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PRODUCTION OF MESOPHASE PITCH FROM GASIFIED LIGNIN-DERIVED TARS

by

Adedayo Oluwafemi Idowu
Bachelor of Science, University of North Dakota, 2015

A Thesis

Submitted to the Graduate Faculty

of the

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in partial fulfillment of the requirements

for the degree of

Master of Science

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May
2017

This thesis, submitted by Adedayo Oluwafemi Idowu in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota, has been read by the Faculty Advisory Committee under whom the work has been done and is hereby approved.

Dr. Wayne Seames, Chairperson

Michael D. Mann

Dr. Michael Mann

Dr. Brian Tande

This thesis is being submitted by the appointed advisory committee as having met all of the requirements of the School of Graduate Studies at the University of North Dakota and is hereby approved.

Grant McGimpsey
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Department	Chemical Engineering
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Date: May 9th, 2017___________

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I would first like to thank my family for all of their support and encouragement over the years. Thank you to Dr. Seames, my advisor, who always held me accountable and provided me great knowledge and support. I wish to express my sincere appreciation to my advisory committee, Dr. Mann and Dr. Tande, for all their help and guidance with my research. Last, thank you to Sara Pourjafar and Ian Foerster for all the work they put into helping with my research.

To Mom and Dad and our Lord and Savior Jesus Christ!

ABSTRACT

Lignin tars are created as a by-product of lignin gasification. Significant effort has gone into minimizing tar production. However, no process has been shown to completely eliminate its formation. As a result, the tar is being used to manufacture low value products such as asphalt, or is being used as a fuel in fixed combustion systems.

The research presented here is part of an effort to increase the viability of using ligno-cellulosic biomass as a feedstock to produce high value products. We tested the postulate that tars derived from lignin could be processed into a mesophase pitch allowable for conversion into high quality carbon fibers. Literature demonstrates that coal tar and petroleum pitch can be transformed into a high quality mesophase pitch. However, the processes involved are complicated and expensive. This is because the impurities - ash content for example, in these materials lead to defects in the pitch and must be removed. Since lignin is without these impurities, its transformation into mesophase pitch should be a less complicated and less expensive process than those for coal or petroleum analogs.

Tars were generated using a lab-scale gasification vessel, at an overall conversion rate of 16% tar from kraft lignin. The tar was subsequently filtered and fed to a residue pitching reactor. The pitching reactor was used to generate mesophase pitch under inert conditions. During the pitching step, an unexpected temperature increase likely due to partial oxidation of lignin carbon units with inherent oxygen released during the process was observed. Characterization of both the tar and pitch products was performed by thermogravemetric analysis and differential scanning calorimetry. Further characterization of the pitch products was performed using SEM.

A mixture of apparent coke and mesophase pitch products were produced in the pitching reactor. However, the TGA profiles of both products were very similar while their morphologies differed slightly. The condition of ~215°C with a vacuum pressure ranging from ~0.03-0.13 kPa was at the threshold of coke formation while allowing mesophase pitch formation for lignin tar. These results demonstrated that it is possible to generate a mesophase pitch from lignin-derived tars. However, further work is required to perfect the process such that a commercially viable pitch product is generated.

CHAPTER I

INTRODUCTION AND BACKGROUND

Decreases in nonrenewable resources as well as the concern for sustainability has triggered research into feasible alternatives to high volume, fossil-based raw materials such as coal, oil, and gas. Global climate change is one of the most significant environmental problems in today's society. Increases in atmospheric carbon has been linked to the burning of fossil fuels. Coal, oil, and gas consist mostly of carbon and hydrogen. When these substances are burned, they undergo a chemical reaction where carbon combines with oxygen to form CO_2. Increased carbon dioxide in the atmosphere is a leading contributor to global climate change. Other compounds such as methane, nitrogen oxides, and CFCs also play a large role in the production of greenhouse gases [1]. Figure 1 gives a visual breakdown of the main greenhouse gas contributors [2].

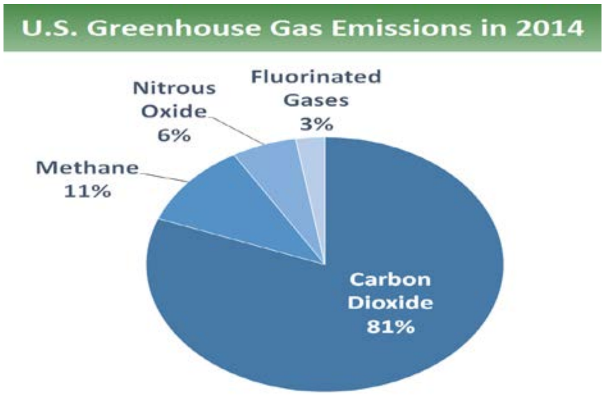

Figure 1. U.S Greenhouse Gas Emissions in 2014 [2]

Biomass has the potential to be the most commonly used raw material to create alternative products to replace those formed from nonrenewable sources. The most common class of biomass resources are ligno-cellulosic biomass, which are comprised of cellulose, lignin, and hemicellulose. Lignin’s uses are more limited compared to the other two components. Many researchers are analyzing lignin because of its high accessibility and high carbon content.

Lignin is an organic structure used to hold the cells, fibers, and tracheids which make up wood and elements of plants. It is the second most abundant renewable carbon source found on earth [3]. However, since uses are limited, it is often seen as an industrial waste product with 40 to 50 million tons being produced annually around the world. There are different types of lignin which result in slightly different chemical structures such as kraft, softwood, alkali, and others.

Researchers describe lignin as polymers possessing a variety of characteristics. These characteristics include polymers made from phenylpropanoid building units, resistance to hydrolysis, readily oxidized, soluble in hot alkaline and bisulfite, and readily condensed with phenols or thiols [4].

Lignin is currently being used as a fuel source for heat and power in the biomass industry and researchers have also been decomposing lignin in a variety of ways to manufacture valuable products. Gasification and pyrolysis are common methods used to generate products to create energy from i.e gasoline, diesel, etc. Pyrolysis is known as the thermal decomposition of biomass occurring in the absence of oxygen. Gasification is the ultimate extension of pyrolysis, where carbon-carbon bond cleavage is complete, resulting primarily in methane and carbon monoxide.

To evaluate the potential to utilize lignin decomposition to produce continuous carbon fiber (CCF) precursors, our research focused on tar formed during gasification. The gas generated during this process usually contains an unacceptable level of tar, which cannot be removed. This leads to operational problems by blocking gas coolers, filter elements and engine suction channels [5]. As a result, conscious efforts are being made to mitigate gasification tars. Thus, tar generation and removal remains a major research objective in the field of biomass gasification [6]. Lignin has a higher tar yield and produces more stable components in tar, due to its molecular structure, compared to either cellulose or hemicellulose. We believe this tar can be used as a feedstock to generate products of higher value and create a new and impactful revenue for the biomass gasification industry.

The desired product is mesophase pitch, a commonly used precursor for the production of high modulus CCF. Carbon Fibers are long, strong, stiff, carbon chains. They have exceptional strength and modulus, roughly four times that of steel yet at a fraction of the density [7]. Two of the main precursors used to produce CCF are PAN and pitch (coal and petroleum products). The uses of PAN-based carbon fiber are rapidly increasing. However, the production frequency cannot meet the current level of demand. PAN-based carbon fiber is expensive to produce which limits its use to high end applications such as sporting and aerospace equipment [8].

Pitch based CCF is a less expensive alternative to PAN –based CCF. Mesophase pitch specifically, has a higher tensile modulus than PAN (800 GPa for pitch compared to 500 GPa PAN) however, its tensile strength is typically lower; 7000 MPa for PAN and 3000MPa for mesophase pitch [7]. Tensile strength usually depends on its elongation which is determined by the degree of defects [9]. These defects are typically due to weld and mineral contaminants that concentrate in the pitch when derived from petroleum or coal processing. Decreasing the concentration of defects in the carbon fiber can greatly increase its tensile strength, allowing it to be comparable to the strength of PAN. A lignin-derived pitch will contain a much lower concentration of the contaminants that lead to CCF defects since lignin is a cleaner starting material compared to coal or crude oil. In addition, mesophase pitch has a higher carbon yield and is formed from cheaper raw materials (commonly coal tar and petroleum) compared to PAN, which is why it is frequently proposed as a less expensive precursor to produce high performance carbon fibers.

I.I BACKGROUND

While lignin and its characteristics have been studied for over a century, it has recently received renewed attention [10]. It possesses a complex structure which is partly why its uses have been scarce over the years. Lignin’s structural diversity emerges from three phenylpropane derivatives that are the main building blocks of its unique structure. These phenolic compounds are typically hydroxycinnamyl alcohols or monolignols that share the most abundant phenylpropane unit and differ in phenyl functionalization [10]. Lignin is a physically and chemically heterogeneous material whose structure tends to be significantly different when lignocellulosic material is treated to separate lignin from cellulose [11].

Lignin has a heating value of 26.7 MJ/kg, the highest energy content among all natural carbon polymeric compounds [12]. As a result, roughly 90% its use has been for heat or power production. Lignin also serves as an additive to produce relatively low value products such as asphalt, dyes and inks. It has also been used as a precursor for producing carbon fibers, although to date it has seen limited success. Lignin’s abundance and unique characteristics is why it has been used as the raw material of choice for the research described herein.

2.I.A Tar Generation

When lignin undergoes gasification/pyrolysis it usually produces a far amount of tar. Tar is a complex mixture of condensable hydrocarbons resulting from thermochemical reactions, such as chemolysis, depolymerization, oxidation, repolymerization and cycloaddition [6]. Research has been conducted to better understand such tar formation mechanisms and its composition. Such a study was conducted by Yu [6] where lignin and other biomass components were gasified and their products were analyzed. Reaction conditions varied from 800-1100°C and small samples of tar were collected. Lignin proved to have the higher tar yield compared to cellulose or hemicellulose ranging from 0.27 to 1.99 mg/g depending on the condition. Temperature had a large impact on the tar yield with the highest (1.99 mg/g) occurring at 800°C and the lowest (0.27mg/g) at 1100°C [6]. Research done by Narvaez [13] observed the yield drop from 15 to 0.54 g/Nm^3 when the temperature increased from 697 to 817°C. Other factors were investigated to determine their effects on tar formation. These included pressure, equivalence ratio, heating rate, residence time, and feedstock composition.

The industrial uses of tar are very limited and efforts are frequently being made to minimize its production, which is why studies of its mechanisms are taking place. Methods such as catalytic cracking, filtration, and pyrolysis are amongst those consistently used to accomplish such a task [14, 15]. These techniques, have successfully reduced its production levels. However, none have been able to completely eliminate tar production. Most companies are burning leftover tar as fuel for their respective power plants. In addition, the tar is used as a filler to produce low value-added products like asphalt. Our research involves utilizing generated tar to produce products of much higher value such as mesophase pitch. We postulate this pitch will be capable of producing continuous carbon fiber.

I.I.B Carbon Fibers

Carbonization of fibers dates back to the late 1800s when Thomas Edison was in the process of creating incandescent filaments [9]. Since then, they have evolved into strong stiff lightweight materials with an increasing demand. The most common industries using CCFs include: aerospace, sporting equipment, and automotives. The production level of fibers is limited due to its high costs. There are two main raw materials, polyacrylonitrile (PAN) and pitch.

I.I.C PAN Based Carbon Fibers

PAN is the precursor for roughly 90% of current carbon fiber [16]. Its primary use involves structural reinforcement because of its high tensile strength which ranges from 3000-7000MPa. The absolute tensile strength of CCFs can approach 7 GPa, almost four times that of steel [7].

PAN based CCF production is a very refined process involving many steps. The first steps include polymerization and spinning of fibers. The PAN precursors usually contain about 2-10% of a comonomer such as methyl acrylate, methyl methacrylate, or itacon acids [17]. Wet spinning is the most widely used of the commercial manufacturing processes, however, it is slowly being replaced by dry-jet wet spinning [18]. Melt spinning has also been performed, however it has yet to become a promising manufacturing process of carbon fibers, commercially [19].

The next step is the thermal stabilization/oxidization step. The PAN-based precursor is stabilized by controlled low-temperature heating over the range 200-300°C in air to form a precursor which can be further heat-treated without either melting or fusing fibers [20]. Linear PAN-based polymer molecules are initially converted into cyclic structures. Since cyclization is very complicated, the mechanism is still unclear. The most widely known reaction is shown in figure 2 below.

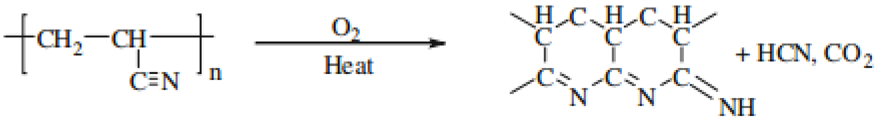

Figure 2. Mechanism of cyclization of PAN polymer precursor [17].

Carbonization and graphitization occur after the fibers are thermally stabilized. The temperature of carbonization is usually determined by the end use of the resulting CCF. During this process, all non-carbon materials are removed from the fiber. For high-strength applications, the carbonization temperature ranges from 1500-1600°C to ensure sufficient tensile strength [21]. Graphitization typically occurs above 1600-1800°C and up to 3000°C. This is required to obtain a high elastic modulus in the carbon fibers, allowing them to be shaped more easily. Both processes are carried out in an inert atmosphere containing either nitrogen or argon. Argon is preferred as it helps provide strength to the carbon fiber because of its higher density and viscosity. Further, nitrogen has a tendency to react with carbon and form cyanogen at temperatures above 2000°C [17]. The rate of heating and residence time are all contingent on the precursor and stabilization conditions.

The surface treatment and washing step is done to improve the mechanical properties of the composite through alteration of the fiber surface [17]. The most commonly used surface treatment methods are categorized as liquid and gaseous oxidation treatments. The liquid oxidation treatment method is well known and can double the composite shear strengths with 4-6% reductions in fiber strengths [22]. The demand for surface treatment of carbon fibers has significantly increased because of the increasing need for high performance carbon fiber composites.

The final step in PAN manufacturing is drying, sizing, and winding. Carbon fibers require protection and careful handling [17]. The fibers are predried for the sizing treatment, and the sizing materials are carefully chosen to help protect the carbon fibers. Finally, the dried and shaped carbon fibers are collected using winders that operate automatically. The overall process of carbon fiber manufacturing is shown in the figure 4 below.

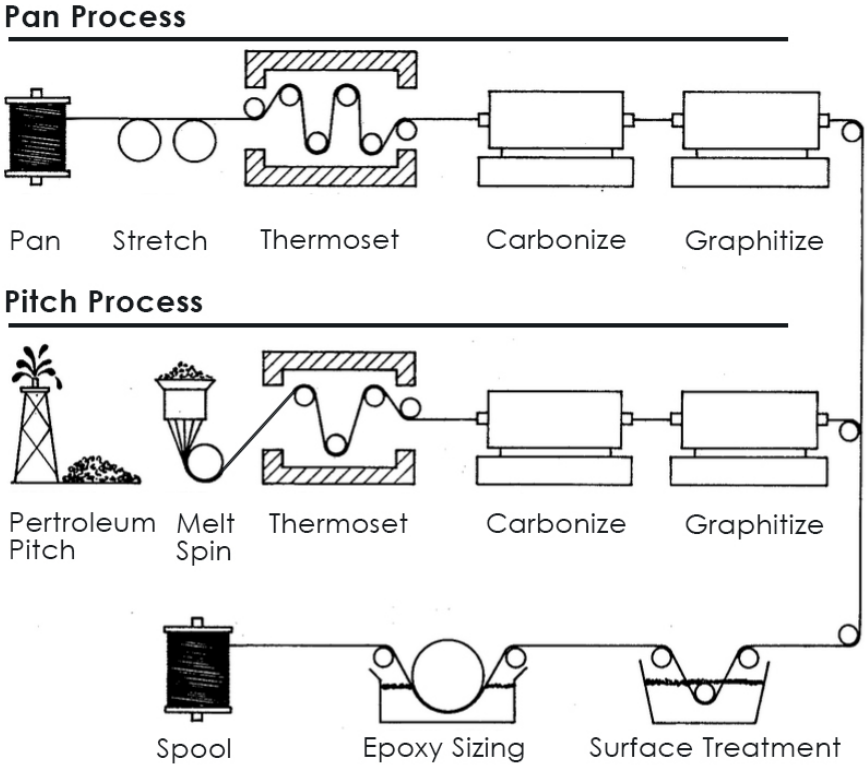

Figure 3. Process for manufacturing of Carbon Fibers [23]

PAN is a relatively expensive raw material, and it requires a lot of refining in order for it to generate carbon fiber. The spinning techniques require a costly wet chemical bath and a long stabilization time. The demand for carbon fibers is increasing and the production total does not meet the demand. The high price of PAN provides incentive for the development of cheaper, more accessible precursors.

I.I.D Pitch Based Carbon Fibers

Pitch is a residue mainly from distillation of either coal tar or petroleum. It is composed of thousands of aromatic hydrocarbons having up to an 80% carbon yield. The average molecular weight is roughly 300-400. It has a varying complex structure where it usually possesses 3-8 fused rings depending on its chemical composition and molecular weight distribution [24]. Pitch is developed when the residue of the raw materials is mixed with other hydrocarbons and undergoes polymerization to obtain a mesophase structure. Mesophase is known as the liquid crystal region that falls in between the solid and liquid phases.

Petroleum pitch is obtained from different sources such as heavy residue from catalytic cracking of either naphtha or gas oils and residue from crude oil distillation or refining [25]. The method used to produce this pitch depends on the technique used in its initial refining process. These methods include one or a combination of the following:

1. Prolonged heat treatment to increase the molecular weight of the components
2. Steam stripping and application of vacuum to remove low boiling components
3. Distillation

Petroleum pitches are typically less aromatic compared to coal tar because of their decreased residence times and lower temperature.

Coal tar is a by-product of the coking of bituminous coals to produce cokes [26]. Coal tar pitch is the residue resulting from distillation and heat treatment processes. The pitches are complex mixtures containing many different organic compounds whose compositions depend on the source of tar and the extraction method used for the light weight fractions. The majority of compounds present in coal tar pitch are aromatic and can be found in figure 4.

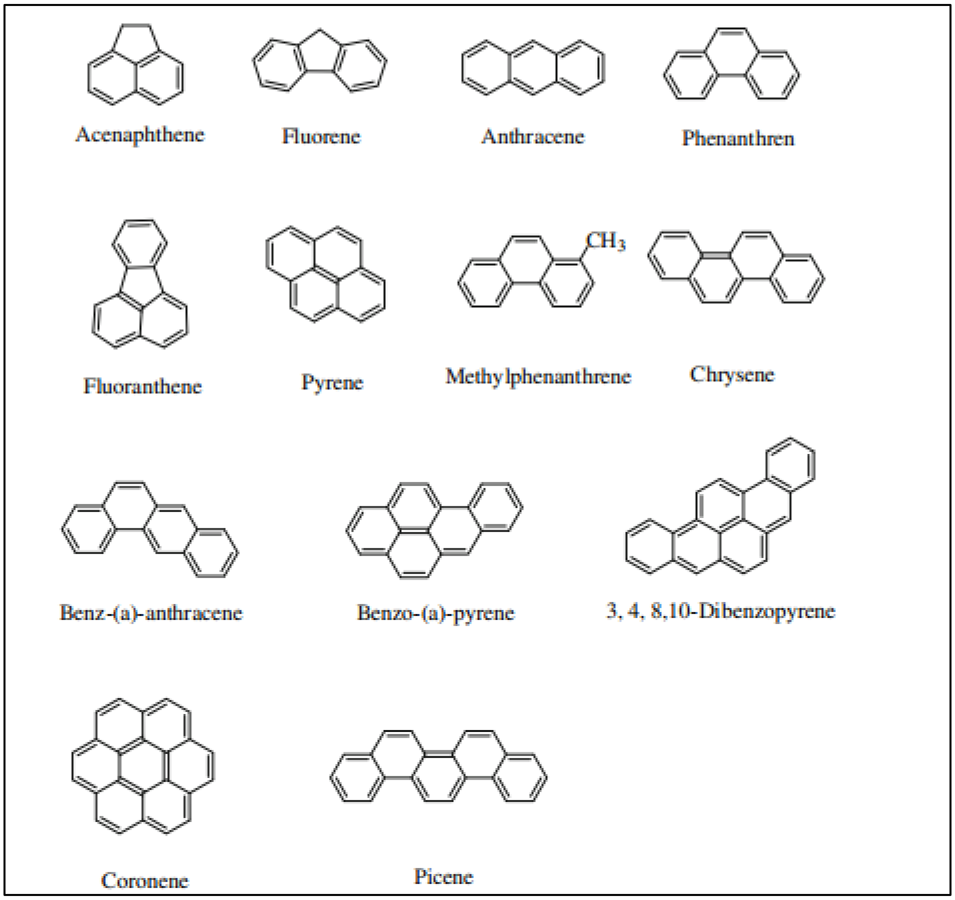

Figure 4. Aromatic hydrocarbons found in coal tar pitch [17]

The techniques used to prepare mesophase pitch include thermal modification, solvent modification, hydrogenation, and catalyst modification [27, 28]. Each method is used in different circumstances to produce pitch spinnable into carbon fibers. In order for mesophase pitch to be spun into high performance carbon fiber, it must possess the following characteristics [24]:

1. Low ash content
2. 100% anisotropic content
3. A softening point between 230 and 280°C
4. High flow at spinning temperature and good viscosity integrity
5. Good spinnability and thermal stability
6. High oxidation activity and high carbon yield

It is essential that the raw material is refined and that the methods listed above are followed properly to optimize mesophase pitch production.

The process of forming carbon fibers from pitch is similar to that of PAN. The manufacturing steps include production of the fibers, stabilization, carbonization/graphitization, and surface treatment.

Production of the carbon fibers is typically done by melt spinning. This part of the process is the primary source of the structure found in mesophase pitch-based carbon fibers. First, the correct melt temperature is needed in order for the proper mesophase structure to occur. Each mesophase has a range of temperatures in which melt spinning is possible. Temperatures below this range result in high viscosities and brittleness, while higher temperatures lead to thermal degradation and low viscosities. The range for melting is very narrow and can have a lasting impact on the mesophase produced. Low melt viscosity has been shown to be the most promising for developing high-quality carbon fibers.

Stabilization for pitch is very similar to the PAN precursor fibers. In order to stabilize the pitch fibers, the oxidization temperature should be below the softening point to help maintain its structure. Temperatures usually range from 250-350°C.

Analogous to PAN, once fibers are stabilized, they are carbonized and graphitized. The carbonization temperature ranges from 1500-1800 °C [17]. Temperatures at that level allow the fibers to maintain their high modulus. Carbonization and graphitization take place in inert atmospheres and help remove most elements except for carbon from the fibers. Nitrogen is used as the inert gas for pitch graphitization whereas argon is the choice for PAN.

Surface treatment and sizing is the final step and its technique is very similar to that of PAN. This step is used to improve the mechanical properties of the composites and help create more high performance carbon fibers.

There are many different kinds of pitches formed but not all of them are capable of producing CCF. Often times pretreatment and adjustments are done to create such quality pitch. Raw tar and pitch, especially coal by-products, contain solid impurities and primary quinolin insoluble (QI) [29]. This leads to an absorbance of impurity and free carbon which hinders sphere growth and coalescence, preventing the formation of a large anisotropic domain with good properties and spinnability [24]. This results in fibers containing cracks and pores which lead to poor quality carbon fiber. Prior to creating mesophase pitch, both the impurity and primary QI need to be removed to obtain a pitch containing mostly hydrocarbon. Coal tar is commonly refined by solvent refinement or thermal filtration and petroleum pitch is done with vacuum distillation or a wiped film evaporator method [30, 31].

The high cost of current pitch-based precursors along with their respective processing costs are understanding more research into low-cost carbon fibers. Efforts involve the use of lower cost materials, reducing the cost of processing, or both.

1.1.E Lignin-Based Carbon Fibers

Lignin's abundance and low ash content have triggered research into its use as a precursor to produce carbon fiber. Looking at the numbers, the estimated cost of a suitable lignin precursor for carbon fiber, considering simple purification and high-speed melt-spinning is about \$0.85/kg (\$1.52 for a carbon fiber yield of at least 55%) [32]. This is much lower than the price of other precursors such as textile grade PAN which ranges from \$4.4-\$13.2/kg depending on the grade used while also accounting for at least a 50% carbon yield [33].

A method for manufacturing carbon fiber from lignin entails preparation of quality lignin that is melt-spun into fiber under an inert atmosphere [34]. Research has shown that the addition of some lignin has increased the carbon fiber yield from tar pitch. Kadla [35] noticed an increase from 33.4-40% when using alcell lignin. Uraki [36] prepared carbon fiber precursors by melt spinning organosolv hardwood lignin obtained from birch wood. Steam-exploded hardwood lignin was spun into a general purpose carbon fiber by Sudo [37]. Other alternatives have involved blending various lignins with other prevalent precursors. Softwood and Kraftwood lignin were combined by Nordström [38] to produce carbon fibers with low tensile strength (300 MPa). Clive Liu [39] produced a lignin/PAN blend (30% lignin) with performance close to that of control PAN-based carbon fibers. Carbon fibers were generated with a 45% yield from a kraft lignin blended with polyethylene oxide, in an experiment also conducted by Kadla [35].

Mesophase pitch possesses both a higher tensile strength and higher elastic modulus than the listed precursors. Converting readily available tar into mesophase pitch could generate a high performance carbon fiber from low material and processing cost.

CHAPTER II

EXPERIMENTAL METHODS

II.I Tar Formation

The first part of this project involved generating sufficient amounts of acceptable quality tars for use in the pitching reactor. The challenge with this task was finding the optimal conditions to generate reasonable amounts of useable tar. Once the necessary tar was collected, different methods were used to help characterize the tar. The final task was to run the pitching reactor and produce mesophase pitch.

A reactor was constructed inhouse and used to gasify lignin and generate residual tars needed for this research. A schedule 40, 60.96 cm (35.56 heating zone) 304 stainless steel tube with an internal diameter of 7.62 cm was used as the gasification vessel. 12.7 cm plugs with a 7.62 cm diameters were inserted in each end of the tube. The inlet and outlet pipes were 0.64 and 0.95 cm stainless steel, respectively. These were installed by screw fittings tapped into the end plugs. All the required parts were purchased from McMaster-Carr (Elmhurst, Illinois). A Carbolite HST 12/300 tube furnace with a maximum capacity of 120 volts, 1500 Watts, and 14.5 Amps was used to heat the reactor. Argon was selected as the inert gas to help move the gas and tars produced during gasification out of the furnace. A rotometer was placed on the Argon tank to regulate the flow of gas into the chamber. A pressure gauge was attached to monitor any back flow that might occur during gasification. A thermocouple was connected to monitor the temperature inside the reaction chamber. A schematic of the experimental apparatus is shown below (Figure 5).

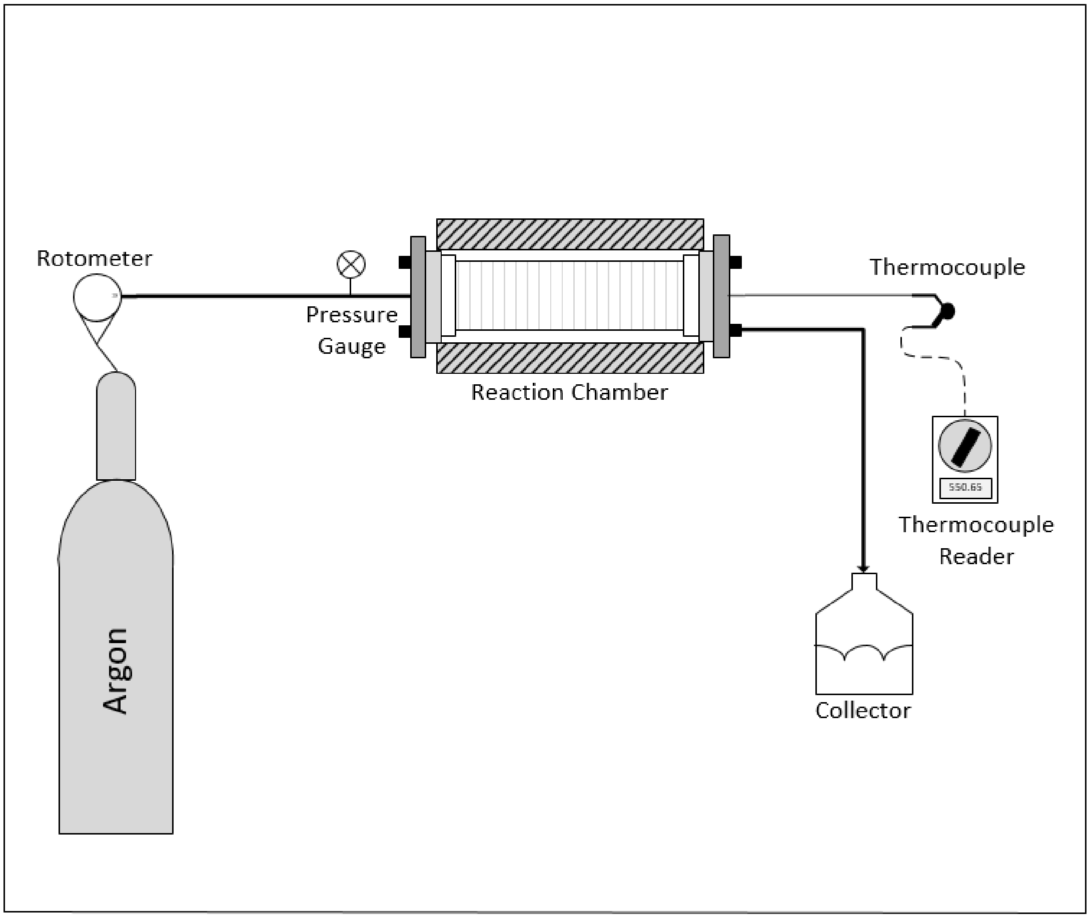

Figure 5. Schematic of the gasification system

Roughly 300 g of Indulin AT-type lignin from MeadWestvaco (Richmond, Virginia) was placed inside the reaction chamber. The chamber was sealed tightly to prevent any gas from leaving or any air from entering the system. A beaker with 150 mL of water was covered with aluminum foil and placed at the end of the exit tube to collect all of the product.

Next, the furnace was purged with Argon for a minimum of five minutes to remove all air from the system. The flow rate used for Argon was 142 L/hour and the pressure was set to 690 kPa. Once the furnace was completely purged, the heating element was turned on. The PID set point was 550°C. Heat was added until the PID controller reached its set point of 550°C. This usually took ~45minutes. Once the temperature was reached, the heating element was turned off and the reactor was left to cool down. The argon supply tank valve was left open to push out all remaining product. Once the temperature controller cooled to 100°C, the Argon was closed.

After all of the sample was collected, the filled beaker was weighed to measure the quantity of tar generated. Next, the entire sample was placed in an oven to evaporate the water from the tar. The oven was set to 120°C and run for 16 hours. Finally, the remaining tar was transferred to a large beaker where it was prepared for pitching. 33 tar gasifier runs were performed and ~400 mL of tar was collected.

II.II Tar Filtration

The tar was filtered to remove any lignin, coke or other solid products that could be mixed in the sample and interfere with the pitching process. Tar was heated at about 100°C until it was flowable. Next, it was passed through two Swagelok inline filters which were located inside the stainless steel feed tanks of the pitching reactor. The first feed tank was connected to an empty one and the bomb was placed upright, in the oven at 100°C. Once most of the tar was removed from the feed tank, it was connected to a gas cylinder to help push out the remaining tar. Finally, the second feed tank with the filtered tar was connected to the pitching reactor.

II.III Pitching Reactions

A residue processing (pitching) reactor was designed and constructed by previous students at UND as described by Linnen [40] to produce quality mesophase pitch from residue samples (Figure 6).

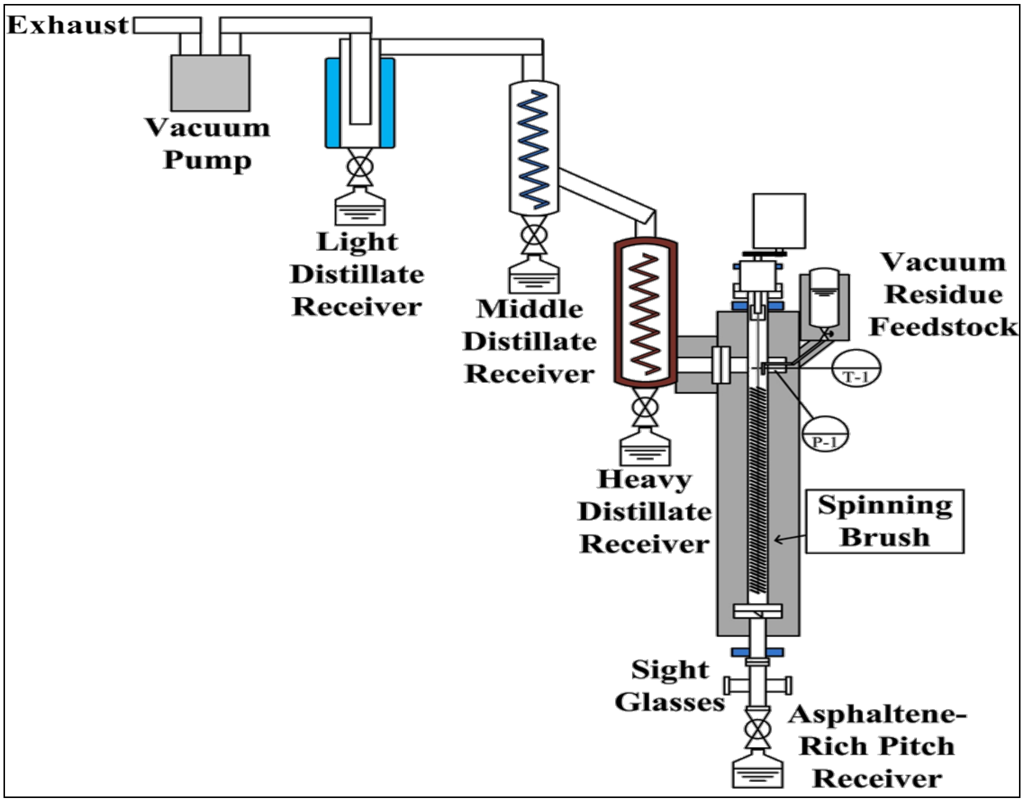

Figure 6. Residue reactor [40] for processing tar into high quality pitch [40]

The removable feed containers (Middle, Heavy, Asphaltene) were weighed and connected tightly before each run. Next, a vacuum check was performed to ensure complete sealing and proper function of the vacuum pump. The steps included: turning on the vacuum pump, opening both cooling water valves, and checking the vacuum gauge. The gauge typically reached ~0.03 kPa (200 millitorr).

Once the vacuum check was completed, the reactor, feed container, and transfer lines were heated. Two PID controllers were used to control the reactor and feed tank temperatures, respectively. The reactor was initially set to run at high vacuum (~0.06 kPa) and high temperature (350-450°C). After characterizing the tar, it was discovered that the lignin residual was not thermally stable at temperatures beyond ~185°C. To determine an adequate reactor temperature, the mass fractions from TGA testing for lignin tar were compared to those from cracked soybean oil derived tar (SODT). The SODT feed was processed in the pitching reactor previously and successfully produced a mesophase pitch. We related the mass fraction of the SODT TGA profile to that of lignin tar to predict the best pitching temperature. SODT was known to pitch well at a temperature of 430°C and a calculated mass fraction of ~84%. At the same mass fraction, lignin is at ~215°C so this is the reactor temperature used. The pressure was not controlled but monitored using a vacuum gauge. The gauge ranged from ~0.03-0.13 kPa. The feed container was weighed prior to being connected to the reactor. Then it was then insulated and jacketed and its PID temperature set to 100°C. The transfer line PID controller box was also set to 100°C.

When the temperature of each unit operation reached its respective set point, the peristaltic feed pump was turned on to its maximum capacity, the spin brush was set to 900 rpm, and the valves were opened to release the feed. The feed flow rate was 1.3 g/min.

II.IV TGA Testing

Using a TA Instruments TGA-DSC Q-Series (SDT Q600) (TGA) machine (Figure 8), thermal gravimetric curves were obtained under an atmosphere of argon at a constant flow of 100 ml/min. A small sample was placed in an alumina crucible and an empty crucible was used as a reference point. Both crucibles were placed in the furnace where they were heated and changes in mass was observed. The temperature program for TGA testing of all our samples were as follows: isothermal at room temperature for 5 minutes, ramp 25°C/min, isothermal for 5 minutes at 300°C, 400°C, 500°C, 850°C, and 870°C.

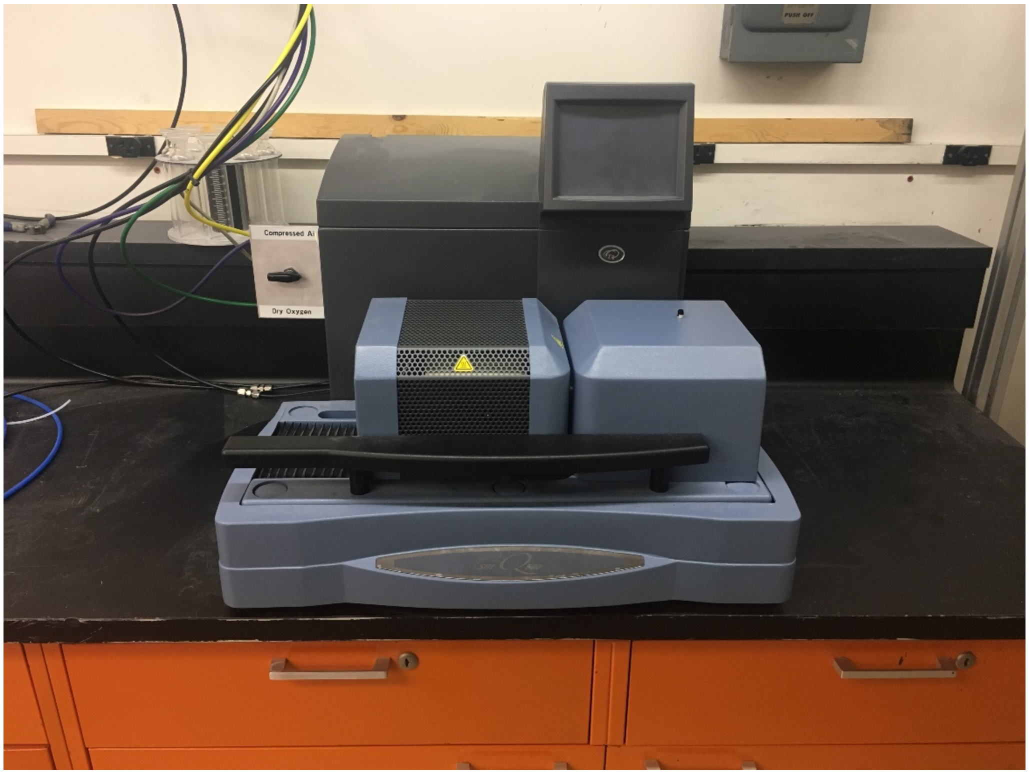

Figure 7. Photograph of TA Instruments SDT Q600 TGA

II.V DSC Testing

A PerkinElmer® Jade DSC (Figure 9) was used to measure the heat flow and determine the glass transition temperature of respective compounds. A small sample of each compound was weighed before being placed in an empty crucible. About 5-10 mg of the sample is needed to run. Next, the weighed sample was placed in the empty crucible where it was covered with a PerkinElmer® crimping press (Figure 8).

The DSC intercooler (Figure 9) was turned on for 30 minutes to let the machine cool down. Later, the crucible was placed inside the system. The temperature program used for all samples went from -50 to 300°C at 10°C/min. Nitrogen was purged at 20mL/min to prevent accumulation in the chamber.

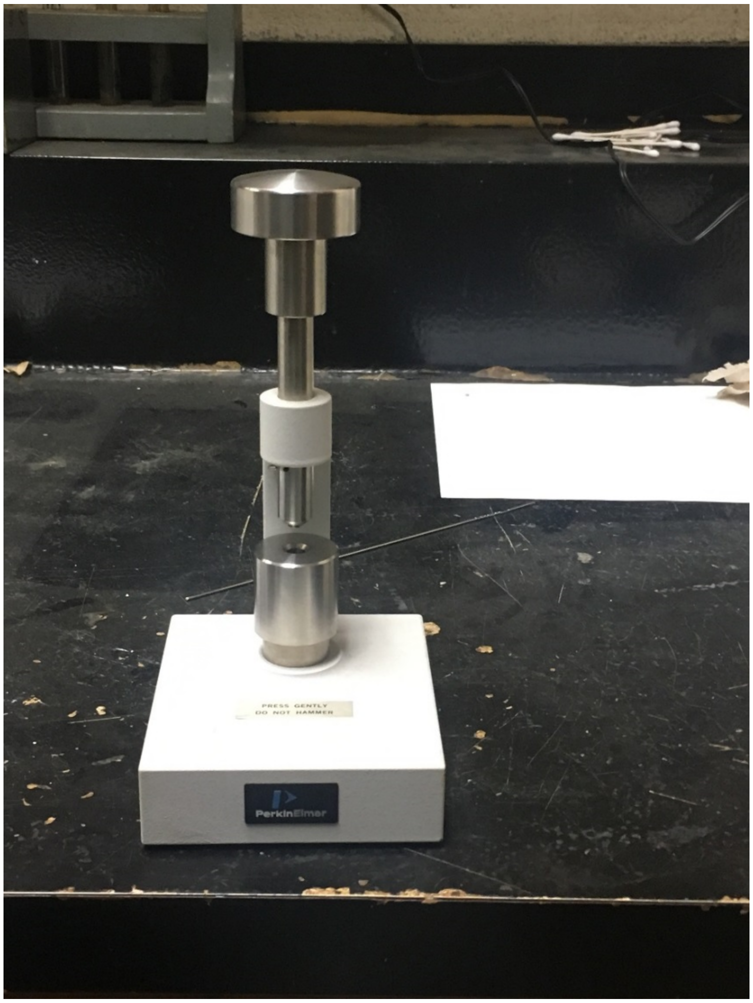

Figure 8. Photograph of the PerkinElmer® Crimper

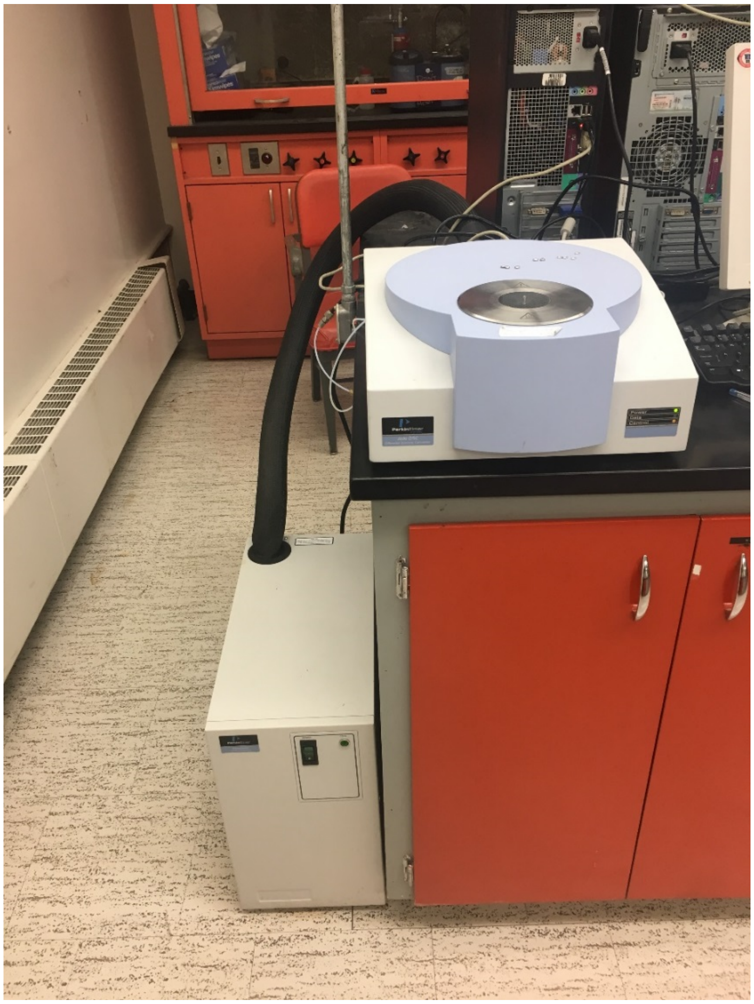

Figure 9. Photograph of the PerkinElmer® Jade DSC

II.VI SEM TESTING

Scanning Electron Microscopy (SEM) Hitachi S-3400N equipped with high TOA ports for EDS, Japan) was employed to study the surface morphology of selected catalysts and reactor residues. All the samples were gold coated for forty seconds.

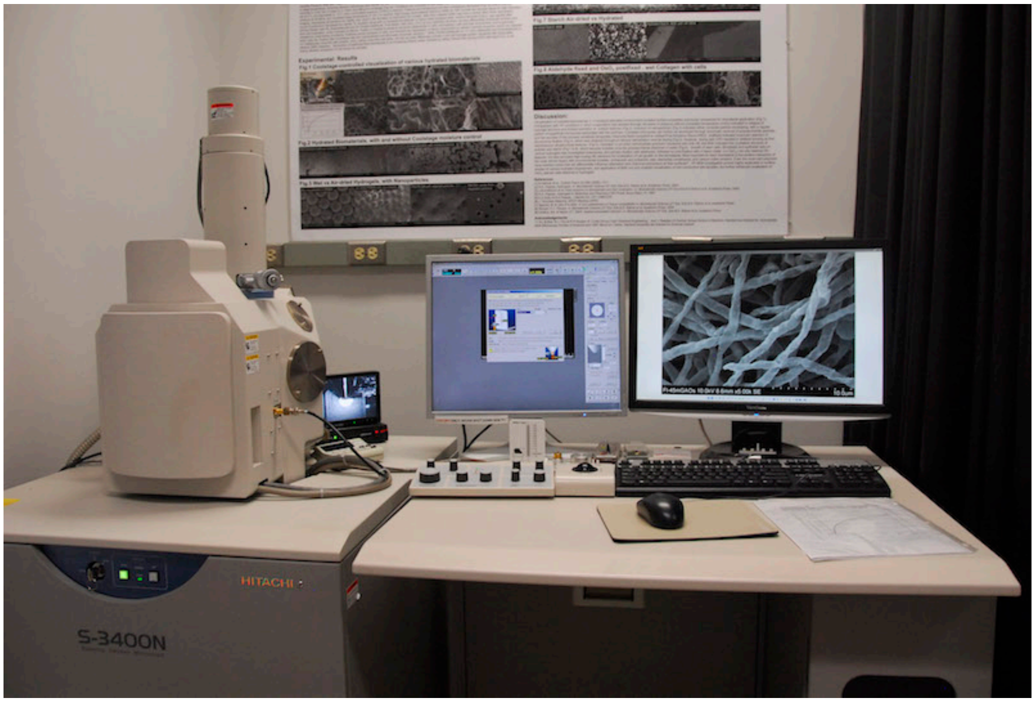

Figure 10. Photograph of Hitachi S-3400N SEM

CHAPTER III

RESULTS AND DISCUSSION

III.I Tar Formation

Tar samples were collected and analyzed to better understand their characteristics. Characterization is important because it allows us to better understand what was generated. In addition, it helps determine the conditions at which to run the pitching reactor and successfully produce mesophase pitch. Comparisons to other tars were done to justify our products and predict its conversion into high performance CCF.

The maximum calculated conversion rate was roughly 16% tar from lignin. This occurred at the conditions listed in Chapter II. No precision on this value was done because operating conditions were constantly changed in order to maximize the yield. In addition, literature on this subject is limited because efforts are typically done to minimize tar production. Before analysis was performed, tar from all experiments were mixed together because only a small amount of tar (~400mL) was generated. Also, compilation was required to give a homogenous feed stock.

Lignin tar was compared with other tar samples in order to gauge its quality and conversion potential. Two comparison samples used were coal tar and soybean-derived bio tar. Coal tar is a commonly used feedstock to produce mesophase pitch industrially. With sufficient purification, this pitch has also been shown to produce high quality CCF. The tar was provided from the Dakota Gasification Company (Beulah, North Dakota). The bio tar was generated under the direction of Ian Foerster using a continuous non-catalytic cracking reactor. This bio-tar has been shown to produce quality mesophase pitch using the same tar processing reactor, as was used in the present study.

III.II Thermal Analysis of Tar

Thermogravimetric analysis and Differential Scanning Calorimetry (TGA-DSC) were used to characterize the tars and study properties such as thermal stability, phase transition, glass transition and other properties needed to determine pitching conditions.

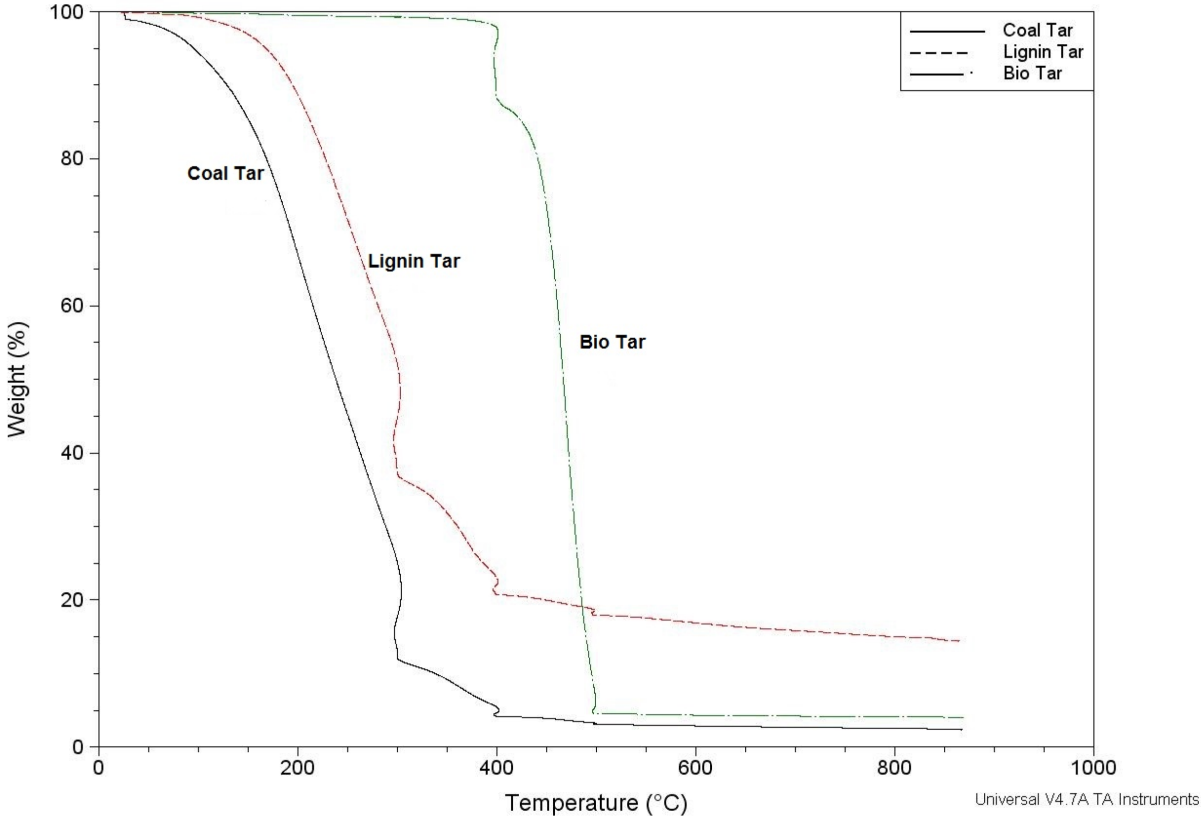

Figure 11. Mass loss of Lignin Tar, Bio Tar, and Coal Tar vs. Temperature

Lignin tar started to vaporize at ~184°C, bio tar at ~398°C, and coal tar degraded the earliest at ~40°C. The concentrations for all compounds were 92% at their respective vaporization points. Each compound displayed temperature ranges where distinct amounts of mass were lost. As shown in Table 1, from 200-400°C, lignin lost ~66% of its mass and coal tar lost ~61% of its mass. Bio tar lost ~92% from 400-600°C. Lignin shows small declines occurring throughout the whole test. About 14.5% of its mass remained at 900°C. Almost no bio tar mass (0.284%) was lost after 600°C. At 900°C, ~ 4.1% of the solid residue was left. Coal tar lost the most mass throughout with about ~97.5% lost before 900°C.

Table 1. Mass percent losses for each tar sample.

Sample	**Mass (wt%) loss 0-200°C**	**Mass (wt%) loss 200-400°C**	**Mass (wt%) loss 400-600°C**	**Mass (wt%) loss 600-900°C**	**Total Mass (wt %)**
Lignin Tar	11	66	6.1	2.4	~86
Bio Tar	0.48	3.4	92	0.28	~96
Coal Tar	33	61	2.6	0.50	~98

The thermal analysis of lignin tar is difficult to compare with other lignin because literature on this topic is limited. The differences in chemical structure as well as the method used to form each tar, account for the various behaviors observed from testing.

Lignin tar appeared to be more viscous than the other two samples. We believe the high viscosity is attributed to phenolic groups present in lignin which resulted in hydrogen bonding within the tar. Lignin tar decomposes earlier than bio tar because oxygen is present in the tar and has been shown to cause reactivity at low temperatures. Coal is essentially aged lignin. It possesses a similar chemical structure to lignin. However, coal tar’s characteristics vary based off the method used for recovery. The coal tar used in this study was formed from distillation. As a result, oxygen was still present in the coal tar sample and once again forced the tar to decompose quickly. We postulate most of the residue heavy enough to remain at 900°C was not distillable and therefore did not show up in the tar, which is why less than 3% mass remained at the end of testing. Bio-tar had the latest decomposition because no oxygen was present. All of the oxygen from soybean oil was removed during the cracking process.

III.III Pitch Products

The lignin tar generated was analyzed and processed to produce a mesophase pitch following the methods described in Chapter II. Figure 12 shows a TGA chart of both tar and produced pitch.

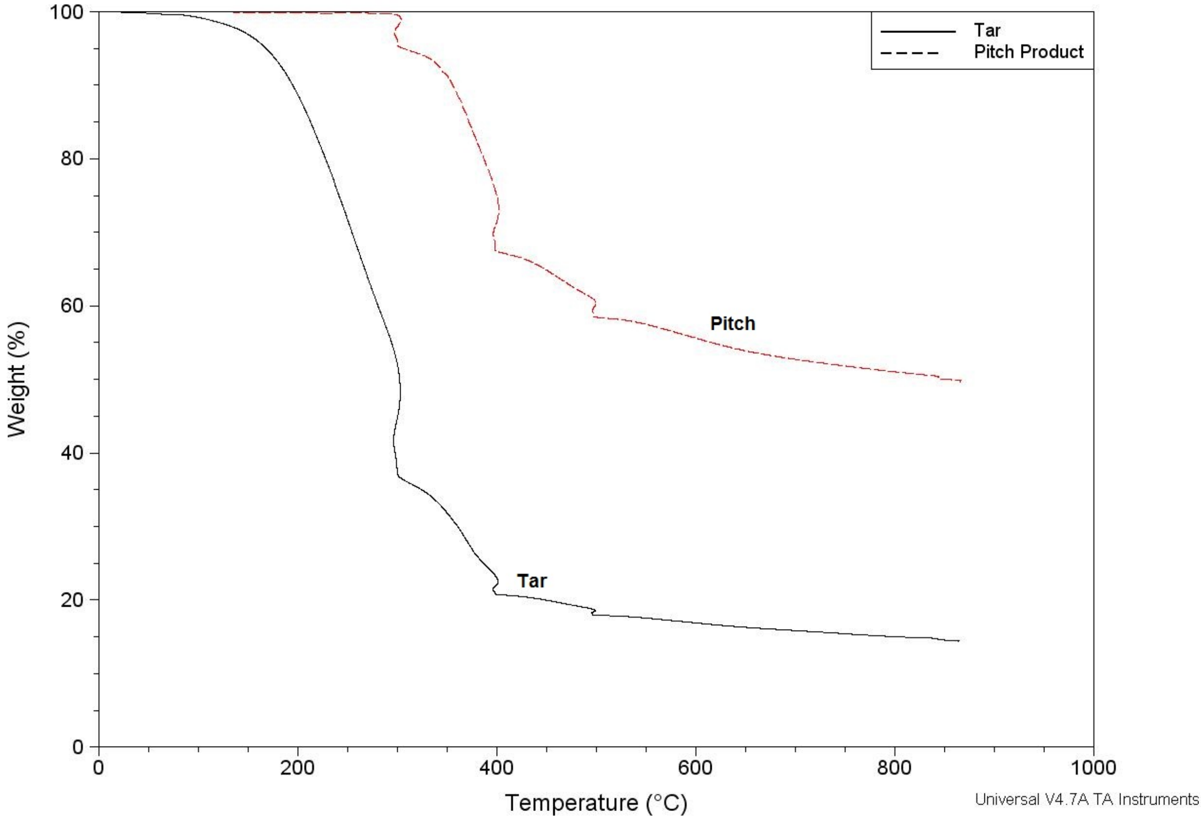

Figure 12. Lignin Tar and Pitch Product vs. Temperature

Pitch degraded later than lignin and did not vaporize until around 300°C. This trend is expected because the residue processing reactor was designed to drive off most volatiles and rearrange the intermolecular forces to increase the thermal stability of the compound. The change in mass appears to be steadier with its decomposition also occurring throughout the whole temperature range. There are no apparent temperature ranges with a distinct mass loss. The most mass loss

(25%) however, occurred from 200-400°C, the same region where tar had its greatest loss. Residue left from pitch at 900°C was higher than tar (~50 wt %).

A similar result occurred when the soybean based bio tar was run through the processing reactor. A visual of the TGA result for this process is found in figure 13 below.

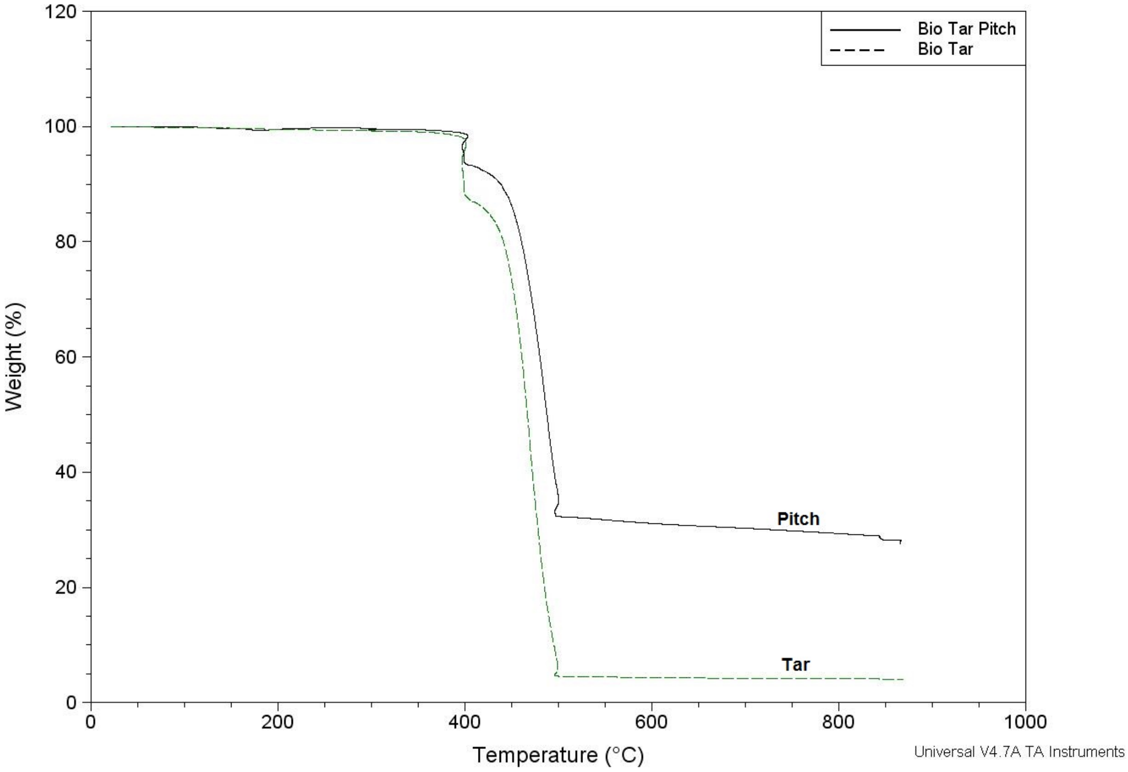

Figure 13. Bio Tar and Pitch Product vs. Temperature

Similar to lignin tar and its pitched product, bio tar also increased its thermal stability after being processed in the pitching reactor. Both tar and pitch began to vaporize at similar temperatures, however, the pitch had a slower decrease in mass loss. The majority of the decomposition also came in the range of 400-600°C. The change in vaporization temperature for pitched bio tar however, is not as dramatic as lignin because bio tar first underwent a devolatization process. During this process, tar was placed under high vacuum and high temperature to help remove light volatile matter from the tar. As a result, a large difference for bio tar and its pitched product is identified from the mass left behind after the run. ~28% of residue was left at 900°C compared to its tar's ~4%. As shown in figure 13 it still appears to be slightly decomposing at 900°C whereas the tar reached a plateau close to 500°C.

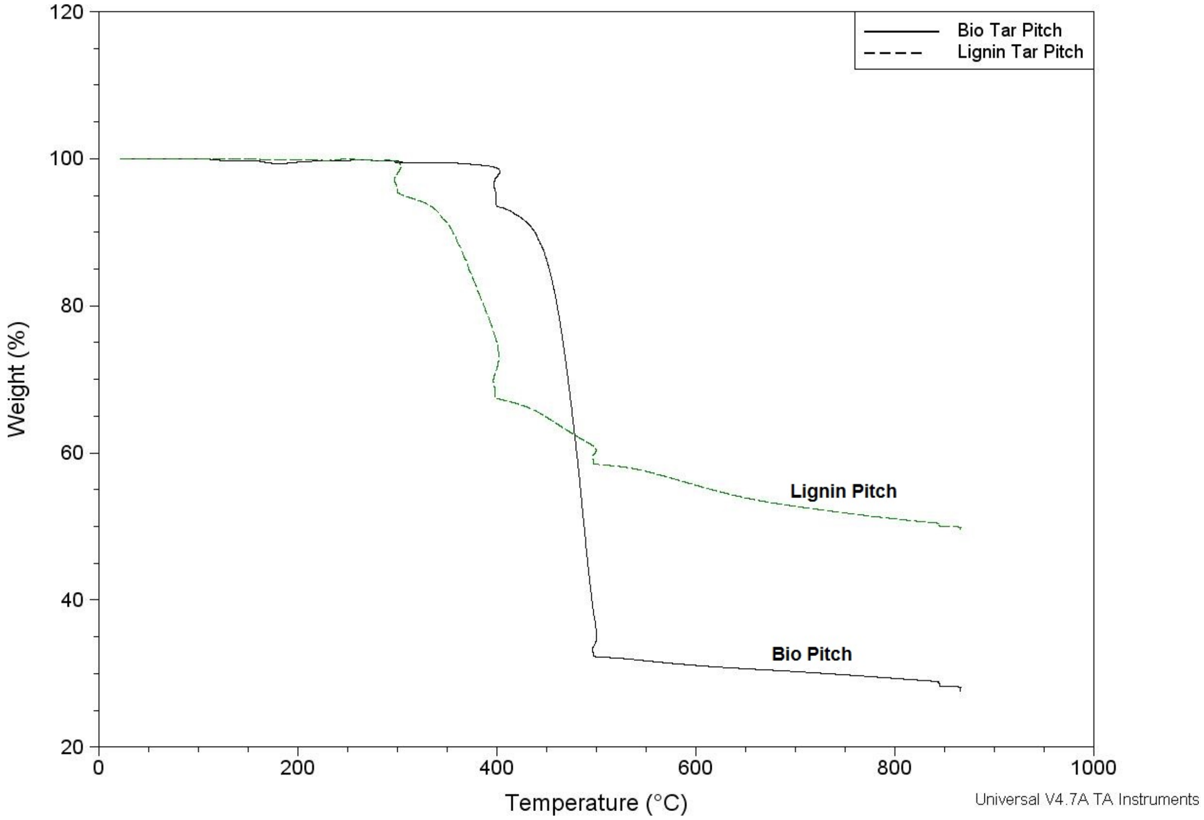

Figure 14. Bio Pitch and Lignin Pitch vs. Temperature

Figure 14 compares the pitch from each source. Lignin's pitch product shows a more steady decomposition compared to Bio tar and both products relate to their tar feedstock. The complex structure of lignin causes it to degrade over the entire temperature range, where bio tar lost ~63% of its mass from 400-600°C. Figure 14 indicates both products are still slightly degrading at 900°C. The final mass fractions lost for Lignin and Bio Pitch are ~50% and ~72%, respectively. The mass lost for each temperature range can be found in Table 2 below.

Table 2. Mass percent loss for both lignin and bio pitch

Sample	Mass (wt%) loss 0-200	Mass (wt%) loss 200-400	Mass (wt%) loss 400-600	Mass (wt%) loss 600-900	Total Mass (wt% loss)
Lignin Pitch	0.10	25	19	5.7	~50
Bio Pitch	0.46	5.9	63	3.0	~72

The TGA profiles of the pitched products matched up similarly to the tars as expected. The chemical structures of each tar were not significantly altered which is why the profiles look similar. Mesophase pitch was formed as a result of repolymerization that occurred in the pitching reactor. Small polymers molecules were joined together to form longer chained polymers and strengthened overall bonds. As a result, the decomposition temperatures were increased and more residue was left over at 900°C.

III.IV Coke Formation

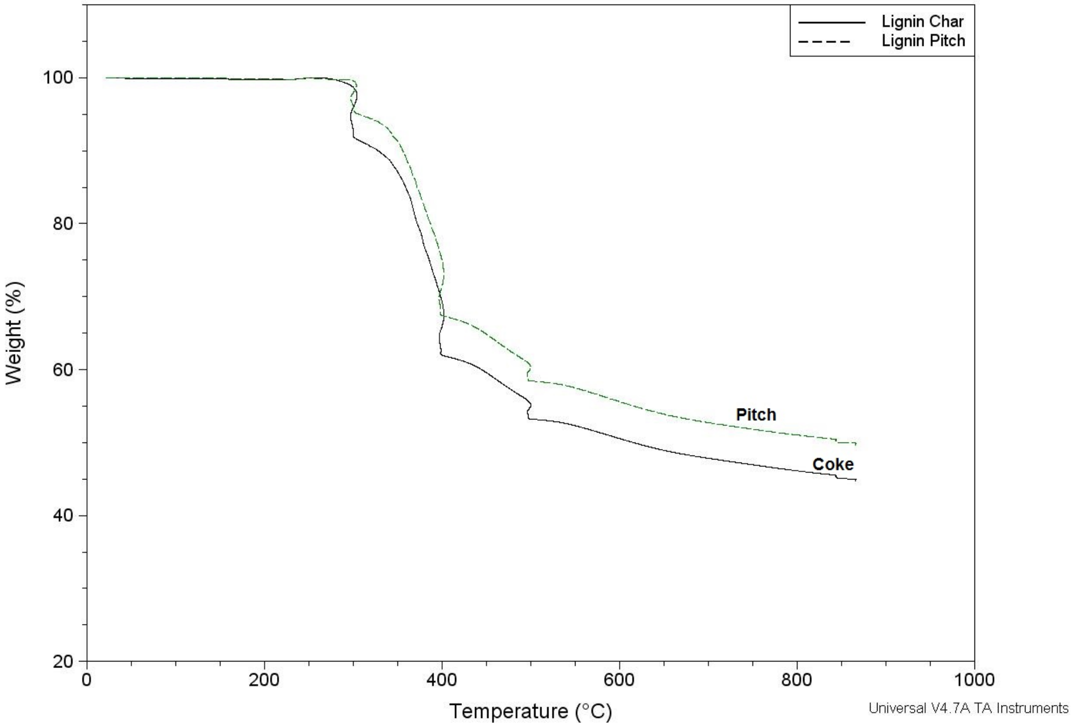

Figure 15. Lignin Pitch and Coke vs. Temperature

When lignin was pitched, it generated material that appears to contain mesophase pitch as well as other material that appeared to be char. TGA was performed on the char and its results were aligned with the simultaneously generated mesophase pitch. These are shown in figure 15.

Within the accuracy of the TGA test, the concentrations and trends of both products match up very closely. This implies that while they looked different visually, they are actually the same material.

Lignin is known to self-oxidize because of the many oxygen molecules present in its structure. Because tar is essentially unreacted, decomposed lignin, the tendency for oxidation to occur is even more likely than for regular lignin because of weaker intermolecular forces. We suggest the oxygen presented from lignin was sufficient to cause some oxidation to occur. However, differences between the apparent coke and pitch materials seem to be in residue and physical appearance rather than chemical makeup. This is most likely the result of small temperature differences that occurred from possible combustion in the reactor.

Bosquez conducted research on the formation of coke from heavy residual crop oil tars as a result of commercial cracking [41]. Figure 16 is an initial TGA profile of his feedstock used to determine adequate coking conditions.

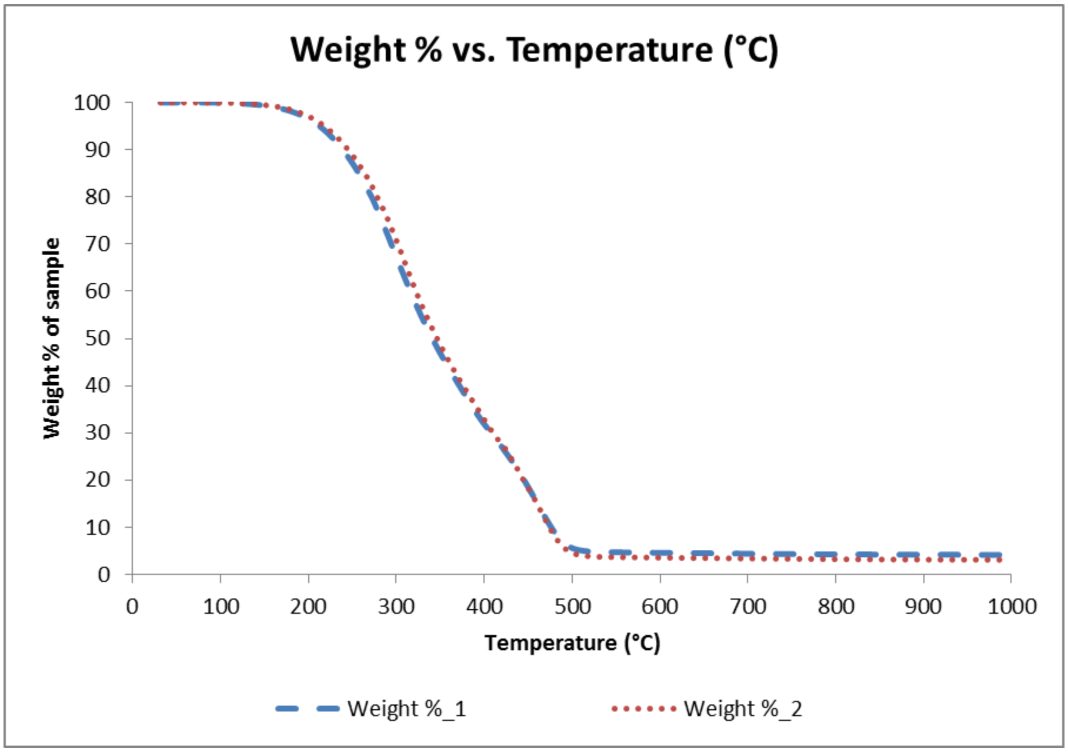

Figure 16. Crop Oil Residual Tar vs. Temperature [41]

The results for this graph look similar to that shown in figure 10 for lignin. It appears that most of its mass was lost from 200-400°C. However, no actual values were presented so it cannot be quantified. In addition, the quantity of residue left behind after analysis looks to be less than lignin. These were based on coking conditions tested at 450-490°C. Results show that temperatures above 460°C and at atmospheric pressure generated maximum coke [41].

The equipment used to produce this coke had a few similarities to our residue processing reactor: no oxygen present, inert nitrogen, and vacuum pressure (39.4 to 59.3 kPa) [41]. Our tar was processed at 215°C where 84% of its mass remained. Significantly less than 84% remained when crop oil tar underwent coking at >460°C. We were well underneath the temperature range for desired coking.

SEM analysis allowed us to look at the morphologies of each product to further analyze differences in our pitch. Figure 17 shows pitch product made from bio-tar. There are no apparent cracks or pores seen in its structure. This along with the properties discussed earlier, suggest that mesophase pitch was successfully made from bio-tar.

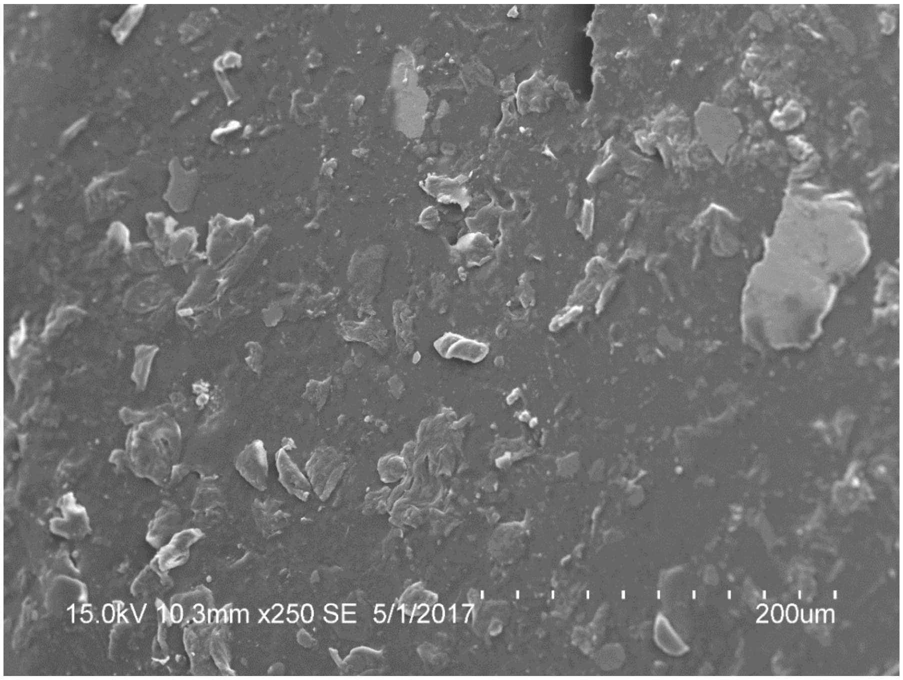

Figure 17. SEM photograph of mesophase pitch from bio-tar

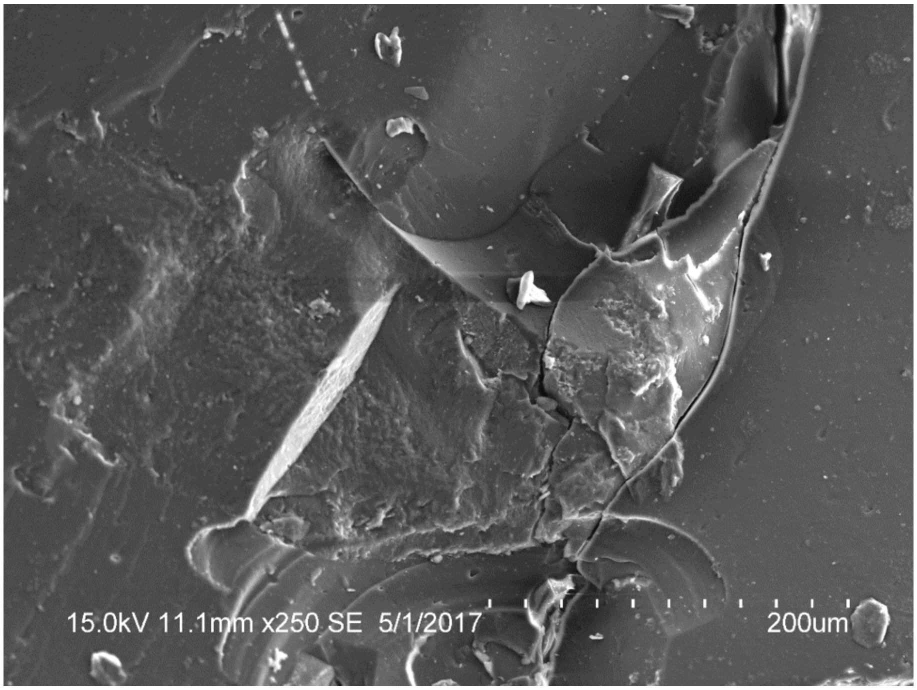

Figure 18. SEM photograph of mesophase pitch from lignin tar

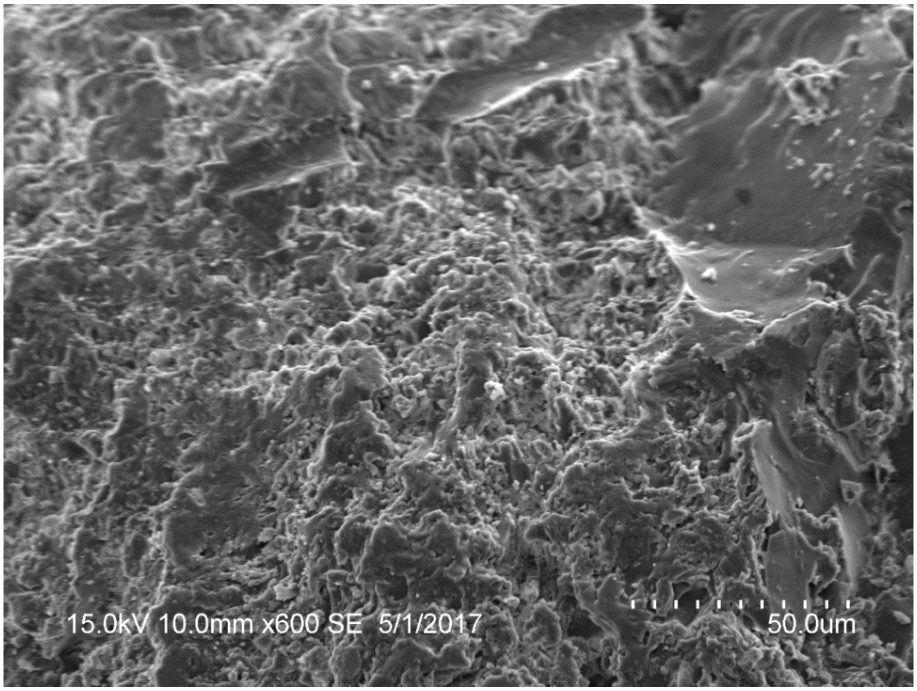

Figure 19. SEM photograph of oxidized mesophase pitch from lignin tar

Figure 18 represents the glass-like pitch product and figure 19 is the oxidized pitch. Mesophase pitch shown in figure 18 has a morphology similar to that from bio-tar. The pitch surface was mostly homogenous. However, there is a small porous region as well as an evident crack in the sample. We suggest the crack is due to an impurity from unfiltered lignin that settled in the tar during gasification. Figure 19 is predominately porous with a small glass-like region seen in its upper right hand corner. Lignin tar contains numerous aromatic hydrocarbons which are known precursors for forming coke. With combustion likely occurring, water molecules were formed, allowing cross linking to occur between carbon molecules.

Figures 18 and 19 are similar where both show pores and glass-like regions. These photos indicate that we did generate mixed samples of both mesophase pitch and coke. We believe the conditions used for pitching lignin are right at the threshold of producing both mesophase pitch and coke. More analysis however, is required to determine the quality of this pitch in regards to its spinnability into CCFs. Samples of the pitch will be sent to the Advanced Carbon Fiber Research lab at Clemson University to determine other important characteristics i.e ash content, anisotropic content, softening point, among others. These results were not available at the time of Thesis publication.

CHAPTER IV

CONCLUSIONS

Tar was successfully generated using an inhouse tube furnace from lignin gasification. The observed condition for maximum tar generation was 550°C and an argon flow rate of 142 L/hour. A 16% tar yield was observed as a result.

The tars created were treated in an inhouse pitching reactor to produce a mixture of presumed glass-like and oxidized mesophase pitch. The reactor was set to 215°C with a vacuum pressure of (0.03-0.13 kPa). We believe the conditions used for pitching were right at the threshold of mesophase pitch and coke formation. Combustion likely occurred inside the reactor most likely due to the release of oxygen molecules. This resulted in a ~10°C increase above the reactor set point (225°C). Oxidized mesophase pitch mixed with glass-like pieces was likely the result of fluctuating temperature in the pitching reactor. Further analysis would need to be done to determine the compositions of the products generated from the residue processing reactor.

IV.I Future Study

The next step for this research is to analyze other important properties for our generated pitch product to determine its quality. Recommended characteristics needed for high performance CCF include: 100 anisotropic content, a softening point between 230 and 280°C, high flow at spinning temperature with good viscosity integrity, high oxidation activity and carbon yield. This will be performed by another university who will also help to spin the fibers.

An important area of concern is the oxidation occurring in the pitching reactor. We believe this occurred because bound oxygen released from tar and then oxidized nearby carbon groups. In order to prevent this, deoxygenation of the tars may need to be performed prior to processing the tar in the pitching reactor. A first step would be devolatilizing the tar to remove any volatile matter. Removing the volatile matter initially would increase the tar's thermal stability and potentially reduce redox reactions if bound oxygen is released when pitched. If this is insufficient, more aggressive techniques may be required. For example, hydrotreating the tar may replace some of the oxygen groups such as those forming carboxylic acid, with hydrogen terminators.

A different feedstock to look at is black liquor. It is a mixture of both cellulose and lignin that is commonly produced as a result of paper manufacturing. Sulfur typically is added to black liquor to separate out lignin from cellulose. As a result, lignin usually has a foundation of sulfur in its structure. The sulfur helps lignin maintain its structure by essentially strengthening its intermolecular forces. Leaving black liquor as is and using it as a direct feedstock for pitching could produce promising results because cleavage of oxygen from lignin is less likely than tar. The absence of sulfur allows it to decompose easier while still having stronger bonds than tar.

The last recommendation involves efficient tar formation. While, literature on tar generation is limited, some studies have used thermal shock as a way to efficiently produce tar. Lignin has a tendency to oxidize with sufficient residence time. Drastically minimizing the residence time could potentially reduce the amount of char formed while increasing the tar yield.

APPENDICES

APPENDIX A

RHEOLOGICAL PROPERTIES OF TARS

Table 3. Rheological Properties of Lignin Tar

Point No.	Shear Strain (%)	Phase Shift Angle (°)	Complex Shear Modulus (Pa)	|G*|/sin(delta) (Pa)	|G*|·sin(delta) (Pa)
1	0.00989	86.1	50.8	50.9	50.7
2	0.0146	89.4	51.1	51.1	51.1
3	0.0215	88.6	53.3	53.3	53.3
4	0.0316	88.3	51.8	51.9	51.8
5	0.0463	88.7	51.9	51.9	51.9
6	0.068	88.8	51.9	51.9	51.9
7	0.0998	88.8	52.3	52.3	52.3
8	0.147	89.1	52.1	52.1	52.1
9	0.215	89.1	52.4	52.4	52.3
10	0.316	88.9	52.1	52.2	52.1
11	0.464	89.0	52.2	52.2	52.2
12	0.681	88.8	52.0	52.0	52.0
13	0.999	88.7	51.9	51.9	51.9
14	1.47	88.9	51.9	51.9	51.9
15	2.15	88.9	51.8	51.8	51.8
16	3.16	88.9	51.8	51.8	51.8
17	4.64	88.9	51.7	51.8	51.7
18	6.81	89.1	51.6	51.6	51.6
19	9.99	89.0	51.6	51.6	51.6
20	14.7	89.3	51.5	51.5	51.5
21	21.5	89.3	51.4	51.4	51.4
22	31.6	89.4	51.3	51.3	51.3
23	46.4	89.5	51.2	51.2	51.2
24	68.1	89.6	50.9	50.9	50.9
25	99.9	89.6	50.8	50.8	50.8

Table 4. Rheological Properties of SODT

Point No.	Shear Strain (%)	Phase Shift Angle (°)	Complex Shear Modulus (Pa)	|G*|/sin(delta) (Pa)	|G*|·sin(delta) (Pa)
1	0.00992	90	5.44	5.44	5.43
2	0.0146	90	3.70	3.70	3.70
3	0.0215	90	5.48	5.48	5.48
4	0.0316	79.1	4.12	4.20	4.05
5	0.0464	75.6	2.78	2.87	2.69
6	0.068	66.1	2.14	2.34	1.96
7	0.0994	90	2.12	2.12	2.12
8	0.147	79.2	2.04	2.08	2.00
9	0.215	86.1	2.19	2.19	2.18
10	0.316	86.8	2.25	2.26	2.25
11	0.464	87.4	2.11	2.11	2.10
12	0.681	90	2.05	2.05	2.05
13	0.999	90	2.11	2.11	2.11
14	1.47	78.9	2.19	2.24	2.15
15	2.15	79.5	2.15	2.18	2.11
16	3.16	88.6	2.11	2.12	2.11
17	4.64	89.1	2.14	2.14	2.14
18	6.8	87	2.05	2.06	2.05
19	9.99	84.3	2.06	2.07	2.05
20	14.7	88.2	2.06	2.06	2.06
21	21.5	87.9	2.06	2.06	2.06
22	31.6	87.3	2.06	2.06	2.06
23	46.4	87.4	2.05	2.05	2.05
24	68	88.5	2.05	2.05	2.05
25	99.9	89.3	2.05	2.05	2.05

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Table 5. Rheological Properties of Coal Tar

Point No.	Shear Strain (%)	Phase Shift Angle (°)	Complex Shear Modulus (Pa)	|G*|/sin(delta) (Pa)	|G*|·sin(delta) (Pa)
1	0.00989	11.3	3.40	17.3	0.669
2	0.0145	7.41	5.04	39.1	0.650
3	0.0216	21.9	5.72	15.3	2.14
4	0.0314	11.2	4.39	22.5	0.854
5	0.0462	12.2	5.5	26.1	1.16
6	0.0679	10.2	5.72	32.3	1.01
7	0.0995	11.6	4.95	24.6	0.995
8	0.147	14.5	4.51	17.9	1.13
9	0.215	11.6	4.39	21.8	0.884
10	0.316	17.0	3.84	13.1	1.13
11	0.463	19.6	3.28	9.76	1.10
12	0.681	20.2	3.03	8.77	1.04
13	0.999	21.2	2.81	7.78	1.01
14	1.47	22.2	2.42	6.43	0.915
15	2.15	24.9	1.91	4.53	0.804
16	3.16	28.1	1.46	3.09	0.685
17	4.64	31.7	1.12	2.13	0.589
18	6.8	34.6	0.775	1.36	0.441
19	9.99	35.4	0.648	1.12	0.375
20	14.7	45.7	0.454	0.634	0.325
21	21.5	51.5	0.365	0.466	0.285
22	31.6	60.5	0.286	0.329	0.249
23	46.4	58.9	0.250	0.292	0.214
24	68	57.2	0.220	0.263	0.185
25	99.9	61.2	0.195	0.223	0.171

REFERENCES

1. Cohen, Bernard Leonard, The nuclear energy option: An alternative for the 90s. New York Plenum Press, New York, NY (1992).

2. Overview of Greenhouse Gases, EPA. (2017). https://www.epa.gov/ghgemissions/overview-greenhouse-gases (accessed 2017).

3. R. Vanholme, B. Demedts, K. Morreel, J. Ralph, W. Boerjan, Lignin biosynthesis and structure, Plant Physiol. 153 (2010) 895-905.

4. F. Lu, J. Ralph, Chapter 6-Lignin, Cereal Straw as a Resource for Sustainable Biomaterials and Biofuels, Amsterdam: Elsevier (2010) 169-207.

5. L.P. Rabou, R.W. Zwart, B.J. Vreugdenhil, L. Bos, Tar in biomass producer gas, the Energy research Centre of the Netherlands (ECN) experience: an enduring challenge, Energy Fuels 23 (2009) 6189-6198.

6. H. Yu, Z. Zhang, Z. Li, D. Chen, Characteristics of tar formation during cellulose, hemicellulose and lignin gasification, Fuel 118 (2014) 250-256.

7. A.A. Ogale, M. Zhang, J. Jin, Recent advances in carbon fibers derived from biobased precursors, J Appl Polym Sci 133 (2016) para. 2.

8. University of Tennessee | Creative Services, Carbon Fiber Production, Carbon Fiber Production. (n.d.). http://www.utsi.edu/research/carbonfiber/cf.htm (accessed 2017).

9. T. Matsumoto, Mesophase pitch and its carbon fibers, Pure and applied chemistry 57 (1985) 1553-1562.

10. F.G. Calvo-Flores, J.A. Dobado, Lignin and lignans as renewable raw materials: chemistry, technology and applications, John Wiley & Sons, Hoboken, NJ 2015.

11. G. Gellerstedt, Softwood kraft lignin: Raw material for the future, Industrial Crops and Products 77 (2015) 845-854.

12. B. Jenkins, L. Baxter, T. Miles, Combustion properties of biomass, Fuel Process Technol 54 (1998) 17-46.

13. I. Narvaez, A. Orio, M.P. Aznar, J. Corella, Biomass gasification with air in an atmospheric bubbling fluidized bed. Effect of six operational variables on the quality of the produced raw gas, Ind Eng Chem Res 35 (1996) 2110-2120.

14. G. Chen, C. Liu, W. Ma, B. Yan, N. Ji, Catalytic Cracking of Tar from Biomass Gasification over a HZSM-5-Supported Ni–MgO Catalyst. Energy Fuels 29 (2015) 7969-7974.

15. J. Han, H. Kim, The reduction and control technology of tar during biomass gasification/pyrolysis: an overview, Renewable and Sustainable Energy Reviews 12 (2008) 397-416.

16. N. Yusof, A.F. Ismail, Post spinning and pyrolysis processes of polyacrylonitrile (PAN)-based carbon fiber and activated carbon fiber: A review, J. Anal. Appl. Pyrolysis 93 (2012) 1-13.

17. S. Park, G. Heo, Chapter 6 - Precursors and manufacturing of carbon fibers, in: Carbon Fibers, Springer, Netherlands, 2015, pp. 31-66.

18. V.B. Gupta,V. Kothari, Manufactured Fibre Technology, Chapman & Hall, London, (1997).

19. M. Paiva, P. Kotasthane, D. Edie, A. Ogale, UV stabilization route for melt-processible PAN-based carbon fibers, Carbon 41 (2003) 1399-1409.

20. L. Peebles Jr, Carbon fibers, formation, structure and properties, CRC Press, Boca Raton, FL,1995.

21. J. Mittal, R. Mathur, O. Bahl, M. Inagaki, Post spinning treatment of PAN fibers using succinic acid to produce high performance carbon fibers, Carbon 36 (1998) 893-897.

22. L.T. Drzal, M.J. Rich, P.F. Lloyd, Adhesion of graphite fibers to epoxy matrices: I. The role of fiber surface treatment, The Journal of Adhesion 16 (1983) 1-30.

23. A.R. Bunsell, Fibre Reinforcements for Composite Materials, Elsevier, Amsterdam, 1988.

24. J. Donnet, R.C. Bansal, Carbon fibers, CRC Press, Boca Raton, FL, 1998.

25. Otani, Sugio. "Production of carbon filaments from low-priced pitches." U.S. Patent No. 3,629,379. Washington D.C21 Dec. 1971.

26. F. Smith, T. Eckle, R. Osterholm, R. Stickel, A. Hoiberg, Manufacture of coal tar and pitches, Bituminous materials 3 (1966) 57.

28. X. Cheng, Q. Zha, X. Li, X. Yang, Modified characteristics of mesophase pitch prepared from coal tar pitch by adding waste polystyrene, Fuel Process Technol 89 (2008) 1436-1441.

29. M. Pérez, M. Granda, R. Santamarıa, T. Morgan, R. Menendez, A thermoanalytical study of the co-pyrolysis of coal-tar pitch and petroleum pitch, Fuel 83 (2004) 1257-1265.

30. V.A. Weinberg, J.L. White, T.F. Yen, Solvent fractionation of petroleum pitch for mesophase formation, Fuel 62 (1983) 1503-1509.

31. X. Wang, M. Cao, Z. Min, Y. WANG, H. YANG, X. LIN, Purification of coal tar pitch for removing quinoline insolubles by hot filtration, Carbon Techniques 26 (2007) 10.

32. J. Michels, K. Wagemann, The German Lignocellulose Feedstock Biorefinery Project, Biofuels, Bioproducts and Biorefining. John Wiley & Sons, Hoboken, NJ (2010) 263–267

33. D.A. Baker, T.G. Rials, Recent advances in low-cost carbon fiber manufacture from lignin, J Appl Polym Sci 130 (2013) 713-728.

34. D.A. Baker, N.C. Gallego, F.S. Baker, On the characterization and spinning of an organic-purified lignin toward the manufacture of low-cost carbon fiber, J Appl Polym Sci 124 (2012) 227-234.

35. J. Kadla, S. Kubo, R. Venditti, R. Gilbert, A. Compere, W. Griffith, Lignin-based carbon fibers for composite fiber applications, Carbon 40 (2002) 2913-2920.

36. Y. Uraki, S. Kubo, N. Nigo, Y. Sano, T. Sasaya, Preparation of carbon fibers from organosolv lignin obtained by aqueous acetic acid pulping, Holzforschung-International Journal of the Biology, Chemistry, Physics and Technology of Wood 49 (1995) 343-350.

37. K. Sudo, K. Shimizu, N. Nakashima, A. Yokoyama, A new modification method of exploded lignin for the preparation of a carbon fiber precursor, J Appl Polym Sci 48 (1993) 1485-1491.

38. Y. Nordström, R. Joffe, E. Sjöholm, Mechanical characterization and application of Weibull statistics to the strength of softwood lignin-based carbon fibers, J Appl Polym Sci 130 (2013) 3689-3697.

39. H.C. Liu, A. Chien, B.A. Newcomb, A.A. Bakhtiary Davijani, S. Kumar, Stabilization kinetics of gel spun polyacrylonitrile/lignin blend fiber, Carbon 101 (2016) 382-389.

40. Linnen, Michael J, Advanced Reactors and Novel Reactions for the Conversion of Triglyceride Based Oils Into High Quality Renewable Transportation Fuels, Doctoral Dissertation, University of North Dakota, Grand Forks, 2014.

41. Bosquez, N, High Grade Carbon From Crop Oil Tars, Masters Thesis, University of North Dakota, Grand Forks, 2012.