ALBERTA INNOVATES

CLEAN RESOURCES FINAL REPORT PACKAGE

Project proponents are required to submit a Final Report Package, consisting of a Final Public Report and a Final Financial Report. These reports are to be provided under separate cover at the conclusion of projects for review and approval by Alberta Innovates (AI) Clean Resources Division. Proponents will use the two templates that follow to report key results and outcomes achieved during the project and financial details. The information requested in the templates should be considered the minimum necessary to meet AI reporting requirements; proponents are highly encouraged to include other information that may provide additional value, including more detailed appendices. Proponents must work with the AI Project Advisor during preparation of the Final Report Package to ensure submissions are of the highest possible quality and thus reduce the time and effort necessary to address issues that may emerge through the review and approval process.

Final Public Report

The Final Public Report shall outline what the project achieved and provide conclusions and recommendations for further research inquiry or technology development, together with an overview of the performance of the project in terms of process, output, outcomes and impact measures. The report must delineate all project knowledge and/or technology developed and must be in sufficient detail to permit readers to use or adapt the results for research and analysis purposes and to understand how conclusions were arrived at. It is incumbent upon the proponent to ensure that the Final Public Report **is free of any confidential information or intellectual property requiring protection**. The Final Public Report will be released by Alberta Innovates after the confidentiality period has expired as described in the Investment Agreement.

Final Financial Report

The Final Financial Report shall provide complete and accurate accounting of all project expenditures and contributions over the life of the project pertaining to Alberta Innovates, the proponent, and any project partners. The Final Financial Report will not be publicly released.

CLEAN RESOURCES FINAL PUBLIC REPORT TEMPLATE

1. PROJECT INFORMATION:

Project Title:	**Cost-efficient production of high-quality carbon fibres by floating catalyst chemical vapor deposition method**
Alberta Innovates Project Number:	G2020000332 (202010062)
Submission Date:	
Total Project Cost:	100,000
Alberta Innovates Funding:	50,000
AI Project Advisor:	Shunlan Liu

2. APPLICANT INFORMATION:

Applicant (Organization):	**University of Alberta**
Address:	10-367 Donadeo Innovation Center for Engineering, Mechanical Engineering, Advanced Water Research Lab (AWRL), Edmonton, AB T6G 1H9
Applicant Representative Name:	Mohtada Sadrzadeh
Title:	Associate Professor
Phone Number:	780-492-8745
Email:	sadrzade@ualberta.ca

3. PROJECT PARTNERS

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

RESPOND BELOW

A. EXECUTIVE SUMMARY

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

RESPOND BELOW

The exploration of the high-value application of Alberta oil sands by-product asphaltene is essential to control environmental pollution and maintain the sustainability of the oil sands industry by adding value from the by-product utilization. Here, we have explored the possibility of fabrication of high-quality carbon fibers (CFs) by well-known floating catalyst chemical vapor deposition (FC-CVD) using aromatic carbon-rich asphaltene precursor. The main project objective is the proof-of-concept production of high-quality CFs from asphaltene precursors using FC-CVD. We have proven that different quality CFs can be fabricated simply by varying the growth zone temperature in the furnace tube. The higher the growth zone temperature, the better the CF quality. Based on SEM, Raman, and electrical conductivity assessment, the best CF product constitutes graphene and carbon nanotube phases in its structure. Meanwhile, optimization of the evaporation temperature revealed that the precursor asphaltene contains a high-molecular-weight carbonaceous by-product, presumably a mesophase, that cannot be evaporated even at as high a temperature as 800 °C, leading to an optimized usable amount of ca.70% of the precursor at 600 °C evaporation temperature for CFs production. The finding of phase 1 of the project is the proof that FC-CVD can yield carbon fiber, and temperature plays a crucial role in determining the quality of the CFs. However, the limitation of our existing FC-CVD setup has set the limit of the quality, forms, and continual large-scale production of the CFs, which need to be addressed in phase 2 with proper instrumentation and process flow design.

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

Carbon fibre (CF) is proven to be a promising material for many applications, such as aerospace, military, automobiles, and energy storage, due to its unique high tensile strength in contrast to its extremely lightweight. However, the potential to capture a large global market in the near future is obstructed by the high manufacturing cost of high-quality CF. The high manufacturing cost is imposed by the high cost of raw materials and tedious multistep high-temperature processing. Alberta oil sand asphaltenes is a carbon-rich (almost 90%) aromatic hydrocarbon that can be a vital raw material in reducing CF's manufacturing cost if the fabrication process is designed judiciously. The current project is proposed considering these two purposes of cost and quality of asphaltene-derived CF. Floating catalyst chemical vapor deposition (FC-CVD) will is used to fabricate CF. It is a single-step continuous process, utilizing two zones heating furnace in contrast to multistep high-temperature conventional methods. Vaporized carbon and catalyst precursors are injected from Zone 1, at relatively low temperature, to zone 2 where the temperature is about 800 $^{\circ}$C to grow CFs, which is collected as CNT aerogel by rotational motor rolling. Hence, adjusting the FC-CVD process for asphaltene can potentially allow the fabrication of CF from this industrial waste material. CF manufacturing cost is expected to reduce substantially due to the single-step low energy demanding manufacturing process.

In phase 1, we have provided a proof of concept for the fabrication of CFs using asphaltene as raw material and single-step FC-CVD as a cost-effective technique. We also optimized the evaporation temperature and explored the effect of growth zone temperature on the carbon fiber quality. However, while carrying the experiments, some predicted and unexpected challenges relevant to asphaltene precursor materials and instrumentation revealed a need for more work on material processing, instrumentation, and process flow design. One such material related problem is the presence of 30% non-evaporable carbonaceous mass in the asphaltene raw materials that limits the continuous large-scale production and can be solved either by precursor purification or reactor design. The second challenge is the temperature limit that our existing furnace can reach, which ultimately limits our access to the quality of CFs. We have observed that the higher the temperature in the growth zone, the better the quality of the CFs. In conventional FC-CVD, a molecular precursor is used for CF fabrication where the molecule decomposes at around 800 ^{o}C, and the fragment condenses on the nanocatalyst leading to the growth of CNT aerogels. However, asphaltene as a polymeric material does not decompose as easily as the molecular precursor. Instead, the polymeric precursor decomposes incompletely and fuses to form a less ordered CFs. Fabrication of highly ordered CFs would require a higher annealing temperature beyond the limit of our current furnace.

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

The prime objective of the project is the proof of concept for the fabrication CF using FC-CVD. The second objective is to reduce CF fabrication costs by using asphaltene as a cheap raw material and FC-CVD as a single-step continuous process. The third objective is the improvement of CF quality in terms of purity and order of the CF structure. The last objective is to produce different forms of CFs by tailoring the fibre collection process and post-fabrication processing of CFs. The key parameters that need to be resolved are the continuous injection of asphaltene and ferrocene into zone 1, optimizing temperature in zone 1 and zone 2, and optimizing the ratio of asphaltene to ferrocene. Solid asphaltene and ferrocene can be hot melt-injected using an injection molder or dissolved in toluene for injection. An appropriate toluene amount will be necessary to balance the cost versus quality of CFs for solution-phase injection.

During phase 1, many of these desired parameters have been optimized, and nano-scale graphene and nanotube phase CFs can be generated successfully by this proposed approach. We have learned that the fabrication of high-quality CFs using asphaltene precursors needs a relatively higher temperature in both zone 1 and zone 2 than expected, especially for the injection zone since asphaltene did not have a single temperature evaporation point. The continuous production process is still not achieved with our current available lab equipment. We believed that the fabrication process could be made continuous for large scale-production by modifying or re-designing the precursor delivery process and using a high-temperature furnace. The high-temperature furnace will also facilitate the improvement of the CF crystallinity.

SEM, Raman, and electron conductivity characterizations have proven that graphene and CNT phase structure nano-scale CFs materials were successfully fabricated by the FC-CVD method. The important learning from this phase 1 results, for example, the effect of evaporation temperature on the percentage of precursors asphaltene to be utilized in FC-CVD, and the impact of growth zone temperature on the ordered phase, and electrical conductivity of the CFs, has enabled us to plan for the design of a continuous large-scale fabrication of high-quality CFs.

D. METHODOLOGY

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

RESPOND BELOW

The proposed methodology for the fabrication of CFs using FC-CVD and the fabrication mechanism is described in Figure 1 (left)). The asphaltene precursor and the catalyst precursor (i.e., ferrocene) would be injected as a melt or as a solution in toluene into the injection zone, and the would-be carried forward into the growth zone as vapor by the Ar/H_2 gas flow. In the growth zone, ferrocene would decompose to form an iron nanoparticle catalyst. The asphaltene molecules would decompose into reactive fragments that would condense on the nanocatalyst's surface to form CNT-based aerogels and would be spun into CFs using a mechanical roller. However, while carrying the experiments, it was observed that after injecting the asphaltene solution in toluene into the evaporation zone, there are about 30% carbonaceous residues in the evaporation zone that inhibit the continuous production. Therefore, we had to limit our experiments to optimize the evaporation temperature to use the maximum possible asphaltene precursors and growth zone temperature to enhance the CF quality as high as our furnace temperature limit allowed using the setup presented in Figure 1 (right panels). In this setup, the asphaltene precursor was placed on a ceramic boat without adding the catalyst precursor. The temperature was varied from 400 °C to 800 °C where 800 °C evaporation zone temperature resulted in the evaporation of ca. 70% of the asphaltene precursors, which was very close to ca 65-67% at 600 °C evaporation zone temperature. Therefore, 600 °C was selected as the evaporation zone temperature, and the effect of temperature on the quality of CFs was studied by varying the growth zone temperature from 800 °C to 860 °C.

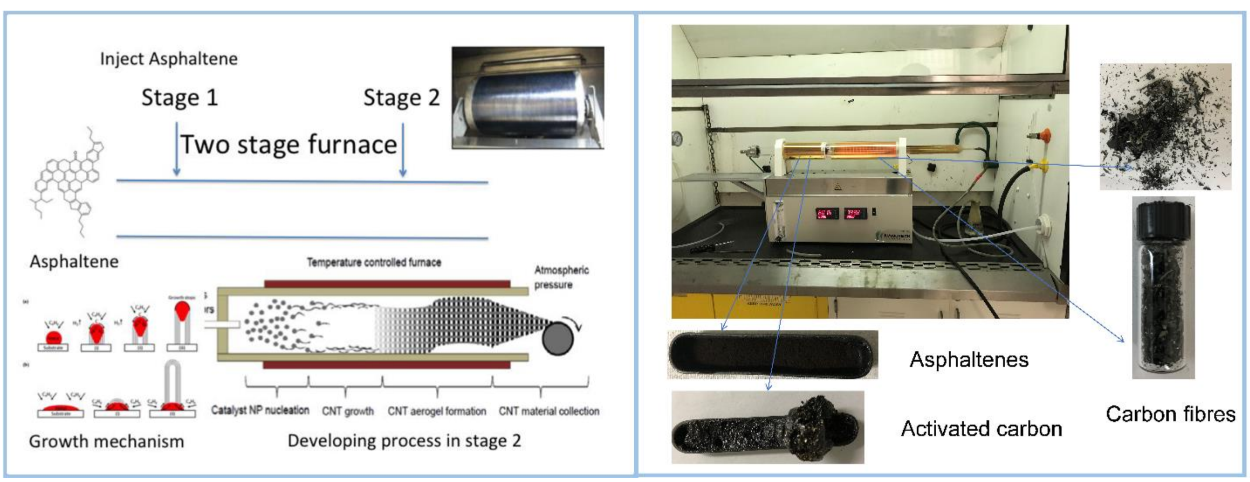


Figure 1. The proposed experimental setup and mechanism for the growth of CFs using FC-CVD (left panels) and the experimental setup used to conduct the experiments in phase 1 of this project (right panels).

Solid ferrocene (0.5 wt%) was mixed with solid asphaltene and ground into fine powder by mortar and pestle. 3.0 g of powder mixture was loaded to a ceramic boat and transferred to the boat in the evaporation zone 1 inside the quartz tube. Both ends of the quartz tube were sealed and bowed with a 5.0 % H_2/Ar gas mixture with a flow rate of 1.5 liters per minute (LPM) for 20 minutes. The temperature of furnace growth zone 2 was set up to the desired temperature. After the growth zone 2 temperature became stable, the evaporation zone 1 was set to 600 °C. After one hour, the furnace was switched off to cool down to room temperature under 0.5 LPM 5.0 % H_2/Ar gas flow rate.

The boat loaded mixture was shown in Figure 1 (right panels) before and after the process in stage 1, and the fabricated carbon nanofibers were shown on the surface of a paper and inside the glass vail as shown in Figure 1 (right panels).

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.

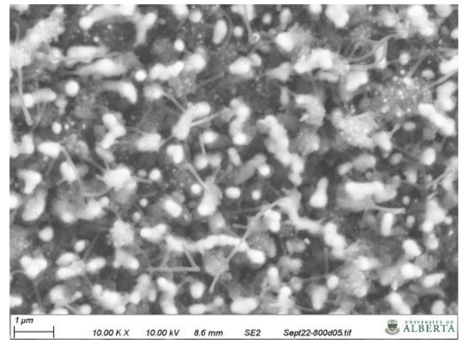
RESPOND BELOW

1. Optimization of the asphaltene evaporation temperature

It was observed that there was some residue in the evaporation zone after placing the asphaltene precursor, 30 wt% even at 800 °C evaporation zone temperature. The asphaltene powder received from AI consists of a weight percentage of 93.8% carbon, 4.5% oxygen, 0.1% aluminum, and 1.6% sulfur, as estimated by EDS elemental composition analysis. Therefore, the high amount of residue must be some carbonaceous mass, for example, the mesophase, which cannot be evaporated.

The evaporation temperature was varied from 400 °C to 800 °C to maximize the amount of asphaltene precursors usable for the fabrication CFs by the FC-CVD method. Either in solid or liquid (dispersed in toluene) was delivered into furnace stage 1; the correlation between evaporation (%) at different temperatures was listed in the table as shown in Figure 2 (top left). The evaporation increased significantly from 400 °C to 500 °C, and a small difference in evaporation was observed by increasing temperature from 500 °C to 800 °C where ca. 70% of asphaltene precursor can be evaporated at 800 °C. Only 7.0% is increased from 500 to 800 °C; the evaporation temperature was selected as 600 °C and the temperature of the growth zone 2 was varied to examine the effect of temperature on the quality of the CFs.

Deliver format	T (°C)	Evaporation (%)	Residual (%)
Solid powder	400	31	69
Solid powder	500	63	37
Solid powder	600	65	35
Liquid (dispersed in toluene)	315/600	67	33
Solid powder	800	70	30



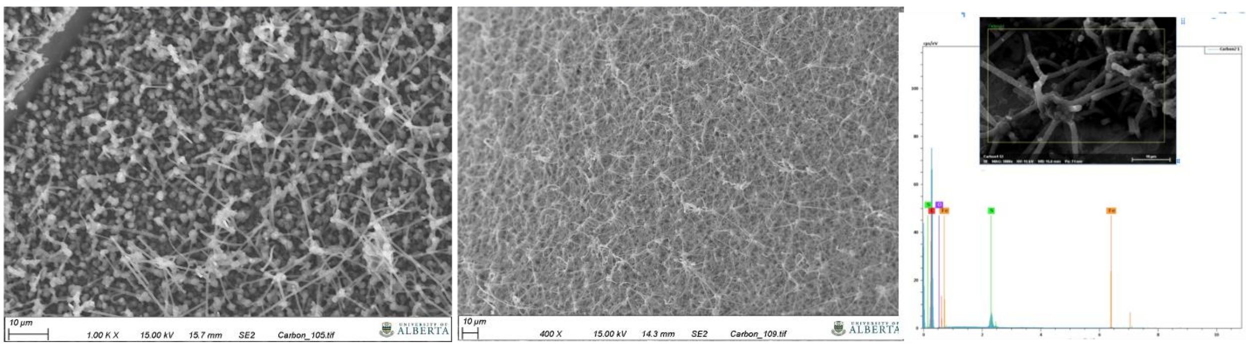


Figure 2. Optimization of asphaltene evaporation temperature and effect of growth zone temperature on the property of the generated CFs.

2. The key results for the fabrication CFs

The growth zone temperature has a substantial effect on the property of the CFs. An increase in temperature by only 30 °C increases the fibrous structure significantly. It can see that the product obtained at 800 °C growth zone temperature consisted of short nanowires and small nanoparticles (Figure 2, top right). An increase in the temperature to 830 °C resulted in a relatively higher population of longer nanowires and a relatively lower population of small nanoparticles (Figure 2 bottom left). Finally, at 860 °C, the maximum reachable temperature with our existing furnace, the product consisted of significantly fewer small nanoparticles and very long nanowire fibers (Figure 2, bottom middle). These results indicated that the growth zone temperature is a critical parameter to the fabrication CFs using asphaltene. These results have proven the possibility of producing carbon nanofibers using asphaltene as a precursor and FC-CVD as a single-step technique.

3. Characterization of the residual in the evaporation zone

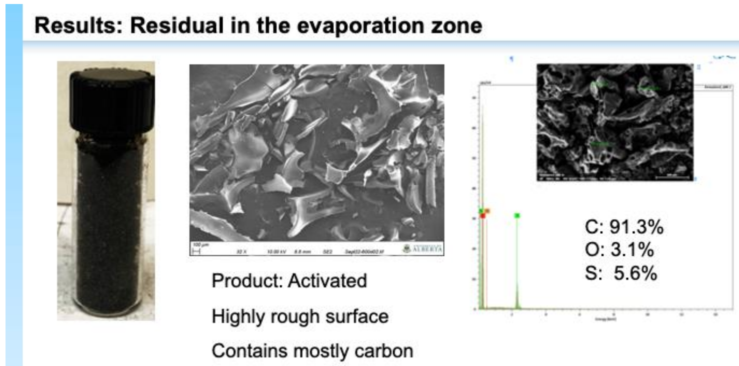


Figure 3. Characterization of residual in evaporation zone by SEM and EDS.

The residual of fine powder similar to charcoal was characterized by SEM and EDS, as shown in Figure 3. SEM images showed small pieces of blocks, and this residual can be useful for applications similar to that for activated carbon materials. It contains 91.3 % carbon, 3.1% oxygen, and 5.6% sulfur. This residue may be the result of the coking of high-molecular-weight asphaltene molecules that could not be evaporated. Even low molecular weight asphaltene could have been coked and converted to this residual.

4. Characterization by Raman and electrical conductivity

The CF products fabricated at various temperatures were characterized by Raman spectroscopy (Figure 4 left). Compared to the residual, G band intensity increases while the D band intensity decreases with the rise in temperature from 800 ^{o}C to 830 ^{o}C to 860 ^{o}C. This indicated that the higher the temperature in the growth zone, the better the degree of ordering in fabricated CFs. Evaluating the electrical conductivity of the fabricated CFs is essential for their electroconductive applications, such as electrode material and electroconductive nanocomposite membrane. We have selected two samples of CFs with different iron content, the residual and the asphaltene powder sample. Asphaltene has no electrical conductivity. The residual shows very low conductivity; meanwhile, the two CF samples show a high conductivity where CF with lower iron content is more electrically conductive (Figure 4 bottom right). The electroconductivity results demonstrate that the CFs consisted of a conjugated structure, and the structure is different than asphaltene, indicating the formation of a new carbon structure.

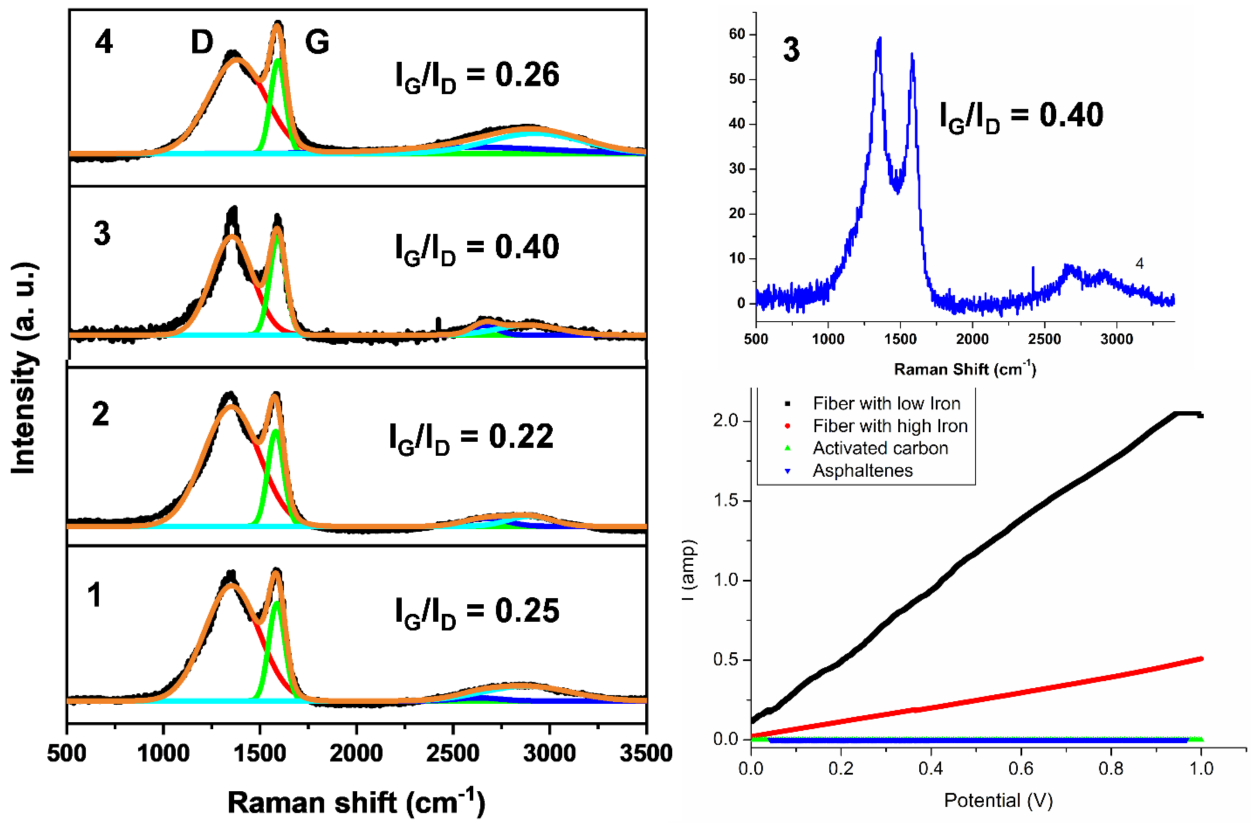


Figure 4. Raman spectra and electrical conductivity measurements; 1, 2, 3, represents the CFs product obtained at 800 °C, 830 °C, and 860 °C, respectively, and 4 represents the residual in the evaporation zone. Number 3 on the top right-hand corner shows the high magnification of the Raman spectrum of CFs fabricated at 860 °C growth zone temperature.

F. KEY LEARNINGS

Please provide a narrative that discusses the key learnings from the project.

- Describe the project learnings and importance of those learnings within the project scope. Use milestones as headings, if appropriate.
- Discuss the broader impacts of the learnings to the industry and beyond; this may include changes to regulations, policies, and approval and permitting processes

RESPOND BELOW

There are three key learnings of the project. Firstly, asphaltene can be used as a cheap precursor for the low-cost fabrication of CFs using the single-step FC-CVD method. Secondly, only ca. 70% of the precursor asphaltene can be evaporated even at as high temperature as 800 ^{o}C, leaving ca. 30% residue obstructing the continuous production of the CFs and needs to be addressed by precursor processing or reactor design. Thirdly, the extent of the fibrous structure, the ratio of ordered phase over the disordered phase, and the electrical conductivity of the CFs increase with the increase in growth zone temperature; therefore, a high-temperature furnace can be utilized to fabricate high-quality CFs. Overall, the continuous production of high-quality CFs requires an efficient technique to evaporate the asphaltene precursor completely and decompose the asphaltene rapidly.

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

The project outcomes are 1) the proof of concept production CFs using asphaltene as raw material and FC-CVD as a simple fabrication, 2) optimizing the evaporation temperature for asphaltene, and 3) effect of the growth zone temperature on the quality of CFs. The phase's outcome has led to the development of a new methodology for the fabrication of CFs using asphaltene for the first time. No major deviation from the proposed plan in the Investment Agreement – Schedule C is encountered.

The project target for the clean energy metrics was one publication, two HQPs, one patent, and one new product/service. We created a new CFs based product and the experimental procedure involving a Postdoctoral Fellow and a Research Associate. However, the target for publication or patent can be met when the process optimization is completed. The team is now working on the quality of the CFs product for patenting the idea and publication in peer-reviewed journals. The unexpected evaporation behavior of asphaltene precursor and much higher temperature requirement for the CFs growth beyond our existing instrument's limit are the reasons behind the delay to accomplish the clean energy metrics completely.

The target for program-specific metrics was to use the CFs by AWRL members to manufacture electroconductive nanocomposite membrane. This metric will be met shortly when the CFs quality is improved, as mentioned above.

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 potential impact of this phase 1 results on the oil sands industry and CF fabrication industry is remarkable. This study shows that the waste by-product asphaltene can be used as a precursor for fabricating value-added products. It benefits the oil sands industry with environmental pollution control and gives additional profits from CF fabrication. Meanwhile, the potential for large-scale, low-cost fabrication of CFs using cheap asphaltene raw material and single-step FC-CVD will benefit the CF fabrication industry. Provided that the process can be optimized and scaled up to commercial capacity, it will create Alberta's new economic opportunities, such as job creation, sales, investment attraction, and increased exports. The conductivity of the CFs will enable many applications, such as electroconductive membrane for water purification, electrode material for battery, and electronic devices. Phase 1 of this project has provided an opportunity to train a postdoc and a research associate, which is beneficial for Alberta to add highly qualified and skilled personnel to the job market. The infrastructure used to complete phase 1 of the project was a simple two-zone furnace, which is beneficial for the low-cost production of CFs.

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

We have proven that it is possible to prepare carbon nanofibers with precursors of asphaltene from our tested results. However, the large scale continuous production was not possible due to residual in the evaporation zone of the 2 zone furnace in the horizontal alignment. Moreover, the quality of the CFs could not be increased significantly due to the temperature limit of the two-zone furnace. Therefore, we plan to design a new process flow and use a high-temperature furnace shown in Figure 5 to address these issues. The proposed process will rely on a one-zone furnace's vertical alignment at a very temperature of ca. 1200 – 1500 ^{o}C. The asphaltene and catalyst precursor can be added as a solid mixture or a melt mixture, or a toluene solution from a container where flow rate will be controlled by combining a valve, H_2/Ar gas flow, and a motor. A simple heating coil can be used to melt the asphaltene sample at about 200 ^{o}C for melt injection. In the furnace's vertical alignment, all the asphaltene samples will enter the growth zone, where the high temperature will decompose all the asphaltene samples leaving no residue. The furnace will long enough, and the temperature will be high enough to decompose all the asphaltene before it drops to the bottom of the furnace and contributes to the CFs growth. This modified process design will enable the continuous large-scale production of CNT-based short form CFs. The high temperature will also increase the degree of ordering and the electrical conductivity of the CFs. The CNT-based nanofibers can be spun into long CFs using a spool where the CNT-based nanofibers will physically adhere to each other via π- π interaction. The long CFs produced in this method will be mechanically weaker compared to the CFs made using convention methods. However, the mechanical strength can be improved by passing and stretching the spun fibre through chlorosulfonic acid bath followed by acetone bath; this process is known as the densification process.

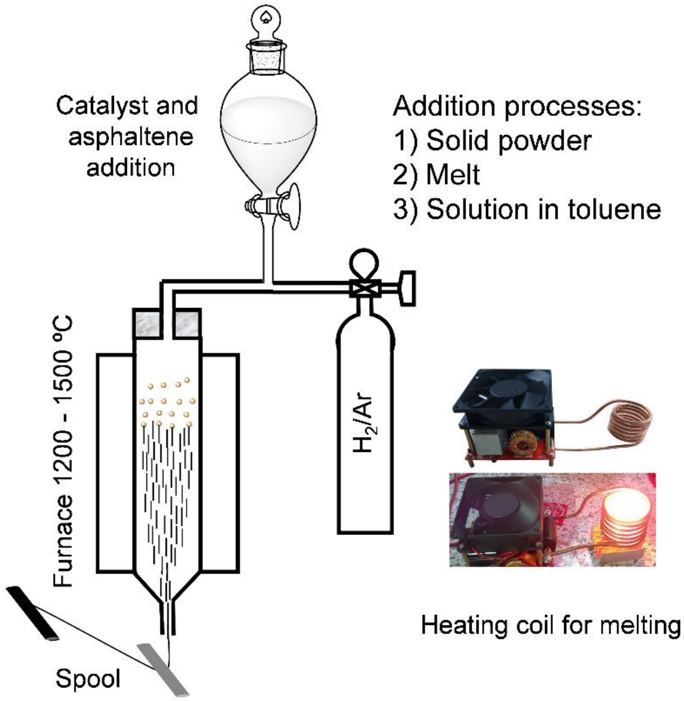


Figure 5. Modification for the production process for continuous production, improvement of CF quality, and weaving CNT aerogel into long CFs. Note: An addition funnel is shown as the asphaltene sample container for the simplicity of the drawing.

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

This project has explored FC-CVD as an alternative low-cost fabrication of CFs using oilsand asphaltene precursors. A simple in-house-designed sample delivering process combined with a high-temperature furnace can lead to a continuous large-scale commercial production of a high-quality CFs.

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

We provided a proof of concept that our method works to produce carbon fiber from Alberta's asphaltenes. The optimum evaporation temperature was found to be 600 °C. We found that higher growth zone temperature gave better fibrous structure and length of CFs. The evaporation zone's residual is considered to be similar to activated carbon powders that can be potentially used in many other applications. Continuous large-scale manufacturing of high-quality CFs will be possible using an appropriate continuous delivery device and a high-temperature furnace.