Final Report

on

One-step plasma-assisted technology for manufacturing high performance carbon fibers using asphaltene precursors

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Executive summary

This report summarizes the work completed in the project entitled “One-step plasma-assisted technology for manufacturing high performance carbon fibers using asphaltene precursors”, which was co-sponsored by Alberta Innovates and Nexen Energy, now CNOOC International. The project was completed in collaboration between the University of Alberta and the Université de Sherbrooke. This report deals with only the work completed at the University of Alberta. A second report from the Université de Sherbrooke report is found in Appendix A of this document.

The University of Alberta has focused on the modification of asphaltene feed stocks, fabrication of asphaltenes-based carbon fibers through melt-spinning, thermal processing of the as-fabricated asphaltene fibers into carbon fibers using conventional approaches, and characterization of asphaltene feed stocks and asphaltene-derived fibers at various stages of processing. At the Université de Sherbrooke, the asphaltene-derived green fibers supplied by the University of Alberta were treated in plasma environments to convert the green fibers into carbon fibers.

It was found that asphaltene feed stocks can be treated to mildly increase the size of aromatic structures within asphaltenes via dehydration and cyclization reactions between the polycyclic aromatic hydrocarbon (PAH) molecules. Green fibers can be obtained by melt-spinning directly using the asphaltenes produced from an industrial C5 solvent deasphalting process at NEXEN Long Lake Upgrader in Alberta. The as-melt-spun green fibers are very brittle and must undergo a stabilization/oxidation process at temperatures ranging from 150^{o}C to 350^{o}C for an extended time up to 20 hours. The stabilization process does not only introduce polymerization and crosslinking between the PAH molecules, but also effectively promotes the growth of aromatic structures.

The stabilization/oxidation process is followed by the carbonization in nitrogen gas environment. Carbonization is usually performed at above 400^{o}C and up to 1600^{o}C. Because of limitation of heat treatment furnace, carbonization was performed only up to 1000^{o}C in this investigation. Both tensile strength and tensile modulus of asphaltene based fibers were improved by carbonization. The highest tensile strength and modulus were obtained when the asphaltene-derived carbon fibers were carbonized at 800^{o}C. Reduction of mechanical properties was observed when the asphaltene-derived carbon fibers were carbonized at around 900^{o}C. This reduction appears to be associated with the formation of defects such as voids and flaws within the fibers after carbonization.

After carbonization, other processes such as graphitization up to 3000^{o}C, surface etching and sizing are also required before carbon fibers are delivered to end users. These processes were not initially planned in the project and therefore were not performed.

The project was targeted to fabricate and to process asphaltene-derived carbon fibers to reach a tensile strength over 2,500 MPa and modulus above 250 GPa. With a carbonization treatment up to 1000^{o}C, the asphaltene-derived carbon fibers with a diameter of 10 μm has reached a tensile strength of 1,300 MPa and tensile modulus of 60 GPa. By reducing the diameter of carbon fibers, optimizing spinning and stabilization conditions, and increasing carbonization temperatures to 1,600^{o}C, the tensile properties of asphaltene-derived carbon fibers are expected to increase to a level reaching the targets set in the proposal.

Carbon fibres developed at the University of Alberta were sent to the the Université de Sherbrooke where the focus was to plasma treat asphaltene fibres as well as benchmark plasma treatment by using polyacrylonitrile (PAN).

Benchmarking with PAN resulted in fibres that were successfully stabilized under plasma process in 30-40 minutes. By comparison the plasma stabilized the PAN fibres six times faster than a conventional oven-based process. The plasma treated PAN fibres displayed considerably improved mechanical properties compared to the conventional approach.

Asphaltene based fibres subjected to plasma were stabilizer over a longer period (1-3 hours). Although, this is comparatively shorter than the 4-13 hour stabilization for asphaltene fibres being prepared using conventional methods, it is still quite longer than the plasma stabilization of PAN fibres. Optimizing processing time remains an area of importance and future study. Due to time constraints the carbonization, graphitization and the one-step plasma process were not investigated during this project.

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One-step plasma-assisted technology for manufacturing high performance carbon fibers using asphaltene precursors

1. Introduction

The project is aimed at developing an efficient and low-cost technology for the production of carbon fibers using asphaltenes as precursors. It is targeted to produce carbon fibers with excellent mechanical properties through an efficient and low-cost plasma-assisted technology. Specifics of the objectives are as follows.

1) To develop a proof of concept plasma-assisted technology for the production of carbon fibers using asphaltenes as precursors.
2) To develop a fabrication technology with substantially reduced processing time, especially reducing the time for fiber treatment, the most energy-consuming step of fabrication, to less than 0.5 hour. The fabrication process should be further optimized to achieve a production cost of ≤ $11/kg.
3) To fabricate carbon fibers with the following mechanical property targets: a minimum tensile strength of 2.5 GPa, a minimum tensile modulus of 250 GPa, and a strain about 1%.

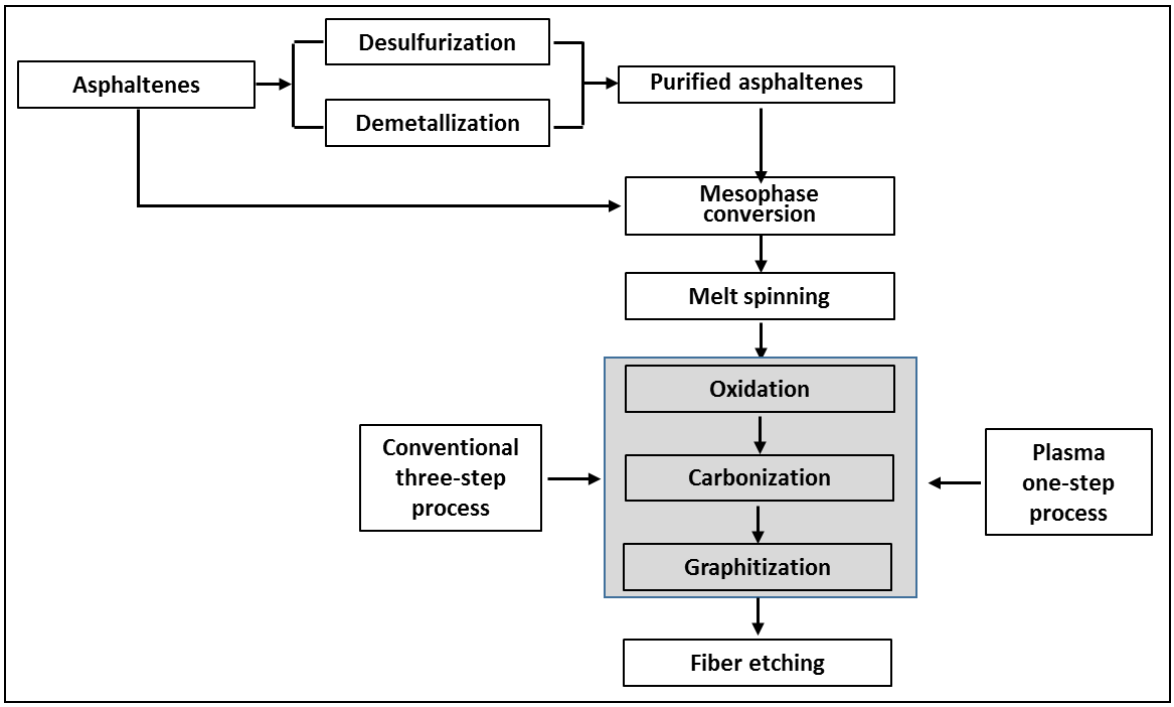


Figure 1 Simplified process flow chart for converting asphaltenes into high performance carbon fibers

The main processes for the conversion of asphaltenes into high performance carbon fibers are summarized in Figure 1. The first step of processing generally involves the conversion of asphaltenes raw materials into anisotropic mesophase materials, which could be done with or without the intermediate process of purifying raw asphaltenes for desulfurization and demetallization. The mesophases obtained will then be processed by melt spinning to produce asphaltene fibers, or green fibers. It was agreed to by the sponsors that the conversion of the as-received asphaltene feedstock into mesophase materials was not performed as long as the as-received asphaltene feedstock can be melt-spun into green fibers.

The as-melt spun asphaltene fibers, or the so-called “green fibers”, must go through a process of oxidation, carbonization and graphitization with increasing temperatures in different environments.

Oxidation is used to cross-link the molecules to the point where the fibers do not melt or fuse together. It is usually performed at about 200-400^{o}C for several hours in air. This step is extremely important because it produces fibers that are stable at the high temperatures of carbonization and graphitization. Without cross-linking, the fibers would fail in these process steps.
Carbonization is achieved by heating the fibers to high temperatures, typically about 1000-2000^{o}C, in an inert atmosphere in an environment without oxygen. This step removes most of the impurities (e.g., hydrogen, oxygen, nitrogen, sulfur) from the fibers, leaving mainly crystalline carbon in mostly hexagonal rings.

Graphitization is the process of treating the fibers at high temperatures in order to improve the alignment and orientation of the crystalline regions along the main fiber axes. Having the crystalline regions aligned, stacked, and oriented along the main fiber axis increases the overall strength and stiffness of the carbon fibers. In order to obtain carbon fibers with higher modulus and higher carbon content, graphitization are performed at higher temperatures up to 3000^{o}C.

After the above indicated thermal treatment, surface treatment or often referred to as etching, and sizing of carbon fibers are also needed before carbon fibers are sold to customers. Surface treatment may be applied to improve the adhesion of carbon fibers to binding matrices for making composite materials. Sizing for carbon fiber, which will coat surface treated carbon fibers with polymers to

prevent individual filaments from breaking, to improve handling of the very fine carbon filaments, and to provide compatibility with the molding process.

It was agreed that the green fibers after fabrication will be treated up to the stage of graphitization. Conventionally, the processes of oxidation, carbonization and graphitization are done separately and sequentially, for example, by exposing carbon fibers in different furnaces with controlled environments. It was initially proposed a one-step plasma process in order to achieve the processes of oxidation, carbonization and graphitization. The project will be carried out collaboratively by the University of Alberta and the Université de Sherbrooke. The work scope of entire project has been divided into three modules as shown in Figure 2 and the scope of work for each university is summarized in Table 1.

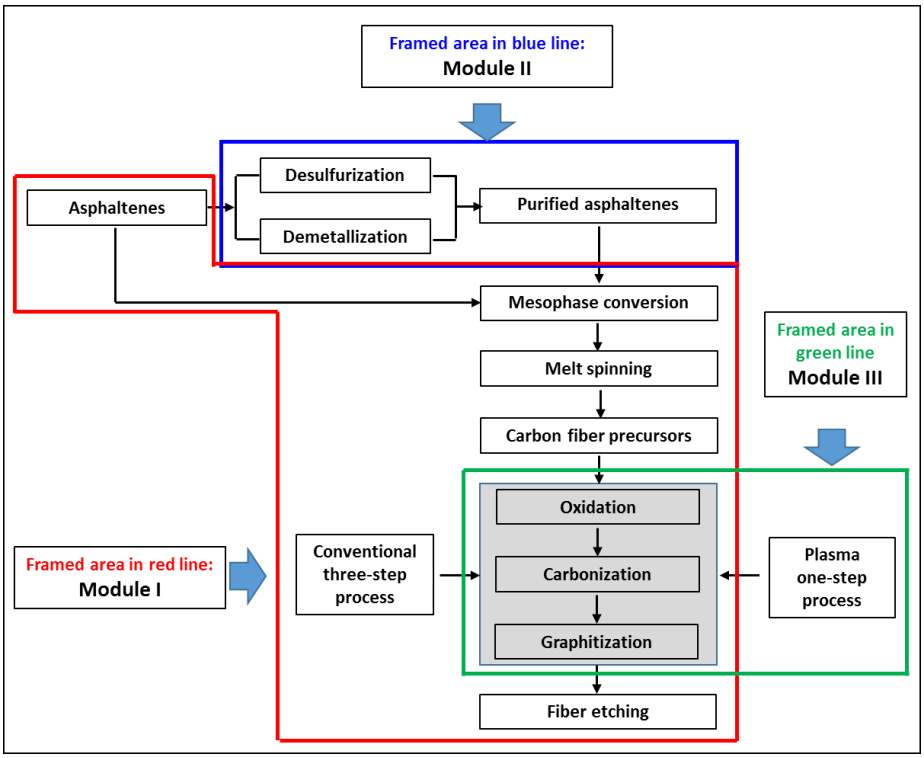


Figure 2 Three project modules for converting raw carbon fibers into high performance carbon fibers

As indicated in Table 1, the University of Alberta will focus on the work defined in Module 1 and Module 2. Because of limited resources, the project was budgeted with only one postdoctoral fellow to work on the project at each university. As a result, the scope of research at the University of Alberta was limited to Module I, the fabrication of green fibers using the as-received asphaltenes and the oxidation and

carbonization treatment of the green fibers. It has also been agreed that the carbonization treatment be performed up to 1000°C because of the availability of furnaces for heat treatment. Module I will serve as an important baseline by which the work at the Université de Sherbrooke can be compared against and enable an understanding of the factors in manufacturing that influence carbon fibre quality.

Because of extensive past experiences with plasma processing, the Université de Sherbrooke team will focus on Module III, that is, developing a plasma one-step process to achieve oxidation, carbonization and graphitization. This report covers the work completed by the research team at the University of Alberta, which focused primarily on Module I: fabrication of green fibers using the as-received asphaltenes and conventional three-step process of green fibers. The report by the Université de Sherbrooke can be found as an Appendix to this report.

Table 1 Original project design: three project modules and partition of research work

Module	Description	Partners	Notes
I	Conventional three-step process without purification of raw asphaltenes	University of Alberta	• Major focus on mesophase formation and melt spinning and conventional three-step processing of green fibers.
II	Purification of raw asphaltenes	University of Alberta	• Module II will start with raw asphaltenes received from CNOOC. • Purified asphaltenes after a removal of metallic- and sulfur-species may also be tested, depending on available time and funding. • Different types of asphaltenes, for example, C3-, C5- or C7- insolubles, may also be tested, depending on the findings from testing the as-received asphaltenes.
III	Plasma-one-step raw-carbon-fiber processing	Université de Sherbrooke	• Main focus

2. **Experimental**

2.1 Materials

The asphaltenes used in this investigation were extracted from the oilsands obtained from an industrial C5 solvent deasphalting process at the Long Lake Upgrader in Alberta, Canada and were supplied by CNOOC International Limited, formerly, Nexen Energy ULC. Nitrogen gas (99%) was purchased from Praxair. Silicone oil purchased from Sigma Aldrich (Lot # X27D026, CAS: 68083-14-7) was used for oil bath.

2.2 Characterization

In this study, pretreated asphaltenes, green fibers and carbon fiber products after thermal processing were characterized using the following methods: Dynamic scanning calorimetry (DSC), Thermogravimetric analysis (TGA), Elemental analysis and FTIR spectroscopy.

The tensile strength tests were carried out following ASTM-D3822 methods using an Instron tensile testing machine model 5565 (max. load = 100 N). The tests were carried out with 10 – 20 single carbon fibers, the average value was taken for each set of tests in this study and the standard deviation were calculated and presented as error bars. Tensile strength was determined by dividing the maximum force recorded with cross sectional area of the fiber being tested. Tensile modulus was the value of slope of stress – strain curve of carbon fibers.

2.3 Carbon fiber preparation

The green fibers were obtained using melt-spinning method with AT-255 melt spinning machine (purchased from Anytester Co., Ltd.). The green fibers were converted into carbon fibers by the following two major processes:

Stabilization: In the stabilization step, the green fibers were heated to various temperatures between 150 – 350 °C in air and fused together. Due to the fact that the asphaltene has a 'softening point' at ~ 120 °C, beyond which the fibers become adhesive and tend to fuse, the asphaltene fibers were treated in a silicon oil bath set to a temperature between 150 - 220°C for at least two hours, as the asphaltene molecules become partially crosslinked during this process, the fibers can be considered stable for treatment at higher temperature. After washing off the silicon oil with toluene, the asphaltene fibers were oxidized under aerobic conditions at 300 – 350 °C for 2 hours before the next stage of treatment.

Carbonization: In the carbonization step, the stabilized asphaltene fibers were heated under nitrogen above 500 °C, as the heteroatoms leave the asphaltene molecules, the crosslinked polymers start to transfer into ordered graphite structure, and hence, the fibers should obtain an enhanced tensile strength. The oxidized fibers were all carbonized at 500 °C for 2 hours at first (1^{st} stage carbonization process) before further carbonization treatment above 800 °C (2^{nd} stage carbonization process) for varying times and temperatures (*vide infra*).

3. Results

3.1 Characterization of asphaltene precursor

Table 1 shows the chemistry of the asphaltene supplied by CNOOC International Inc., which was produced from an industrial C5 solvent deasphalting process at the Long Lake Upgrader in Alberta, Canada. The samples have also been analyzed and were found to contain trace amount of metallic species, less than 2000 ppm.

To determine the temperature for melt spinning, differential scanning calorimetry (DSC) heat flow test was performed on raw asphaltenes. As shown in Figure 3, two distinct endothermic features are observed during heating. The first is related to the evaporation of light molecules and the onset of softening of asphaltenes. The second is caused by melting of asphaltenes over a wide range of temperature because of varied molecular sizes of asphaltenes.

Table 2 CHNSO analysis of the received-asphaltene precursor for carbon fiber fabrication (wt%)

Elements	%N	%C	%H	%S	%O (calculated)	C:H ratio (mol %)
Raw asphaltene	1.12	82.16	8.00	7.66	0.92*	0.855

*excluding trace amount of metallic species.

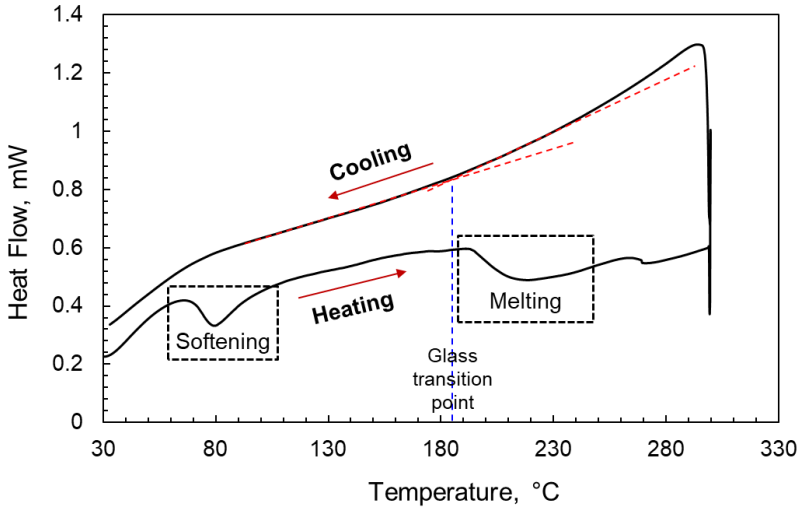
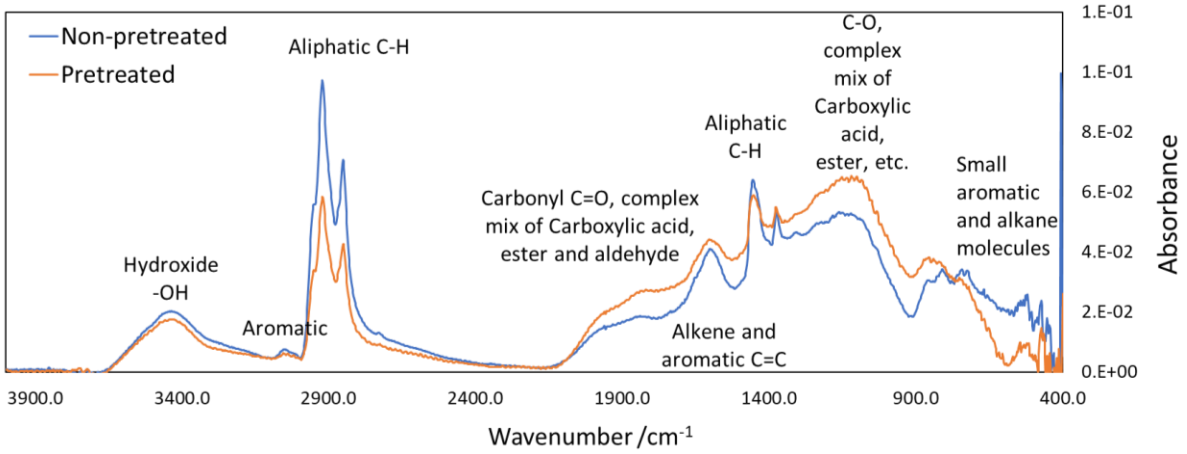


Figure 3 Differential scanning calorimetry (DSC) heat flow curve obtained for the as-received asphaltenes. The endothermic features displayed at heating is due to softening and melting of asphaltenes.

No distinct exothermic peaks are found during cooling, indicating crystallization of asphaltenes either did not occur or occurred over a wide range of temperature. It is seen that the cooling curve exhibits different slopes. One of the slope changes occurs at around 185°C during cooling, indicating some structural evolution. Considering the fact that melting starts at around 185°C, the change of slope marks the glass transition point of asphaltenes.



Figures 4 FTIR spectroscopy of the as-received asphaltenes with and without pretreatment at 350°C for 1 hour in nitrogen.

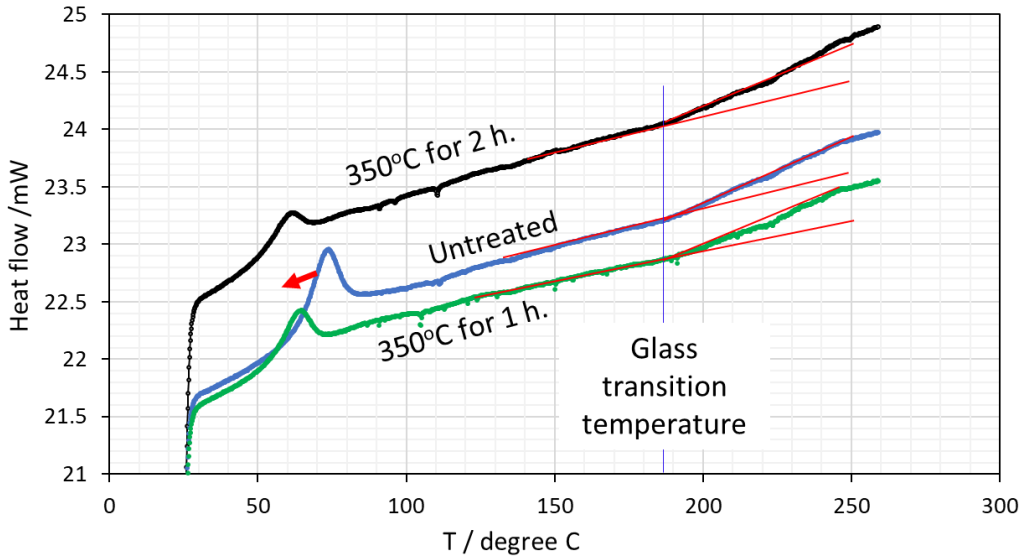


Figure 5 Differential scanning calorimetry (DSC) heat flow curve obtained for the as-received asphaltenes with and without treatment at 350°C in nitrogen.

The as-received asphaltene samples were also pre-treated before melt-spinning. Figure 4 shows FTIR spectroscopy of the as-received asphaltenes with and without pretreatment at 350^{o}C for 1 hour in nitrogen. The results in Figure 4 suggest formation of carbonyl bonding, unsaturated C=C bonds during the Oxygen-free heat pre-treatment and notable reduction of small alkanes, aromatics and alcohols. Differential scanning calorimetry (DSC) heat flow test was performed on pretreated asphaltenes to determine if the glass transition point of asphaltenes can be changed. As shown in Figure 5, a shift of endothermic peak from ~85 °C towards 65 °C for material after pre-treatment was observed. Since it occurs in the solid state of asphaltenes, this shift should not have any effect on the temperature for melt-spinning, but could potentially affect the property of fibers after melt-spinning and subsequent thermal treatment. On the other hand, the glass transition points after pre-treatment remain the same as that of untreated asphaltenes. The latter indicates the same temperature could be used for melt-spinning of asphaltenes with or without the pretreatment.

The chemistry of asphaltenes after the pre-treatment has also been determined. As listed in Table 3, subtle increase of C, S and N, but decrease of H was found.

Table 3 CHNSO analysis of the received-asphaltene precursor with and without treatment at 350^{o}C in nitrogen (wt %)

Treatment	%C	%H	%N	%S	%O (calculated)	C:H ratio (mol %)
Raw asphaltene	82.16	8.00	1.12	7.66	0.92	0.855
After pre-heat treatment at 350 °C for 2h in nitrogen	82.30	7.88	1.14	7.62	0.84	0.870
After pre-heat treatment at 400 °C for 1h in nitrogen	83.67	5.95	1.56	7.60	0.98	1.17

3.2 Fabrication of asphaltene fibers by melt-spinning

Based on the characterization of asphaltene precursors in Section 3.1 and by trial and error, green fibers using 100% as-received asphaltenes were able to be melt-spun at around 190°C under a pressure of 400 kPa in nitrogen gas environment. Molten asphaltene can be pushed through the spinneret with an inner

diameter of Ø = 150 µm. The molten asphaltene was then directed to the spinning wheel with a diameter of 20 cm, and asphaltene fibers were drawn as the winding speed gradually increased, until reaching a speed corresponding to the desired fiber diameter. Figure 6 shows the correlation between the fiber diameters (D) experimentally measured on SEM and winding speed (as revolutions per minute, RPM).

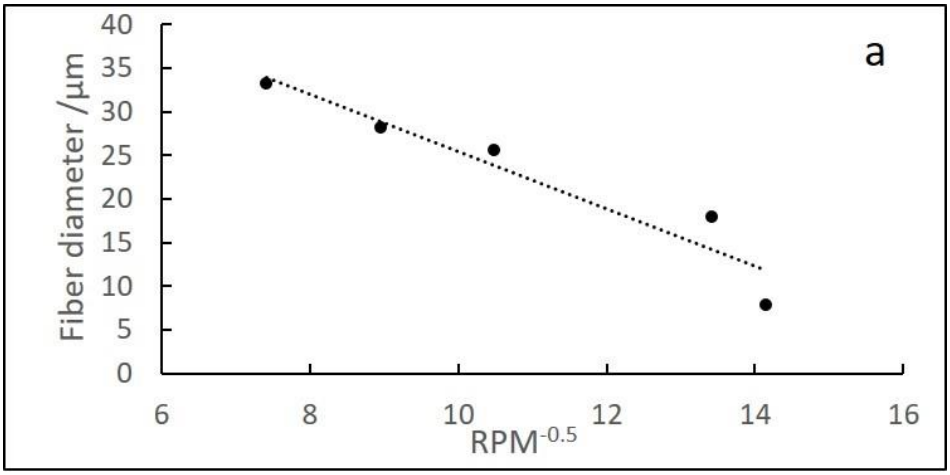


Figure 6 Correlation between the fiber diameter (D) and winding speed (as revolutions per minute, RPM.

At constant temperature, extruding pressure, and steady state there is a constant viscosity and volumetric flow rate of the asphaltene. The mass balance is

$$M = \rho \frac{\pi}{4} D^2 v \qquad 1)$$

where M is the mass of asphaltene flowing through the spinneret per unit time, ρ is the density of asphaltene, D is the diameter of the resulting asphaltene fiber, and *v* is the spinning speed, which is proportional to the winding speed in RPM. Therefore:

$$D = \sqrt{\frac{4M}{\pi\rho}} \cdot \sqrt{\frac{1}{v}} = A \cdot v^{-0.5} \qquad 2)$$

where A = $\sqrt{4M/\pi\rho}$ is a constant.

This correlation appears to be consistent with the results shown in Figure 6; a linear relationship is found between the fiber diameter and the winding speed raised to the power of -0.5. It is expected that a spinneret with smaller diameter would yield a smaller M and, therefore, a smaller diameter of green fibers can be fabricated. In this study, fibers were drawn through spinneret with a diameter of 150 μm at 190 °C at a winding speed of 188 revolutions per minute (RPM), which should result in fibers with cross-section diameter at around 16.6 μm, which was experimentally confirmed.

3.3 Stabilization/oxidation treatment of green fibers

The green asphaltene fibers are not strong at room temperature. Stabilization or oxidation treatment is needed to enhance their strength for further treatment. It has been observed that green fibers were fused into bulky masses when they came in contact to each other during heating after melt-spinning. To avoid the problem of fusing, the first step of stabilization/oxidation treatment of green fibers was performed by placing green fibers in a ceramic crucible filled with silicone oil. Individual green fibers were placed separately in the ceramic crucible to avoid direct contact with each other during the stabilization in silicone oil exposed to air environment.

The green fibers exhibited drastic changes in chemistry after being stabilized or oxidized at elevated temperatures in air. As shown in Table 4, with a treatment at a temperature as low as 220 °C, the content of oxygen within the asphaltene has increased by nearly 10 times, such an increase is accompanied with a jump of C:H ratio from 0.855 to 1.00, indicating a growth of aromatic structures. As the stabilization further proceeded to 350 °C, there appears to be a mild increase of the oxygen content, with a more notable growth of C:H ratio (1.277) which should correspond to a further growth of the aromatic structures. In contrast, the treatment in nitrogen gas leads to minimal chemical changes.

Table 4 CHNSO analysis of green fibers after stabilization/oxidation treatment (wt %)

Treatment	%N	%C	%H	%S	%O (calculated)	C:H ratio (mol %)
Raw asphaltene	1.12	82.16	8.00	7.66	0.92	0.855
220 °C for 2 hour in air	1.22	76.30	6.35	7.50	8.63	1.001
350 °C for 2 hour in air	1.29	75.97	4.96	7.90	9.87	1.277
350 °C for 1 hour in N2	1.14	82.30	7.81	7.62	0.85	0.871

FTIR analysis was also performed on the green fibers after oxidation at 350 °C for 2 hour in air. As shown in Figure 7, similar to the effects of non-oxidative pre-treatment, notable reduction of aliphatic chains and small aromatics, and increase of carbonyl groups were observed after the stabilization. Notable increase of –OH bonding is also observed due to effects of oxidation. The FTIR curve also shows increased complexity for absorption peaks between 1900 – 1000 cm^{-1}, indicating potential formation of different types of intra- and intermolecular bonding (oxidation and cross-linking).

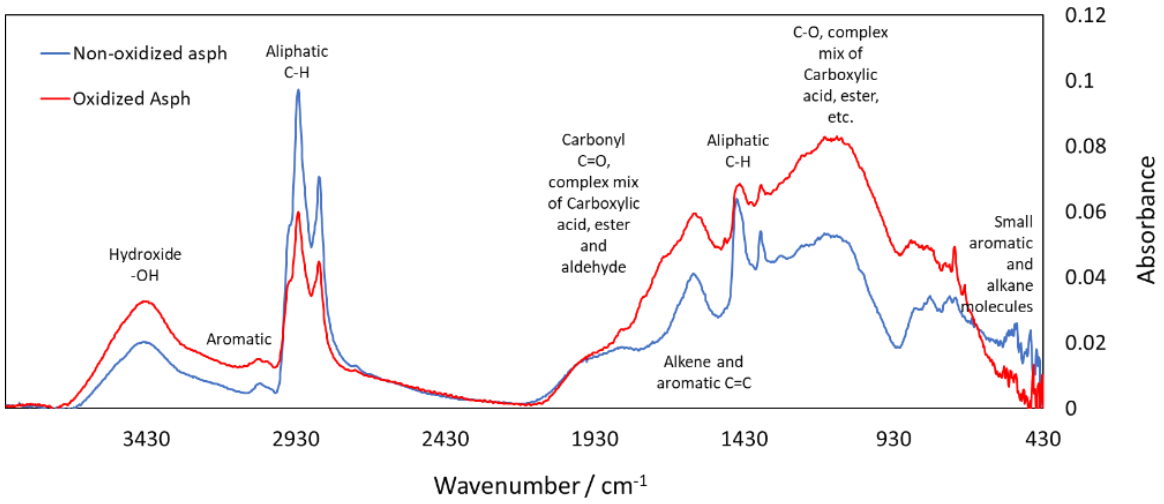
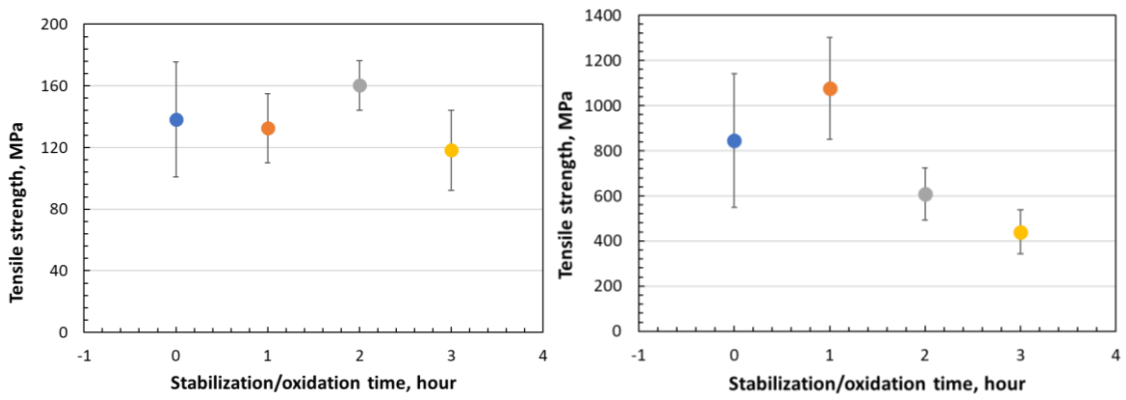


Figure 7 FTIR spectroscopy of the green fibers after stabilization treatment at 350°C for 2 hour in air.

The green fibers are too fragile to be tensile tested. The green fibers were stabilized first at 220°C for 2 hours in silicone oil to prevent fusing during subsequent thermal treatment. This is followed by stabilization/oxidation at 350°C in air. Figure 8a) shows the tensile strength of green fibers after stabilization at 350°C for various lengths of time. The initial treatment at 220°C for 2 hours in silicone oil has reached a tensile strength that is quite similar to those after further stabilization at 350°C in air. Increasing the stabilization time at 350°C does not seem to improve the mechanical properties of stabilized green fibers. However, these stabilized fibers after carbonization exhibit different tensile strengths, with the highest tensile strength reached when the fibres were previously stabilized at 350°C for one hour (Figure 8b). Increasing the stabilization time at 350°C beyond 1 hour reduces the tensile strength once carbonization is performed at 800°C for 2 hours.



a) b)

Figure 8 The tensile strength of the as-spun green fibers after stabilization/oxidation at 350°C in silicone oil bath for various lengths of time (a); and after carbonization of stabilized fibers at 800°C for 2 hours (b).

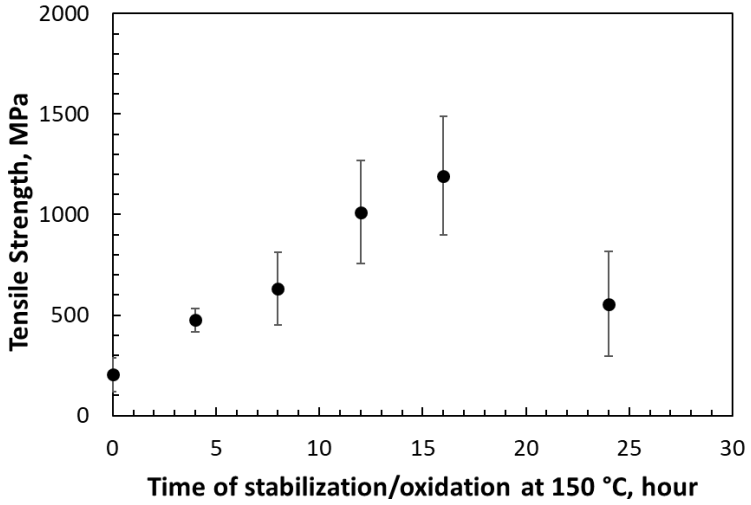


Figure 9 Tensile strength of green fibers after the following sequential treatment: 1) stabilization at 150°C for various length time in silicon oil, 2) stabilization at 220°C for 2 hours in silicon oil, 3) carbonization at 800°C for 2 hours in nitrogen.

It has been found that stabilization at lower temperature for extended length of time can achieve similar improvement of tensile strength to that stabilized at 350°C for short time (Figure 8b). Figure 9 shows the tensile strength of green fibers after stabilization at 150°C for various length time in silicone oil before the 2nd stabilization at 220°C for 2 hours in silicon oil and final carbonization treatment at 800°C for 2 hours in nitrogen. The highest tensile strength was found when the time of stabilization at 150°C was at around 16 hours. With this stabilization condition, the tensile strength on average was found to be at

around 1200 MPa, which is very comparable to the tensile strength measured when stabilization was at 350 °C for 1 hour (Figure 8b). This may reflect the fact that stabilization involves the diffusion of oxygen to the fiber centers, which should follow the law of diffusion in terms of time and temperature required.

3.4 Carbonization treatment

Treatments above 400 °C in the absence of oxygen result in cleavage of heteroatoms (e.g. oxygen, nitrogen) from the asphaltene fibers in the process known as carbonization, which brings further enhancement to the carbonized asphaltene fibers [4]. In this investigation, carbonization was performed in two sequential temperatures steps: 1) Pre-carbonization at temperatures between 400°C and 600°C, and final carbonization treatment at temperatures above 700°C.

Figure 10 shows the effect of pre-carbonization temperature on tensile strength. All the fibers have been stabilized at 220°C for 2 hours in silicon oil and 350°C for 2 hours in air before pre-carbonization at various temperatures. After pre-carbonization, all the fibers were subjected to carbonization at 800°C for 2 hours. As seen in Figure 10, pre-carbonization at 500°C for 2 hours leads to the highest tensile strength after final carbonization at 800°C.

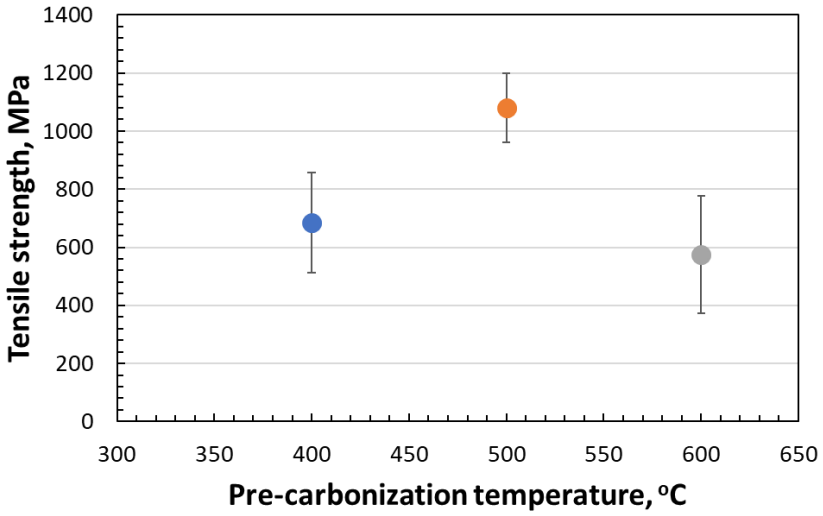


Figure 10 Tensile strength of carbon fibers obtained from the following steps of treatment: stabilization treatment at 220°C for 2 hours in silicon oil, and 350°C for 2 hours in air; carbonization at temperatures ranging from 400°C to 600°C for 2 hours in nitrogen and 800°C for 2 hours in nitrogen.

After optimization of the pre-carbonization temperature, the effect of final carbonization temperature on tensile strength was studied. The final carbonization temperatures used in this investigation were limited to 1,000^{o}C due to the furnace specifications.

Figure 11 shows the tensile strength obtained after final carbonization at various temperatures up to 1,000^{o}C. The fibers were obtained from asphaltenes with 1 hour pre-treatment in nitrogen at 350°C for 1 hour, 4 hour stabilization at 180-220 °C for 2 hours in silicone oil bath followed by 300-350 °C for 2 hours in dry air, and a 2 hour 1st stage carbonization process at 500 °C, but with varied 2nd stage carbonization process: in which, the fibers were treated at 800 °C for 1 hour, followed by additional 1 hour treatment at unchanged temperature (800 °C), 850 °C, 900 °C and 1000 °C with a heating rate of 5 °C/min as suggested by a number of literature [1, 2]. It has been reported that carbonization at higher temperature results in continuous development of graphite structures, and hence significantly enhanced mechanical strength to the carbon fibers [1-3]. It is surprising that the increase of tensile strength with increasing carbonization temperature was not observed. Instead, a lowest tensile strength was found when the final carbonization temperature was at around 900^{o}C.

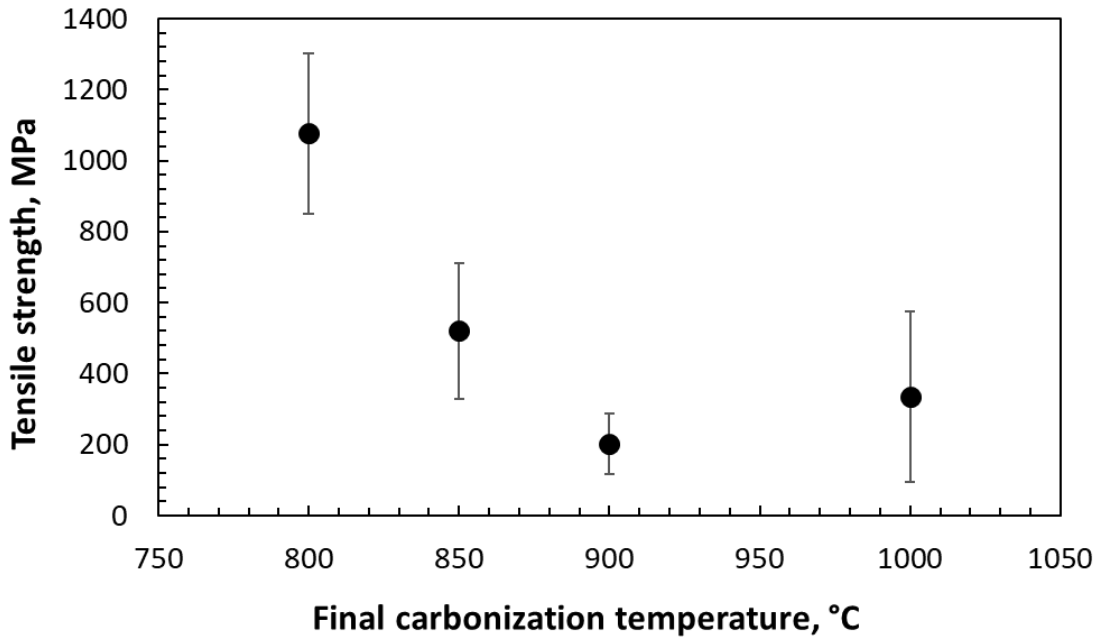


Figure 11 Comparison of tensile strength for asphaltene-based CF carbonized at varied highest temperature from 800 to 900 °C for the 2nd carbonization process.

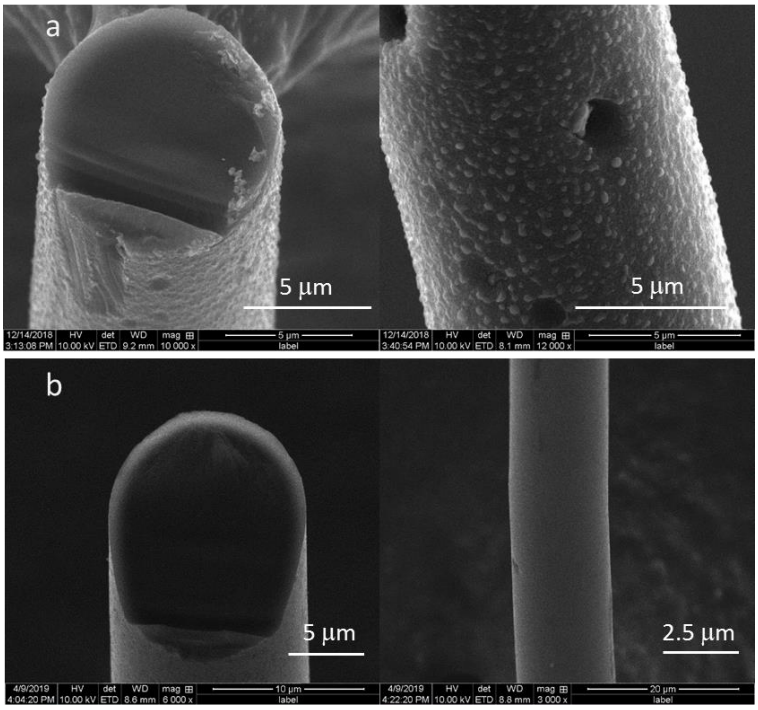


Figure 12 SEM images for asphaltene based CF without the optimization treatment (a) and the CF with 12 hours treatment at 150 °C and reduced heating rate above 800 °C (b). Both CFs were carbonized at 1000 °C.

It has been commonly reported that at temperatures up to 1000 ^{o}C, some degradation of the carbon fibre structure occurred with attendant reduction of modulus, but as the temperature increased there was a marked increase in preferred orientation as the hetero-atoms were continuously released, forming a graphite-like structure [4]. Strength and the modulus of carbon fiber made from a mesophase pitch increased with temperature. At 1500 ^{o}C, mesophase fibers could develop tensile modulus of the order of one third of the theoretical value for graphite (about 1000 GPa). As with PAN based carbon fibers, the strength of mesophase pitch carbon fibers is limited by flaws. Possible reasons for the origin of flaws:

1) Interfilament fusing, where individual fibres join together, could occur during spinning, insufficient oxidation, or thermal processing. This is unlikely to occur in this investigation since fibers were placed in separation during treatment.
2) Internal voids, caused by gas bubbles in the spun fiber, termed bloating, or due to the volatilization of foreign matter during the carbonization process. (In practice, gas bubbles should be released by venting the spinneret).

3) Inclusion of foreign particles, due to inefficient cleaning of the precursor pitch.

4) Surface defects, due to mechanical damage or surface contamination.

The above indicated reasons of degradation seem consistent with the low tensile properties of asphaltene-derived carbon fibers when carbonized at around 900°C. As shown in Figure 12a), internal voids, inclusion of foreign particles and surface defects have been found to be associated with carbon fibers with low mechanical properties.

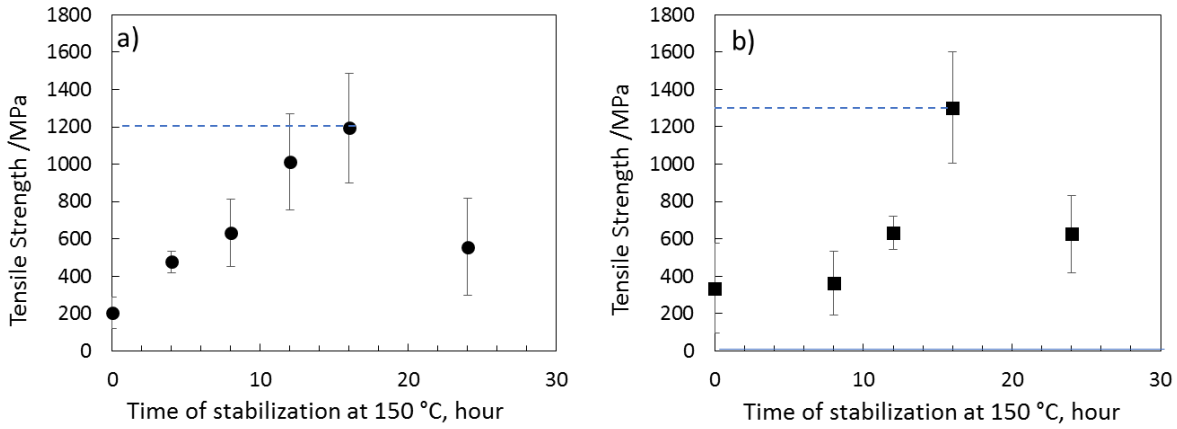


Figure 13 Tensile strength for asphaltene based CF with the highest carbonization temperature at 900 °C (a) and 1000 °C (b) with varied extended treatment at 150 °C.

In order to eliminate such effects, the methods of fiber treatment were modified in the following ways:

- Additional heat treatment was performed at lower temperature (150 °C) for longer period (4 – 24 hours) during the stabilization stage, and
- Reduced heating rate for the carbonization process above 800 °C (down to 1.6 °C/min). The resulting effects are compared and shown in Figure 12.

Figure 13 shows tensile strength for asphaltene based CF with the highest carbonization temperature at 900 and 1000 °C with varied extended treatment at 150 °C. The modulus data are cross-plotted against the tensile strength for CF carbonized at 900 °C (Figure 14a) and 1000 °C (Figure 14b).

As shown in Figure 13a, the additional treatment at 150 °C effectively enhanced the strength of asphaltene-based CF. With 16 hours treatment under such a condition, notably higher strength was

obtained for the fibers carbonized at both 900 °C and 1000 °C, which exceed the carbon fibers carbonized at 800 °C. With the treatment further extended to 24 hours, however, the CFs appear to degrade to lower quality. Such a degradation may be attributed to unaligned structures that developed during the long period and lead to negative effects in both the carbon fiber strength and modulus (Figure 14a and 14b).

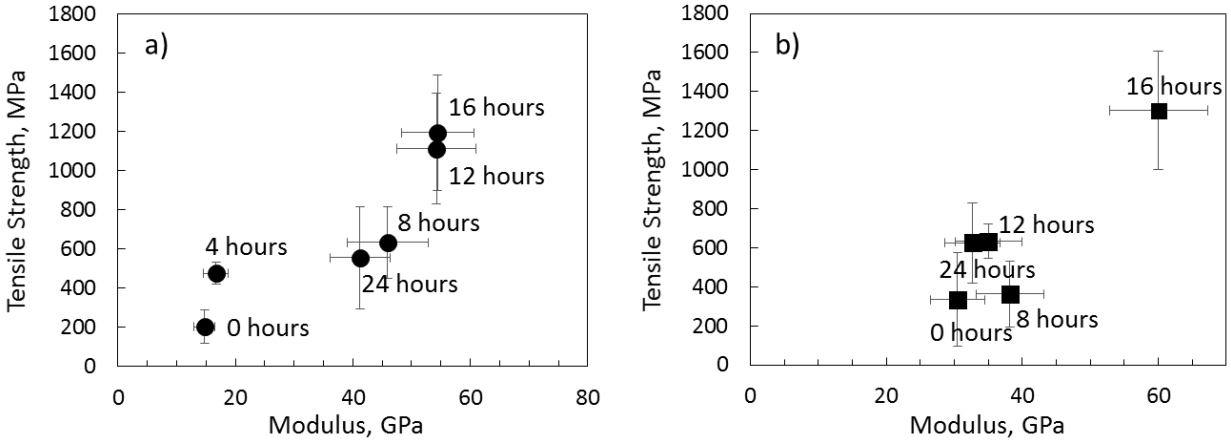


Figure 14 Relationship between tensile strength and tensile modulus of asphaltene-based CF with extended oxidation treatment at 150 °C for various time and the carbonization temperature at 900 °C (a) and 1000 °C (b).

4 Discussion

4.1 Optimized carbon fabrication flow chart

Based on the results obtained from this investigation, a six-step process flow chart for the fabrication of long carbon fibers has been proposed, as shown in Figure 15. Additional description of each step is provided below.

Step 1 Pre-treatment of asphaltene precursor:

This step is applied to remove volatile phases and generate more aromatic structure. It has been proven from this study that improved mechanical properties of carbon fibers can be obtained with the treatment. In addition, this step could be applied to modify the feed stocks including:

1) To remove sulfur and metallic-contaminants

2) To generate other alkane-insolubles, for example, C7-insolubles that might have different melt-spinning and carbon fiber characteristics.
3) To increase the fraction of mesophases in the bulk asphaltenes.
4) To mix with other chemicals for various special purpose.

Treatment through 2) and 3) could yield asphaltene precursors that can be melt-spun at higher temperatures. Green fibers spun at higher temperatures could avoid fusing during heating for stabilization and oxidation treatment and yield higher strength of the green fibers and final carbon fiber products.

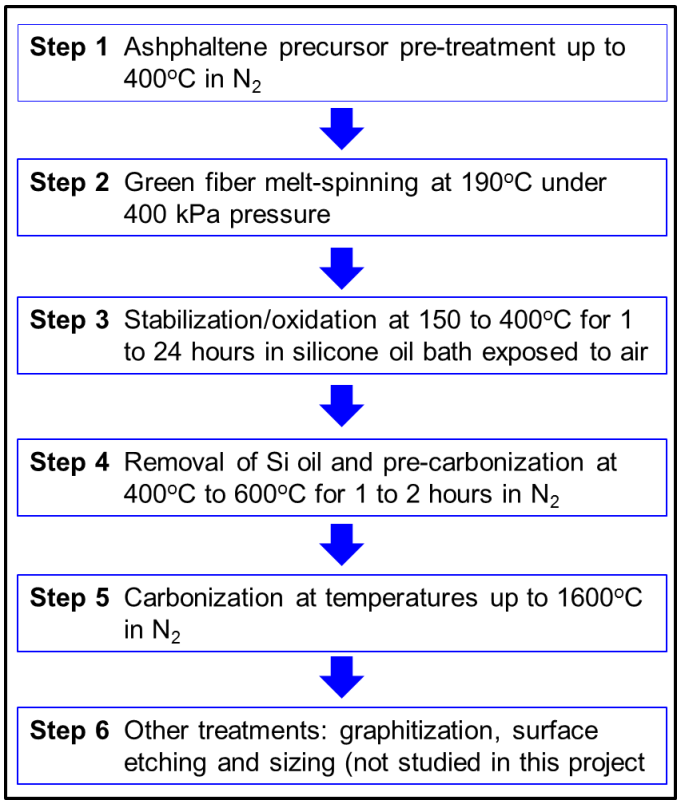


Figure 15 Optimized carbon fabrication flow chart

Step 2 Green-fiber melt-spinning:

The temperature and pressure for melt-spinning determined in this investigation are applicable only to the current as-received asphaltene feedstock. The change of glass transition point of asphaltene precursor would require different temperatures for spinning. The winding speed in

order to reach a given diameter of green fiber would depend not only on the size of spinneret orifice but also the ambient air temperature the green fibers are pulled into.

Step 3 Stabilization/oxidation:

Step-wise process, instead of stabilization at one temperature step, could be used. This process involves the ingress of oxygen into the core of green fibers. Stabilization at lower temperature would require longer time, which would increase the length of processing time, but seems to yield improved mechanical properties after carbonization. There is also an issue of inter-fiber fusing during stabilization that must be resolved. The silicone oil must be removed prior to next step treatments.

Step 4 Pre-carbonization:

Carbonization is required to remove hetero-atoms like H, N, O and S in the form of H_2O, CO_2. CO, N_2, SO_2, CH_4. H_2 and tars. Above 1,000 ^oC, the principal gas evolved is H_2 [4]. Pre-carbonization at 500^oC for 2 hours has led to improved mechanical properties after carbonization at 800^oC. This improvement could be caused by slow and gradual release of chemical species such as H_2O, CO_2. CO, N_2. Quick release of these species at high temperatures could cause formation of large defects within the fiber that limit their tensile strength.

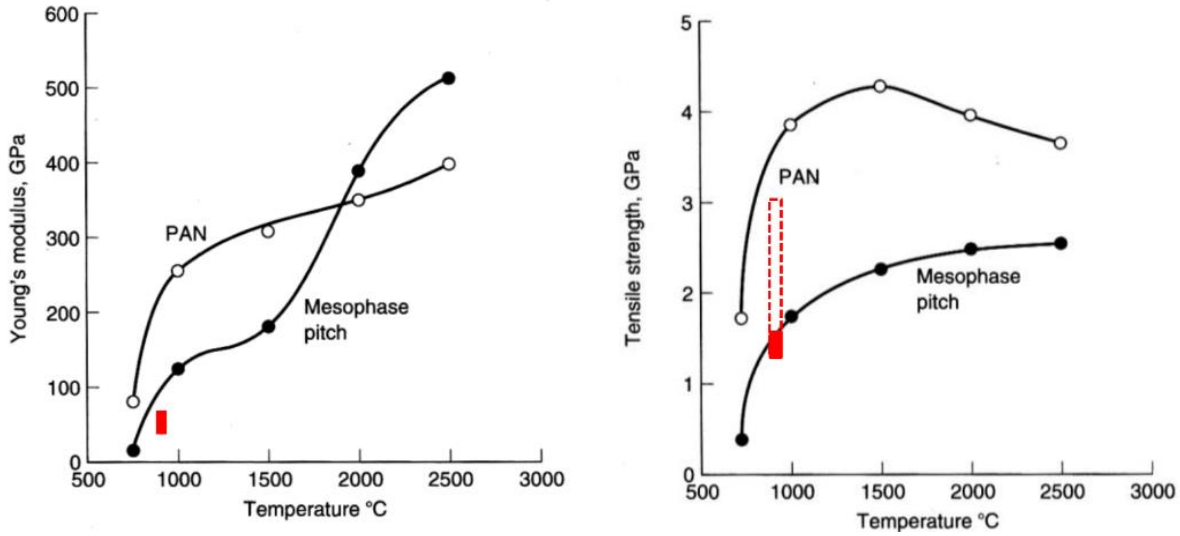


Figure 16 (a) Tensile modulus and tensile strength as a function of carbonization temperature for PAN and pitch-based carbon fibers. [5] **Red ranges are those from current investigation (Red solid: achieved after carbonization at 900^oC, Red dash: projected value after carbonization up to 1600^oC).**

Step 5 Carbonization up to 1600°C:

The tensile properties of mesophase pitch-derived carbon fiber increases quickly with carbonization temperature up to 1600°C, as shown in Figure 16. Carbonization at temperatures at around 900°C has caused substantial reduction of tensile strength as shown in Figure 11. This reduction could be minimized by varying heating rate and step-wise temperature hold before reaching the final carbonization temperature, according to limited results from this investigation.

Step 6a Graphitization:

This step has not been performed in the current investigation. Graphitization is the process of treating the fibers at high temperatures in order to improve the alignment and orientation of the crystalline regions along the main fiber axes. Having the crystalline regions aligned, stacked, and oriented along the main fiber axis increases the overall strength and stiffness of the carbon fibers. In order to obtain carbon fibers with higher modulus and higher carbon content, graphitization is typically performed at higher temperatures up to 3,000 °C.

Step 6b Other treatments including, surface etching and sizing of carbon fibers:

Surface etching is applied to improve the adhesion of carbon fibers to binding matrices for making composites. Sizing for carbon fiber, which coats surface etched carbon fibers with polymers, prevents individual filaments from breaking, improves handling of the very fine carbon filaments, and provides compatibility with molding processes.

Graphitization, surface etching and sizing of carbon fibers are equally important as other steps, although they were not studied in this investigation.

4.2 Tensile properties of asphaltene-derived carbon fibers

Pitch-based carbon precursors are usually melt-spun into green fibers with diameters that do not need stretching to further reduce their diameter. (Stretching, however, is used to align the graphite domains along the fibre axis.) The diameter of green fibers after carbonization can be reduced by a few micrometers because of the reduction of graphitic lattice, evaporation of volatile species, and removal of majority of non-carbon atoms. The tensile properties of carbon fibers are known to be a strong function of fiber diameter, as shown in Figure 17. There is an increase of tensile strength by 1,000 MPa

when the diameter of carbon fibers is reduced from 10 μm to 8 μm for Torayca T300 as an example. Diameters of commercial carbon fibers are normally in the range of 5 to 8 μm. With this range of diameter, carbon fibers can reach the highest force to fracture, although the stress to fracture carbon fibers increases with decreasing fiber diameter.

In this investigation, carbon fibers with a diameter at around 10 μm were obtained by carbonization at 900°C. They have an average tensile strength of 1300 MPa and 60 GPa. By extrapolating the tensile strength of 10 μm diameter carbon fibers to that of 8 μm diameter carbon fibers based on the results in Figure 17, an increase in tensile strength by 1,000 MPa can be expected. Based on Figure 17, this would yield a tensile strength of above 2,500 MPa when the asphaltene-derived carbon fibers were fabricated to a final diameter below 8 μm. The projected tensile strength at lower carbon fiber diameters is also marked in Figure 17 for the purpose of comparison. Further increase of tensile properties can be achieved by carbonizing asphaltene-derived carbon fibers at higher temperatures up to 1600°C, according to Figure 16, provided that the degradation of tensile properties seen at a carbonization temperature of around 900°C could be avoided when such fibers were to be treated at higher carbonization temperatures.

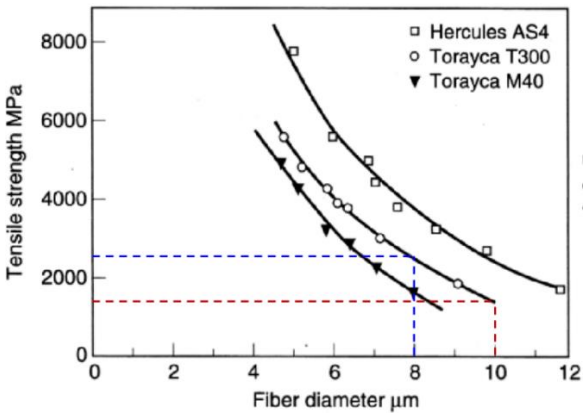


Figure 17 Tensile strength of carbon fibers as a function of fiber diameter [4].

It is a surprise that Young's modulus of asphaltene-derived carbon fibers after carbonization at temperatures up to 900°C is lower than that of mesophase pitch-based carbon fibers carbonized at the same temperature. This lower Young's modulus of asphaltene-derived carbon fibers should be related to the carbon structures of fibers in the following ways:

1) The lattice spacing of graphitic layer in the carbon fibers: Young's modulus is a measure of the relative resistance to elastic stretching of graphitic lattice. A larger lattice spacing corresponds to weaker bonding between graphite layer and can produce larger lattice stretching, therefore, lower elastic modulus.
2) The orientation of graphitic layers with respect to the length direction of carbon fibers: Graphite is highly anisotropic. For example, the elastic modulus is measured to be 1,015 GPa in the direction parallel to the graphite layer planes, but only 35 GPa in the direction perpendicular to the layer plane (c-axis) [6]. Therefore, the graphite layer planes in the asphaltene-derived carbon fibers, could be most likely oriented in a direction more perpendicular to the length direction of carbon fibers.
3) It is observed that a fiber with larger diameter filaments, spun from a mesophase pitch tended to elongate, whilst smaller diameter filaments shrank, presumably because they were more highly oriented. The elastic modulus of spun fibers increased with the draw ratio, but decreased with increasing thermosetting temperature and is attributed to a relaxation effect. (Morgan 2005). Therefore, the modulus of asphaltene-derived carbon fibers could be further improved by optimizing spinning conditions and modifying asphaltene precursors.

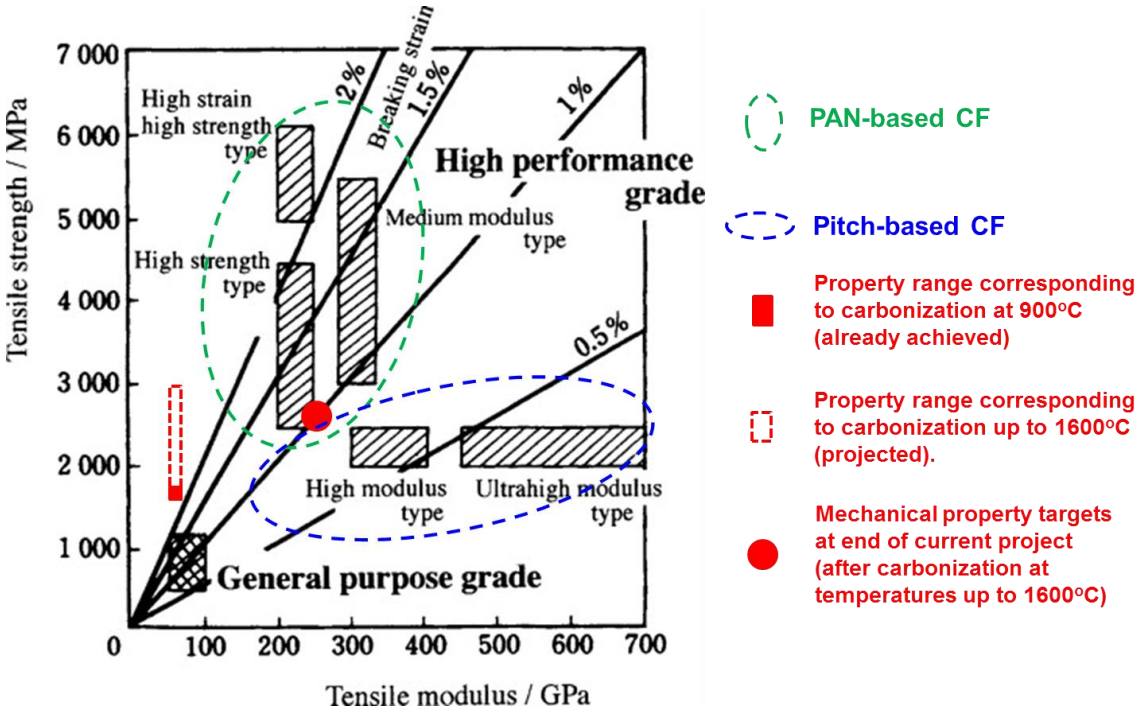


Figure 18 Correlation of tensile strength with tensile modulus of various types of carbon fibers. [7]

As indicated previously, it is common that some degradation of the structure occurred with attendant reduction of modulus at temperatures up to 1,000 °C, but as the temperature increased there was a marked increase in preferred orientation as the hetero-atoms were continuously released, forming a graphite-like structure.

The tensile properties of the current asphaltene-derived carbon fibers are compared with other categories of carbon fibers, in Figure 18. It appears that the tensile properties of asphaltene-derived carbon fibers follow the strength-modulus trajectory of PAN-based carbon fibers. That is to say, asphaltene-derived carbon fibers are able to yield higher elastic strain before tensile failure, and would, therefore, be less brittle than commonly used pitch-based carbon fibers. Because of their stress-strain responses, sizing for asphaltene-derived carbon fibers, which is necessary to prevent individual filaments from breaking during mechanical loading when they are embedded into composite matrix, would differ from that of brittle pitch-based carbon fibers with high modulus. On the other hand, the asphaltene-derived carbon fibers could find applications where PAN-based carbon fibers are required, provided that their tensile strength can be sufficiently improved.

4.3 Toward pilot-scale production of long carbon fibers using asphaltenes as feedstock

The pilot-scale production of long carbon fibers using asphaltenes as feedstock could be achieved following existing technology of fabricating pitch-derived carbon fibers. A brief summary of production technology of pitch-based carbon fibres is given below.

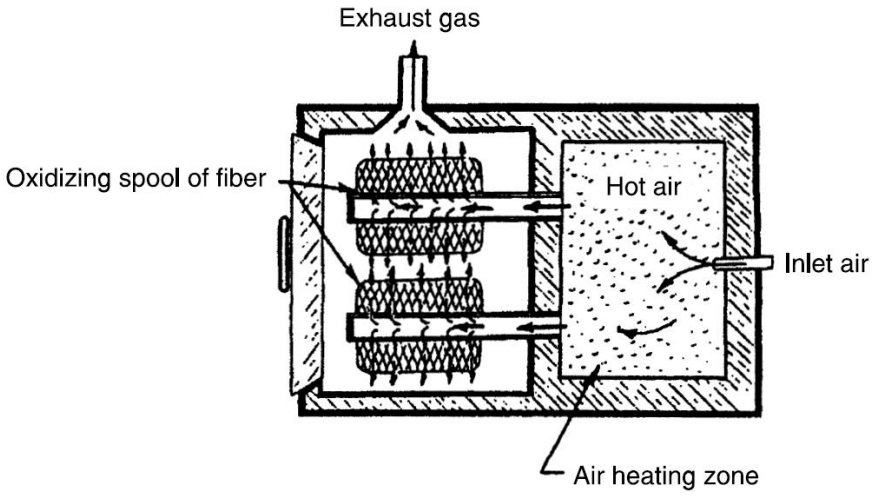


Figure 18 On the spool oxidation of mesophase fibers [4 – page 297]

- Stabilization (thermosetting) of spun fiber: Similar to asphaltene fibers, all pitch precursor fibers, are very weak. They must be stabilized through oxidation treatment in either gas or liquid environments. Because of their brittleness, the precursor fibers are usually treated through a batch process, such as, by placing precursor fibers wound onto a heat resistant spool in an oxidation furnace as illustrated in Figure 18, or by placing spun fibers on conveyor belt and carrying them into oxidation furnace.

- Carbonization: A typical carbonizing furnace using a graphite hairpin heating element and capable of achieving 2000 ^{o}C is shown in Figure 19. [4 – Page 301]. Carbonization can be achieved in a string of separate furnaces with individual temperature settings, or one or more furnaces with zoned temperature control. After the initial carbonization stage, the temperature is increased to about 2,000 ^{o}C.

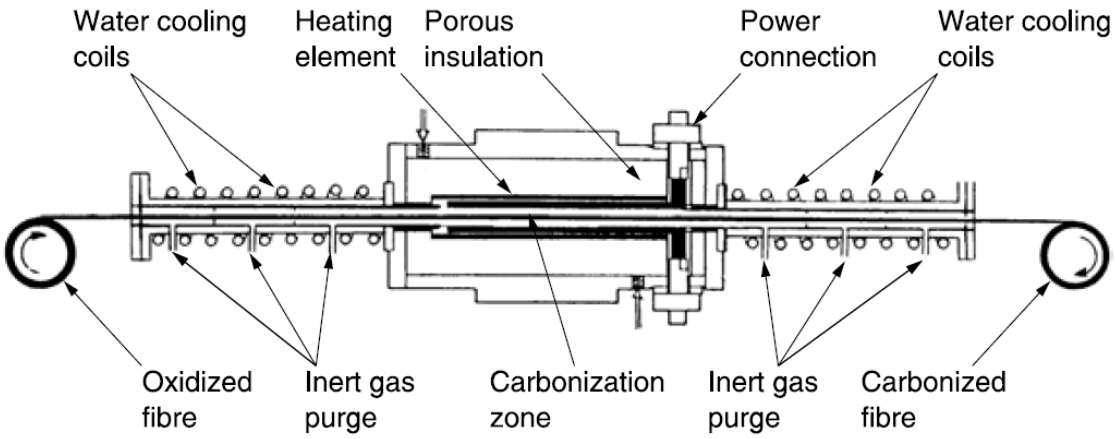


Figure 19 Diagram of a hairpin element furnace used to carbonize mesophase pitch fibers [4]

- Graphitization: It can be further heat treated in a similar type of furnace, using a highly controlled inert atmosphere, at temperatures in the range 2,500-3,300 ^{o}C, preferably 2,800-3,000 ^{o}C.
- Surface treatment: If carbon fibers are to be introduced into a resin matrix, it would be expected that some form of oxidative treatment would be applied to improve resin wetting and to increase surface roughness that could enhance bonding through mechanical and physical interlocking.

5 Conclusions and future works

The objectives set forth at the outset of the project were quite ambitious. It is clear that to achieve the objectives of the project additional research and development will be required beyond the work performed in this study. This investigation, however, did advance knowledge for fabricating carbon fibers using asphaltenes as carbon precursors. This is a very valuable for future comparisons with carbon fibres manufactured using alternative schemes. The major findings for the University of Alberta component of the study are as follows:

1) Green carbon fibers can be fabricated by melt-spinning directly using the asphaltenes produced from an industrial C5 solvent deasphalting process at NEXEN Long Lake Upgrader in Alberta. The green fibers can be fabricated to achieve different diameter by controlling fiber winding speed during spinning and the diameter of spinnerets.
2) The green fibers must be first stabilized/oxidized in order to reach sufficient strength before further thermal processing. The green fibers during stabilization/oxidation treatment must be placed in a silicone oil bath without physical contacts in order to avoid fusing.
3) The stabilization/oxidation treatment must be performed at various temperatures between 150 – 350 °C for sufficient length of time up to 15 hours in open air in order to achieve best mechanical properties.
4) Carbonization is performed after stabilization in nitrogen protected environment. Because of the limit of furnace temperature, the carbonation was carried out at temperatures up to 1000^{o}C. Carbonization first at 500^{o}C for 2 hours prior to the final carbonization at temperatures up to 1000^{o}C or at reduced heating rate to the final carbonization temperature has yielded higher mechanical properties.
5) Best mechanical properties of asphaltene-derived carbon fibers were found when the final carbonization temperature was 800^{o}C. The lowest mechanical properties were observed when carbonization temperature was at around 900^{o}C. At his later temperature, defects such as voids and flaws were found to be formed within the fiber, and may be responsible for the reduction of mechanical properties.
6) With a carbonization treatment up to 1000^{o}C, the asphaltene-derived carbon fibers having a diameter of 10 µm has reached a tensile strength of 1,300 MPa and tensile modulus of 60 GPa. It is expected that the mechanical properties of asphaltene-derived carbon fiber could be further improved by increasing carbonization temperatures to 1,600^{o}C, optimizing spinning and

stabilization conditions, and reducing the diameter of carbon fibers to a value between 5 to 8 µm (diameters of commercial carbon fibers).

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One-step plasma-assisted technology for manufacturing high performance carbon fibers using asphaltene precursor

FINAL REPORT
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EXECUTIVE SUMMARY

In the present report, the results of project entitled “One-step plasma-assisted technology for manufacturing high performance carbon fibers using asphaltene precursors” will be presented. This project was realized in collaboration between the University of Alberta who contracted Université de Sherbrooke and with support of CNOOC International and Alberta Innovates. This report summarizes only the work completed at the Université de Sherbrooke.

The Université de Sherbrooke received as mandate to produce asphaltene carbon fibers through plasma technology in one-step process as a means to bring added value to asphaltene-spun fibers. This part of overall project was divided in 6 steps. The three first steps were concentrated on investigating the first carbon fiber step: stabilization.

In the first step, and to have a process baseline, a commercial polyacrylonitrile (PAN) precursor was successfully stabilized at 300°C during a three hours conventional process in air. In the second step, and the most project consuming time, a set of optimized processing conditions of a PAN plasma stabilization/oxidation process were determined. PAN fibers were successfully stabilized under a plasma process during 30 minutes at 40 cm from plasma discharge. At this discharge distance the temperature of oxidizing environment, composed of a mixture gas of 2.0 % (v/v) of oxygen and 98.0 % (v/v) of argon, was 350°C at 100 torr. PAN fibers, stabilized by both conventional and plasma processes, were characterized by Fourier Transform Infrared spectroscopy (FTIR), elemental analysis, differential thermal analysis (DTA), scanning electronic microscopic (SEM) techniques and tensile mechanical tests. The characterization confirmed that PAN fiber was completely stabilized by both processes. However, plasma process resulted in a stabilized PAN fiber with considerably improved mechanical properties. The plasma stabilization process proved to be six times faster than conventional stabilization. However, the total time required to do this work was longer than expected which limited the time to achieve the final proposed objectives.

In the third step, and based on optimal stabilization conditions of plasma process, an asphaltene carbon fiber feedstock was attempted to be stabilized by a plasma process. Asphaltene fibers were placed at 40 cm from plasma discharge where the oxidizing gas coming from the plasma discharge was at 315°C. Partial stabilization was achieved between 1 to 3 hours. Plasma was generated at 110 torr by a gas mixture composed by 1.0%(v/v) of O_2 and 99.0% (v/v) of Ar. The asphaltene fibers stabilized by these plasma processes were compared with a 13-h and a 4-h conventional process proposed by the Carbon Fiber research group of University of Alberta. Under these processing conditions, the infrared spectrum of stabilized asphaltene fibers showed a possible indication of the beginning of asphaltene stabilization/oxidation by the plasma process. In order to enhance this asphaltene plasma stabilization process, further experimental work was proposed. An optimization of processing time must be necessary to complete this project step.

The final steps, Carbonization, Graphitization and a complete one-step plasma process, were not investigated in this project.

INTRODUCTION

Low-value asphaltenes (derived from Athabasca oilsands bitumen) are highly aromatic compounds and as such were investigated for their potential to be converted into higher value carbon fibres. Therefore, in collaboration with University of Alberta (UofA) and with support of CNOOC International and Alberta Innovates, the Plasma Laboratory of Université de Sherbrooke (UdeS) received the mandate to explore an innovative process of manufacturing carbon fibers from asphaltenes raw feedstock in a one-step plasma process.

A simplified process flowchart of complete process for the conversion of raw asphaltenes into high performance carbon fibers are summarized in Figure 1. The first step of processing involves the conversion of asphaltenes raw materials into anisotropic mesophase materials, which could be done with or without the intermediate process of purifying raw asphaltenes for desulfurization and demetallization. The mesophases obtained will then be processed by melt spinning to produce raw carbon fiber precursors.

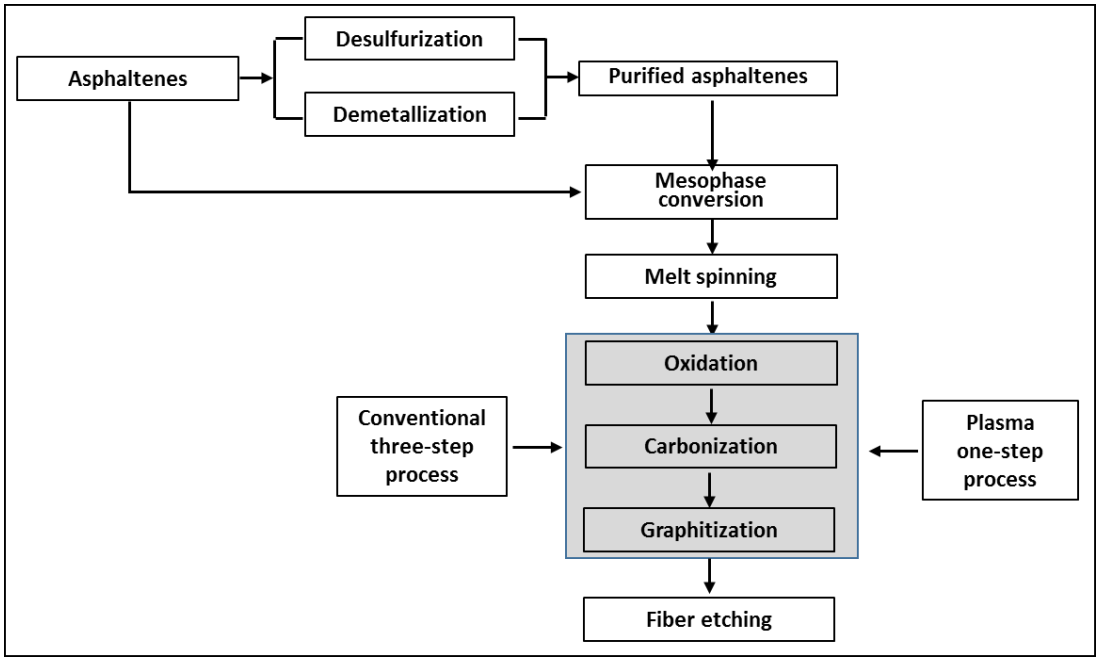

Figure 1. Simplified process flow chart for converting raw carbon fibers into high performance carbon fibers

The production of carbon fibers is typically a multi-step process in which the raw precursor fibers must go through a process of oxidation, carbonization and graphitization with increasing temperatures in different environments. In the oxidation stage, the precursor fibers are treated in an oxidizing atmosphere at temperatures ranging from ambient up to about 200-400^{o}C. This processing step converts the precursor into a thermoset material, stabilizing it both chemically and thermally so that it will resist higher temperatures of subsequent carbonization process [1–5]. The fiber precursor acquires stability by oxidation and cross-linking, which leads to thermally stable, ladder-structured carbon though oxidation, dehydrogenation and cyclization [1, 4–9]. Typically, this oxidation or stabilization process is the most time-consuming and rate-limiting step in conventional carbon fiber manufacturing [10–12]. The terms oxidation and stabilization are both used to describe this processing step because both processes occur simultaneously, so both terms can be used interchangeably. To avoid confusion, hereinafter this processing step will be called the Stabilization Process. The carbonization step occurs at an intermediate temperature about 1000°C to 2000°C and graphitization the highest up to 3000°C where both processes are carried out under inert environments of nitrogen or argon gases.

This project was divided into three modules as shown in Figure 2 and summarized in Table **1**.

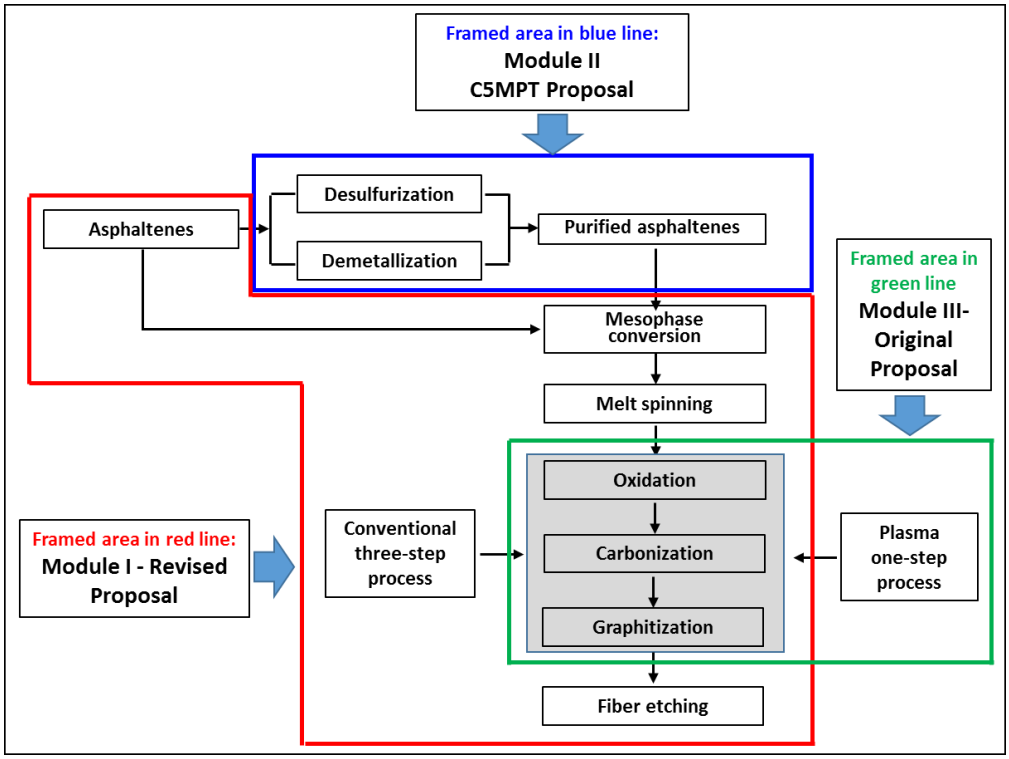

Figure 2. Three project modules for converting raw carbon fibers into high performance carbon fibers

Table 1.Three project modules and partition of research work

Modules	Description	Partners	Notes
I	Conventional three-step process without purification of raw asphaltenes	University of Alberta	• Major focus on mesophase formation and melt spinning • Minor focus on conventional three-step processes
II	Purification of raw asphaltenes	University of Alberta	• Secondary, depending on available time and funding

III	Plasma-one-step raw-carbon-fiber processing	Université de Sherbrooke	• Main focus

The work of UofA was focused on Module I and Module II and the Module III was assigned to UdeS. This report concerns the work reached out at UdeS.

The principal mandate of UdeS was to provide a 'proof of concept' of a Plasma-one-step carbon fibers process using asphaltenes as precursors. A Plasma-one-step process means that the feedstock fibers will be exposed to thermal plasma environment at a sequential set of operation conditions to produce Oxidation, Carbonization and Graphitization. From a technical point of view, to find the operation conditions of carbonization and graphitization steps by plasma process is not difficult because the temperature range of thermal plasma is between 1000 and 10^4 K. Furthermore, the main gas used to generate the plasma state is argon which provides the inert environment for carbonization and graphitization processes. In contrast, the stabilization step represents the biggest challenge concerning the research of operation conditions.

Plasma state consists of an electrically neutral mixture of electrons, neutral molecules, and atoms as well as ions, in the fundamental or excited states [13]. The high reactivity owing to formation of these free ions and radicals species makes the plasma process a powerful technique to promote chemical reactions [14]. In an oxidizing thermal plasma discharge, i.e. an argon/oxygen plasma mixture, the oxygen is present in different atomic-molecular states such as O, O^+, O^{++} and O_2 [13, 15–17]. These high reactive species allow them to react with the fibers faster than molecular oxygen used in conventional processes. The main difficult of applying this more efficient technique is to achieve the correct temperature for oxidation. In carbon fiber manufacturing, the oxidation process requires temperatures < 400°C. Furthermore, asphaltene fibers are susceptible to melt at around 120°C (softening point). Given that the temperature in the plasma state can reach 10^4 K, but decreases dramatically away from the plasma core concomitant with the density of plasma-reactive species. This means that the carbon fiber precursor cannot be placed either too close to the plasma discharge (since it would burn burn or melt) or too far away to have any contact with the plasma-reactive species.

The working hypothesis was that an appropriate working distance from the plasma exists at which: h1) the fibers are oxidized by the incoming gases (between 200 to 400 °C) and h2) longer-lived chemical species generated by the plasma state survive and interact with the fiber precursor.

To verify the first hypothesis (h1) a set of thermocouples were placed at different distances from plasma source. It is important to mention that due to the magnetic field produced in the plasma state, a thermocouple can not be placed very close to a plasma discharge. However, at the oxidation temperatures this magnetic effect was totally negligible. The second hypothesis (h2) was more difficult to verify. The characterization of plasma discharge in terms of active species by optical emission spectroscopy is not feasibile, with our equipment, at temperatures below 1000 °C. The best strategic approach to find the optimal plasma discharge conditions was trial and error. Hence the need to consider, a priori, a commercial carbon fiber precursor, the polyacrylonitrile (PAN), to facilitate the study of stabilization by plasma process. PAN commercial precursor has two advantages, firstly, its proven reactivity to stabilization process. Secondly, PAN fibers change color when stabilization process progresses. This change processing-color can be use as an 'easy' indicator of progress of stabilization reaction. The optimal operation conditions to PAN fibers stabilization will constitute a baseline to the stabilization of asphaltene fibers. The next and less complex step would be to explore carbonization and graphitization by plasma process. Unfortunately, the stabilisation study took longer than expected, and thus the carbonization and the graphitization steps could not be investigated. In summary, the principal objective of the present study was to provide a 'proof of concept' for effective and efficient plasma stabilization of raw asphaltene fibers produced by the Carbon Fiber Research group at the University of Alberta.

EXPERIMENTAL

Materials

Two types of carbon fiber precursors were used in this study: a commercial grade polyacrylonitrile fiber (PAN) and a green asphaltene fiber produced by the Carbon Fiber Research group of UofA.

Polyacrylonitrile Fiber

The commercial grade PAN fiber was supplied by Shenzhen Xiangu High-Tech. Co. Ltd. Properties indices of this fiber are listed in Table ***2***.

Table 2. Properties of PAN fiber [18]

Model	Filament Number	Linear density [tex*]	Linear density of monofilament [tex*]	Elongation at Break [%]
XG-3K	3000	360	0.122 ±0.003	12±3

(*) 1 tex=1 g/1000m

This commercial fiber has 3000 single fibers per sample contrarily to raw asphaltene fibers which were treated by UofA team in an individually manner, i.e. the fibers were separated in individual filaments during each treatment. According to literature review [1–3, 5, 7, 19–29], the manufacturing process of carbon fiber process is carried out by fiber bundle. In the present study this commercial PAN was treated in its purchased state, i.e. in a fiber bundle of 3000 single filaments named hereinafter the PAN fibers.

Asphaltene Fiber Stabilization by a Conventional Process

The green asphaltene fibers was supplied by the Carbon Fiber Research group of the University of Alberta (UofA). The UofA produced asphaltene fibers with a diameter of ~16.6 μm by melt spinning n-C5 (*n*-pentane) asphaltenes, supplied by CNOOC International's, formerly known as NEXEN, facility in Long Lake oil sands site, Alberta, Canada.

The raw asphaltene fiber has a 'softening point' at ~120°C where fibers become adhesive and tend to fuse. In order to prevent these fusing behavior UofA proposed a silicon oil treatment. However, when UdeS began the stabilization study of asphaltene fibers, UofA suggested to change this oil pre-treatment to an acid one instead. The acid pre-treatment consisted to soak the raw fibers in a

10% (v/v) nitric acid solution for 15 minutes and then left to dry for one hour. This protocol was suggested by Dr Weixing Chen. The acid effect is not completely understood yet, however, it is considered that the acid reacts with the fiber by capping its active sites possibly with carboxylic groups, which prevents that asphaltene fibers fused together. After acid pre-treatment, green asphaltene fibers was named asphaltene fibers.

Methods

Asphaltene Fiber Stabilization by a Conventional Process

Conventional Stabilization of fibers was performed in a Carbolite Gero® Tube Furnace, model CTF 12/75/700 provided with a temperature control system using a thermocouple positioned in the center of furnace. The furnace has a 750 mm heated zone and it is provided with a cylindrical quartz tube which dimensions are 1600 mm long and 7.5 cm diameter. The temperature profile inside the tube is characterized by a parabolic distribution. Figure **3** presents a schematic diagram of the setup used in this study.

In the case of PAN fiber, a constant tension of 10 kPa was applied during each test (Figure **3**B), whereas the asphaltene fiber was laid flat in a ceramic crucible (without tension) and was placed in the center of the furnace, as is shown in Figure 3A.

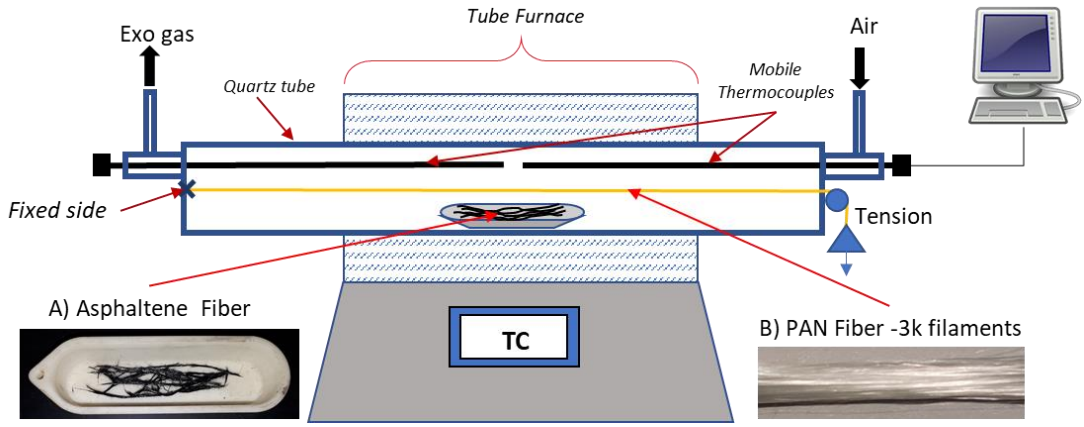

Figure 3. Setup of Stabilization in a Conventional Process: A) asphaltene fiber and B) PAN fiber.

Table 3 summarizes the conditions used in the conventional stabilization process. All tests were performed under a constant air flowrate. Based on: a) thermal properties of PAN sample, b) the literature review and c) a set of temperature tests, a heat treatment of three hours for Stabilization by conventional process of PAN fiber was used.

In case of Asphaltene fibers, the stabilization by conventional process was assigned to UofA. However, based of stabilization treatments developed by UofA, two conventional treatments were carried out at UdeS and these are shown in Table 3. Here, the air flowrate was an approximate of value used by UofA team in their conventional process.

Table 3. The heat treatments of the Stabilization Process of PAN and Asphaltene Fiber in a Conventional Process.

Fiber	Air Flowrate [SLPM]	Cycle	Heating rate [°C/min]	Holding Temperature [°C]	Holding Time [min]	Time of treatment [h]
PAN	4	1	2	300	60	3
Asphaltene	2	1	5	220	120	4
		2	5	350	60	
Asphaltene	2	1	1.3	100	120	13
		2	3.3	200	120	
		3	1.7	250	120	
		4	1.7	300	120	
		5	1.7	350	120	

Stabilization in a Plasma Process

The stabilization tests were carried out in the plasma laboratory of Plasma Process and Integration of Nanomaterials (2PIN) research group of the Université de Sherbrooke.

The schematic diagram of the Figure 4 illustrates the experimental setup used for the present study. It consists of a (Lepel) radio-frequency power supply, a water-cooling system, a vacuum pumping system and a plasma reactor. The power supply has a nominal oscillator frequency of 5MHz and a maximum power plate of 25 kW. The pumping system has a control system which can maintain the reactor pressure over the range from 2 to 110 torr.

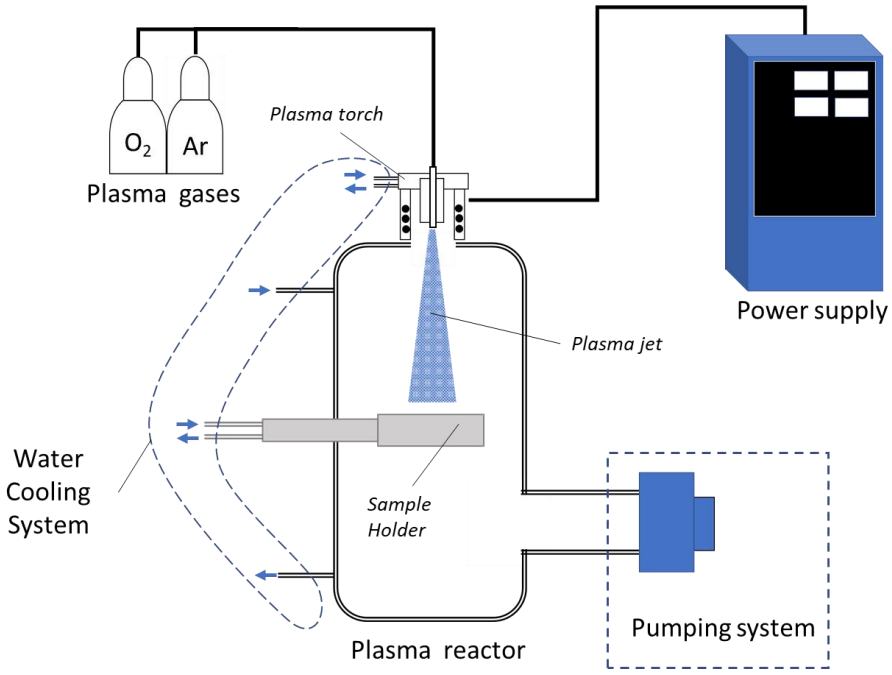

Figure 4. Schematic diagram of Plasma System

Figure 5 shows the reactor chamber. The plasma reactor consists of a sealed water-cooled cylindrical chamber (20 cm inside diameter, 1000 mm long). It is equipped with two quartz windows which allow the observation of either the plasma jet (named the plasma discharge too) or the sample holder. A video camera was placed over one of two windows to have a visual recording of sample evolution during each test.

The plasma torch is driven by a radio-frequency Tekna induction plasma torch model PL-35® which has a 35 mm inner-diameter, water-cooled ceramic plasma confinement tube with five-turn induction coil similar to those shown in Figure 6. The plasma gas is introduced into the discharge chamber as two distinct gas streams, sheath and central gas. In the torch chamber, both gases are separated by a concentric quartz tube. The plasma was formed from a mixture of pure argon and oxygen molecular gas. The oxygen gas was introduced premixed with the argon sheath gas [13]. No carrier gas was used in this study.

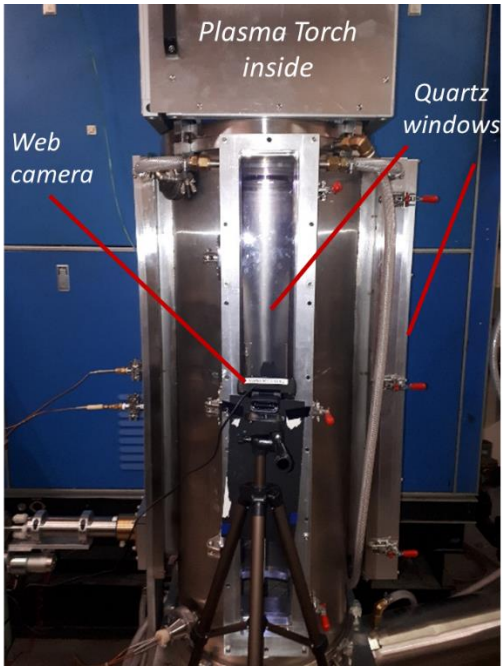

Figure 5. Plasma reactor chamber.

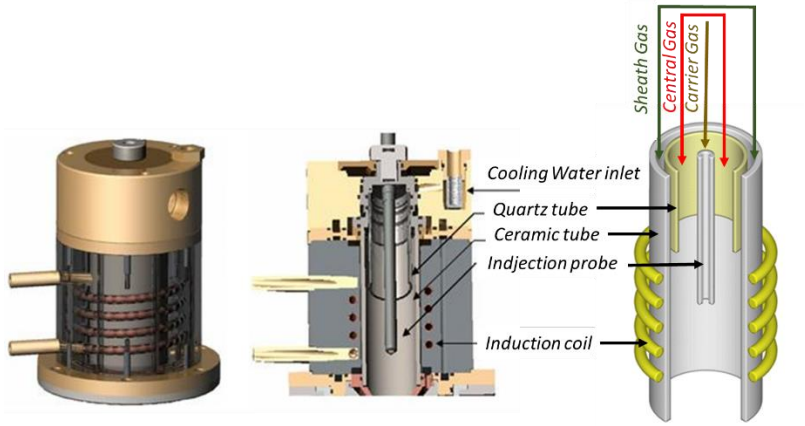

Figure 6. Tekna RF plasma torch model PL-35®*[30]*.

Table 4 summarizes the range of plasma torch operating conditions based on the stability of plasma jet discharge. Due to technical considerations related to thermal stability of plasma torch, the plasma state must be generated (plasma ignition) by a gas composed by argon only. After plasma

ignition (generation of plasma state) the oxygen gas can be injected as a sheath gas. The range of oxygen composition was chosen having as a limit the air composition as it is shown in Table 4.

Table 4. Range of plasma torch conditions.

Torch Parameters		Oxygen gas	Argon gas
Flowrate [SLPM]	**Central**	0	4-20
	Sheath	0.4-10	30-50
Composition [% v/v]		1-21	99-79
Pressure [torr]		20 -110*	

(*) maximum pressure that can be achieved on vacuum system installed

Figure 7 presents the Plasma Stabilization setup used for PAN fibers. Unstabilized PAN fiber was placed under constant tension and it was exposed to the plasma jet discharge under the range of conditions shown in Table 5. In this case, the PAN fibers do not come into direct contact with the plasma jet, but are situated at a considerable distance where, at least, the longest-lived chemical species (seen above) generated by the plasma discharge interact with the PAN fibers.

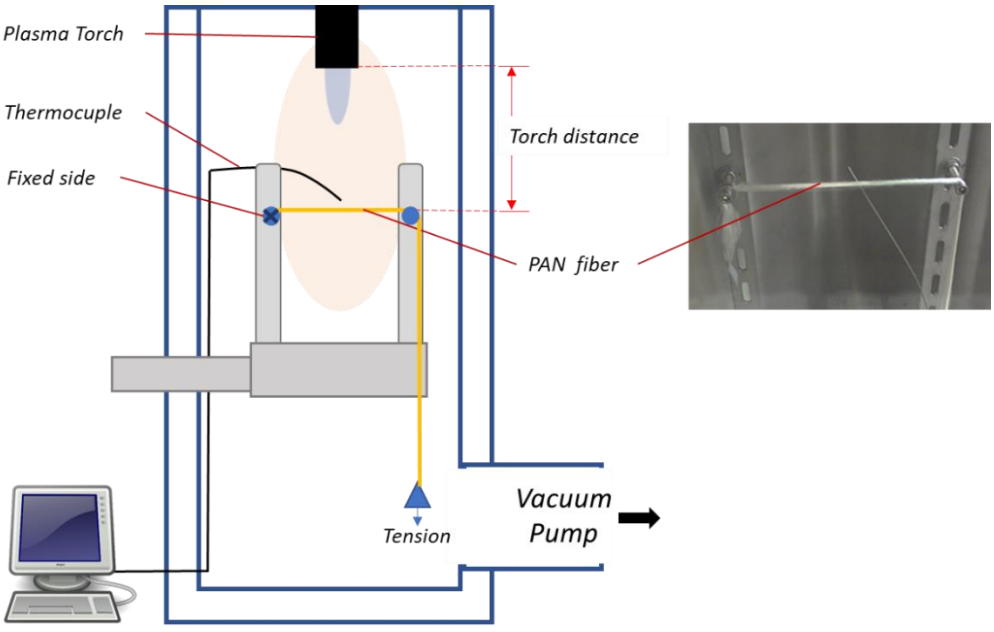

Figure 7. Plasma Stabilization Setup of PAN fiber.

Table 5. Range of processing conditions of Plasma Stabilization by Plasma Process.

Setup parameter	Range of values
Time [min]	30-60
Distance from torch [cm]	12 - 58

Based on optimized processing conditions of PAN plasma Stabilization, plasma Stabilization of asphaltene fibers was investigated. Figure 8 presents the Plasma Stabilization setup used to oxidize several asphaltene fibers in each experiment. At the beginning of this study, the poor mechanical properties of asphaltene fibers made it difficult to expose them to plasma discharge without breaking them. Diverse sample holder models were tested before to find the optimal one. Finally, the asphaltene fibers were placed in a ceramic crucible sample holder positioned at a given distance from the plasma torch. The fiber filaments were fixed with a heat resistant epoxy. In the interest to have a point of reference, a PAN fiber sample was also placed at a same distance from the plasma torch.

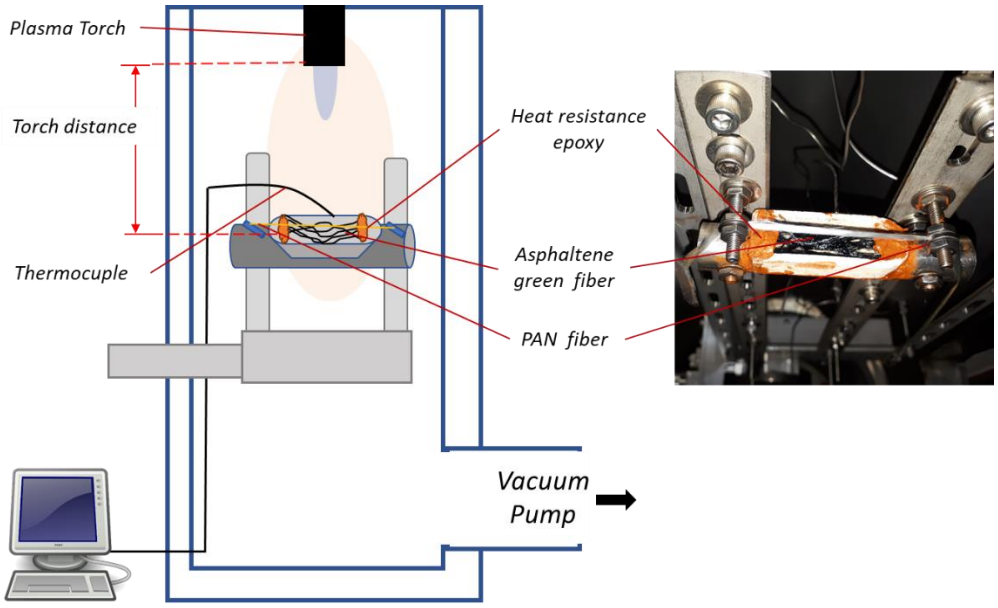

Figure 8. Plasma Stabilization setup of asphaltene fiber.

Experimental Strategy: a proof of concept

In order to provide a 'Proof of Concept' of a plasma one-step Process a schematic of the proposed experimental strategy to achieve this mandate was initially proposed and it is presented in Figure *9*.

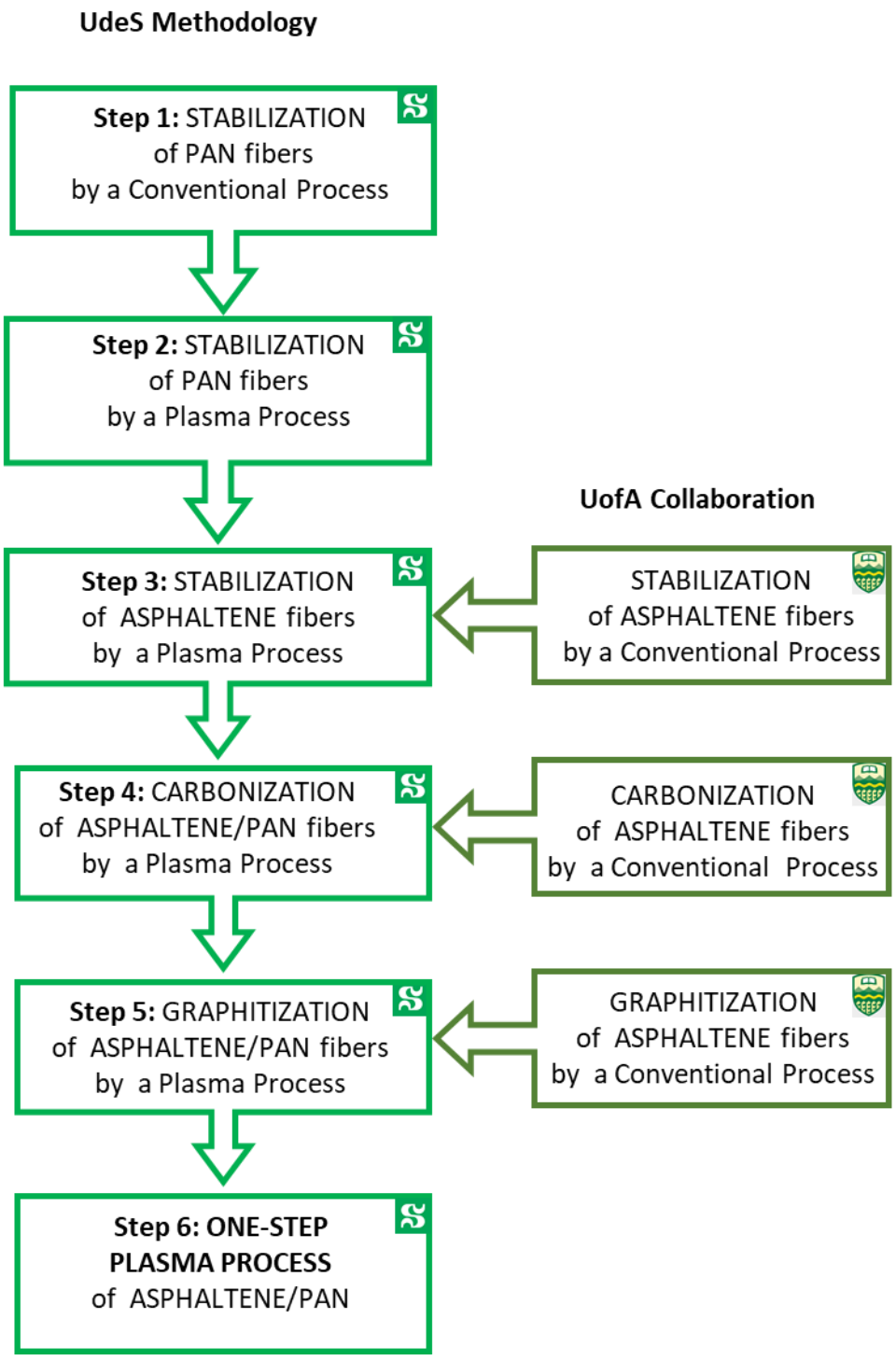

Figure 9. Schematic of the initially proposed experimental strategy.

The experimental strategy consists of 6 steps, with; its specific objectives described below:

Step 1 – PAN Stabilization by a Conventional Process

- To determine stabilization conditions in terms of: air flowrate, temperature profile and heating rate.
- To establish and validate an efficient stabilization progress indicator which gives a 'point of reference' to evaluate the reaction progress.

Step 2: PAN Stabilization by a Plasma Process

- To determine the PAN Stabilization conditions in terms of: central and sheath flowrate of plasmagen gas (Ar), flowrate of oxygen gas, pressure and distance from plasma torch.

Step 3: Asphaltene fibers Stabilization by a Plasma Process

- Based on; i) The optimized conditions of PAN Plasma Stabilization process and ii) the optimized conditions of asphaltene fiber Stabilization by a conventional process developed by UofA, to determine the conditions of Plasma Stabilization of asphaltene fibers.

Step 4: Carbonization process by a Plasma Process

- To determine the Carbonization conditions of PAN and Asphaltene fibers in terms of: central and sheath flowrate of plasmagen gas (Ar), pressure and distance from plasma torch.

Step 5: Graphitization process by a Plasma Process

- To determine the Graphitization conditions of PAN and Asphaltene fibers in terms of: central and sheath flowrate of plasmagen gas (Ar), pressure and distance from plasma torch

Step 6: One-step Plasma Process

- To integrate Stabilization, Carbonization and Graphitization in a one-step process. Once the process conditions for stabilization, carbonization and graphitization are determined, each step will occur sequentially in a one batch process.

Characterization

Fourier-transform infrared spectroscopy (FTIR)

The unstabilized and stabilized fibers were characterized using an ABB Bomem® FTIR Spectrometer analysis system in an Attenuated Total Reflectance (ATR) mode. The recorded spectra were obtained by averaging of 32 scans per sample at a resolution of 4 cm^{-1}. Each spectrum was collected at a wavenumber range of 600 to 4000 cm^{-1}.

In this study, the use of infrared spectroscopy technique has been found to be very useful to follow and understand the chemistry of the stabilization and to monitor the structural transformations taking place during the stabilization process.

Further, in case of PAN fibers, this technique allows to follow the progress of stabilization reaction through a reaction index which can be calculated using the following formula[23]:

$$R_I = \frac{I_0}{I_0 + I_V}, \qquad (1)$$

where R_I is the reaction index, I_0 is the measured intensity of a conjugated infrared band at 1595 cm^{-1} which is generally associated with C=C/C=N bonds and hence represents transformed structures. I_v is the intensity of the band associated with the nitrile group of the uncyclized PAN fiber at 2241cm^{-1}.

In case of asphaltene fibers, the progress of stabilization reaction was followed by the increasing intensity of the conjugated band located between 1800 and 1600 cm^{-1} which is associated with C=O bonds and hence represents transformed structures by oxidation process, according to standard processes described in the litteratue.

Elemental Analysis

Elemental Analysis of all samples were performed in a Leco TruSpec® Micro Elemental system.

Thermal Analysis (TGA/DTA)

Thermal properties of fiber samples were determined by simultaneous Thermogravimetric and Differential Thermal Analysis (TGA-DTA) carried out on a Setaram SETSYS 24 TGA system at 2°C/min, under argon and an air-like argon/oxygen mixture flow, from room temperature up to 600 °C.

Thermal behavior of unstabilized PAN is a determinant factor to define the processing operation conditions for the stabilization process. Generally, the temperature of stabilization reactions is determined by the study of DTA thermograms of precursor fibers[19]. Since oxidation reactions do not occur in an inert atmosphere, comparing the thermal behavior of fibers between an argon and an oxidative atmosphere helps us separate the oxidation from cyclization reaction [6, 8, 19].

Scanning Electronic Microscopy (SEM)

The microsurface structure of unstabilized and stabilized fibers was observed by scanning electron microscopy using a FEG-SEM Hitachi S-4700 scanning electro microscope operated at 5 kV.

Tensile Mechanical Tests

Tensile properties of a monofilament of the unstabilized and stabilized fibers were performed following the ASTM D2256 with a Zwick/Roell z050 machine. Tensile tests were performed using a load cell of 5 N and a crosshead speed of 1 mm/min. Reported values are the averages obtained over at least seven measurements. Young's modulus of a monofilament sample was calculated from initial slope of the load-elongation curve.

RESULTS AND DISCUSSION

FTIR characterization results

PAN fiber infrared spectrum

Figure 10 presents the FTIR spectrum of PAN fiber. The most important infrared absorption band were identified, and its values are shown in Table 6. The infrared bands around 2960, 1450 and 1261 cm^{-1} region are due to the presence of methyl (C-CH_3) and methylene (H-C-H) vibrations and deformations bending of the respective groups of polyacrylonitrile structure. The 2241 cm^{-1} band was associated with the stretching vibration of nitrile groups in the polyacrylonitrile structure. The absence of infrared bands between 2835 and 2815 cm^{-1} confirm the absence of methyl ether monomeric units (O-CH_3) related to methyl acrylate units. The absence of any vinyl ester structure suggests that the 1732 cm^{-1} infrared band are due to the presence of carbonyl units (C=O) related to the itaconic acid structure.

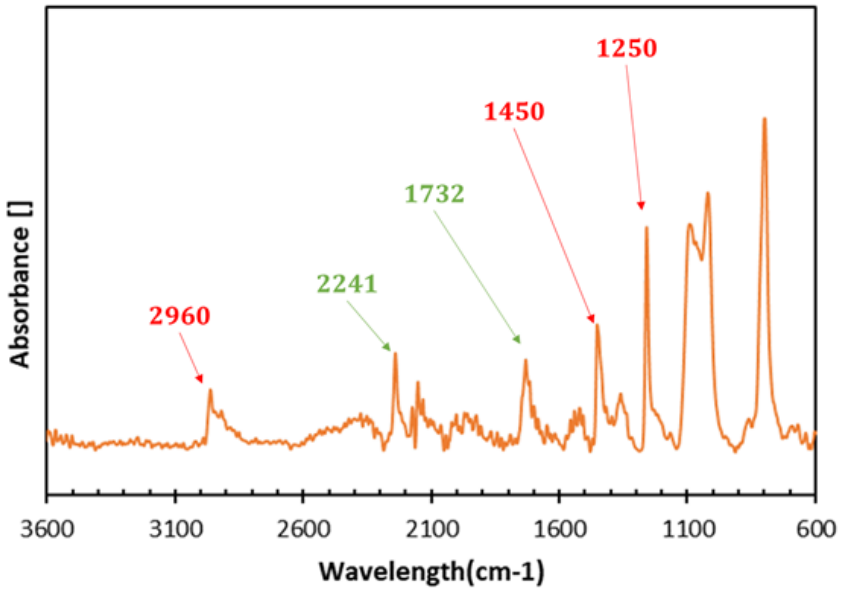

Figure 10. FTIR Spectrum of unstabilized PAN fiber.

Table 6. Assignment of PAN infrared absorption bands in the 4000-600cm^{-1} region *[28, 31, 32]*.

Wavenumber [cm^{-1}]	Assignment
2960	Methyl and methylene vibrations
2241	-C=N (stretching)
1732	-C=O (stretching)
1450	-CH_2 (twisting or bending)
1250	-CH (bending)

Asphaltene fiber infrared spectrum

Figure 11 shows the asphaltene fiber infrared spectrum. Two infrared bands at the wavelength range 3000-2800 cm^{-1} correspond to the functional groups producing vibrations of the aliphatic CH bond corresponding to CH_2 and CH_3, as well as, the strong absorption near 1630, 1450 and 740 cm^{-1}. The presence of the bands near 1630 and 820 cm^{-1} in the asphaltene infrared spectrum indicated its aromaticity [33–36]. The absence of absorption bands in the wavelength range 1800-1600 cm^{-1} shows that no carbonyl groups (C=O) are present in the asphaltene chemical structure of the raw (untreated) asphaltene fibres.

Table 7. Assignment of asphaltene infrared absorption bands in the 4000-600 cm^{-1} wavelength region [33–37].

Wavenumber [cm^{-1}]	Assignment
2920	C-H (stretching) from CH_2
2850	C-H (stretching) from CH_3
1560	Deformation vibrations C=C from benzene ring
1450	Bending vibrations C-H from CH_2
820	Nonplanar deformations of substituted benzene rings
740	Rocking vibrations C-H from CH_2

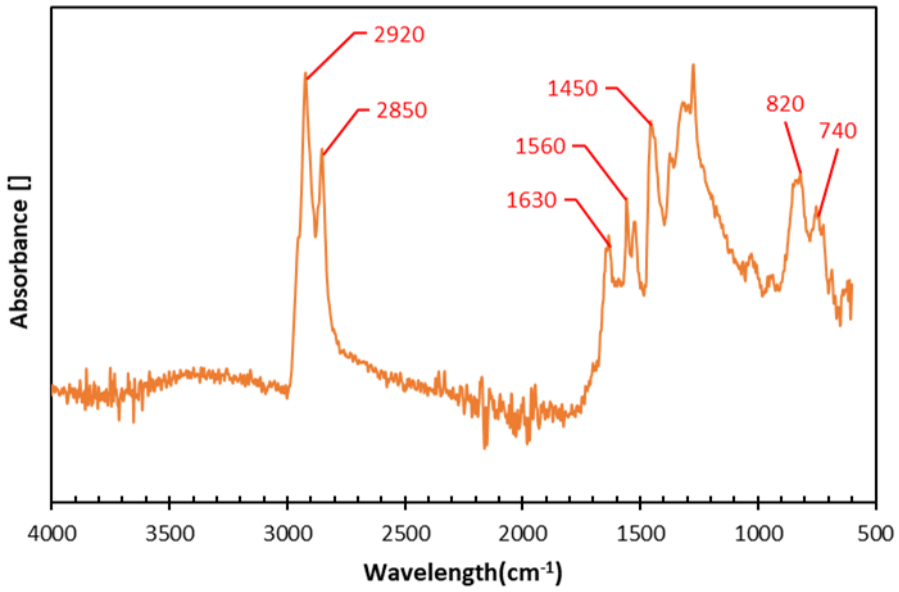

Figure 11. FTIR Spectrum of unstabilized asphaltene fiber.

Stabilization of PAN fibers by conventional and plasma process

This section presents the results of PAN fiber stabilization by a conventional process, plasma process conditions optimization, and a comparison of PAN fiber properties stabilized by either conventional or plasma process.

PAN fiber Oxidation by a conventional process

PAN fibers were first successfully stabilized by a conventional process at 300ºC for 3 hours. The most evident indicator of the stabilization process was the color transition during stabilization reaction as is shown in Table 8.

Table 8. Color transition during PAN Stabilization in a conventional process

PAN sample	PAN fiber color	Reaction Index []
Unstabilized		0
Transition		0
Stabilized		0.8 - 1

Before any heat treatment, unstabilized PAN fibers have a white color. During the stabilization process, the PAN fibers became copper in colour at the beginning of heat treatment, followed by a change to black color upon complete stabilization. The PAN fiber treated between 250 to 300^{o}C exhibited a black color with reaction index values of 0.8 to 1, respectively, whereas the lower temperature treatments produced non stabilized, yellow or copper fibers. This change of color became an indirect but convenient indicator to evaluate the oxidation progress in a plasma process.

Optimized processing conditions of a plasma process

In order to provide a lowest possible temperature in the plasma discharge the torch parameters of plasma ignition was investigated. The best argon flowrate values (sheath and central gas) are those shown in Table 9. Once the plasma ignition conditions were established, a wide range of sheath oxygen flowrates and at different distances from torch was explored. A set of optimized plasma processing conditions was obtained (Table 9).

Table 9. Optimized processing conditions of PAN Plasma Stabilization (temperature measured next to fiber.

Torch Parameters		**Oxygen gas**	**Argon gas**
Flowrate [SLPM]	**Central**	0	6
	Sheath	0.8	33
Composition [% v/v]		2	98
Pressure[torr]		100	
Time [min]		30	
Distance from torch [cm]		40	
Temperature [^{o}C]		350	

The most relevant result to stand out was the short process time of plasma processing. PAN fibers were stabilized after only 30 minutes of plasma processing, comparing to three hours for the conventional one. It means that the plasma process stabilization process was six times faster than the conventional one.

Figure 12 presents the temperature profile of Plasma Stabilization at 40 cm from the plasma torch and the visual appearance of stabilized PAN fiber at various torch distances. The abrupt increase of the temperature illustrates why in the plasma process the stabilization process must compete

with the melting process to avoid any fiber damage. The black color in the center of fiber placed at 40 cm from the plasma torch was used as an indicator of stabilization progress. Incomplete stabilization was observed at higher torch distances, whereas at the closer (36 cm), the fiber was melted completely.

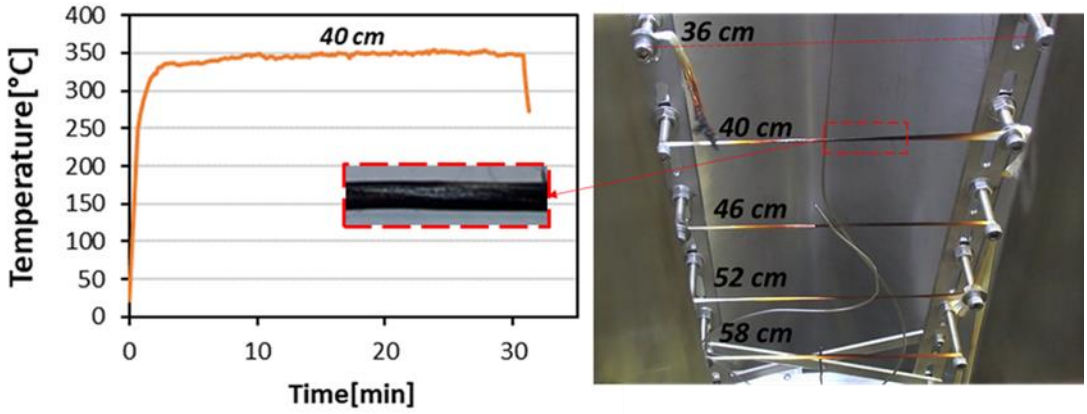

Figure 12. Temperature profile of Plasma Stabilization process at 40 cm of plasma torch (left side) and visual appearance of stabilized PAN fibers at various torch distances (right side).

FTIR Results

Figure 13 presents the FTIR spectra of unstabilized PAN, stabilized PAN in a conventional process at 300°C for 3 hours under air environment, and stabilized PAN in a plasma process at optimized processing conditions (Table 9). After PAN stabilization by the two studied processes, a prominent infrared band at 1595 cm^{-1} (I_0) appeared whereas the band at 2241 cm^{-1} (I_v) decreased, confirming that the cyclization reaction had occurred in PAN fibers. The degree of cyclization, which is denoted as RI (reaction index), was quantified through equation (1) and the relative values were indicated on each FTIR spectrum. The RI ranged from 0 (no cyclization as PAN unstabilized fiber) to 1 (complete cyclization). The RI results confirmed that PAN fiber was successfully stabilized by both studied processes.

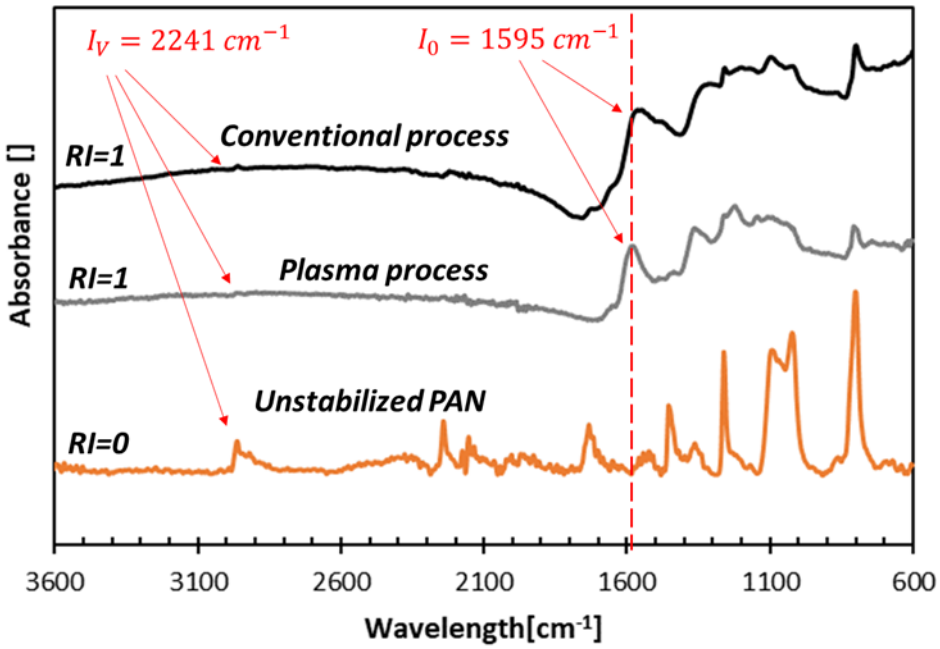

Figure 13. FTIR spectra of unstabilized PAN, stabilized PAN in a conventional process and stabilized PAN in a plasma process..

Elemental Analysis results

Elemental analysis of unstabilized and stabilized PAN fibers by the two studied processes is shown in Table 10. The PAN fibers showed different chemistry changes after stabilization in both processes. In a conventional process, the content of oxygen reached out to 10 wt% whereas in a plasma one the content was around 7 wt %, 30% less. The aromatic structures can be studied by the C:H evolution. In this case, plasma process evidenced a less impact of growth of aromatic structures of PAN fibers.

Table 10. Elemental Analysis of unstabilized PAN, stabilized PAN in a conventional process and stabilized pan in a Plasma Process

Treatement	N [wt %]	C [wt %]	H [wt %]	O[wt %]	C:H ratio [mol%]
Unstabilized PAN	24.6	68.7	6.4	--	0.895

Stabilized by a Conventional Process	21.6	61.4	4.0	10.0	1.28
Stabilized by a Plasma Process	22.2	65	5.1	7.3	1.05

Thermal behavior results

Thermal behavior of unstabilized and stabilized PAN fibers by the two studied processes is shown in Figure 14. According to the unstabilized PAN DTA curves, initiation temperature of exothermic peak in air and argon atmosphere was, in both cases, 190^{o}C. In Figure 14A, the DTA curve of unstabilized PAN in an oxidizing atmosphere (oxygen/argon mixture) presented two exothermic peaks at 230 and 272^{o}C, respectively. The first peak was associated with cyclization reactions whereas the second one is due to the occurrence of an oxidation reactions. Otherwise, in an argon atmosphere (Figure 14B) and caused by the absence of oxidation reactions, the cyclization peak shifted to 244^{o}C. After stabilization by the two studied processes, cyclisation and oxidation peaks were substantially attenuated and/or disappeared. This significant decrease confirmed the efficient stabilization by plasma and conventional processes. However, as was shown in elemental analysis too, the differences found in baseline of PAN stabilized thermograms can be an indicative of chemical differences between the structure of stabilized PAN of both processes.

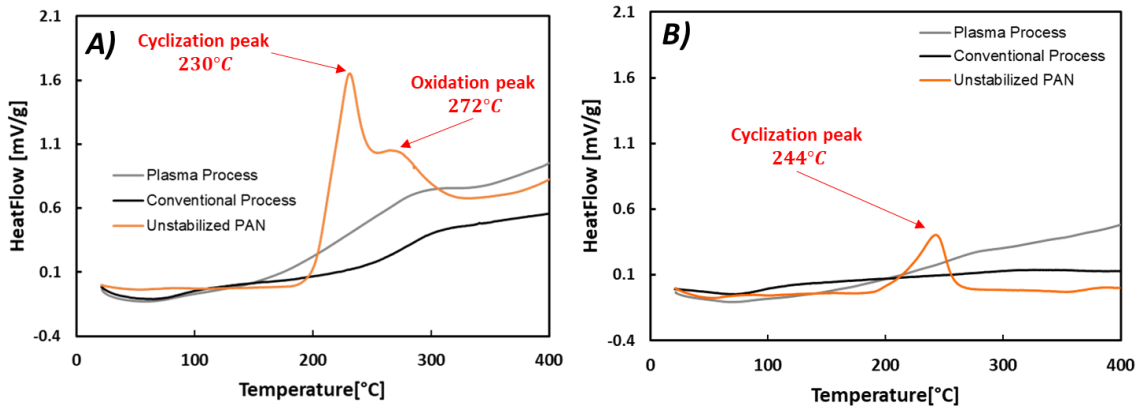

Figure 14. DTA thermograms of unstabilized PAN, stabilized PAN in a conventional process and stabilized PAN in a Plasma Process: A) under like-air atmosphere B) under argon atmosphere.

Cross-sectional SEM images

The cross-sectional SEM images of unstabilized and stabilized PAN fibers are given in Figure 15. After stabilization, the cross-sectional surface is presented as a compact and homogeneous surface with the absence of any voids in the PAN fiber bulk at this microscopy measurement scale. Moreover, it can be noted that the shape of the cross-section of PAN fibers has not changed after stabilization in both studied processes. Otherwise, no damage due to plasma treatment was found on plasma stabilized PAN fibers. Another indication of successfully stabilization process was the reduced fiber diameter resulting in both of the studied processes. The fiber diameter decreased from ~15.3 μm to ~11.7 μm and ~11.3 μm, after stabilization in a conventional and plasma processes, respectively. This decrease in the diameter of the fibers has been currently ascribed to the mass loss resulting from structural and chemical transformation occurring within the bulk fiber during stabilization stage [38].

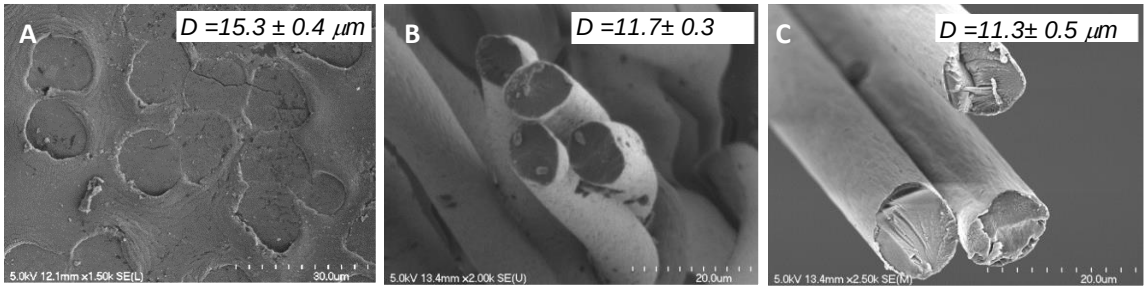

Figure 15. SEM images of cross-sectional and average fiber diameters of unstabilized PAN and its stabilized PAN fibers: A) Unstabilized (fibers embedded in an epoxy resin); B) stabilized in a conventional process; C) stabilized in a plasma process.

Evolution of tensile mechanical properties

The stabilization process is a bottle neck in carbon fibers processing and the most influential step in determining mechanical properties of final carbon fibers [2, 3, 25, 38]. Normally, fiber tensile strength decreases in the stabilization step, but once carbonized, it has an abrupt increase, whilst elongation at break has an abrupt decrease [2, 5, 7, 29].

The tensile mechanical properties of unstabilized PAN, stabilized PAN in a conventional process and stabilized PAN in a plasma process, and the strain-stress tensile plots of select samples are shown in Figure 16. After stabilization in a conventional process the Young modulus of PAN fibers increased from 5.6 GPa to 6.8 GPa whereas its tensile strength and elongation at break decreased from 300 MPa to 180 MPa and from 10.7% to 5.2%, respectively. Surprisingly, all tensile mechanical properties of PAN fibers were improved after the plasma stabilization step. Elongation at break had a 16% improvement increasing from 10.7% to 12.4%, whereas the Young's modulus increased from 5.6 GPa to 7.1 GPa, which represents an improvement of 27%. Even more, the tensile strength of PAN fiber treated in a plasma process increased from 300 MPa to 480 MPa, which is an improvement of 40%.

These surprising results might be indicative that the surface of the plasma-treated PAN fibers was more oxidized/stabilized than the core. However, this hypothesis was not verified in the framework of this project.

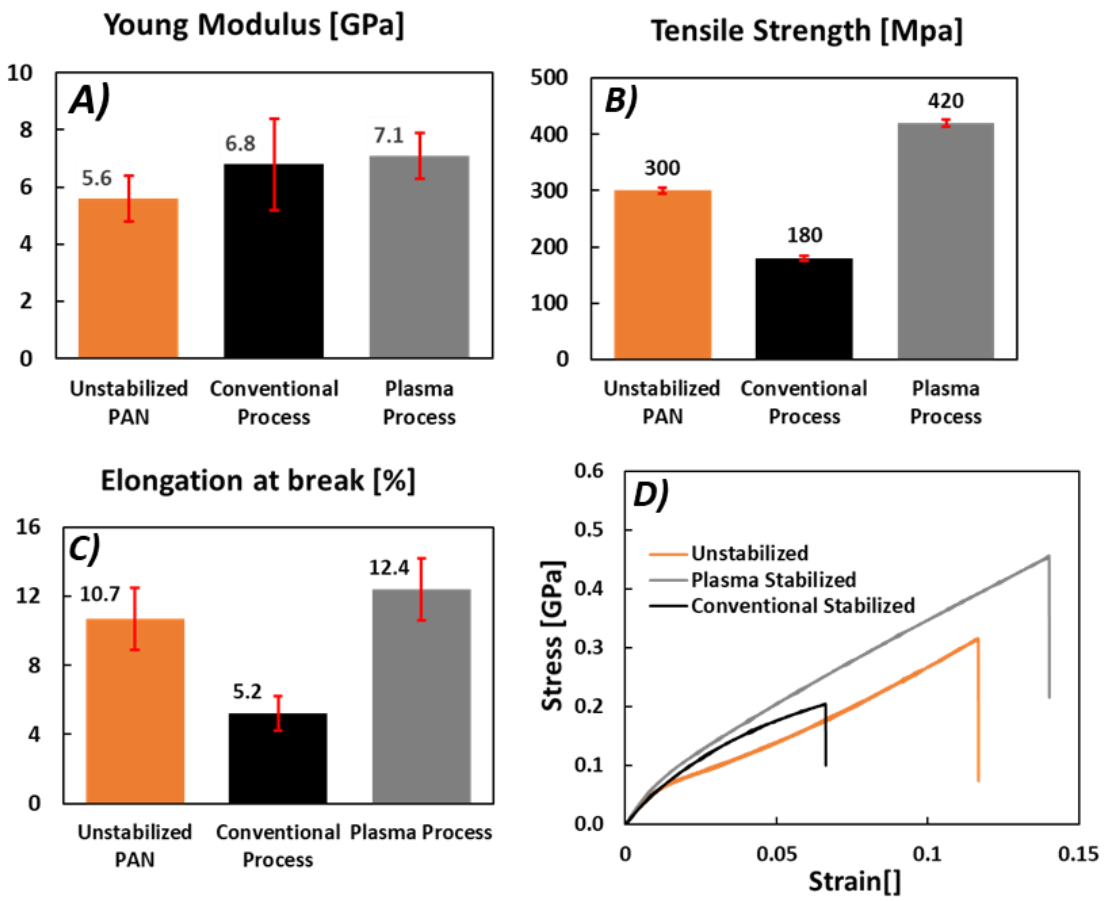

Figure 16. Mechanical properties of unstabilized PAN, stabilized PAN in a conventional process and stabilized PAN in a plasma process (A, B and C) and the stress-strain tensile plots of its selected samples (D).

Stabilization of Asphaltene fibers

This section presents the results of asphaltene fibers stabilization by a conventional process and a set of plasma process conditions, and a comparison of asphaltene fibers properties stabilized by either conventional or plasma process.

Figure 17 shows temperature profiles of stabilization by plasma process at three oxidative plasma treatments at 40 cm from the plasma torch. The temperature profile shows a steep increase of temperature in plasma process produced after by plasma ignition. At a fixed distance from the plasma torch, a decrease in oxygen concentration in the plasma source resulted in a decrease in temperature of plasma gases. For example, the maximal temperature of plasma gases at 40 cm from plasma torch were 350, 342 and 335 °C of 2.0%, 1.5% and 1.0% (v/v) oxygen plasma, respectively. This cooling effect is related to decreasing the higher energetic oxygen species due to oxygen concentration decrease in the plasma gas.

Asphaltene fiber was, at first, treated under the same processing conditions as in plasma PAN stabilization. At a 2% (v/v) oxygen plasma and 350^{o}C for 30 minutes (orange line) the asphaltene fibers were completely melted. Asphaltene plasma stabilization was tested at two additional oxygen plasma gas concentrations: 1.5% and 1.0% (v/v). In this lower oxygen concentrations, asphaltene fibers showed were an evident improved resistance to melting process. This means that the stabilization reactions rate was higher than the melting process induced by the high plasma temperature.

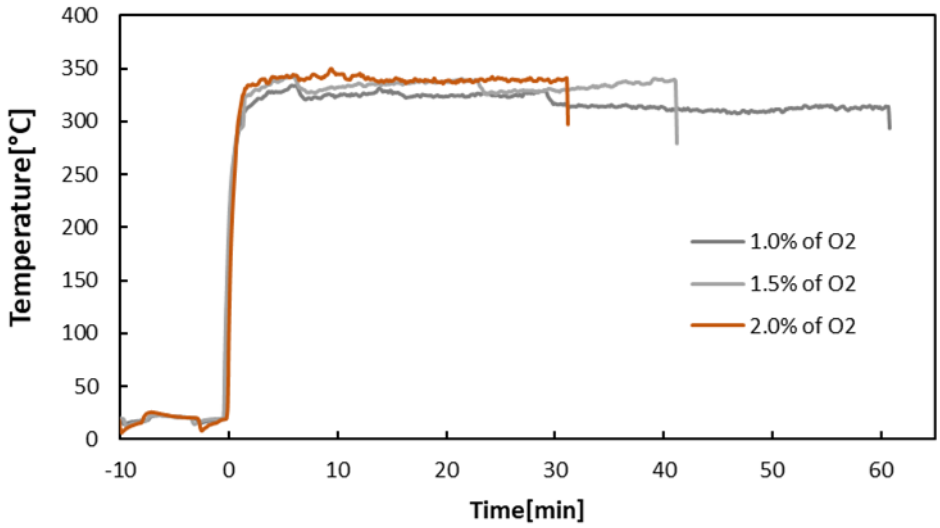

Figure 17. Temperature profile of oxidizing plasma treatment at 40 cm from plasma torch at 1.0%, 1.5% and 2.0% (v/v) of O_2 concentration in plasma gas.

Figure 18 presents the FTIR spectra of unstabilized asphaltene fiber, stabilized asphaltene fibers in a conventional process and fibers treated at 1.5% and 1.0% of oxygen in the plasma gas. The infrared spectra of stabilized asphaltene fibers in two conventional processes (black lines) evidenced several changes in the functional groups relative to the starting fibers. Firstly, no differences between FTIR spectra of asphaltene fibers after 4 and 13 hours of stabilization process were found. A very broad area is showing around 3000 cm^{-1} band which represents the molecular vibrations of hydroxyl and carboxyl groups together. Even the aliphatic vibrations represented by the two peaks at 3000-2800 cm^{-1} and such as those at 1400-1200 cm^{-1} have disappeared completely or have a lower intensity. Furthermore, a new band at 1730 cm^{-1} concerning carbonyl groups C=O has appeared which is evidence of oxidation (stabilization) progress.

A plasma treatment at 1.5% of oxygen concentration in plasma gas for 40 minutes (pale gray line) showed only a very short attenuation on 1630 cm^{-1} and 1530 cm^{-1} bands, however, there is no evidence of asphaltene oxidation while the asphaltene fiber was exposed to plasma environment. Conversely, at 1.0% of oxygen concentration in plasma gas for several length times, the FTIR spectrum of asphaltene stabilized fiber revealed the slight improved results (dark gray lines). While the C-H stretch double peak in the 3000-2800 cm^{-1} wavelength range shows a progressive decrease without complete attenuation, there is a progressive increase of a peak at 1730 cm^{-1} band, which could indicate the beginning of an asphaltene stabilization by a plasma process. At this plasma

conditions (1.0% O_2), the successfully stabilization of PAN fibers confirmed the power of oxidizing environment at this distance from plasma torch. However, apparently the asphaltene fibers shown a lower degree de stabilization than the asphaltene fibers stabilized by a 4h-conventional process. Another kind of characterization would be necessary to reach a conclusion. Obviously, the best way to clarify the degree of stabilization process is to submit stabilized samples to a carbonization test. Unfortunately, the deadline of this project ended before being able to verify these results.

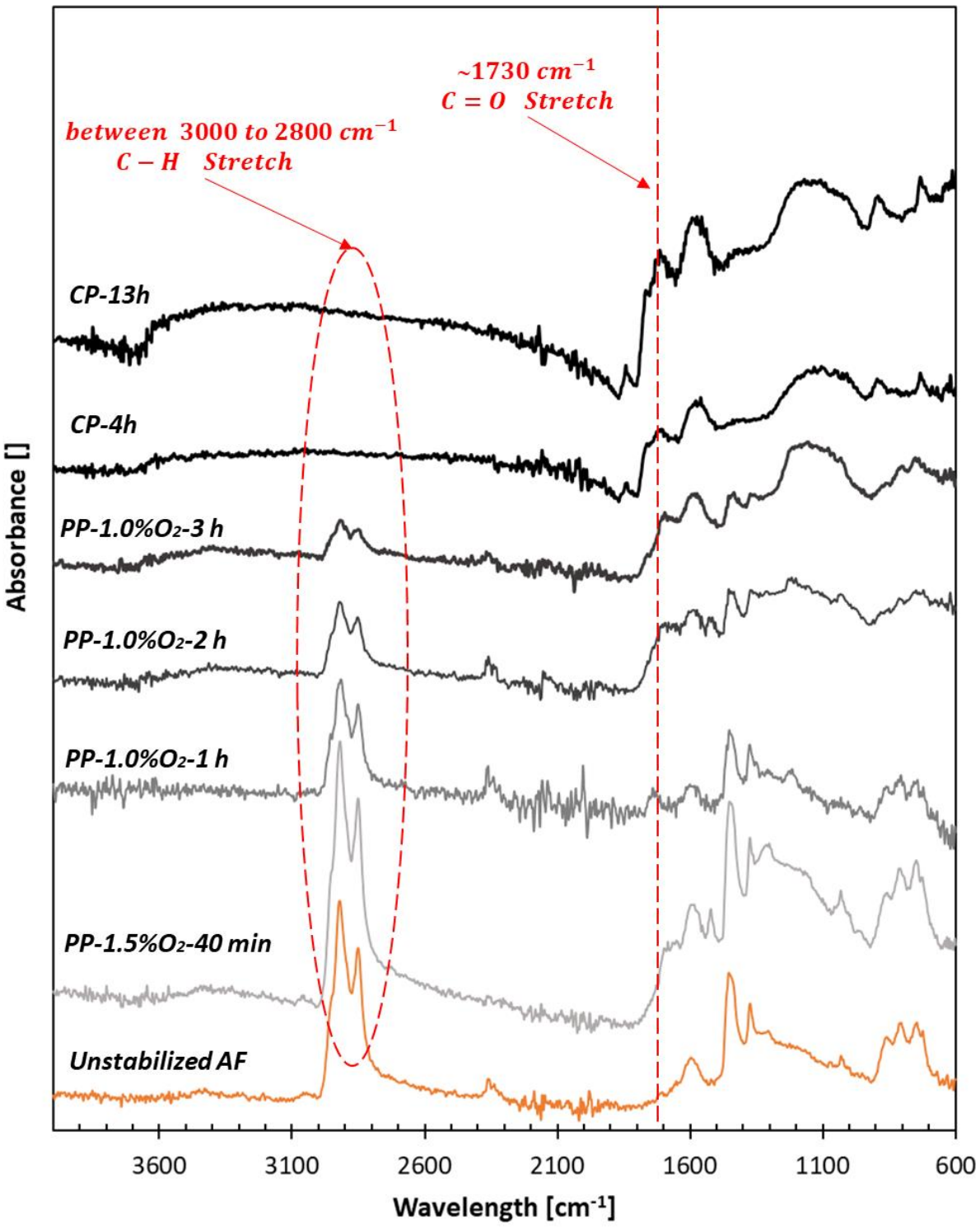

Figure 18. FTIR Spectra of unstabilized asphaltene fiber (AF), stabilized asphaltene fiber in two Conventional Processes (CP); and the asphaltene fibers treated in a Plasma Process (PP) at 1.0%(v/v) of O_2 for various length time and at 1.5%(v/v) of O_2 for 40 minutes. All asphaltene fibers treated in plasma process were placed at 40 cm from the plasma torch.

Figure 19 presents a comparison of the visual appearance of PAN and asphaltene fiber before and after stabilization in a 1% of oxygen gas plasma content for various time of treatment. At this stabilization conditions, the PAN fibers placed at the same distance as the asphaltenes (40cm) from the torch changed from yellow to black (image not shown), confirming the oxidizing environment of coming plasma gases. The stabilized asphaltene fibers could be separated and did not show signs of fusing together. Ensuring that the fibres do not fuse is important for the success of the stabilization process.

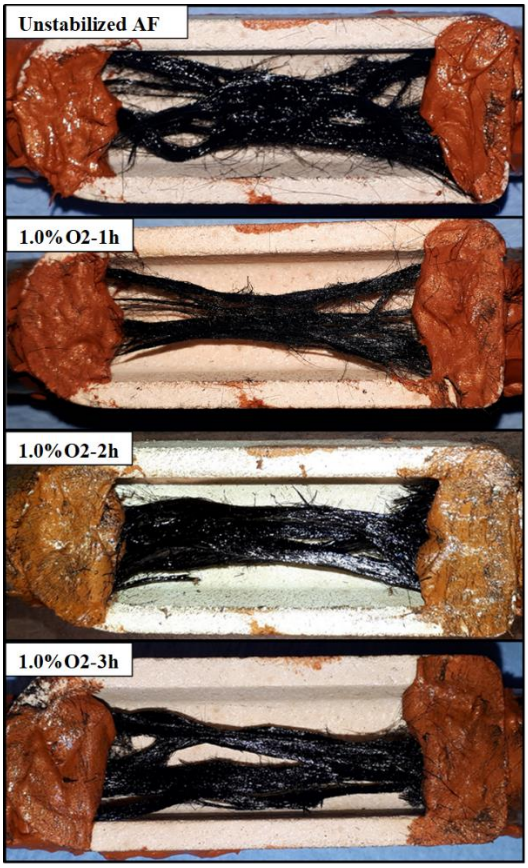

Figure 19. Pictures of asphaltene fibers before and after stabilization in a Plasma Process at 1.0% of O_2 for various time of treatments.

CONCLUSIONS AND FUTURE WORKS

In the present report, the results of project entitled "One-step plasma-assisted technology for manufacturing high performance carbon fibers using asphaltene precursors" were presented.

In the first step of the project, commercial PAN fibers were efficiently stabilized by a three-hour conventional process at 300°C under 4 SLPM air flowrate. The PAN Stabilization progress was confirmed, by 1) the black color of PAN stabilized fibers, 2) a reaction index which indicated a completely cyclization process (RI=1) and 3) a completely attenuation of oxidation and cyclization peaks in DTA thermograms.

In the second step of the project, the PAN Stabilization optimized plasma processing conditions were determined. PAN commercial fibers were efficiently stabilized with a 30 minutes plasma process in a 2%(v/v) oxygen plasma gas at 40 cm from plasma torch. Once again, plasma PAN stabilization was confirmed by 1) the black color of PAN stabilized fibers, 2) a reaction index which indicated a completely cyclization process (RI=1) and 3) complete attenuation of oxidation and cyclization peaks in DTA thermograms. **The plasma technique proved to be six times faster than the conventional stabilization process**. Surprisingly, **plasma stabilized PAN fiber showed significant enhancement of all its tensile propertie**s.

In the fourth step of the project a set of asphaltene stabilization conditions by plasma process were determined and are summarized in Table 11. With these processing conditions, the appearance of the carbonyl 1730 cm^{-1} band in the FTIR spectrum of asphaltene stabilized fiber was possible evidence of the beginning of the asphaltene stabilization by a plasma process. This premise was confirmed by the improved heat resistance of asphaltene fibers during stabilization temperatures, around 300°C. Apparently, and contrary to PAN carbon fiber precursors, the asphaltene fibers exhibited a greater resistance to reaction with oxidizing species coming from the plasma gas. In terms of time of process, a 1-3 hours range was determined for stabilization to be observed. An optimization of this processing time is necessary.

Table 11. Preliminary processing conditions of asphaltene Plasma Stabilization process.

Torch Parameters		**Oxygen gas**	**Argon gas**
Flowrate	**Central**	0	6

[SLPM]	**Sheath**	0.4	33
Composition [% v/v]		1	99
Pressure[torr]		100	
Time [hours]		1-3	
Distance from torch [cm]		40	
Temperature [ºC]		315	

In order to enhance the asphaltene stabilization conditions of the plasma process, the following future work should be considered:

1. optimize stabilization time depending on the characterization of asphaltene fibers (as mechanical properties) after subsequent process stages (carbonization and graphitization)
2. complete stabilization analysis by incorporating a carbonization test to verify stabilization degree.
3. explore less aggressive plasma configurations such as cold plasma systems.
4. investigate alternative oxidizing plasma gas mixtures to control the chemical potential of highly energetic oxygen species. Gas mixtures as H_2O/H_2 or CO_2/CO systems are potentially less energetic alternatives.

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APPENDIX

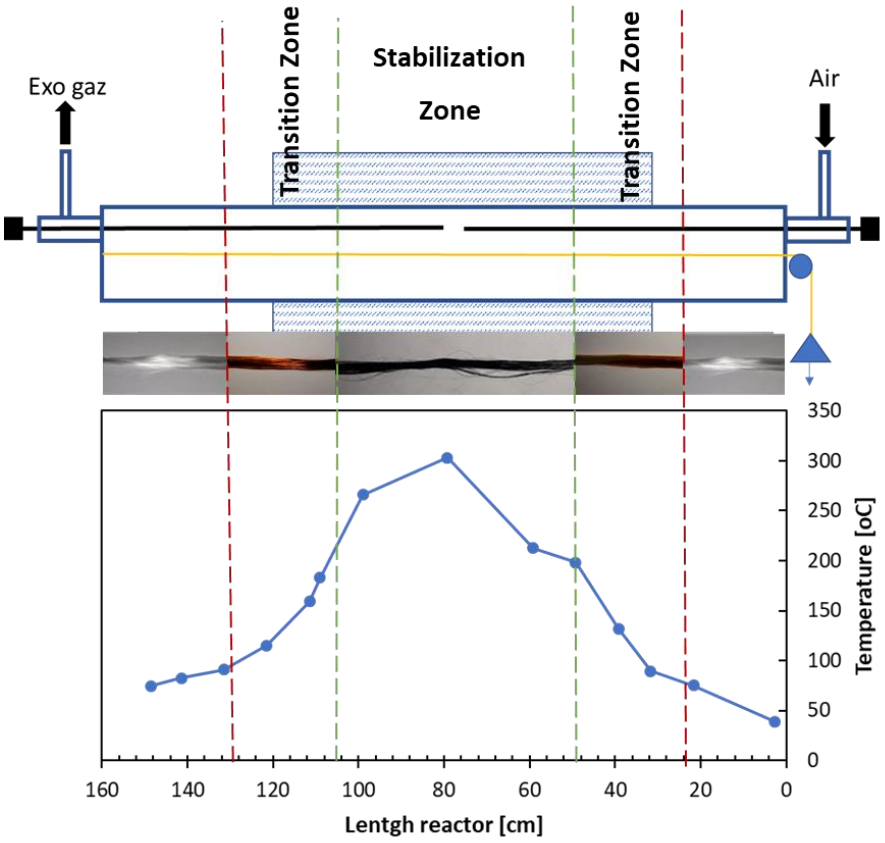

Figure A.1. Evolution of PAN fiber color and temperature profile in a thee hours stabilization conventional process.