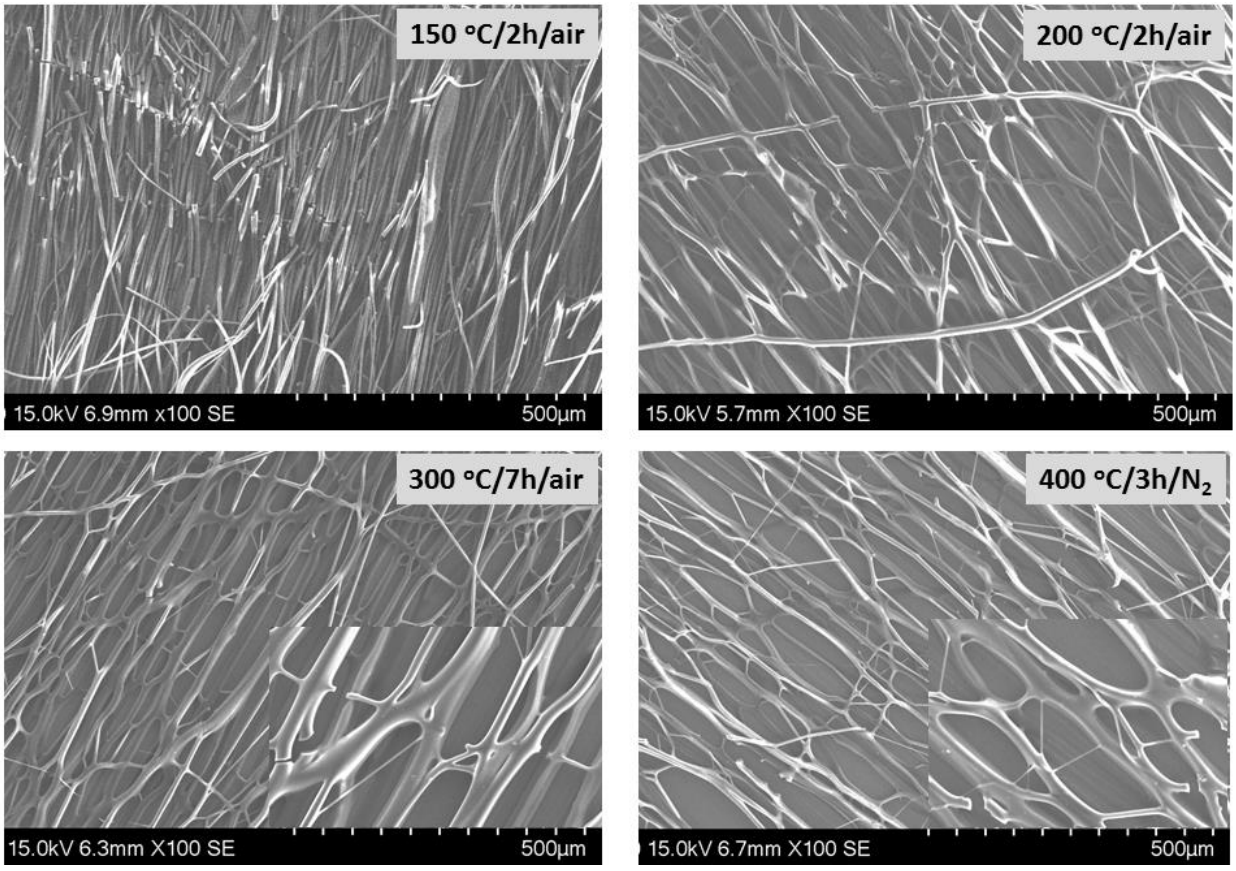

Figure 13 SEM images of S1-green fibres from xylene solution at elevated temperature treatment

(3) Protocol establishment of AOA-based green fibres from pentane-purified S1 in xylene by electrospinning

It is known from Alberta Innovates sample bank that the as-received AOA S1 contains about 22 wt% maltenes that are mostly alkane hydrocarbon species and may not likely be beneficial to the carbon fibre conversion by forming graphitic structures during the carbonization process. Hence, the purified S1 (S1-pent) is about removal of maltenes through pentane pricipitation, and the remaining fractions were applied for electrospinning to produce green fibres, using the same protocol as established in the previous sections of S1-toluene and S1-xylene. Namely, the spinning conditions are the electric field of 60 kV/m, the feeding rate of 3 µL/min and the drum rotating speed of 520 rpm was applied. We found, however,

that 50 wt% solution of S1-pent in xylene is too viscous to be electrospun due to the removal of maltenes fraction and therefore the concentrated fraction of aromatic species of AOA. We found that xylene solution of S1-pent at 40 wt% is perfectly applied to the above mentioned electrospinning conditions. As shown in Figure 14, a large size of S1-pent green fibre mat has successfully produced with pretty uniform sizes and smooth surface morphologies. The green fibre mat seems to be better stretchable and relatively stronger than unpurified S1-green fibre mats, although the individual fibres are still broken under SEM electronic beam focus as shown in Figure 15, obviously, less fractured fibre sections and slow rate of broken speed have been visually observed with the purified S1 green fibres.

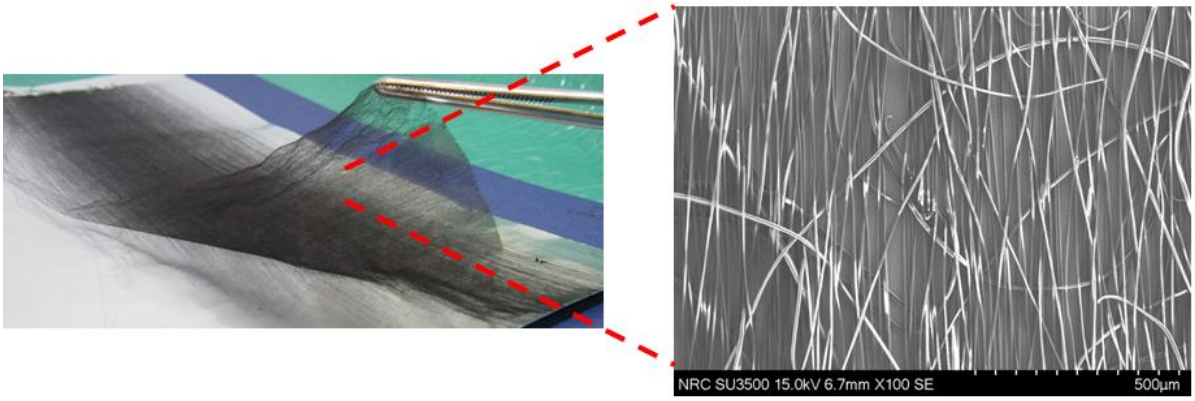

Figure 14 Digital photo of S1-pent green fibre mat and SEM image with uniform fibre sizes and smooth surface morphology

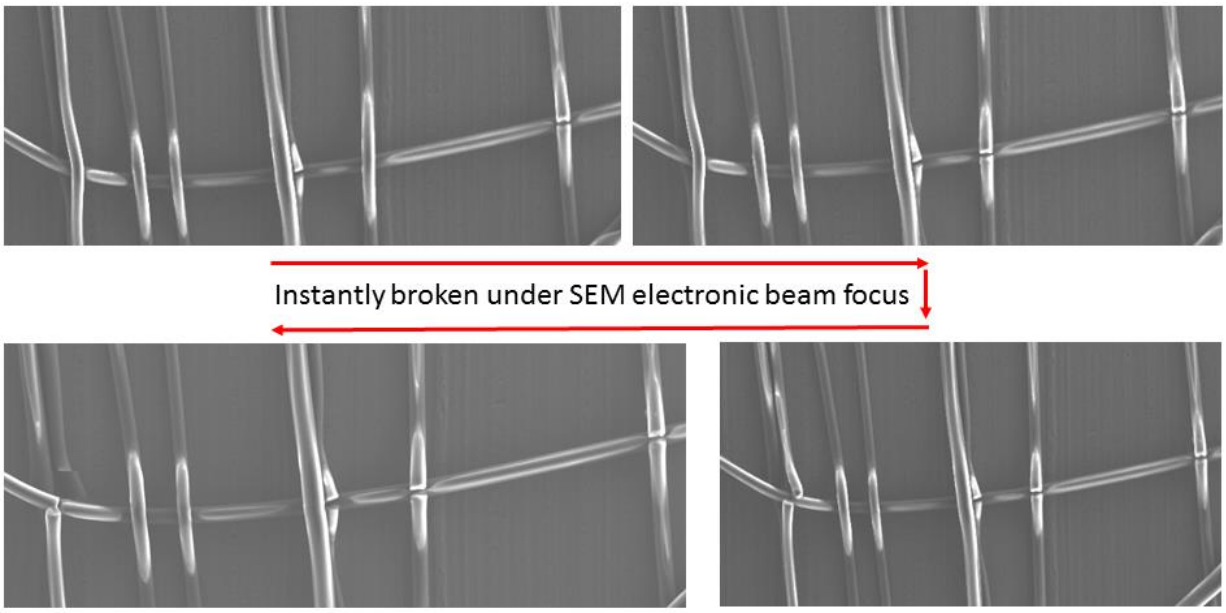

Figure 15 Observation of S1-pent individual green fibre broken instantly under SEM electronic beam focus

To our surprise, with the similar thermal treatment profile of the unpurified S1-green fibres to the purified S1-pent green fibre sample, the results of the SEM images, shown in Figure 16, revealed that the individual S1-pent fibres are strongly withstanding the elevated temperature up to at least 300 °C without obvious fusing and crosslink each other with adjacent fibres for 7 hours duration tested. Unlike S1-green fibres that are heavily crosslinked at as low as 200 °C within a short period of time. Only until the temperature reached to 350 °C, the S1-pent fibres started to partially fuse together and tiny fibres formed and crosslinked between the large fibres. In addition, much less fractured fibre sections are observed, and the crosslink degree is in magnitude less than the S1-green fibres. We intended to interpret that maltenes in S1-green fibres play a solid solvent role during elevated temperature due to their lower softening points and alkane characteristics, which promoted fibre fusing each other at relatively low temperature, while lack of maltenes in the purified S1-pent fibre sample and enriched polyaromatic AOA components resulted in good withstanding of the individual fibres at high temperature.

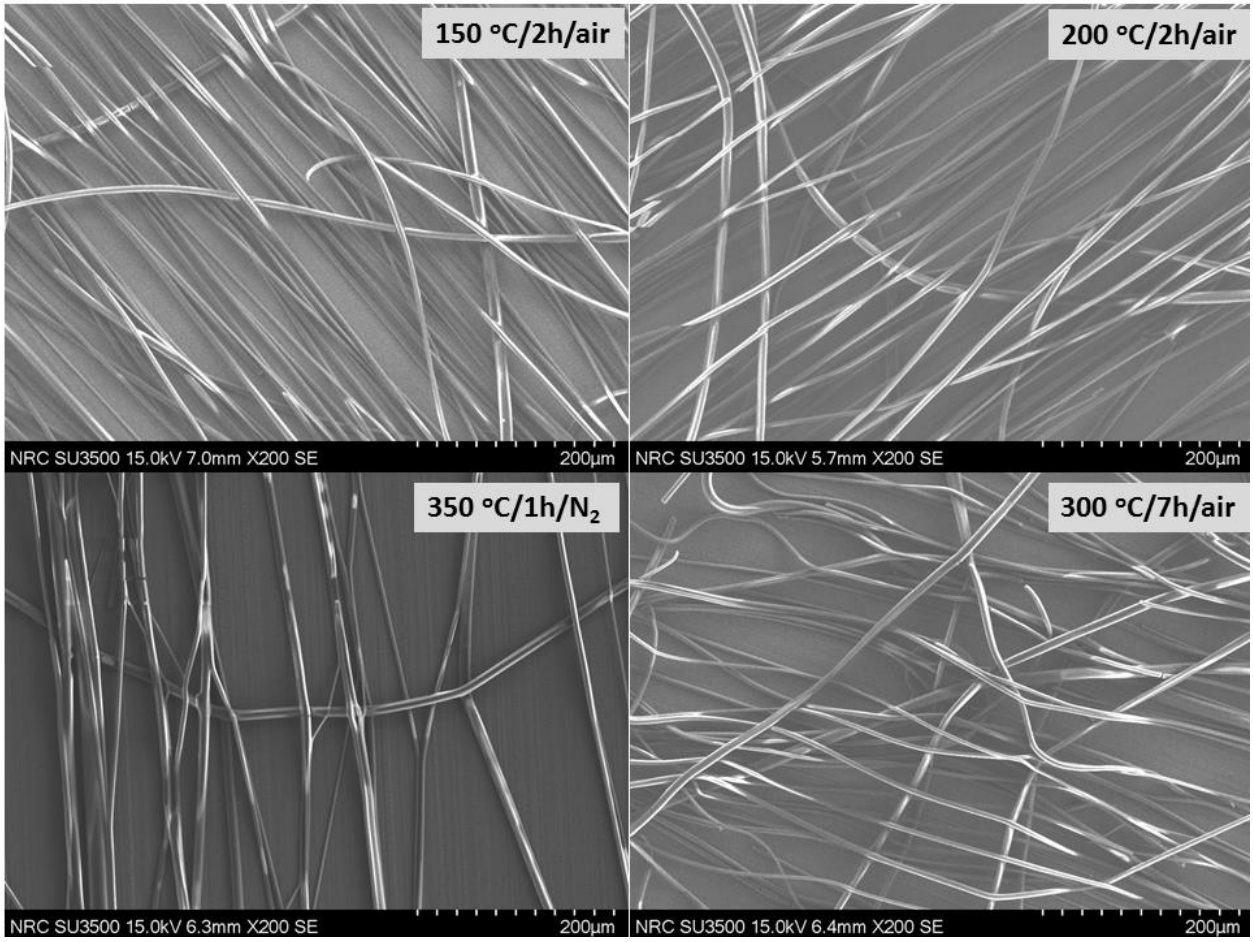

Figure 16 SEM images of the purified S1-pent green fibre morphologies at elevated temperature treatment with improved mechanical strength visually and delayed crosslink behaviors

In summary of this section, three protocols of S1-green fibres from toluene solution, S1-green fibres from xylene solution and purified S1-pent green fibres through electrospinning process have been established. These three protocols are the foundation and the baselines as references and starting points for future

chemically modified AOA sample processing. The thermal treatment up to the stabilization and oxidization temperature levels revealed that maltenes fractions are playing a key role for the fibre crosslink with elevated temperature. All AOA green fibres are extremely brittle and some improvement of mechanical strength has been qualitatively observed with thermal treatment. The removal of maltenes is beneficial for delaying fibre crosslink and mechanical strength improvement. Large sizes of fibre mats can be produced, however, insufficient mechanical strength and fibre crosslink at the stabilization and oxidation temperature levels make it impossible to do additional thermal treatment at high temperature for carbonization towards the formation of quality carbon fibres with sufficient mechanical strength for practical usefulness. Therefore, chemical modification and composition to the as-received asphaltenes S1 is the only way to explore the opportunity for the potential conversion of AOA to the value-added carbon fibres.

Chemical modification of the as-received asphaltenes S1 with incorporation of commercial high molecular polyacrylonitrile (PAN)

(4) Chemical modification of as-received asphaltene S1 and material behaviors

The as-received asphaltene sample S1 from Alberta innovates sample bank was applied to chemical modification and composition with commercial polyacrylonitrile (PAN) in a solvent system as described in our invention Form-1 submitted as NRC-2021-100. The modified asphaltene with its additive must fulfil two critical requirements that are homogenous and spinnable in the selected solvent system. These pre-acquisitions will make sure that the modified asphaltene composite can be spun into green fibres as a first step and no any fraction of AOA and additive is missed out from the asphaltene composite and during the spinning process. Such modified asphaltene composite slurry demonstrated an adaptive viscosity and homogeneity visually as shown in Figure 17.

Figure 17 Chemical modified asphaltene S1 composite slurry in a solvent system and drop-casted on a glass slide

Further qualitative assessment of its mechanical strength was conducted by drop-casting a thin layer of the modified asphaltene composite slurry on a glass slide. For comparison, the unmodified asphaltene S1 and toluene-purified S1-T/W and pentane-purified S1-pent were also prepared in the same way. After

solvents evaporated, the resulting thin films, as shown in Figure 18, behaves significantly different amongst the samples tested. All the unmodified asphaltenes including the as-received S1, toluene-purified and pentane-purified S1 are fully cracked into pieces and stayed on glass slides as seen in optical microscopic images in the first row in Figure 18, while the chemical modified S1 thin film self-pilled off from glass slide and twisted during dry-up. Unlike the unmodified asphaltenes, a zoom-out look at the twisted thin film surface showed a smooth and crack-free surface morphology. This observation strongly suggested that the mechanical property of the modified S1 is improved in magnitude with respect to the unmodified asphaltene samples.

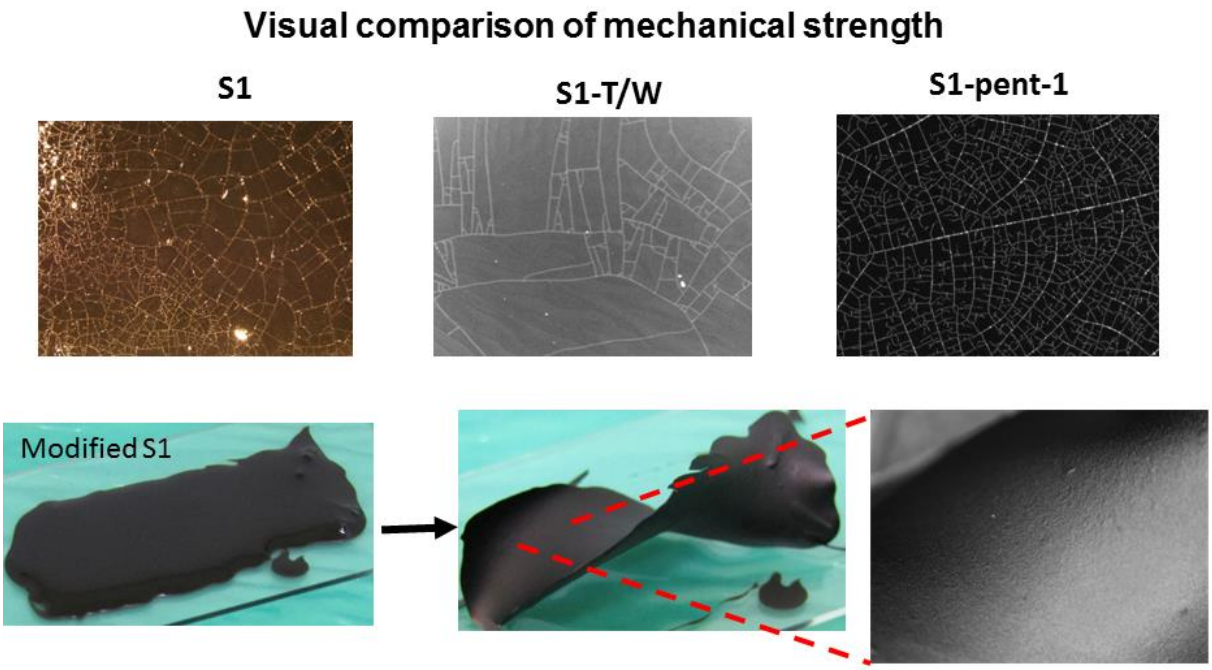

Figure 18 Drop-casted asphaltene and modified asphaltene composite thin films on glass slides

(5) *Green fibre production of the chemically modified S1 and composite with commercial PAN through electrospinning using similar to S1-xylene spinning protocol*

The chemically modified S1 and composite with commercial PAN mentioned above was concentrated in the solvent system to about 30 ~35 wt% concentration, and a similar slurry as shown in Figure 17 was obtained and spun with an optimized spinning condition as the S1-xylene protocol. The resulting fibres, one of the examples shown in Figure 19, gave us a few surprised observations. One of the observations we found is the fibres generated are very small in diameters and very long; secondly, unlike the S1-green fibres, the modified green fibres are not breakable under SEM electronic beam focus; thirdly, it is out of our expection that there are full of beads and particles inside the fibres. Although efforts have been made for tunning the electrospinning conditions, the all-size beads and fibre morphology remained unchange.

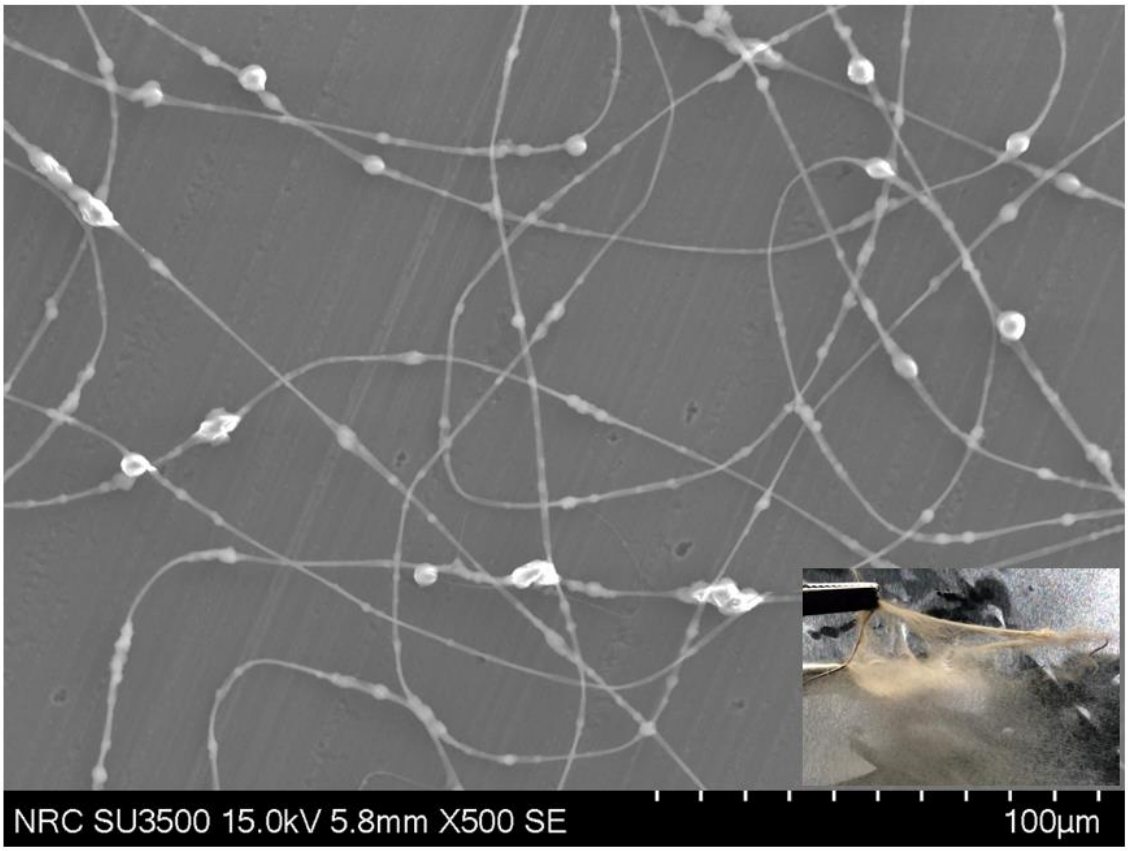

Figure 19 SEM image of chemical modified S1 and its composite with commercial PAN

To identify the species of the beads and it is important to know if the beads from asphaltenes or from PAN, different fibre samples from different spinning conditions were thermally treated with elevated temperature in air in a hope to observe the morphology change of the beads with temperature increase if the beads are from asphaltene due to its low softening point as we observed from the thermal treatments of the S1-green fibres in the previous sections. As shown in Figure 20 and Figure 21, the beads in the fibres did neither disappear nor change their morphologies regardless the temperatures and the treatment durations. During such treatments it was barely to observe any broken fibres under the SEM electronic beam focus like S1-green fibres, where the fibres were extremely brittle and broken instantly. This is a good indication that such modified S1 green fibres are truly getting strong.

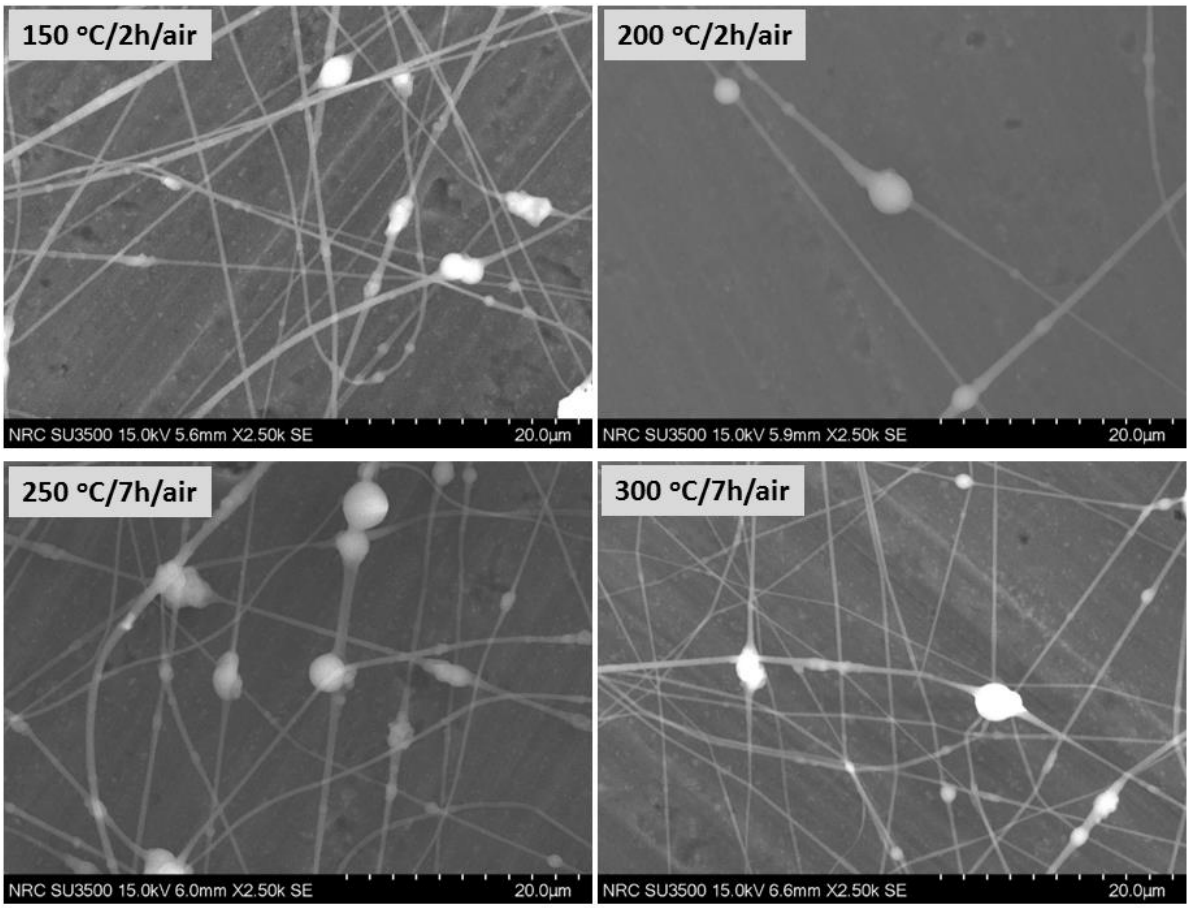

Figure 20 SEM images of thermally treated chemically modified S1-green fibres (slurry concentration ~30 wt%, electrical field 100 kV/m, feeding rate 3 µL/min)

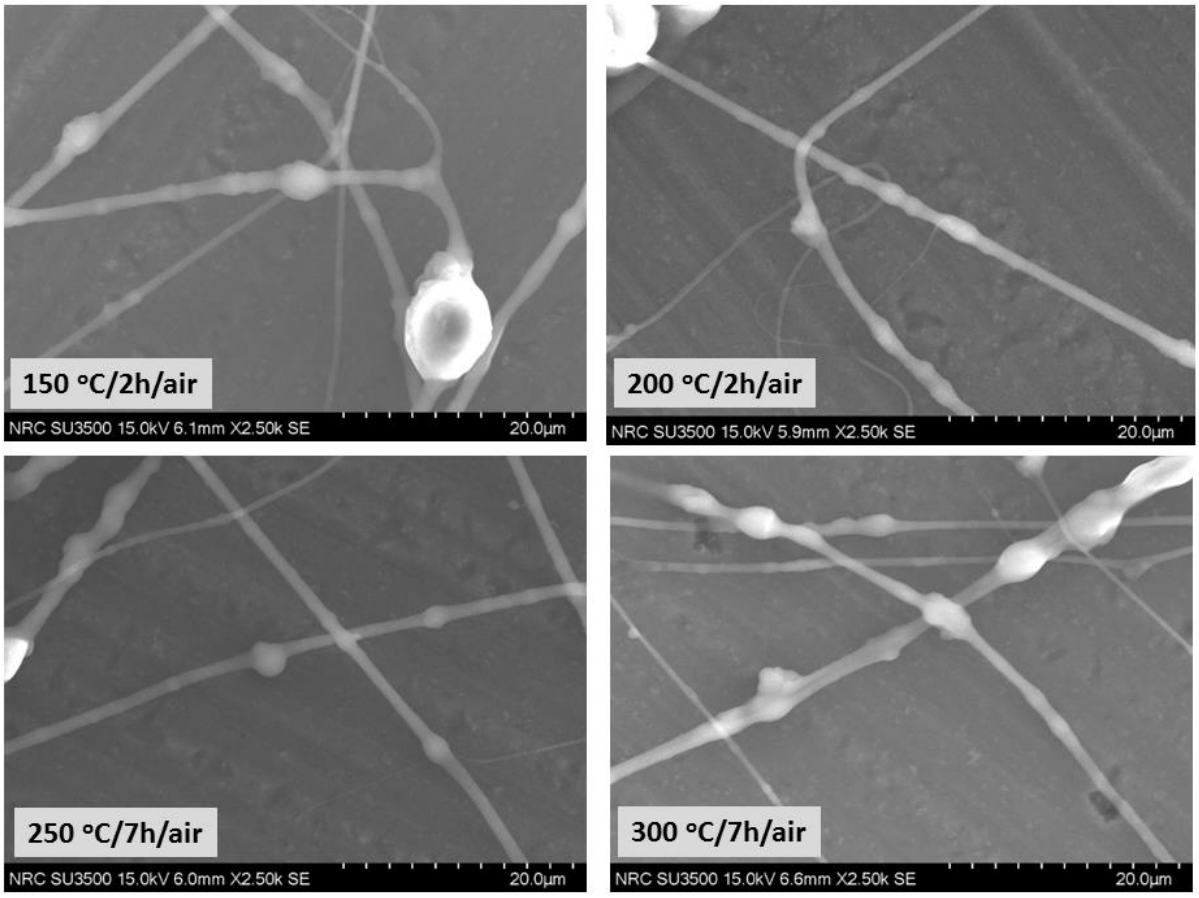

Figure 21 SEM images of the thermally treated chemical modified S1-green fibres (slurry concentration ~35 wt%, electrical field 75 kV/m, feeding rate 1 µL/min, drum speed 1080 rpm)

Further a proof of assumption experiment was conducted to confirm if the beads was caused by the in-situ polymerization, hence, a reduced amount of monomer of acrylonitrile was used and the same reaction conditions as the above experiments were applied. The resulting chemically modified S1-green fibres have the similar SEM morphologies to the previous examples with different sizes of beads inside the fibres. In addition, a new observation have been noticed that the fibre diameters were further reduced down to small sizes than that from the previous experiment, as shown in Figure 22.

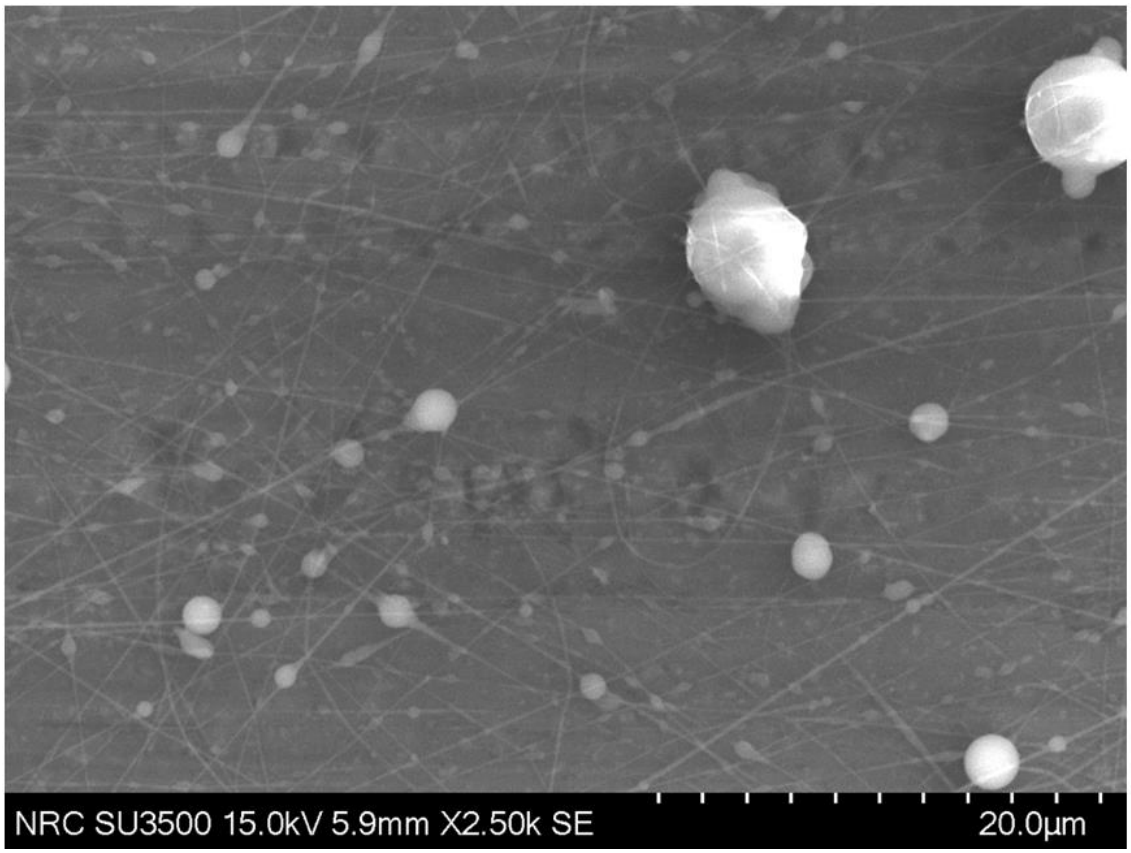

Figure 22 SEM image of chemical modified S1-green fibres with reduced amount of monomer used

Looking for further evidences if the beads are caused from the impurities or the insoluble mineral residue in as-received asphaltene S1 sample, therefore, the previous chemical modification reaction was repeated using pentane-purified S1 instead of as-received S1. Again, the resulting modified S1-green fibres have no different morphology and content of beads inside the fibres even with additional thermal treatments as shown in Figure 23.

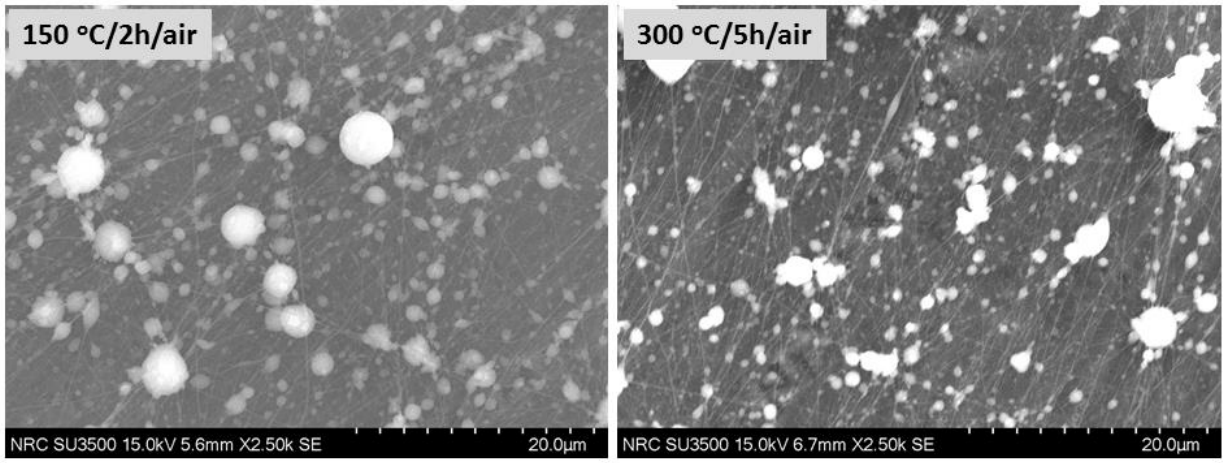

Figure 23 SEM images of chemically modified pentane-purified S1 green fibres with same morphology and beads content

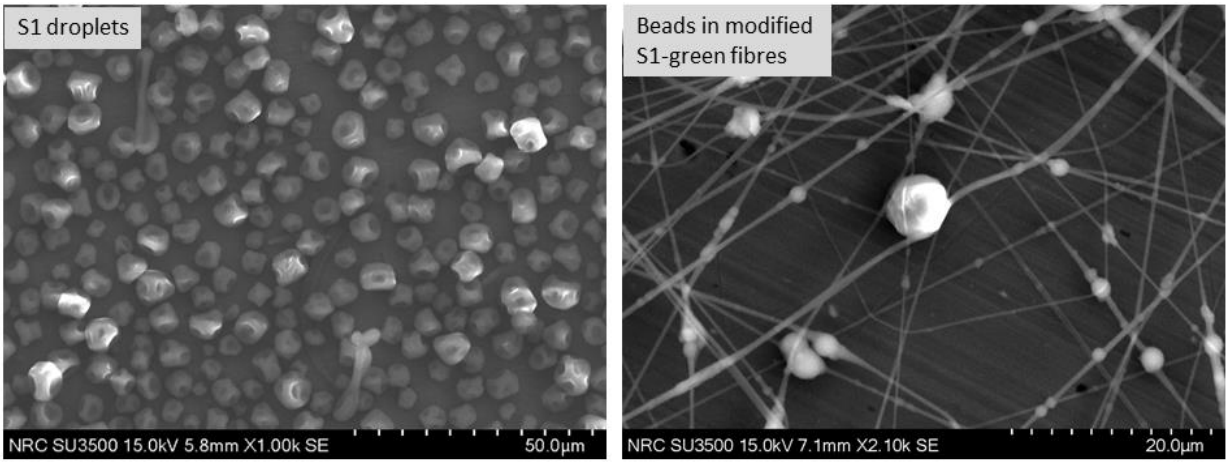

Figure 24 SEM morphology comparison between asphaltene droplet/beads and beads existed in chemically modified S1-gree fibres

Further SEM morphology comparison, as shown in Figure 24, clearly indicated that the beads existed in the chemically modified S1-green fibres are neither from asphaltene components nor from its impurities. According to all the evidences and observations up to this point, we concluded that the beads existed in the modified S1-green fibres must be commercial PAN that was incorporated into the system. Since asphaltene and PAN do not have a common favorable solvent, the high molecular commercial PAN partially aggregated into different sizes of beads due to its unfavorable solvent in the solvent system used, while the soluble fraction of PAN bring the beads into the modified asphaltene system during the electrospinning process. To further prove our conclusion, in the next series of chemical modification of S1, the commercial high molecular PAN was completely omitted.

Chemical modification of the as-received asphaltenes S1 without incorporation of commercial high molecular polyacrylonitrile (PAN)

(6) Chemical modification of as-received asphaltene S1 in a solvent system I (confidential, ref. submitted Form-1: NRC-2021-100) and its modified green fibres through electrospinning and wet-spinning processes

The challenge of PAN beads formation in the chemically modified S1-green fibres from the last section needs more experimental optimization for proper solvent systems selection, some of them have been identified. Alternatively, in this section of material development and chemical modification of as-received and/or purified S1 asphaltenes, we are exploring the potential of homogeneity and spinnability of modified asphaltene S1 and/or its purified derivatives using the same chemical approach without interfering from the commercial high molecular PAN in selected solvent system.

In solvent system I, the chemical modification of asphaltene S1 was conducted with the similar chemical reaction conditions as in the previous sections, and the obtained concentrated solution/slurry was successfully electrospun into nicely aligned fibre mat and able to be spun for any large size of mat sample technically as an example shown in Figure 25.

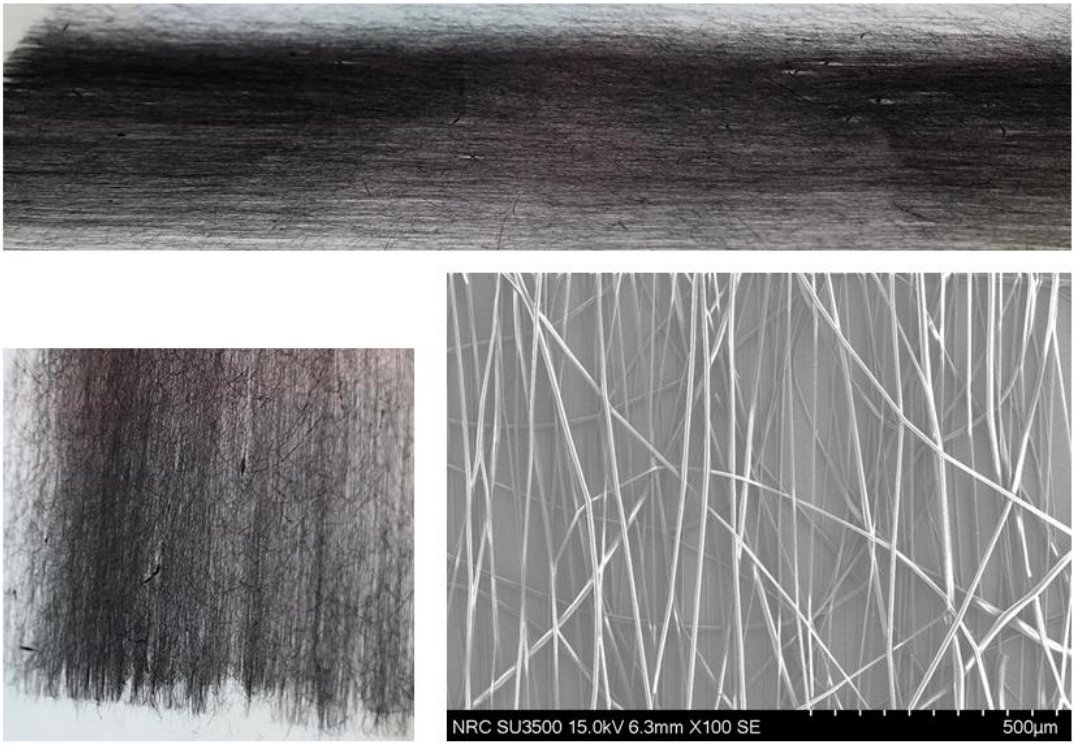

Figure 25 digital photos and SEM image of chemically modified S1-green fibres from solvent system I

Such chemically modified S1 has also been successfully demonstrated by wet-spinning into a double-layered coagulation bath for any arbitrary duration without break of continuing fibre formation, an example illustration shown in Figure 26, a consecutive 5 hrs spinning with adjustable spinning rates.

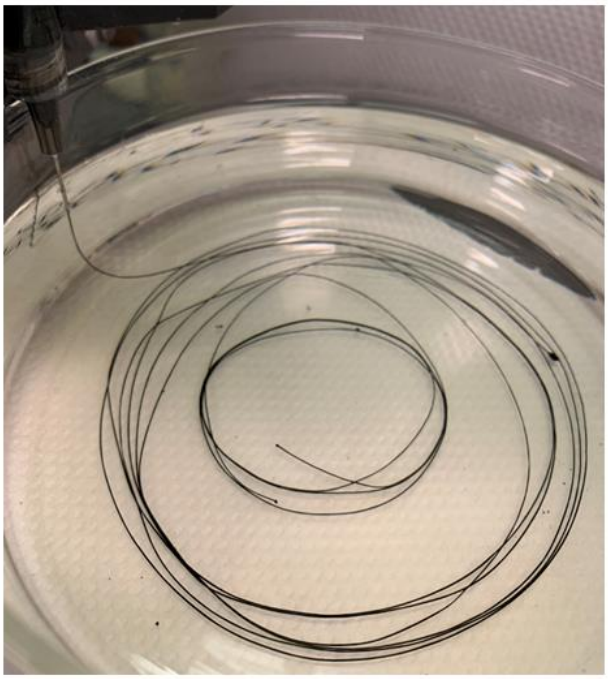

Figure 26 Wet-spinning of chemically modified S1 in solvent system I for any during with adjustable spinning rate and draw ratio

(7) Chemical modification of as-received asphaltene S1 in a solvent system II (confidential, ref. submitted Form-1: NRC-2021-100) and its modified green fibres through electrospinning and wet-spinning processes

The chemical modification of as-received asphaltene S1 was conducted in the selected solvent system II, wherein the solvent system is more conductive. However, the inherent property of this solvent system II makes the electrospinning very challenge as illustrated in Figure 27 for continuing long fibres. Either only short fibres produced or visible large fibres hit on the drum collector piece by piece. With any adjustment of the electrospinning parameters, it was unsuccessful. However, the observation of the slurry and its spinnability during the trial of electrospinning implied that there is a good chance for wet-spinning with a proper coagulation. As illustrated in the Figure 28 of the wet-spinning process with slurry of the chemically modified S1 in the selected solvent system II, where the electrospinning is very challenge for long fibres with a continuing spinning. It seems to be easy however, for wet-spinning process, the fibre can be picked up from the coagulation bath and pulled out and wrapped on a beaker just by hand.

A simple and quick bending test by hand was visually checked for the mechanical strength improvement as shown in Figure 29. The performance demonstrated a great promise and high potential for scaling up green fibre production and post-drawing through the chemical modification to the as-received asphaltene S1.

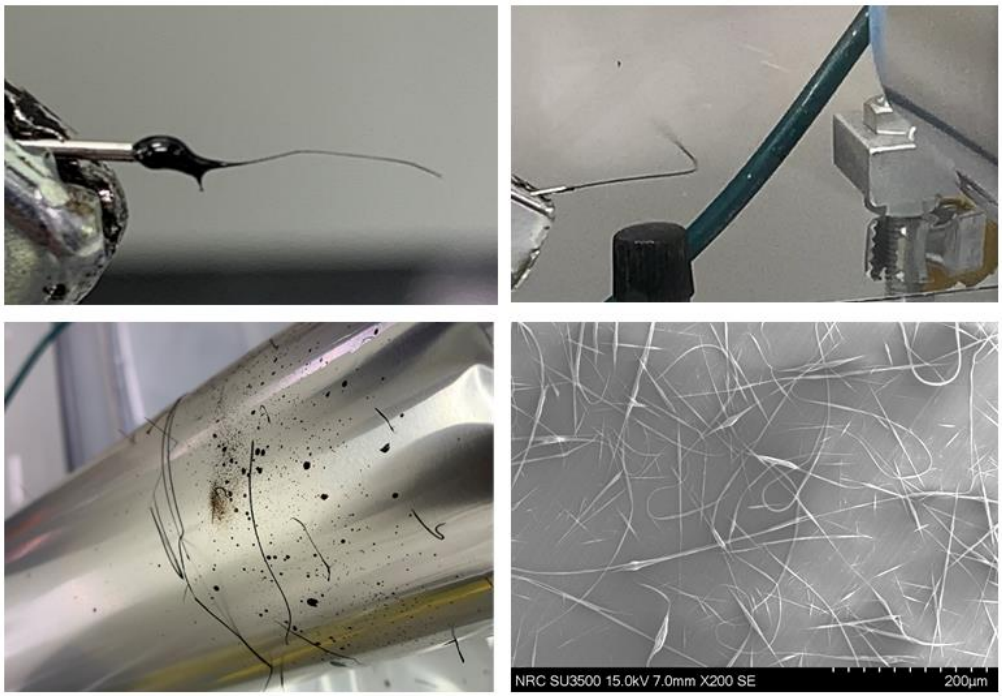

Figure 27 Challenge of electrospinning for long fibres from the chemically modified S1 slurry in solvent system II

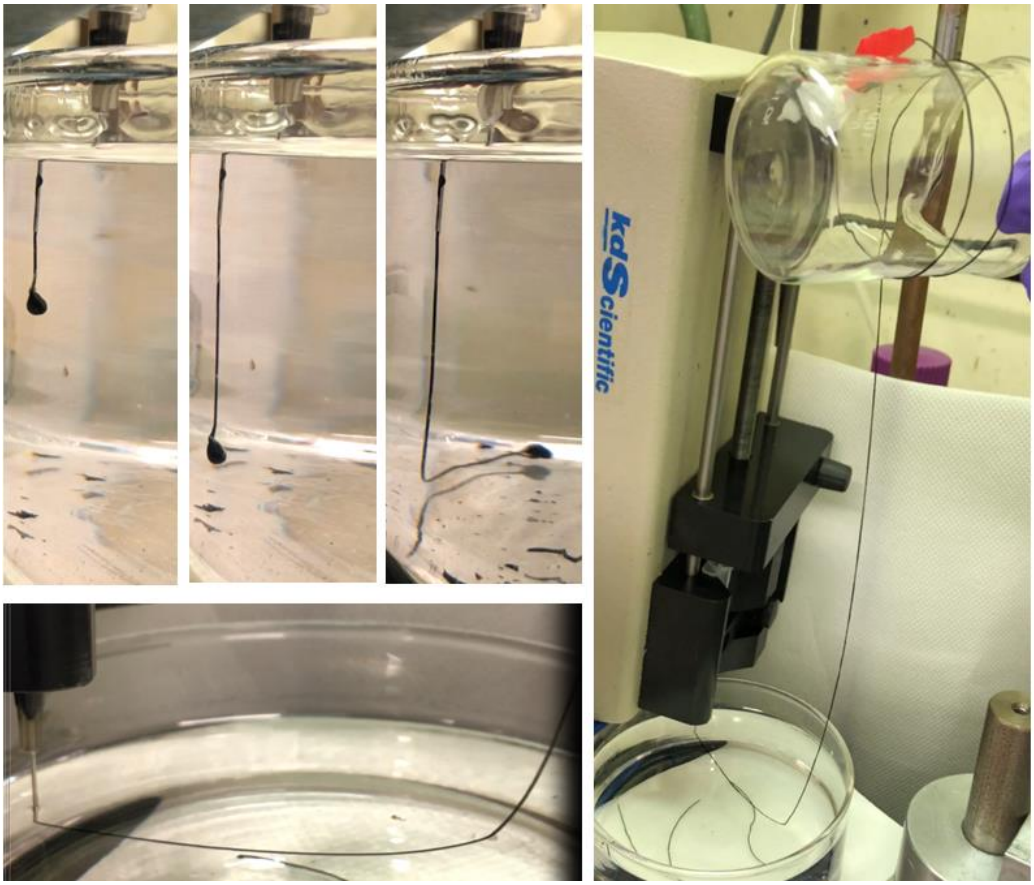

Figure 28 Wet-spinning process of the chemically modified asphaltene S1 from the selected solvent system II in a double layered coagulation bath

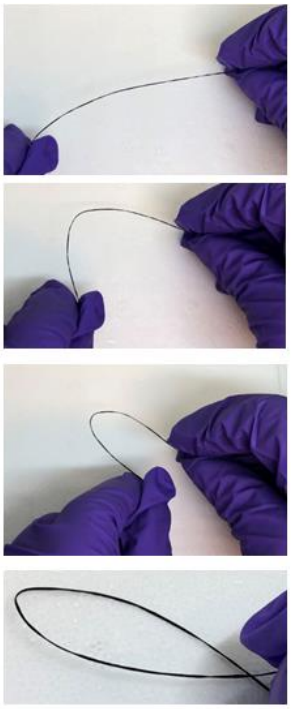

Figure 29 Visual bending test to check to its mechanical strength of a piece of the chemically modified S1-green fibre obtained from wet-spinning process from the selected solvent system II

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[6] A. A. Lach, H. L. Morris, J. A. Martins, E. T. Stace, A. J. Carr, and P. A. Mouthuy, "Pyridine as an additive to improve the deposition of continuous electrospun filaments," *PLoS One*, vol. 14, no. 4, pp. 1–16, 2019.

[7] C. J. Luo, M. Nangrejo, and M. Edirisinghe, "A novel method of selecting solvents for polymer electrospinning," *Polymer (Guildf).*, vol. 51, no. 7, pp. 1654–1662, 2010.

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

ASPHALTENE GREEN FIBRE PRODUCTION FROM AS-RECEIVED ASPHALTENE SAMPLE S1

- We learned that the as-received asphaltene sample S1 from Alberta Innovates sample bank and its purified derivatives from EME lab at NRC can be electrospun into large diameter (~10-15 µm) asphaltene green fibres from static spinning to drum collector pickup, and from small size of fibre samples to a large fibre mat.
- We learned that the proper solution concentration in toluene and xylene is about 50 wt%, higher than that it will be getting hard in operation, and lower than that short fibres and more droplet formation have observed.
- We learned that those fibres are extremely brittle and chopped into pieces just under slight SEM electronic beam focus.
- With the thermal treatment at the stabilization and oxidation stage, we learned that the unpurified asphaltene green fibres get heavily fused and crosslinked at as low as 200 ^{o}C, while the purified (maltenes removed) asphaltene fibres have a better thermal profile than the unpurified S1 green fibres and are able to withstand to the temperature at 350 ^{o}C in air, however, afterward, individual fibres are starting to combine together and crosslink each other.
- We realized that the extreme brittleness and crosslink of the green fibres at low temperatures have brought the matter to the dead corner for any high temperature process towards the final carbon fibre conversion.
- Therefore, we have proposed and conducted the chemical modification to the as-received asphaltene S1 and its derivatives, since this is the only approach to be able to connect the variety of fragments and components within asphaltene mixture into large domains through chemical bond formation for potential macromolecule assembly.

Chemical modification approach to the as-received asphaltene S1 and its purified derivatives

- We learned that chemical modification of S1 and its purified derivatives can produce a homogenous and spinnable asphaltene sample system (or a composite).
- We learned that a proper solvent system is needed to accommodate the modified asphaltene sample system.

Chemical modification to the as-received asphaltene S1 and its purified derivatives and composition with commercial polyacrylonitrile (c-PAN)

- We learned that there is a big challenge that asphaltene and c-PAN do not have a common solvent that is able to bring them into a common solution, therefore, to form a homogenous system of asphaltene and c-PAN is rather challenge.
- The chemical modification to the asphaltene S1 is able to tune the modified asphaltene solubility, especially through intermediate species generated in situ, and bring the modified asphaltene to a close compatible with c-PAN in a solvent system.
- Most importantly, we learned and evidenced that such quasi-homogenous system can produce very small in diameter but strong fibres with fully up-taken of asphaltene. However, the c-PAN beads inside the small fibres are still remaining as a challenge to be resolved in further study.

Spinning and green fibre production

- We learn that the chemical modified asphaltene sample system in different solvent system have significant differences of spinnability and may be favor for one spinning process but unfavorable to another spinning process.
- We understood that the different solvent systems have different polarity, conductivity, solubility and viscosity, this makes the chemically modified asphaltene sample system behaves different in different solvent system and different performance and format in different spinning system, such as from electrospinning to wet-spinning, as mentioned in the project results section.
- We learned that more polar and conductive solvent system is more favorable for composite fibre product and wet-spinning process, which will be our future focus.

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

Asphaltene has been considered a waste produced from the OIlsands industry. Considering the amount produced every year from oil sand in Canada, possibility of the novel application of asphatene is break through. Moreover, the carbon fibre (CF) industry is one of the current key industries to deliver strong and light-weight products. However, due to the expensive feedstock, polyacrylonitrile (PAN), alternative cheaper feedstock to produce CF are being sought. Asphaltene is considered a bitumen beyond combustion (BBC) product and a carbon-rich hydrocarbon material. The outcome of thise project is the chemically modified AOA to be used as a feedstock for CF production, which will implement a few technology knowledge gaps identified currently and open a gate for the road map from a waste asphaltene to a value-added and economic carbon fibre product, meanwhile, the chemistry of asphaltene, asphaltene composites, asphaltene fibres and spinning processes will also be developed to a new era. We have also characterized the asphaltene and the fibre using TGA-MS-FT-IR, and CHNS to find the effect of the impurities. The information generated by thermal characterization and the techniques to modify AOA to CF feedstock will not only solve the waste problem of AOA but also generate potential business for CF industry manufacturing. Furthermore, we have succeeded to synthesize green fibres and optimized parameters for electro and wet-spinning. The following summaries provides the metrics achieved during the projects.

Clean Resources Metrics

Table 4 shows the Clean Resources Metric that we have targeted at the beginning of the project and resulting metrics at the end of the project. Currently, we are working on publication in process for converting AOA to spin-able green fibre methods. A patent creation is also on the way in NRC for the

method we have created. With the new method we have developed, to make a CF from AOA, a new modified AOA was synthesized to prepare green fibre. We have initially planned to hire students for the project, but instead, we have decided to hire HQSP to be trained for AOA-green fibres and CF manufacturing.

Table 4 Clean Resources Metric table.

Metric	Project Target	Results
# of Publications (manuscript)	1	(1)
# Students (Msc., PhD, Postdoc)	**2**	0
# Patents filed (in process)	**1**	*(1)*
# New products/services created	**1**	1
# Sector HQSP trained	**0**	1

Program Specific Metrics

The program specific we chose for the project was the end users participating, Table 5. The knowledge and technology in this project is synthesis of green fibre for scale up process. This can be used in scale up process for CF manufacturing in NRC facility in Boucherville.

Table 5 Program Specific Metrics

Metric	Project Target	Commercialization / Implementation Target	Comments (as needed)
# of End Users participating	1	For commercial implementation we will require NRC facility for carbon fibre scale up process and validate the performance of the fibres.	This project is targeting to produce carbon fibre using asphaltene

Project Outputs.

Table 6 shows the project success metrics that we have targeted initially. It also shows the target achieved during the project. Few target such as carbonization and characterization of the CF could not be achieved due to the resource shift and underestimated work load on milestone 2.

Table 6 Project Success Metrics

Metric	**Project Target**	**Target**
Fabrication of carbon fibre	Validate the initial feasibility to fabricate AOA-green fibres using an electrospinning process in Phase 1.	Achieved Achieved

	Validate the initial feasibility to fabricate AOA-green fibres using a wet-spinning process in Phase 1.	
Impurity content tracking (e.g. Sulfur)	To understand the mechanism of the reactions on the stabilization and carbonization process using AOA-based carbon fibres.	Achieved
Chemical modification of AOA asphaltenes	Visual assessment of viscosity changes before and after modification	Achieved
	Developing of homogeneous and spinnable system Discovering proper solvent systems for the system	Achieved Achieved
Thermal treatments	Thermal treatment/stabilization of AOA green fibres in air up to 400 ^{o}C	Achieved
Carbon fiber demonstration	The spun AOA-green fiber precursor oxidization and stabilization Further carbonization to the least temperature about. Characterizing the mechanical property of the obtained carbon fibers and their morphology	Achieved Not performed yet Not performed yet

H. BENEFITS

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

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

RESPOND BELOW

The successful implementation of this technology could result in:

- Value-added product from asphaltene waste currently produced.
- Extension of market and partners for Alberta oilsands companies with carbon fibre manufacturers.
- Environmental benefit by converting the asphaltene waste from Alberta oilsands bitumen production to economic products, generating economic values and creating a cleaner environment for Alberta and Canada.

ECONOMIC

The cost of Carbon fibre could be reduced, and reduce the cost of the apshaltene waste management by adding value as CF feedstock. The second is the jobs can be created to build the plant to repurpose the asphaltene and relevant business can be developed within Alberta, Canada and worldwide. New opportunity will rise due to the cost reduction of CF.

ENIVIRONMENTAL

The success of the technologies from this project will transform the wasted asphaltenes from the Alberta oilsands to value-added carbon fibre. The large fraction (15 to 20%) of the Alberta oil sands is asphaltene that has little to no utility and considered as wasted byproducts. The technology will convert the waste into value-added product for CF industry that can reduce significant waste accumulation in oil and gas

industry. Indirectly, sufficient CF supply to the market will reduce the demand or replace other high-energy-cost product such as metal, plastics.

SOCIAL

The success of the technologies will create new market and new business to the CF industry due to the reduced price. The new market will bring more entrepreneurship opportunities to the province. The augmentation of the safeguarded investment, and strengthened stake holder will come together on the oilsands industry in Alberta as well. The new business will create new job market and new demand for raising new relevant high quality expert and talent working people.

BUILDING INNOVATION CAPACITY

The success of the technology will required to train HQSP in Alberta to modify the AOA for CF feedstock, and also to manufacture the CF using AOA. HQSP will be necessary to build and CF industries. Furthermore the CF from AOA. This will also need university education system to implement new innovative education plan to raise such HQSP who can timely fulfil the highly demanded job market in the AOA-CF business.

I. RECOMMENDATIONS AND NEXT STEPS

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

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

RESPOND BELOW

- Long-term plan for commercialization if the technology of chemically modified AOA and its composite is succeeded to the carbon fibre stage with adaptable mechanical strength, within 3 years, a facility for a kilogram carbon fibre production should be implemented for pre-commercialization stage, wherein a chemical modification reactor facility in multi-kilogram scale capacity is needed and a fibre spinning production to carbonization production line should be available for one step and multi-stage treatment of fibre from feeding, spinning, post-treatment, stabilization/oxidization, and carbonization to and above 1000 ^{o}C.
- Long carbon fibre and short carbon fibres should be in parallel considered during the facility implementation.

- This will need relevant industrial partner or a dedicated R & D research centre as partnership to be involved in the scaling process.
- Based on our current output and knowledge obtained during the current phase I, in the next step, we will need to focus on the repeating production of the chemically modified asphaltene, optimizing the reaction conditions, catalyst selections, solvent system combination, scaling up modified AOA feedstock, the current challenge of solid polymer beads inside the fibres, implement post-draw capacity, tune the stabilization and oxidization temperature profile and establishing carbonization steps. This will aim to produce certain level of mechanical strength for full characterization and two year time frame is expected to carry out the expected work load.
- And this will need partnership collaboration amongst the NRC research centres of SDTech, EME and AST as initially planned, whereby, SDT will carry out the chemical modification, proof of concept fibre spinning, post treatment, stabilization and carbonization, EME will take care of full characterizations, and AST will take care of the reproduction of the lab-scale samples from the SDT and the scaling-up production to its facility capacity.

It is expected that once the scaling up stage completed and the resulting carbon fibres are adaptable for industrial application, Alberta Innovates may find proper industrial partners to facilitate the technology developed within NRC, and NRC's innovation and technology can be transferred to the industrial partners with IP protection by the time.

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 inventive technology of chemically modified AOA materials and processing obtained from this project will be protected from patent application and can be licenced to industry partner for technology transfer.

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

This project objective is to prove a concept for a potential feasibility of asphaltene from AOA to the formation of carbon fibre. Within the current Phase I of this project, the following 6 major components have been performed and carried out thus far:

1. Material analysis and characterization,

2. Protocols establishment of asphaltene green fibres from as-received and purified asphaltene from AOA,
3. Innovation technology development by chemical modification of as-received asphaltene S1 and its composition,
4. Asphaltene green fibre production from chemically modified asphaltene sample system,
5. Electrospinning and wet-spinning processes development,
6. Asphaltene green fibre stabilization and oxidization

Three protocols of S1-green fibres from toluene solution, S1-green fibres from xylene solution and purified S1-pent green fibres from xylene solution through electrospinning process have been established. These three protocols are the foundation and the baselines as references and starting points for the chemically modified AOA sample processing. The thermal treatment up to the stabilization and oxidization temperature levels revealed that maltenes fractions are playing a key role for the fibre crosslink with elevated temperature. All AOA green fibres are extremely brittle and some improvement of mechanical strength has been qualitatively observed with thermal treatment. The removal of maltenes is beneficial for delaying fibre crosslink and mechanical strength improvement. Large sizes of fibre mats can be produced, however, insufficient mechanical strength and fibre crosslink at the stabilization and oxidation temperature levels make it impossible to do additional thermal treatment at high temperature for carbonization towards the formation of quality carbon fibres with sufficient mechanical strength for practical usefulness. Therefore, chemical modification and composition to the as-received asphaltenes S1 becomes essential to explore the opportunity for the potential conversion of AOA to the value-added carbon fibres.

Protocols of chemical modification and composition of as-received asphaltene S1 and its purified derivatives have been developed, and a novel invention Form-1 (NRC-2021-100) has been developed and submitted for US provisional and full patent application. This patent application is the core technology development for the success of AOA conversion to carbon fibres.

A few solvent systems that are suitable to the modified asphaltene sample system have been identified, and both electrospinning and wet-spinning process have been demonstrated with the chemically modified asphaltene sample system. We learned that the chemically modified asphaltene can be achieved from small size to large size of samples. The feasibility for a homogenous and spinnable slurry with a proper solvent system selection. Such homogenous system may be favorable for electrospinning process, scale-up production has been evidenced through wet-spinning process or both depending on that is more adaptable for industrialization. Furthermore, the conductivity, viscosity and solubility of the solvent system.

With the established protocols, scalable asphaltene green fibre samples have been repeatedly produced and both electrospinning process and wet-spinning process have been demonstrated.

The chemically modified asphaltene resulting green fibres have been thermally treated up to 400 ^{o}C in air, unlike the unmodified asphaltene green fibres, fibre breakage under SEM electronic beam focus and fibre

fuse and crosslink have not been observed under electron microscopy, indicating that the chemically modified asphaltene fibres becomes stronger and can be treated at further high temperature. More noticeable is that such chemically modified asphaltene green fibres are much smaller in diameter than the unmodified fibres. The mechanical strength improvement is further confirmed with the visually for many hours and demonstrated certain flexibility by stretching and bending test that was conducted with a piece of dried fibre from wet-spinning process tests.

Our inventive technology develop through this project will not only beneficial to the conversion of asphaltene waste to a value-added carbon fibre product, therefore generating new business opportunity but also beneficial to the currently existing carbon fibre industry, wherein the incorporation of chemically modified asphaltene to their current carbon fibre production line will be significantly reducing their feedstock costs and hence more profit with less costs will generate. In addition, there is also potential to improve the property of their current carbon fibre product in the vision of light-weighting and stronger carbon fibres.

These exciting output from this project in phase I and the knowledge obtained are strongly promoting us to the next steps. We will focus on in next steps:

- Repeating production of the chemically modified asphaltene and its composites,
- Optimizing the chemical reaction conditions, catalyst selections, solvent system combination,
- Scaling up modified AOA material preparation,
- Optimizing the compositing recipes of chemically modified AOA with commercial PAN and resolving the currently encountered challenge of solid polymer beads inside the fibres, once the polymer beads get resolved, such tiny fibres can be applied to stabilization and carbonization process towards carbon fibre formation, and then establishing stabilization and carbonization protocols,
- Implementing post-draw and post-treatment system for lab-scale fibre sample production, which is critical for immediately improving mechanical strength of the wet fibres for additional handlings in the following steps,
- Optimizing spinning process, fibre pickup, drawing, coagulating, washing, and drying for asphaltene green fibres produced,
- Triggering thermal chemistry during the stabilization and oxidization stage for the formation of polyaromatic condensation, and graphitic domain formation and crystallite growth in the carbonization stage,
- Scaling up fibre sample will be developed, and this will need partnership collaboration amongst the NRC research centres of SDTech, EME and AST as initially planned, whereby SDT will carry out the chemical modification, proof of concept fibre spinning, post treatment, stabilization and carbonization, EME will take care of full characterizations, and AST will take care of the reproduction of the lab-scale samples from the SDT and the scaling-up production to its facility capacity and mass of carbon fibre delivery.
- This will aim to produce adaptable level of mechanical strength of carbon fibres for full characterization and two year time frame is expected to carry out the expected work load.