

## 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.

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# The use of pre- and post-chemical modification to prepare low-cost carbon fibres from electrospun Alberta oilsands asphaltenes

## Public Final Report

Prepared for

Alberta Innovates

Prepared by

Ryerson University

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## CLEAN RESOURCES FINAL PUBLIC REPORT TEMPLATE

### 1. PROJECT INFORMATION:

Project Title:	The use of pre- and post-chemical modification to prepare low-cost carbon fibres from electrospun Alberta oilsands asphaltenes
Alberta Innovates Project Number:	G2020000345
Submission Date:	Feb 28, 2021
Total Project Cost:	\$105,000
Alberta Innovates Funding:	\$50,000
AI Project Advisor:	Paolo Bomben

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### 3. PROJECT PARTNERS

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

*RESPOND BELOW*

In addition to Alberta Innovates and Ryerson University, we'd like to thank Koivisto Materials Consulting for their financial support of this project. Furthermore, a big thank you goes out to our collaborators, Jordan Wilson, Nariman Yousefi (Ryerson), Dr. Stephanie MacQuarrie and Nicholas Magliaro (of Cape Breton University) for their collaboration (helpful discussions, providing lignin, assistance for preliminary pyrolysis and carbon product analysis) on this project.

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## A. EXECUTIVE SUMMARY

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

*RESPOND BELOW*

Owing to their significant presence in bitumen and their propensity to aggregate, asphaltenes decrease pipeline capacity and require costly flow additives. However, if they were removed at source and converted into higher-value carbon based materials, this would increase pipeline capacity, serve as a secondary revenue stream for the province of Alberta and open the pathway for new carbon-based green technologies. We hypothesized that if we disrupt the aggregation using lignin and other additives, that these asphaltene carbon building blocks could find use in a number of sustainable materials including; carbon fibre, activated porous carbon, carbon foam, and versatile high strength composites. To this end, this project has explored the potential of electrospinning a lignin/asphaltene/polymer composite material, that we believe can be converted into high-value carbon materials at reasonably low pyrolysis temperatures. We have demonstrated herein that that aqueous lignin and asphaltene can be electrospun into a composite coaxial fibres that could be used as building blocks in the development of carbon nanofibres and ultimately green technologies.

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## 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*

Asphaltenes are a family of polyaromatic hydrocarbons that exist in all fossil fuel streams (Figure 1).<sup>1,2</sup> The asphaltene family includes a variety of complex structures that continue to be studied and characterized, but generally it is agreed that asphaltene molecular diameters range from 10-20 Å with molecular weights estimated to be between 500 and 1000 g/mol. The strong correlation between colour (they are black in nature owing to their chromophoric content) and asphaltene size indicate that asphaltenes possess 1 or 2 chromophores per molecule with 4-10 fused rings. It is also suggested that asphaltene molecular aggregation occurs at low concentrations, approximately 0.06 g/L, explaining why larger molecular weights are often reported for techniques that require high concentrations.<sup>3,4</sup>

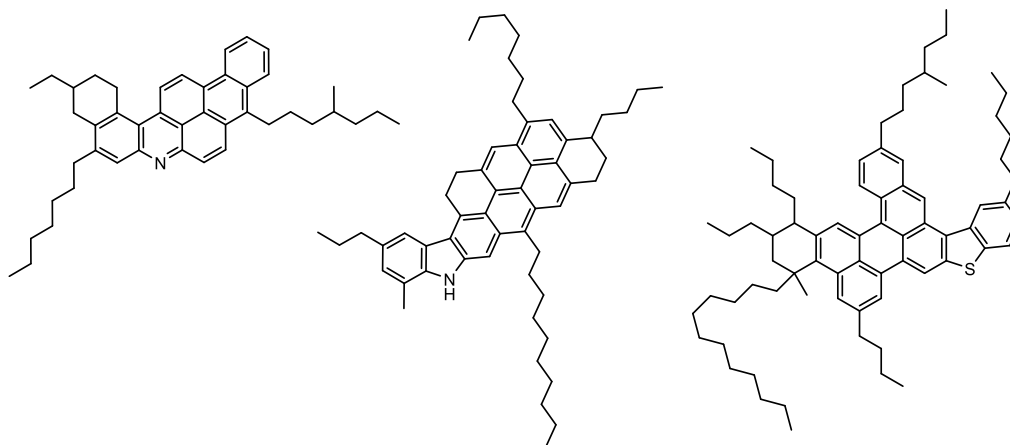


Figure 1. Idealized structures of asphaltene molecules proposed by Groenzin and Mullins based on the molecular weight, heteroatoms present, aromaticity, number of fused rings, and alkane structures.

Oil is, and will remain for some time to come, the most important energy carrier in the world. It is a complex liquid composed of four fractions: saturates (liquid), aromatics (liquid), resins (dispersants), and asphaltenes (dispersed solids). The proportion of each fraction is dependent upon the oil source, and it dictates the properties and the value of the oil. Asphaltenes are denoted as the fraction that is soluble in toluene or benzene and insoluble in n-alkane. Owing to their significant presence in the oil sands, asphaltenes do pose a challenge to Alberta bitumen extraction because of their propensity to aggregate, resulting in decreased pipeline capacity the need for costly flow additives. In addition, Athabaskan oil sands also contain a high level of metal (nickel and vanadium)<sup>5</sup> porphyrins. However, if asphaltenes were removed at source and converted into higher-value carbon-based materials (carbon fibre, etc.), this would increase pipeline capacity, serve as a secondary revenue stream for the province of Alberta and open the pathway for new carbon-based green technologies.

### Fibre formation with electrospinning

Pitch fiber formation begins with using a process known as melt spinning – mechanical extrusion of a hot melt through a die. However, this is not favorable when dealing with systems prone to aggregation (like asphaltenes), because high asphaltene containing coal pitch, for example, shows significant filament clogging and breakage during melt spinning, due to these aggregated asphaltenes.<sup>6</sup> An attractive alternative large-scale carbon nanofibre production method is electrospinning.<sup>7,8</sup> Electrospinning has emerged as an economical, industrially relevant alternative. In many ways, electrospinning is similar to melt spinning, but the difference is the origin of the tensile force initiating the fibre jet. In electrospinning a viscoelastic liquid is ‘stretched’ in a high applied electrostatic field causing fibre jetting after the formation of a stabilized Taylor cone. The extrusion is due to the massive potential difference between the charged droplet in the spinneret and a grounded collector (Figure 2). Mesophase pitch contains a liquid crystalline and an isotropic phase that provides subunit mobility during the pre-carbonization process; however, electrospinning process parameters such as voltage can tune analogous behaviour in fibre morphology.<sup>9</sup> More relevant context on electrospinning will be discussed in future sections, as we elaborate on the opportunities (and challenges) when using this technique.

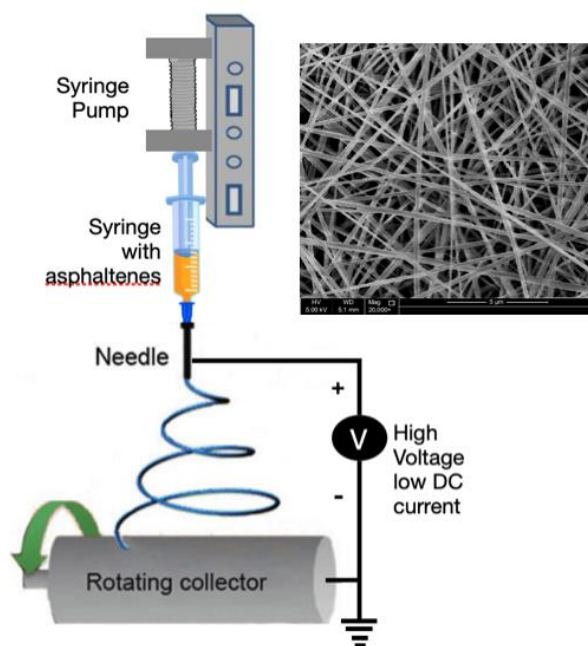


Figure 2. Nanofibre formation using electrospinning

In 2011, a report demonstrated that asphaltenes could be electrospun into fibres using toluene as the solvent.<sup>10</sup> Unfortunately, these fibres were hollow, brittle and there was no disclosed attempt to carbonize them. However, two more recent reports show strong evidence that coal-derived asphaltenes could be converted effectively into CF. It was demonstrated that carbon nanofibres could be generated after electrospinning, oxidative treatment, and carbonization at 900°C (a significantly lower temperature than turbostratic PAN post thermal treatment of >1600°C); however, tensile properties were not discussed.<sup>11</sup> In another report, purified asphaltenes were first converted to a high-grade pitch using a pre-oxidizing heat treatment followed by melt spinning, post oxidation and carbonization to yield 12 micrometer CFs with a tensile strength of 920 MPa.<sup>12</sup> Other reports have also shown that electrospinning asphaltenes as a co-additive in PAN is also possible.<sup>13</sup> With the high cost of CF being the dominant concern associated with its wide scale commercial success, any innovation that converts asphaltenes into CF needs to be cost effective – both in the consumable costs (solvents, additives, polymers, etc.) and the energy used in thermalization/pyrolysis. In the above cases, the additional cost (high purity pretreatment) suggests that economical and robust methods are still required to economically convert asphaltenes into CFs and novel carbon-based materials.

### Disrupting asphaltene aggregation

Oxidative thermal pretreatment is a technique used to oxidize the asphaltene prior to melt or electrospinning. As an alternative strategy to pretreatment of asphaltenes, we sought to examine disrupting aggregation with additives. In order to realize the *material* potential of asphaltenes they need

to be stitched together to create graphitic building blocks during the carbonization process (heating at high temperatures in the absence of oxygen – also referred to as pyrolysis). Just as in oil production, asphaltenes aggregate or  $\pi$ -stack (face-to-face alignment of the polyaromatic core).<sup>2</sup> However, if the asphaltenes  $\pi$ -stack with each other prior to the carbonization process, then brittle petroleum coke is formed as a bi-product. However, if  $\pi$ -stacking/aggregation is disrupted, then there is a greater potential for the thermodynamic edge-to-edge bond-forming and “stitching” together of the asphaltene building blocks to create graphitic subunits (Figure 3).

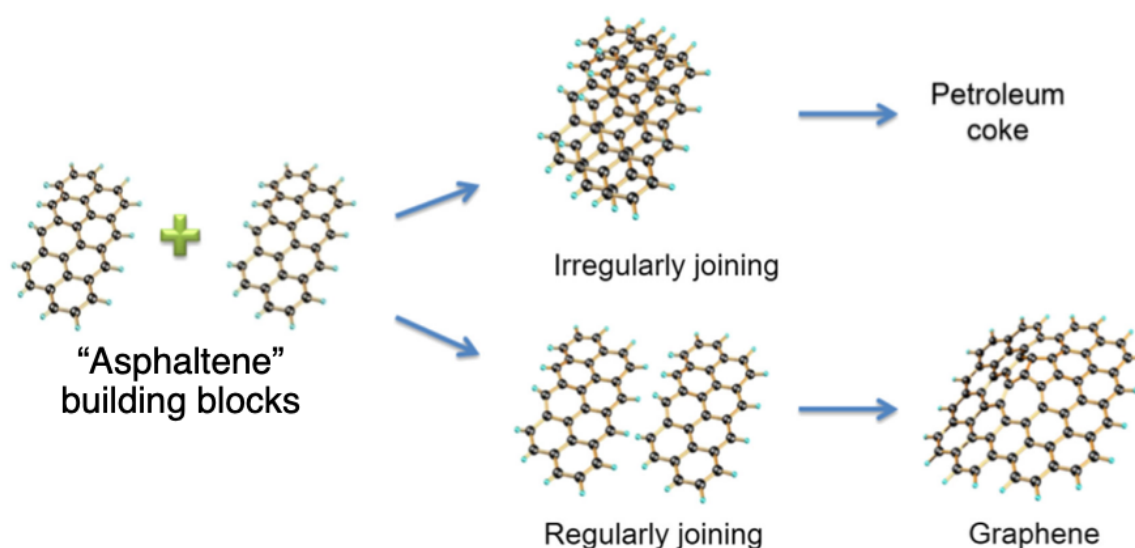


Figure 3. The use of asphaltenes as building blocks for graphitic compounds.<sup>14</sup>

A number of strategies have already been employed to physically disrupt asphaltene aggregation using various templating strategies. Ning and coworkers explored the use of vermiculite (a porous clay-like, layered material) where asphaltene molecules were adsorbed onto the surface. The formation of graphene layers upon calcination was ascribed to not only the regular arrangement of asphaltenes but also the joining of the asphaltene molecules catalyzed by the Fe-containing vermiculite surfaces.<sup>14</sup> This was an attractive example of both catalyzed reactions and templating effects using vermiculite. This example demonstrated the effectiveness of templating strategies coupled with oxidative catalysts (Fe). A similar study explored the adsorption behavior and templating effect using mica.<sup>15</sup>

Once again, we sought to find an alternative to using additives that could not be carbonized. For example, while the templating strategies above do have analogy to a catalytic converter in the auto industry, it would be difficult (and costly) to extract the graphene from the template, and reuse the template. However, the surfactant literature does provide some clues to commercial viability of potential additives. Velásquez et al. analyzed the rheological properties of hydrophilic ethoxylated phenol formaldehyde polymeric resins with asphaltenes to determine their potential as surfactants at an asphaltene oil/water interface.<sup>16</sup> They hypothesized that the structure of the polymeric resins must contain aromatic rings to interact with asphaltene and a hydrophobic back bone allowing the polymer resin and disruption of

aggregation. The researchers did show that asphaltenes oil emulsions were stabilized ultimately as a result of decreased aggregation in solution.

Phenol formaldehyde resins have structural similarity to lignin (Figure 4), a biopolymer of interest that could serve to stabilize asphaltenes in oil/water emulsions. Lignin is found as a natural macromolecule in the cell walls of vascular plants, making it one of the most abundant macromolecules in the biosphere, second only to cellulose. Lignin has attracted renewed attention given its role as a byproduct in the forestry industry and anticipated role in biorefinery operations and bioethanol production. In fact, lignin is already being explored as a renewable and superior asphalt binder modifier in roads and construction materials.<sup>17</sup>

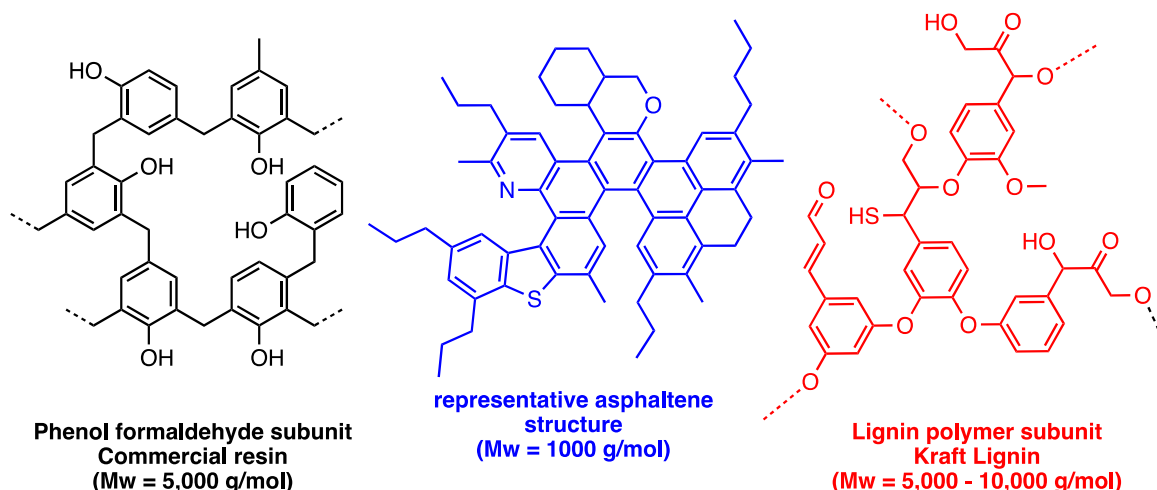


Figure 4. Like dissolves like – a structural chemical comparison between phenol formaldehyde resins, asphaltenes and lignin.

### Electrospinning lignin

As mentioned above, a myriad of precursors, such as coal and pitch, have been used for electrospinning – and lignin has also been used successfully deployed in this effort. As a result, the use of lignin as a building block in the fabrication of new materials has been frequently reported.<sup>18</sup> However, unless chemically modified in advance, Kraft and organosolv lignins must be blended with polymers to produce electrospun fibers, because lignin alone does not have a high enough molecular weight for entanglement. Entanglement is a concept that will be discussed later in the report, but essentially, intermolecular interactions, such as hydrogen bonding and entanglement (Mol wt > 100,000 g/mol) are main factors influencing the electrospinnability of any system. Perhaps the most studied lignin sources have been the composites of commercially available Kraft or organosolv lignin mixed with hydrophilic or hydrophobic polymers, such as polyethylene oxide (PEO), polyvinyl alcohol (PVA), polyhydroxybutyrate (PHB), polyethylene terephthalate (PET), polypropylene (PP) and polycaprolactone (PCL).<sup>19</sup> Each of these



composite polymers, can be thermally processed into fibers (carbon and nano), compostable plastics, and structural materials.

### Technology/Knowledge Gap and Research question

Due to their high surface-to-volume ratio, porosity, and mechanical properties, nanofibers have widespread applications in drug delivery, tissue engineering, sensors, energy storage, and separation membranes. As described above in earlier sections, electrospun films of nanofibers can also be carbonized to create a number of functional carbon materials and composites. While various methods can be used to fabricate nanofibers, including; template synthesis, drawing, melt-spinning, self-assembly, phase-separation, and centrifugal spinning, only electrospinning is a versatile, cost-effective, and facile way to provide great control over the fibers' diameters, characteristics, and morphologies (discussed in greater detail in the methods section). Additionally, having the ability to tune the electrospinning process parameters permits further control of the morphology and the mechanical properties of the fibres formed.

Our proposal makes the following assumptions: 1) Asphaltene cores are responsible for aggregation that encourages undesirable "face-face" irregular joining, and; 2) this prevents edge-to-edge regular joining that is essential for graphitic formation during carbonization. **It is hypothesized that if we disrupt this aggregation there will be a greater propensity to form graphitic structures upon carbonization AND using electrospinning to make high surface areas composite films will permit carbonization at lower temperatures.** Therefore akin to reinforcing lignin-based electrospun nanofibers with cellulose,<sup>20</sup> the knowledge gap that we hope to address is:

- Can we use lignin to disrupt asphaltene aggregation enough (Figure 5) such that we suspend both the lignin and asphaltene mixture in an aqueous polymer suitable for electrospinning?

In 2019, mineral fuels including oil was Canada's largest export (US\$ 98.4 billion – 22 % of all exports), in 7<sup>th</sup> place was forestry (US \$11.7 billion – 2.6% of all exports). While asphaltenes represent a significant byproducts in our fossil fuel extraction, lignin is the largest by product in the forestry industry. In terms of waste valorization, combining these two by-products (lignin and asphaltenes) may offer some convenient synergies that might also be at the industrial scale needed to make new composite carbonaceous materials. If the knowledge gap above can be closed successfully, then it is our opinion that we could carbonize these materials and upcycle these Canadian waste products and transform them into a new value added material. Lignin-asphaltene derivatives should exhibit liquid crystalline mobility that will facilitate asphaltene fibres to possess a preferential edge-to-edge conformation, which should lower the energy required in the carbonization steps. Furthermore, any 'failure' towards our CF goals above could still be a market breakthrough for other asphaltene-derived applications.

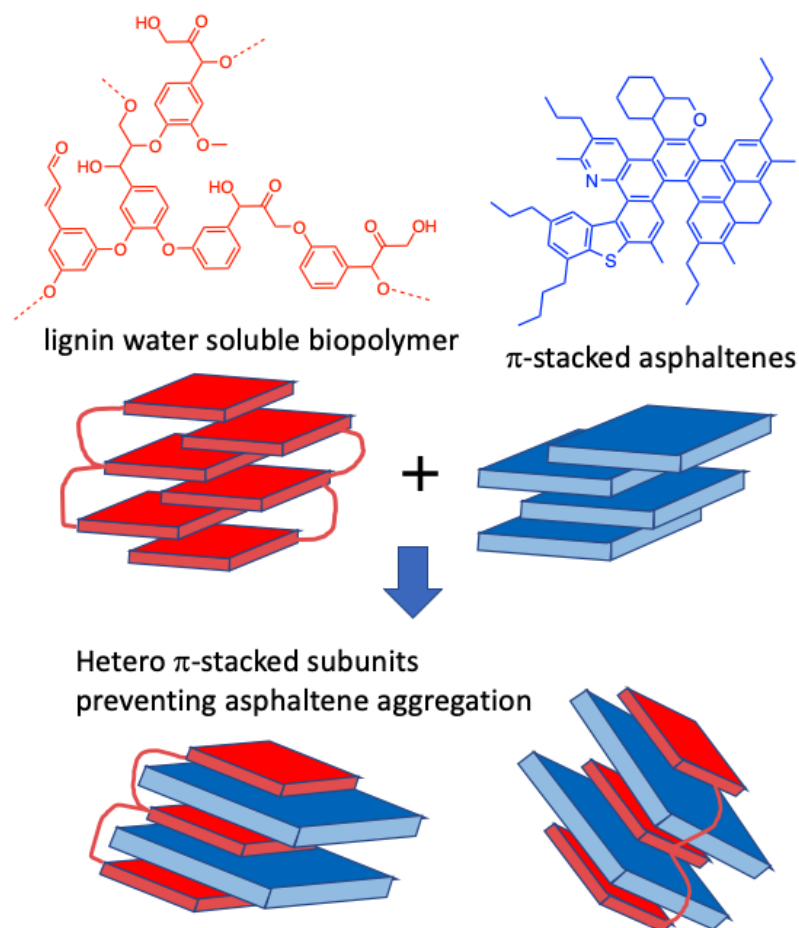


Figure 5. Lignin as a biopolymer template to disrupt asphaltene aggregation

## 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

## Project objectives

As alluded to in the introduction, in 2011 a report demonstrated that asphaltenes could be electrospun into fibres using toluene (and hydrogen peroxide) as a solvent.<sup>10</sup> Unfortunately, these fibres were hollow, brittle and there was no attempt to carbonize them. As a starting point we sought to optimize this existing literature precedent of fibre synthesis by doping our asphaltene solutions in toluene with different oxidants (0 – 3%) prior to electrospinning. Our proposed innovation expanded on the previous work by using hydrophobic oxidants, instead of hydrogen peroxide (organic peroxides catalysts derived from industrially-relevant and low-cost cumene). Peroxides are some of the strongest chemical oxidants known, capable of oxidizing benzylic groups and graphene. In addition, cumene itself was hypothesized to serve as a co-catalyst with oxygen, because cumene readily reacts with oxygen to produce cumene hydroperoxide in situ, which would add a higher level of safety, at a reduced cost. However, our attempts to electrospin asphaltenes to **reproduce the findings this 2011 paper (Original Objective 1)** failed. At this point we quickly realized there were more variables at play than originally thought. A key pivot occurred for the following reason:

- Asphaltene source is critical (and highly variable). While this is generally understood to be true, our work analyzed both a liquid fraction (L2; containing other volatile organic liquids) and a solid sample (S2) provided to us from InnoTech Alberta's Asphaltene Sample bank. As will be discussed (in the following sections), the complexity of the asphaltene mixture affects the viscosity and conductivity and ultimately the electrospinnability. It is likely that every asphaltene mixture will have unique viscosity and conductivity, and therefore, to overcome this, a modified approach using lignin, polymer co-additives and coaxial electrospinning (see below) was required.

The most common process to disrupt asphaltene aggregation is the chemical pre-oxidation with an aqueous oxidants (e.g.,  $H_2O_2$ - see above).<sup>18</sup> Oxidation inserts oxygen functional groups (epoxides, alcohols and carboxylic acid groups) on the asphaltene surface. The addition of these new functional groups weakens the stacking force exerted by  $\pi$ - $\pi$  interactions. While our project always had, at its core, the idea to pre-oxidize the asphaltene using organic peroxides (increased solubility) catalysts with and oxygen, we did not observe **pre-oxidation using organic peroxides (Original Objective 2)** under any of the conditions we employed. As a result, the following key pivot occurred:

- While COVID-19 delayed and hindered every aspect of our project - a silver lining did emerge in the form of a synergistic collaboration that presented itself after our grant submission. Dr. Stephanie MacQuarrie (Cape Breton University (CBU), Nova Scotia) is an organic materials chemist with expertise in biopolymer waste valorization and pyrolysis. CBU has complementary skill set and equipment for analysis. Dr. MacQuarrie has an ongoing lignin project and therefore **we pivoted to focus almost exclusively on lignin (Original Objective 3) as an additive**.

As a result of focusing on lignin-based electrospinning, we made the following additional pivots:

- Lignin is water soluble, and owing to our interest in industrially scalable and green technologies, we elected to focus entirely on water-based solvents AND the challenge then became suspending asphaltenes within lignin (to increase water miscibility), similar to the surfactant behavior discussed above).
- As mentioned in the introduction, a minimum polymer molecular weight is a critical piece for filament formation during electrospinning (often overlooked in electrospinning literature). Commercial lignin does not have enough entanglement for solution based electrospinning therefore a water soluble polymers: polyvinylalcohol (PVA), polyvinylpyrrolidone (PVP) were used as a co-additive. PVA and PVP were selected for this study because we had used them previously in our research and there was literature precedent for their use in electrospinning.
- We quickly realized that the simple single-nozzle electrospinning setup has limitations; for example, forming fibers from low molecular weight or unentangled polymer solutions is challenging. However a modified version of single-nozzle electrospinning, known as coaxial electrospinning, can be (and was) used to overcome these limitations. This technique will be discussed in greater detail in the following section.

As mentioned in the introduction, asphaltenes are toluene soluble, and hydrophobic. Therefore an ancillary objective from this study is to find a way to increase the hydrophilic nature,

- Oxidative pretreatment and asphaltene functionalization were explored as a means to increase hydrophilicity and are discussed in the results section.

## Performance Metrics

Our original proposed research had several performance metrics that quickly changed as a result of the project pivots listed above. Therefore the ultimate performance metric that we established was to incorporate asphaltenes in lignin containing aqueous electrospun nanofibers.

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## D. METHODOLOGY

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

*RESPOND BELOW*

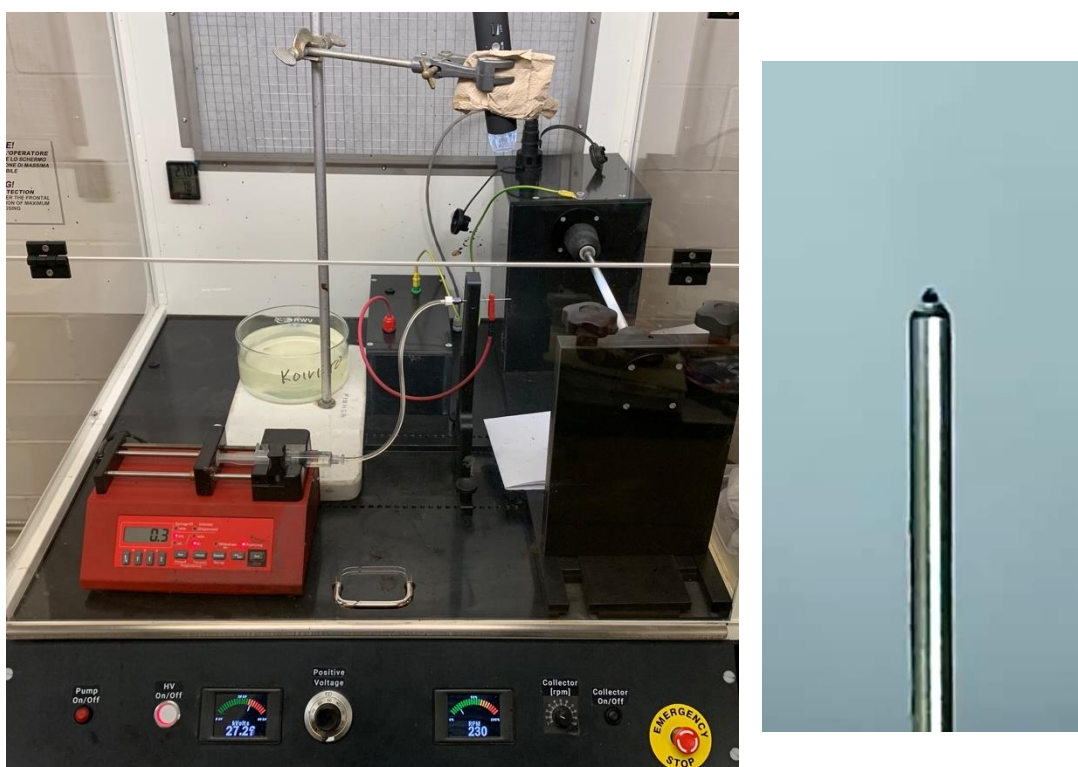
Owing the our long-term challenge goals, we focused exclusively on industrially relevant environmentally-green conditions. Therefore, we ONLY explored water as our electrospinning solvent. The following commercially available reagents were also used in this study: alkaline lignin (low sulfonate content, Sigma Aldrich #471003) and PVA (98% hydrolysed, Mw = 125,000 g/mol, Sigma Aldrich – Moviol20-98, #11773)

and PVP ( $M_w = 1,300,000$  g/mol, Sigma Aldrich #437190). Asphaltene liquid fraction (L2) and a solid sample (S2) were provided to us from InnoTech Alberta's Asphaltene Sample bank.

### Electrospinning

Below is a picture of the electrospinning set up employed at Ryerson University. A syringe pump feeds an aqueous polymer solution to a needle tip. When flow rate, solution viscosity & conductivity and voltage are matched a stabilized Taylor cone forms (right) and nano (or micro) fibres form and collect on the collector.

*Owing to proprietary considerations, the ratio of reagents used, the solution properties and the electrospinning parameters have been omitted from this report.*



*Figure 6 – (left) The electrospinning equipment used in this study - both a drum and plate collectors were used; (right) – stabilized Taylor cone at the needle tip*

As alluded to earlier, there are a number of variables that can be adjusted to tune and later the size and shape of the electrospun fibres (Figure 7). While there are several variables that we can control, we were not able to explore temperature and humidity dependence on our electrospun films. Owing to our lab environment were at the mercy of Fall/winter heating ( $\sim 26-28$  °C in the lab and low humidity of 20%)

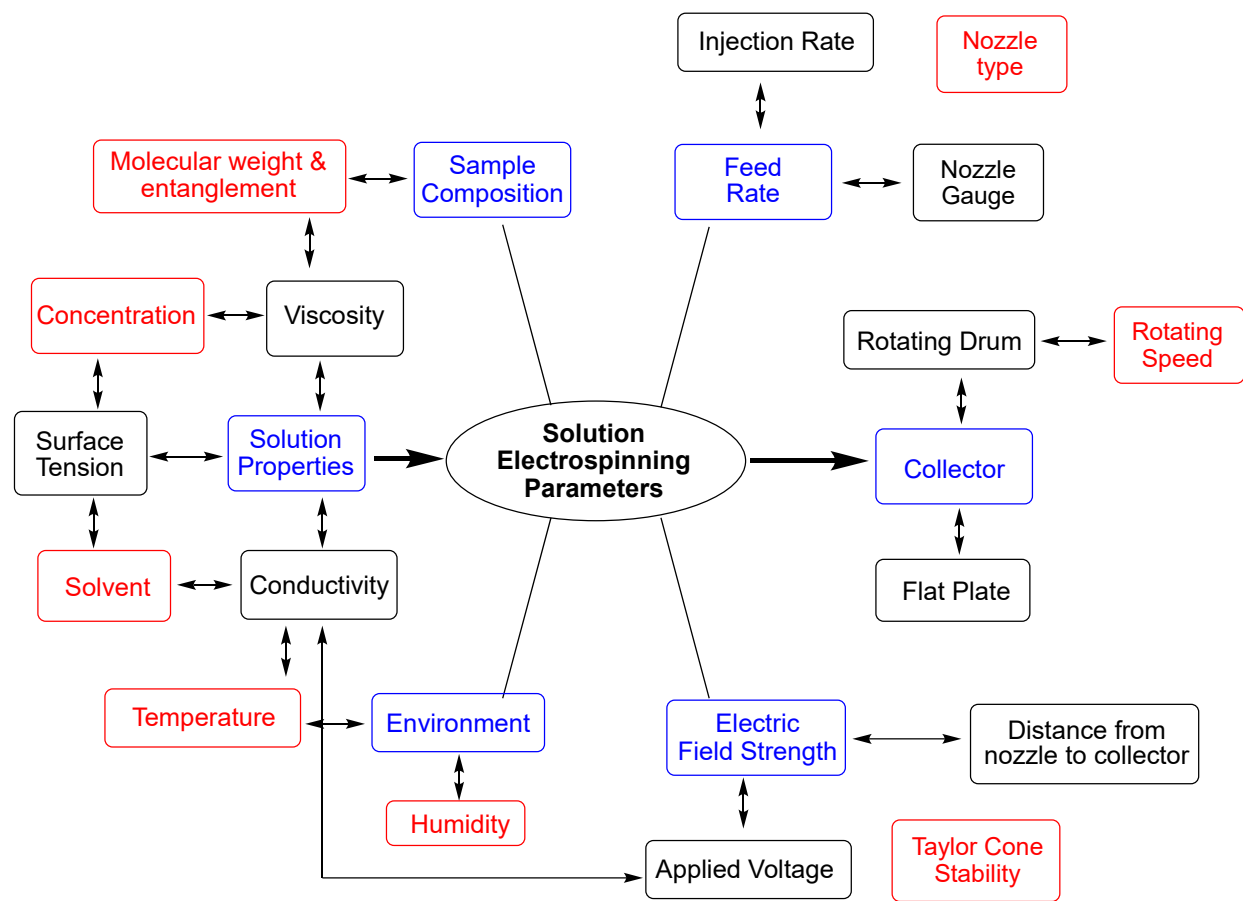


Figure 7. Variable inter-relationships in electrospinning. Left hand side are chemically relevant variables, and the right hand side are largely engineering variables. Nozzle type refers to co- or triaxial design.

## Analytical and physical testing

The following techniques were also used to inform the structure property relationships of the electrospun and pyrolyzed fibres.

- Brookfield Viscometry – Ryerson University – used to measure the viscosity of the electrospinning solutions.
- Conductivity – Ryerson University – used to measure the conductivity of the solutions
- Scanning electron microscopy (SEM) – Ryerson University – used to visualize electrospun nanofibers (and will be frequently visualized below)
- Infrared spectroscopy (IR) – solid state method - Ryerson University – used to monitor the change in asphaltene composition and surface modification upon chemical oxidation
- Ultraviolet-visible spectroscopy (UV-Vis) – solution method - Ryerson University – used to monitor the change in asphaltene composition and surface modification upon chemical oxidation

- Elemental analysis (EA) – Cape Breton University – used to examine chemical (specifically carbon) composition of pyrolyzed films
- Brunauer–Emmett–Teller (BET) gas adsorption – Cape Breton University – used to determine the effective surface area of the pyrolyzed carbon material.
- Transmission Electron Microscopy (TEM) – Cape Breton University – used as a complementary technique so we can further examine core-shell coaxial electrospun fibres.

Below is a summary of the project results. Many proprietary details have been omitted.

## 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

### Chemical pre-modification of Asphaltenes

As one of our updated technology objectives, we sought to functionalize asphaltenes to disrupt aggregation and increase hydrophilicity. To this end there were three approaches explored: PEGylation (adding a polyethylene glycol (PEG)); using organic peroxides to (dicumene peroxide); and Hummers method for oxidation.

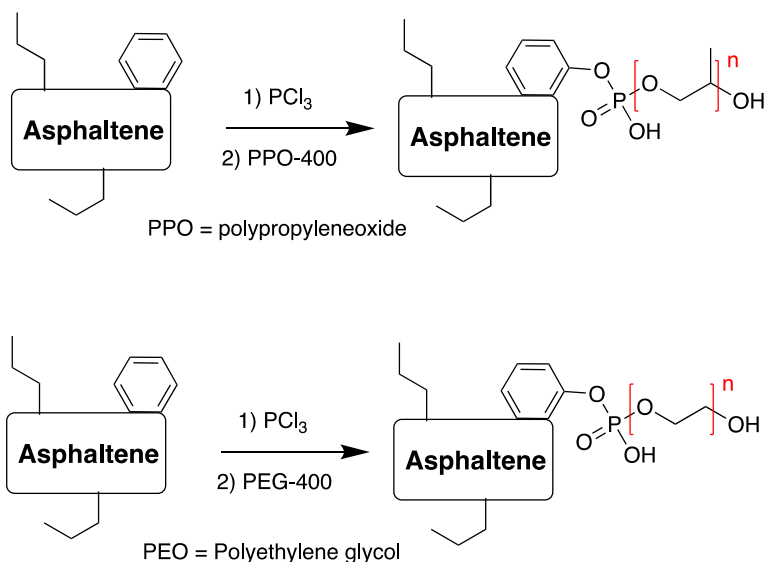


Figure 8 – Cartoon showing the reaction of an asphaltene with  $\text{PCl}_3$  followed by the addition of hydrophilic polymer

PEGYLATION (Figure 8 above): Owing to the additive costs of both the consumables and the additional synthetic manipulation steps, we were hesitant to even consider this approach to asphaltene modification; however, a sense of desperation early on led us to attempt this approach as a possible way to make the asphaltene more water soluble and electrospinnable. Building on a report by Ovaless et al. we sought to make our Athabaskan oil sands derived asphaltenes more soluble by functionalizing it using a phosphoethoxylation reaction.<sup>21</sup> PEGylating nanostructures similar to asphaltenes (corannulene) has shown promise in dispersing graphene nanotubes, and we thought that it might be an effective way to disperse asphaltenes.<sup>22</sup> Unfortunately neither L2 nor S2 showed any spectroscopic evidence of conversion. Moreover, the greater complexity of L2 also made this conversion process impossible to monitor. A number of solvents and temperature conditions were attempted.

ORGANIC PEROXIDES (Figure 9 below): As part of our initial proposal, we sought to oxidize the asphaltene with organic peroxides instead of aqueous peroxides. Two different trials were attempted. Using catalytic cumene and oxygen (A) and stoichiometric (excess) dicumene peroxide. Unfortunately neither L2 or S2 showed any spectroscopic evidence of conversion in either A or B. Moreover, the greater complexity of L2 continued to make this conversion process impossible to monitor spectroscopically. A number of solvents and temperature conditions were attempted.

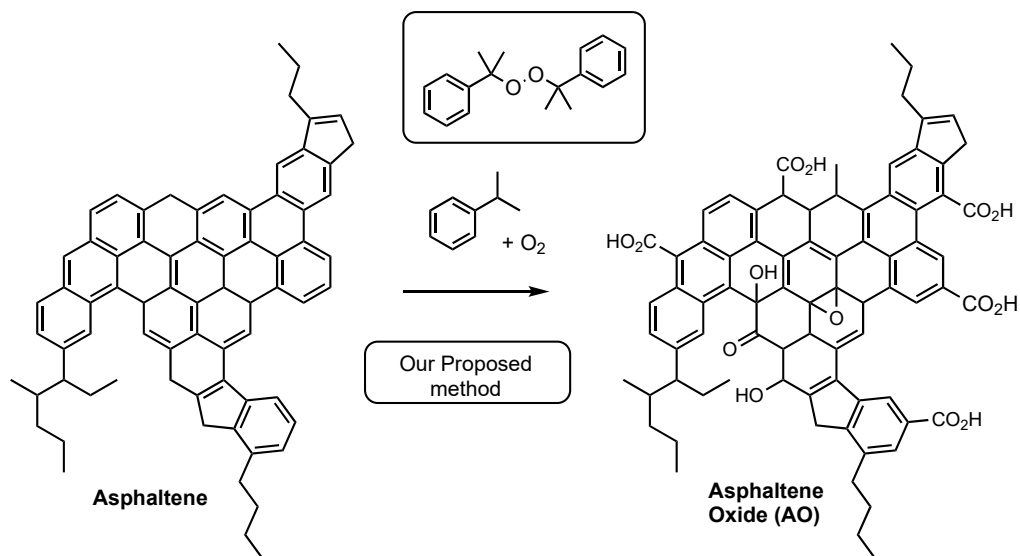


Figure 9 – Representative asphaltene oxidation using A) Cumene and air and B) dicumene peroxide

HUMMER'S METHOD (Figure 10): Another attractive method for oxidation is a modified Hummer's method. In a report by Jung et al., they demonstrated the feasibility of this reaction for asphaltene pretreatment.<sup>23</sup> This reaction was successful in the conversion of the asphaltene in our hands, but BE



CAREFUL – slow addition of the oxidant is needed to avoid pyrophoric conditions. Owing the endergonic nature of this reaction we avoided testing this reaction in the presence of a more combustible mixture.

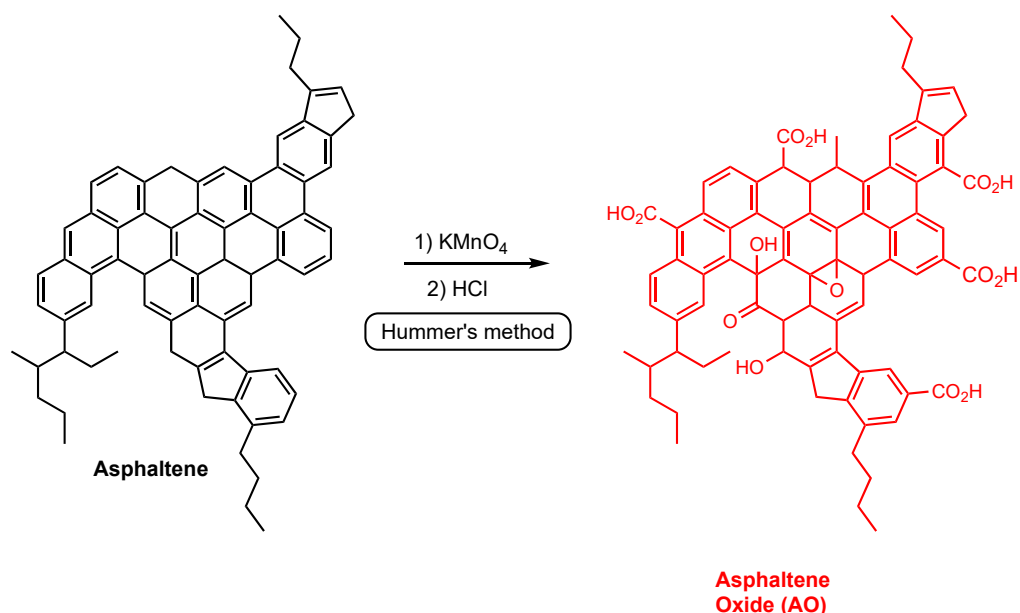


Figure 10 – Representative cartoon of the Hummer's method using Potassium Permanganate in acidic conditions

## Electrospinning

As mentioned in the introduction, we were not successful at electrospinning pure asphaltene fibres from S2 (in toluene) or L1 (neat). In our system, clogging of the needle, and conductivity of the solution are believed to be the major factors preventing electrospinning and Taylor cone stability. Therefore, we focused on lignin-PVA and lignin-PVP combinations as hosts for asphaltene. Both lignin and the polymers have been frequently electrospun, and have been explored in the preparation of carbon fibre.

Using PVA or PVP in (5-10% by weight in water) and lignin (5-10% by weight in water) ratios we were able to produce electrospun fibre mats as a baseline for our asphaltene addition. The two samples below are representative (Figure 11), and showcase the large and small fibres that we can tune and create when we vary the viscosity, solution conductivity and voltage during our electrospinning process. Our results indicate that we can use both PVA and PVP polymers mixed with lignin to form nanofiber mats with fibre diameter ranging from 130 – 1100 nm.

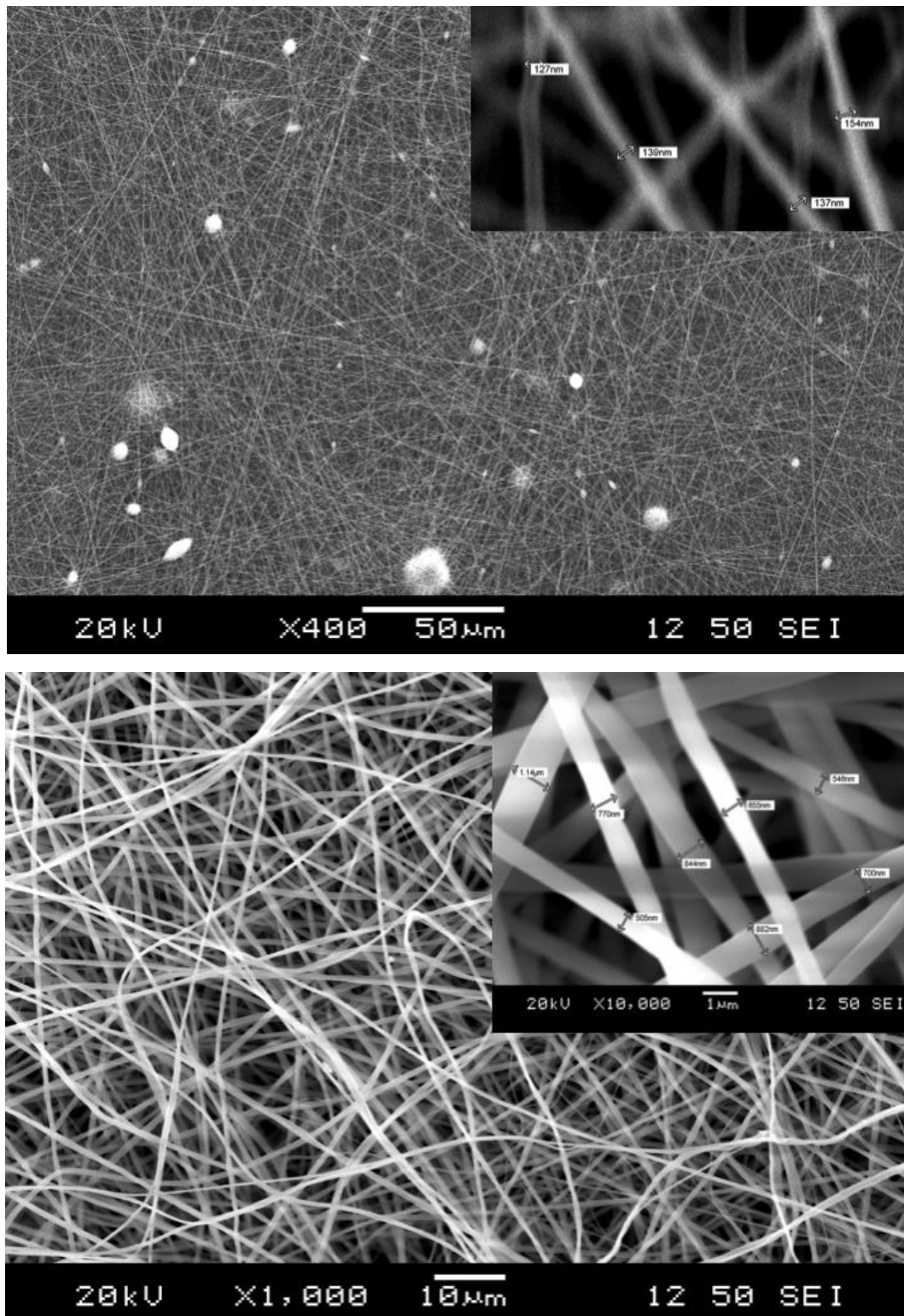


Figure 11 – Representative SEM images for (top) PVA/lignin nanofibers (130-160 nm); (bottom) PVP/Lignin microfibre mats (500 – 1100 nm). Large white spots in the top diagram is sputtered gold used in the SEM imaging

## Coaxial electrospinning

After several failed attempts at loading our control polymer fibres, described above, with asphaltenes (likely owing to immiscibility), we discovered a new approach to asphaltene electrospinning. As mentioned in the introduction, co-axial electrospinning uses a special needle nozzle where one can have a core solution that is different from the sheath. The sheath is usually a higher molecular weight polymer that has greater entanglement (better electrospinnability), allowing a core (that is harder to electrospin), to be cast into fibres.

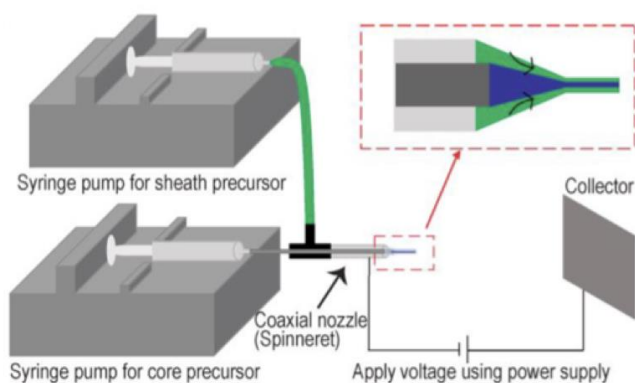


Figure 12. Coaxial electrospinning nozzle set up<sup>24</sup>

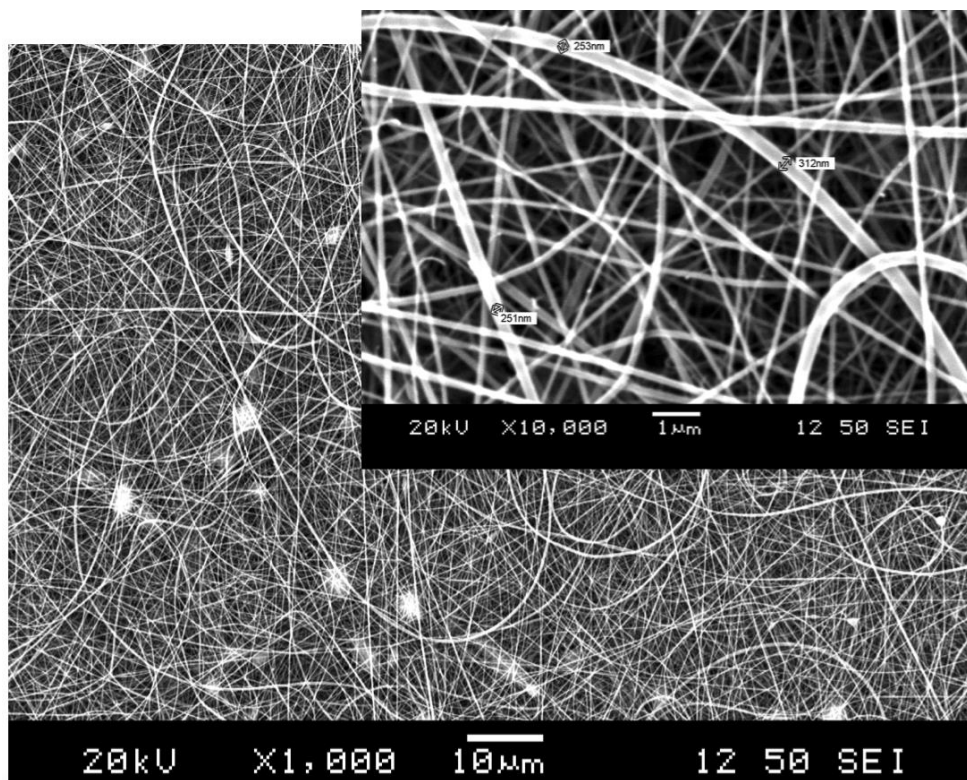


Figure 13. A core-sheath coaxial electrospun fibre (250 -350 nm) with an asphaltene/lignin core

Figure 13 shows our core-sheath asphaltene containing electrospun fibre. While we cannot disclose its composition, improvements can still be made in the lignin:asphaltene ratio with the goal of achieving a 1:1 ratio of the two materials (see future work).

## 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

Table 1: Summary of results

Asphaltene Sample	Electrospinning (Neat)	Sample pretreatment with $\text{PCl}_3$	Sample pretreatment with Organic peroxide	Sample pretreatment with $\text{KMnO}_4$	Electrospinning (in Lignin)
Liquid (L2)	As is, unsuccessful, no stable Taylor cone	Too much hydrocarbon impurity to monitor spectroscopically	Too much hydrocarbon impurity to monitor spectroscopically	Too much hydrocarbon impurity to test	Additional organic solvent makes water miscibility impossible
Solid (S2)	In toluene, unsuccessful - clogs needle - no stable Taylor cone	No evidence of conversion spectroscopically	No evidence of conversion spectroscopically	Successful conversion spectroscopically	Promising initial result with coaxial electrospinning

Table 1 summarizes the key results with respect to the reactivity and spinnability of untreated and treated asphaltene samples using our the electrospinning methodology.

The key insights from our results, include:

- Asphaltene source is critical (and highly variable). While this is generally understood to be true, solution-based electrospinning is highly sensitive to viscosity and conductivity - and both of these properties are directly related to the asphaltene source and its homogeneity.
- While it does not mitigate this impact above entirely, coaxial electrospinning provides a greater opportunity for spinning low molecular compounds (asphaltenes and lignin) by containing them within a polymer sheath.
- This coaxial electrospinning is particularly attractive when making carbon-based materials because it affords a number of structures and compositions for building other novel carbon-based technologies.
- Lignin does help to disperse asphaltenes ultimately increasing their electrospinnability in aqueous solutions.



## 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

### Clean Energy Metrics:

# New products/services created	Estimated = 1 new use for asphaltene Actual = 1 new use for asphaltene
# of Publications	Estimated = 1 review, 1 paper Actual = 1 review, 1 thesis
# Students (Msc., PhD, Postdoc)	Estimated = 3 Actual = 4 (2 MSc, 2 BSc)
# Patents filed	Estimated = 2 Actual = 0
# new jobs created from project	Estimated = 1 Actual = 1
# New Spin-Off Companies created	Estimated = 1 Actual = 1
Partnership agreements / MOUs?	Estimated = 1 MOU Actual = 1 MOU
Unique product/process	Estimated = A scaleable lowcost electrospinning process Actual = A scaleable lowcost electrospinning process
# of End Users participating	Estimated = 1 end user for the unique CF formed above Actual = 0

In terms of our Clean energy metrics, the pivots in our project hindered patents, publications and end user agreements, but serendipity did favor a discovery that has enabled the formation of a new startup company (AIM consulting), and the project has inspired many future research directions that will continue beyond the scope of this funding.

**Program Specific Metrics:** The goal of our project is to enable value-added technological development creating wealth for Alberta. We predict this will be achieved by developing new ways to use asphaltene in green technologies. Owing to our previous described project pivots, we were not able to reach any of our proposed program specific metrics, but the project will continue beyond this funding arrangement

**Project Outputs:** 1 pan-Canadian collaboration (Alberta, Ontario & Nova Scotia) has been initiated; 2 conference presentations; and this project has inspired one MSc thesis (underway)

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## 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*

At this point, other than the training of students, and the key learnings from this project, we have not yet realized any benefits; however, we do foresee this project enabling the following economic, environmental and social future benefits to Alberta (and Canada).

- **Economic** – Our learnings provide a pathway (that we are still pursuing and improving) where we have control over the morphology of nanofibers that incorporate asphaltenes. To this end, we open the door to a wide range of applications (beyond carbon fibre). Some include, optically transparent conducting materials, catalysts for electrochemical cells (like fuel cells and batteries), and as low cost nano-additives/fillers for composite materials (like concrete). In addition, the start-up company emerging from this project will be a future job creator in the province of Alberta, as it's IP is mobile, and incorporated nationally.

- Environmental – Sequestering biowaste (like lignin, as our other templating material) and coupling it with asphaltene from the oil sands to make nanofibres that will be used as feedstocks that will enable an eco-revolution (electric vehicles, and hydrogen economy) will have an enormous positive impact on the planet. In addition, consuming large quantities of organic materials and incorporating them into long lasting composite materials, also sequesters CO2 destined for the atmosphere
- Social and Building Innovators - At the moment, HQP are being trained outside the province, but the collaborations and partnerships formed during this research will enable translational movement of HQP to Alberta as soon as the COVID pandemic has passed. We enthusiastically look forward to that mobility. Additionally one of the co-applicants is based in Calgary. In terms of social impact, we feel that the entrepreneurial spirit within our team, will translate several of our project ideas into commercialize activities that will benefit Alberta in the near future.

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## 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*

While this Alberta Innovates project has come to a close, it has inspired an entirely new direction for our research program. In addition, the graduate student on the project has founded a startup company (AIM consulting), and he is keen to continue to work on this for the remainder of his thesis over the next 2 years, and commercialize these results. The graduate student is keen to travel, and Alberta could be a future destination for him and his company. We also expect this to evolve into several Graduate theses over the next few years (PhD and MSc) because this project has sparked the following questions, current and future directions.

**Follow up project 1:** Pyrolyse the various promising electrospun films that serve as controls and compare them to pyrolyzed samples containing asphaltenes. Examine the major differences in their structure-property relationships.

**Follow up project 2:** Biopolymers have been widely explored in electrospinning and have show promise in a myriad of applications.<sup>25</sup> They are attractive way to disrupt aggregation, and are produced at a relevant scale for industrial processes. Of those lignin remains attractive, but perhaps the wrong lignin industrial by-product was studied. Lignin has two major forms: a sulfonated form (lignosulphonates, LS) and a sulfide from Kraft pulping of wood. A recent study does suggest that we are on the right track with using lignin, but maybe chose the wrong lignin derivative and should examine lignosulphonates as well.<sup>26</sup> The study showed oxidized asphaltene films where adsorbed into lignosulphonates at oil–water interfaces.

**Follow-up Project 3:** Owing to the limited solubility of asphaltenes in aqueous polymers Asphaltene/lignin/polyethylene oxide (PEO) compositions may be more feasible<sup>27,28</sup> than PVP and PVA. Pure lignin solutions usually do not have the enough viscoelasticity for spinning. However, ultrafine microporous and mesoporous activated carbon fibres from alkali lignin and PEO has been described with lignin:PEO ratios as high as 1:1 being possible. In addition PEO micelles have been shown to solubilize polycyclic aromatic hydrocarbons.<sup>29</sup> This particular approach is quite attractive as it may increase the asphaltene composition in our nanofiber. Furthermore, PEO is preferred for carbonization process because of the lower melting point that leads to the fusion of the fibers during pyrolysis.

**Follow-up Project 4:** In terms of an industrial process, it is environmentally and economically feasible to use water as an electrospinning solvent. However, low molecular weight lignin solutions usually do not have the enough viscoelasticity for spinning. Building on the work developing a series of poly(ethylene glycol) methyl ether methacrylate (PEGMA)-grafted lignin hyperbranched copolymers,<sup>30</sup> lignin-acrylic acid copolymers,<sup>31</sup> and graft copolymers<sup>32</sup> we feel that making higher molecular weight lignin copolymers, may eliminate the need for a binder polymer; ultimately lowering the consumable cost of fiber formation, while increasing asphaltene content and dispersity in our lignin-based nanofibers.

**Follow-up Project 5:** Lignin is a polyphenol material that has a low cost, but unfortunately owing to its water solubility, the asphaltenes will always have limited solubility or dispersity. Therefore, finding an organic polymer matrix that could be valorized would be particularly advantageous.





Figure 14 – Plastic waste could be used as an electrospinning sheath during coaxial electrospinning, and better “solubilize” asphaltenes.

At least 8 million tons of plastic end up in our oceans every year and far more in our landfills. Mixed plastics are not recycled because they have varying chemical structures, glass transition temperatures and polydispersity indices (PDI) that impart different polymeric properties. However, in terms of electrospinning followed by carbonization the most significant properties are viscosity, polymer entanglement, conductivity and carbon content. Therefore, we would like to explore blending highly carbon containing and hydrophobic waste plastics (polystyrene, polyethylene, etc.) with asphaltenes. We hypothesize that the asphaltene content would be increased and upon pyrolysis novel carbon-materials could be attained.

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

## J. KNOWLEDGE DISSEMINATION

Knowledge over the next 6 months will be disseminated in the following forms

- A provisional patent on our coaxial electrospun asphaltene containing fibres – this will provide AIM consulting with the opportunity to commercialize this work further.

- An asphaltene review paper for the chemistry community as part of milestone 1.
- At least one publication in a chemistry journal
- Presentations at virtual national and international conferences.

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## 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*

After multiple pivots and delays owing to COVID-19, this opportunity has opened a path to cast asphaltenes into electrospun fibres. The waste valorization approach also appears feasible as an effective technique at making new carbon-based materials with asphaltenes. This work suggests that asphaltene derived materials have far more uses than merely a building block for carbon fibre formation. In fact coaxial electrospinning represents a means to create hierarchical architectures, that should facilitate a number of novel carbon composites; these will be explored as part of an newly inspired research direction in the Koivisto group at Ryerson University. We anticipate the findings in this report will benefit two start up companies (KMC and AIM), as they seek to find new commercial opportunities for asphaltene derived composites

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