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Coal Liquefaction Process Development

Christopher L. Yurchick

Dissertation submitted to the College of Engineering and Mineral Resources at West Virginia University in partial fulfillment of the requirements for the degree of

> Doctor of Philosophy in Chemical Engineering

Alfred Stiller, Ph.D., Chair Christopher J. Bise, Ph.D. Eung H. Cho, Ph.D. Rakesh K. Gupta, Ph.D. Eric Johnson, Ph.D.

Department of Chemical Engineering

Morgantown, West Virginia 2012

Keywords: Coal Liquefaction; Pitch; Coke; Centrifugation; Distillation; Process Development

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ABSTRACT

Coal Liquefaction Process Development

Christopher L. Yurchick

The traditional method of liquefying coal operates at extreme conditions consisting of hydrogen pressures of over 2000 pounds per square inch and temperatures of over 450 °C. The elevated hydrogen pressure is necessary to hydrogenate the reaction mixture and liquefy the coal molecules. As a result, the processing equipment is very expensive and safety is a major concern. The coal liquefaction process invented at West Virginia University does not use hydrogen overpressure and operates below 500 pounds per square inch. The WVU process has produced 4500 pounds of cleaned de-ashed coal extract referred to as centrate. The centrate was processed into coal tar binder pitch by Koppers Inc. and finally into electrodes for the steel industry by GrafTech International Ltd. The electrodes were tested and passed all of the commercialization tests. Quantex, a Canadian company, licensed the technology from the university in 2007 with the intention of commercializing the process. However, the process had several deficiencies to overcome before it could be economically viable and move towards commercialization.

The centrifuge system removes ash and other solid materials from the mixture after the coal has been liquefied. In the process existing in 2007, the centrifuge residue, or tails, contains only 20% by weight of the ash material with the remaining 80% consisting of valuable products or unreacted coal. Without first increasing the efficiency of ash removal from the coal either before or after the liquefaction reaction, the process cannot be economically viable and is unable to be commercialized. Another drawback of the original process is the reaction and centrifuge systems were not designed or operated to produce reliable mass balance results.

The reaction system was redesigned and constructed incorporating the previously redesigned centrifugation system to produce clean, de-ashed centrate and other products from the raw materials. A vacuum distillation system was designed and constructed that produces quality pitches and condensed liquid volatiles from the clean, de-ashed centrate produced from coal in the previous reaction step. The coking system was designed and constructed to process the coal derived pitches into commercial grade coke and additional condensed volatiles. Each of the three operating systems produces reliable and repeatable mass closure results for individual experiments. All of the products can be collected and samples taken for further analytical analysis. A complete mass balance analysis for the overall process was performed from the raw material through the products produced. The end products were subjected to and passed testing for commercial standards. The potential for commercialization has been enhanced by this research and the technology now can be properly analyzed.

Dedicated to my beautiful wife Rebecca, whose love and support made this work possible.

Also dedicated to my late grandfather Stanley Gawlik for all of the knowledge, love, and support that he provided during my childhood.

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I would like to thank Norm Caplin and Coal Innovations for providing the ability to perform research at their facility in Stoystown, PA. I would like to thank the Chemical Engineering Department, the Carbon Products group, and Quantex Energy for the financial support to construction the necessary systems.

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DISCLAIMER

The document is not only a dissertation for the requirements of a Doctoral degree, it is also a legal document for the Technology Transfer division of West Virginia University since this is a licensed process. Therefore, it contains all of the information in great detail so that the legalities of ownership and property rights can be distinctly discerned.

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CHAPTER I: INTRODUCTION

1.1 History of the Carbon Products Group

In 1983, researchers at West Virginia University joined with researchers from the University of Kentucky, the University of Utah, University of Pittsburgh, and Auburn University to form the Center for Fossil Fuel Liquefaction (CFFLS). This consortium was formed under the direction of the Pittsburgh Energy and Technology Center of DOE. The purpose of the consortium was to develop a new technology to liquefy coal under mild conditions. Based on a patent by A.H. Stiller (Stiller et al., 1981), WVU used aprotic dipolar solvents to dissolve coal and make fuels, but during this effort researchers at WVU became acquainted with other direct liquefaction technology. As support for the CFFLS effort faded, a new program, the Carbon Products Program was born. In this program West Virginia University researchers were to develop a method for making nuclear graphite from coal. The primary ingredient for making nuclear graphite is a very isotropic coke, the extract that was produced when coal was solubilized in the dipolar aprotic solvents made the ideal coke for nuclear graphite production.

As the Carbon Products Program progressed it was incorporated into a new consortium, the Consortium for Premium Carbon Products from Coal, (CPCPC). This was again initiated by Pittsburgh Energy and Technology Center (PETC) and directed by Pennsylvania State University. The direction of the WVU Carbon Products program changed. Researchers at WVU were asked to make pitches suitable for use as additives for coal tar binder pitch that is nationally in short supply. This involved a different application of the direct liquefaction processes that were studied in the CFFLS program. As a result of these studies the Carbon Products Program was able to show how purifying coal liquids produced by direct liquefaction could make synthetic pitches that complied with the standards required by Koppers. The preferred process used by WVU involved blending ground coal with the middle cut of coal tar distillate (CTD), and adding a proton transfer fluid. The blend was then put into an autoclave at high hydrogen pressure, ~2000 psig, and brought to a temperature of about 425°C for one hour. After the liquids cooled to room temperature they were filtered to remove the non-soluble material including the ash. The excess solvent was distilled, and the residues in the bottom of the distillation vessel are pitches. The softening point of the pitches could be adjusted by the degree of distillation.

Simultaneously with the CPCPC research effort Carbon Products continued a major DOE program that was designed to test the pitches for the ability to produce in commercial applications. Researchers at WVU were asked to make 4500 pounds of de-ashed extract that could be sent to Koppers for distillation. This would be distilled by Koppers to make a pitch that would be blended with their coal tar binder pitch and used to make commercial test electrodes by GrafTech.

In order to accomplish this task the majority of the synthetic pitch was produced in the room 317 laboratory of the Engineering Research Building using a five gallon autoclave system. An unfortunate failure of this autoclave occurred so a larger, ten gallon, autoclave reactor in the bunker behind the engineering science building was activated. The system in the bunker mirrored the reaction system in the room 317 laboratory. In these systems the coal tar distillate (CTD) blends were mixed, the liquefaction reactions were run, and the extract was de-ashed using the centrifuge system. The cleaned extract

was collected in 55 gallon barrels seen in Figure 1 and sent to Koppers. Intertek at UPARC did the distillation, the pitches were processed, and the graphite electrodes were made. The electrodes were tested and indeed they passed the commercialization tests which can be viewed in Figure 2.



Figure 1: Cleaned, de-ashed extract produced by the Carbon Products Group.



Figure 2: Electrodes made from cleaned extract during commercial testing

Although pitch is a fairly expensive commodity, the expense of the reaction conditions caused the financial viability of the process to be questioned. This technology would only be advanced if the researchers discovered a process that decreased the severity of the reaction conditions. In nearly all previous coal liquefaction runs the proton transfer agent was tetraline. Tetraline has the ability to both transfer hydrogen to the coal molecules and capture hydrogen from gaseous hydrogen that is dissolved in the solvent. It is commonly referred to as "shuttling agent". The higher the pressure of the hydrogen the more dissolves and that facilitates exchange in the solvent. This is the reason for the high hydrogen pressure. The costs for direct liquefaction are the cost of high pressure hydrogen and the reactor vessel that has to be capable of housing a reaction at such extreme conditions. In order to decrease the extreme conditions and costs, a hydrogenated compound that could transfer hydrogen and could be more easily rehydrogenated is needed. After much research it was determined that common

hydrogenated vegetable oil was a suitable hydrogenating agent. By using hydrogenated vegetable oil instead of tetraline the reaction did not need the excessive hydrogen over pressure and the extreme conditions for liquefaction could be significantly reduced. Similar synthetic coal tar pitch was able to be produced by dispersing finely ground coal in the middle cut CTD and using hydrogenated vegetable oil as a proton transfer additive. In this blend coal was effectively liquefied at 425°C and only 400 psig. This invention became the basis for several patents disclosures filed by the university on coal liquefaction (Kennel et al., 2003; Stansberry et al., 2003, Stansberry et al., 2004; Kennel et al., 2008). This completely fulfilled the goals and objectives of the earlier CFFLS project.

In the new process with the milder reaction conditions, 1 part ground coal was blended with 3 parts CTD. Hydrogenated vegetable oil was added in the ratio of 1/5 the amount of coal by weight and the mixture was put into the autoclave. The system was heated to 425°C. The pressure generated during the reaction continued to increase in the sealed autoclave until the run was complete and the vapors vented. The vaporized volatiles generated were passed to a room temperature, large volume, flash tank where they condensed. After heating the system for one hour, the reaction was believed to be complete. The reactor was drained into a receiving vessel. This was repeated until nearly 55 gallons of extract was accumulated. The extract was then taken to the centrifuge system in room 317 where it was centrifuged repeatedly until the centrate had sufficiently low ash at about 0.05%. The cleaned, de-ashed, centrate was distilled by Koppers and a quality pitch was produced. The distillate was believed to be CTD and some unreacted hydrogenating agent. The distilled CTD blend was recycled. An

estimated mass balance indicated that about 16% of the CTD needed to be continually added to keep the mixture in balance. This was the state of the experimentation in 2007 when Quantex licensed the technology from West Virginia University.

1.2 Statement of the Problem

Licensing this technology to Quantex by the university was a "first". Although the university holds many patents, this was the first actual license that was ever granted. The value of the technology however was very limited. The state of knowledge when it was licensed had several deficiencies. First and foremost, there was no complete measured mass balance. A mass balance was developed based upon proximate analysis results and some weights but the system never closed. With no mass balance over the system economic viability of the process could not be determined. Second, the experimental process had several flaws in design. The reactions took place at one location while the de-ashing step took place at another location. The extract had to be heated and cooled and reheated. Third, although the centrate was effectively de-ashed to 0.05%, the centrifuge tails only contained about 20% ash. The centrifuge tails being the compressed material removed from the centrifuge after processing. This meant that 80% of the tails were insoluble coals and volatiles that would need replenished in the process. Those numbers would mean the process was financially infeasible. Fourth, the need for a makeup of 16% of the CTD is a "show stopper". In the state at which the process was licensed the university would realize no royalty income because the process would never be commercialized.

Quantex licensed the technology from the university with the expectation of immediately moving forward with commercialization of the liquefaction process to produce centrate. However, Quantex had very little knowledge of the process and even less knowledge of the deficiencies that existed when they licensed it. Therefore, these deficiencies <u>are</u> to be overcome so the technology can be advanced. The overall system must be considered and the problems analyzed so that some approaches can be derived to solve them. Then a system needs to be constructed in which the tests can be carried out and legitimately measured mass balance results can be obtained to fully assess the potential of this technology. Only then will this technology have value and it will become possible for the university to realize a profit from its technology.

1.3 **Proposed Research**

The overall objective of this research is to analyze the existing technology and eliminate the deficiencies described above. Although valuable products were produced by this technology as licensed, the deficiencies would eliminate this technology from consideration for commercialization. During the carbon products period, the group was charged with making materials for testing. The group did make sufficient cleaned deashed centrate so that it could be distilled to pitch, then used in the manufacture of graphite electrodes from which commercial tests could be made. Little attention was given to mass closure or potential products other than centrate. At the time of licensing, the process was only used to make cleaned de-ashed centrate. WVU never made coal derived pitches or cokes. WVU never considered the process for the production of light volatiles or synthetic crude. The design and construction of facilities needed to manufacture those materials had never been part of the DOE contract. A "cradle to grave" set of operations was never actually done at WVU. Therefore a true and accurate assessment of the technology through the entire process was impossible. In order for this process to be advanced towards commercialization a complete operation from beginning inputs to end products must be completed and mass balances of each operation in the sequence must be measured. This will require the designing and constructing of a new system in which all steps are completely closed so all masses can be directly measured.

A complete understanding and analysis of this process will be complicated by the need to use the WVU process to convert lower rank coals. Researchers at WVU had never processed any coal other than a high volatile bituminous coal. The technology has been licensed by the university to Quantex and Quantex is supported by New Hope, an Australian coal company. Quantex wants us to evaluate this process with Australian sub bituminous and lignite coals. These are lower rank coals and are also ash rich. The bituminous coal that was studied using the previous process had 4.5% ash while the Australian sub-bituminous coal contains roughly 25% ash by weight. The ash in the bituminous coal is basically heavy rock ash. While the sub-bituminous coal ash is basically clay. The heavy rock ash has a specific gravity that is very different from coal 1.6 - 5.5 while the sub-bituminous coal ash has a specific gravity that is nearly the same as the coal 1.6 - 2.0. Although the previous centrifugation process could remove the ash from the bituminous coal extract, the de-ashing efficiency of the centrifugation was very low and caused the economics of the process to be questioned. It is expected that the separation of the ash from the sub-bituminous coal will be much more difficult than separating ash from bituminous coal. Inadequate ash removal would produce an extract with higher ash content. Therefore, it is logical that the first task should be developing a

method for ash removal from the Australian coals. In all chemical processes it is better to react the highest purity chemicals rather than try to react systems with spectators. Therefore it would seem to be better if we can remove the ash from the sub-bituminous coals before they are reacted. Before a 'cradle to grave' system can be developed, a technology that would enable the ash removal from lower rank coals so that these coals could be viable candidates for processing using the WVU technology must first be investigated.

1.4 Research Objectives

Prior to this research, all of the experiments to produce the centrate in the Carbon Products program were performed using the first generation of the reaction system and the first generation of the centrifugation system. A block flow diagram of the original process licensed by Quantex can be seen in Figure 3. The first generation reaction system was loaded from a pre-mixed 55 gallon barrel of reactants with the extract as the only product collected from the experiment. The vapors produced by the reaction were sent to a 60 gallon tank which opened to the hood exhaust. Some of the moisture and volatiles condensed in the tank before the vapors escaped the system. However, there was no attempt to separate or collect any of the products in the vapor stream vented from the reactor.



Figure 3: Block flow diagram of the process licensed by Quantex when the research began.

There was no attempt to weigh any of the vapor products. The only product of the original process, the centrate, was not weighed either on a per experiment basis. After the 55 gallon drum was full, the weight was recorded for the numerous experiments that were performed to fill it. Periodically, the volatiles that did condense in the 60 tank were drained. These volatiles would be added to the drum of extract to reduce the viscosity of the material for the centrifugation step. The volatiles were never collected as a product of the reaction process.

1.4.1 Primary Objectives

The overall objective of this research is to analyze the technology and enhance its potential for commercialization. To complete this task, a primary objective along with several secondary objects must be realized for each section of the process. The primary objectives are to:

(1) Investigate how effective the use of detergent solutions are in removing clay ash from the low-rank Australian coal prior to the liquefaction reaction in the external de-ashing process.

- (2) Increase the efficiency of the internal de-ashing process by evaluating the current centrifuge process and determining the cause of changes that occur in the material as it is processed from ash rich extract into very low ash% centrate and very high ash% tails.
- (3) Design and construct a closed system that performs a single batch process for the digestion reaction and ash removal of lower rank coal that achieves mass closure from the raw materials through the moisture, condensed reaction volatiles, centrate, centrifuge tails, and non-condensable gases.
- (4) Design and construct a system that performs a single batch process for the vacuum distillation of cleaned de-ashed centrate into quality pitch and condensed liquid distillation volatiles while achieving mass closure from input through products.
- (5) Design and construct a system that performs a single batch process for the coking of pitch to produce quality coke from non-caking coals and condensed liquid coking volatiles with an acceptable level of mass closure considering the non-condensable gases produced.
- (6) Develop the coal liquefaction technology to a level where economic and commercial viability can be determined through a mass closure analysis of the entire process from the raw materials through final products, the determination of whether volatile liquids are produced by the process, and performance of final products when subject to commercial testing.

After the method that will be used for de-ashing the coal was determined, the next step towards analyzing the technology and enhancing its potential for commercialization was to re-design the reaction system including any new internal de-ashing methods. The emphasis was placed on achieving mass balance through collecting all of the products of the coal liquefaction reaction process including the vapor phase. The new system will be separate the vapor products into the moisture contained in the coal, the volatile vapors, and the non-condensable gases. The moisture and volatiles will be condensed and collected as products while the non-condensable gases will be sent to a scrubbing system before they are vented to the atmosphere.

The other two products of the new reaction system will be the clean, de-ashed centrate and the centrifuge tails containing the ash material along will the remaining solid material and volatiles. The centrate will be processed through the new vacuum distillation system with the only products being the solid pitch and liquid condensed volatiles. The pitch was further processed into coke using the new coking system. The products of this system are the solid coke, the liquid condensed volatiles, and the non-condensable gases that will be vented to the fume hood. The new coking system also processed the centrifuge tails to recover the remaining volatiles. The concept of this new overall process can be seen in the block flow diagram of Figure 4.

1.4.2 Secondary Objectives

The overall objective is to enhance the potential of the liquefaction technology for commercialization. Each of the first five primary objectives is associated with each of the five steps in the overall process while the final primary objective is the evaluation of the results of all five steps combined. The five steps are external de-ashing, centrifugation or internal de-ashing, reaction, vacuum distillation, and coking and can be seen in the block flow diagram below of the overall process. In order to design, construct, and operate each of the five process steps properly, secondary objectives must also be accomplished.

1.4.3 External de-ashing process secondary objectives

1) To redesign the external ash removal testing system (or Product Development Unit) and test it to determine if it is capable of producing reliable and repeatable results.



Figure 4: Concept for the new coal liquefaction process block flow diagram

- To develop a laboratory to perform proximate analysis testing of the PDU samples, bench scale testing of various detergent blends, and consistent detergent preparation for the PDU.
- 3) Determine if the use of external ash removal for the Australian coals should be pursued.

1.4.4 Internal de-ashing process secondary objectives

- 1) To determine the cause for the increase in viscosity of the extract and centrate during heating and processing of the material.
- To develop and construct a Proof of Concept system to test and verify any new concepts that can improve the efficiency of the process.
- 3) To incorporate any viable internal ash removal concepts into the new production system

1.4.5 Reaction process secondary objectives

- 1) To construct and operate the reaction process to achieve mass closure from the combining of the raw material to the collection of all products from the process.
- To design and construct a new process that combines the digestion reaction process and an ash removal process that is redesigned to increase the efficiency of internal de-ashing of the extract.
- 3) To construct and operate the updated reaction process to produce a high quality centrate suitable for further processing in the vacuum distillation system along with products from the moisture collection system and the volatile collection system.
- 4) To construct and operate the reaction process to minimize or eliminate all of the safety hazards that occur prior to operation, during operation, and during the collection of the products.
- 5) To construct the bunker process with the ability to test control variables by altering the operation conditions and obtaining well representative samples for further evaluation from the analytical laboratory.

1.4.6 Vacuum distillation process secondary objectives:

- To design and construct a vacuum distillation process that inputs a homogenous sample of de-ashed centrate and produces a quality pitch suitable for further processing the coking system, and distillate that could be recycled as CTD in future experiments.
- To design and construct a process to alter and evaluate the control variables with an extensive ability to monitor process conditions.
- To design and construct a distillation column that is capable of extracting pitch samples at different points during the distillation run without affecting the operation of the experiment.
- 4) To design and construct a condensation system that is capable of extracting condensed volatile samples from specific ranges of distillation conditions.

1.4.7 Coking process secondary objectives:

- To design and construct a process that produces condensed liquid coking volatiles and determine if commercial quality coke could be produced from the pitch of non-caking liquefied coal.
- To test a new method of removing solid coke from the coking vessel where the product was produced.
- 3) To design and construct a coking process that achieves a reasonably high mass closure considering the process was not design to collect and weigh the amounts of noncondensable gases produced.
- To design and construct a coking system that not only processes pitch but also processes centrifuge tails to recover the remaining volatiles.

1.5 Accomplishing the Objectives

The customer, Quantex, had a client from Australia, New Hope Coal, who wanted to test the WVU coal liquefaction process with their coal. This coal is a sub-bituminous coal containing about 26% ash. Sub-bituminous and lignite coals had never previously been tested with the WVU process. Furthermore, a coal with such a high ash% has never been tested. The ash in this coal is also primarily clay in origin so the traditional float sink methods for removing the ash from bituminous coal were not suitable.

In order to accomplish the overall research objectives a method for de-ashing lowrank coals that contain clay based ash materials must be determined. There are two approaches to be tested: ash removal before reaction, external de-ashing; and ash removal after reaction, internal de-ashing. In order to de-ash the coal before reaction; the application of the technology being developed by Coal Innovations in Stoystown, Pennsylvania will be tested. The second approach will be accomplished by evaluating the centrifugation procedure that is already incorporated in the WVU process. The first approach will involve studying the equipment and procedures that are being tested in Stoystown and determining what changes must be made so the technology can be adapted for low rank coals. Two different aspects of the external de-ashing will be considered. First, is the process effective when the entire mass of the material is collected and analyzed and second is the process economically viable? The second approach will involve an analysis of the tails from the centrifuge. It was hypothesized that by heating the extract to decrease the viscosity of the fluid, a polymerization reaction between the dissolved coal and CTD occurred. This reaction increased the viscosity which caused the centrifuge to operate will less efficiency. No real proof of such a reaction existed and that hypothesis needs to be tested. If it is true then a different separation procedure, such a high pressure filtration, is needed to accomplish the internal de-ashing task.

The second component of the research objectives requires that a measured mass balance for the entire process is obtained. This is a cradle to grave approach from input materials to products that meet commercial standards. Although there have been attempts to measure a mass balance in the carbon product grant time period, the major goal was in manufacturing samples of materials that could be used for commercial testing; could the material actually be produced at a high enough quality? If commercial grade material could not be produced, then the mass balance was of no consequence. The mass balance was a secondary task with the sample preparation as the primary task and it was very successful. The funded research program was discontinued before a complete mass balance effort could be completed. Now mass balance must be established over the process. The product of the process as defined in the license agreement is the de-ashed extract, however the licensee needs to understand the complete processing from reacting the coal and solvents all the way through coking. This would provide a complete mass balance for the entire process. Several procedures in the process that were previously done by carbon products collaborators will now have to be done at WVU. First, the deashing of coals portion of the project needs to be solved then the appropriate technology incorporated into the dissolution procedure. This will produce a de-ashed extract referred to as centrate. Second, the distillation of the de-ashed extract to distillation volatiles and pitch, which was previously done at Intertek, will have to be done at WVU. Third, a system to produce coke will have to be designed, constructed, and tested. This was previously done by GrafTech.

1.6 State of the Processes When This Research Began

1.6.1 Summary

This section describes the state of this research when the current effort began in 2007. In particular it contains a description of the various laboratory equipment and facilities that were available for the de-ashing of coal located at Coal Innovations in Stoystown, PA. It also contains a description of the facilities and coal dissolution equipment at WVU where the coal dissolution technology was invented. Finally this section deals with the operation of the de-ashing system in Stoystown and the operation of the coal dissolution experimentation at WVU.

1.6.2 Pre-reaction De-ashing of Sub-bituminous Coal

In another project, Dr. Stiller was working as a consultant for a company: Coal Innovations. In this activity the company was trying to reclaim gob wastes. Gob waste fines are a complicated composite material. Frequently the particles are a mixture of good coal, heavy rock ash, and clays. The clays are enriched in the cleaning plants and are discarded with the fine coal particles. The clays act as glue to combine the coal and rock ash together as a composite so that the coal particles cannot be separated from the rock ash by gravity methods without first dispersing the clays. The process being tested by Coal Innovations was a procedure invented by Dr. Robert Bender that uses a series of detergents to disperse the clays. This procedure was explained in detail in United States patents 4,328,002 (Bender, et al., 1982) and 4,560,390 (Bender, et al., 1985). Once the clays were dispersed, the composite gob particle would decompose and the coal could be separated from the rock ash by gravity methods. The company had built a small pilot scale unit to test this hypothesis in Stoystown, Pa next to a 2.5 million ton gob pile seen in Figure 5.



Figure 5: Gob pile located in Stoystown, PA.

The gob material was 56% ash on average. Dr. Bender's mixture included an anionic detergent, a nonionic detergent, a defoaming agent, and urea. The test unit shown in Figure 6 and Figure 7 was a square tank of about 400 gallons. It had an aerator in the bottom. Three hundred and fifty gallons of water were mixed with the chemicals and 350 lbs of coal gob was added. The tank was agitated with an external paddle stirrer. The slurry was pumped from a sump in the bottom of the tank through a density differentiating cyclone. The underflow contained the heavy ash rich material while the coal and clays exited the top flow of the cyclone. The top flow was then run through vibrating screen and the coal particles, that are much larger than the clays, are captured on the screen. The underflow from the cyclone went back into the tank for reprocessing. The particles that were collected from the screen were very low in ash, about 6.5%, but only several pounds of material were collected from the 350 lbs of gob fed to the system.

It was apparent that the system only demonstrates the potential that could exist, but in no way was this practical.



Figure 6: Original testing system for the external de-ashing of coal.



Figure 7: Original mixing tank for external de-ashing of coal

1.6.3 The Coal Liquefaction Facility

When the proposed research on coal liquefaction began, the carbon products group had just completed collecting the 4500 lbs of cleaned filtrate and had sent it to Koppers in Pittsburgh. The system that was used to make this material can be seen in Figure 8 and was housed in the walk-in hood in room 317 of the ERB.

It was composed of a 5 gallon autoclave and a flash tank that was attached to a 60 gallon expansion tank. Ground coal was blended with the CTD in a 55 gallon barrel. The mixture in the barrel was heated and stirred. About four gallons were pumped into the reactor and the reactor was heated to 425°C. The pressure rose to around 1000 psi. After heating for one hour the system was vented to the flash tank that was opened to the evaporation tank. While the flashed off contents were still fairly hot, about 200°C, they were permitted to drain into a 55 gallon drum. The process was repeated while the reactor was still kept hot. This way it was possible to make four to five runs per day. After the reactor had been run for three consecutive days, the 55 gallon barrel was filled with the reacted mixture which is referred to as extract. It then needed to be de-ashed. At first de-ashing was done using a scroll centrifuge but this proved too difficult because the extract could not be heated high enough to reduce the viscosity sufficiently for effective separation. The bearings of the centrifuge were only safe at temperatures less than 100°C. The second attempt to de-ash the extract involved the use of a pressure filter. This proved ineffective because the temperature needed to conveniently handle the material causes it to have a thick pasty consistency and soon blinds the filter material. Finally a bowl centrifuge was tested. This is the same type of bowl centrifuge used to clean motor oil from diesel engines and is capable of functioning at higher temperatures.

Initial tests using this centrifuge method proved successful so a large unit capable of cleaning a 55 gallon drum of the reacted mixture was purchased. This type of centrifuge uses the force of a pumped fluid to cause the bowl to rotate. There are relationships between the flow velocity and the rotation speed of the bowl that permit us to closely approximate the gravitational forces on the system. The larger centrifuge required a 15 gallon/minute flow to be effective.



Figure 8: Original Reaction system housed in the Room 317 Laboratory of the Engineering Research Building

The following describes the equipment and procedure for centrifugation. Once a 55 gallon drum of extract was produced it was taken into the next hood where the centrifuge was housed. The extract was heated to about 70° C. At this temperature the fluid did flow but had a viscosity of about 300 cp – the consistency of motor oil. A diaphragm pump was used to pump the extract from the 55 gallon acting as a reservoir through the centrifuge that was attached to the lid of the drum. The cleaned extract then drained back into the reservoir drum. This way the extract could be continuously re-centrifuged until

the proper ash% was produced or the centrifuge turbine filled which can be seen in Figure 9. If the turbine filled before the proper ash% was reached, the turbine was removed and cleaned. The turbine was placed back into the system and the process repeated until the desired ash%, which was less than 0.05%, was achieved in the centrate. The filter cake was removed as batches were centrifuged. The clean de-ashed centrate is the product of the WVU process as defined by the university in agreement with Quantex.



Figure 9: Centrifuge tails from the previous internal de-ashing system.

1.6.4 Beginning of Operation in the Bunker Facility

Soon after the quantity of pitch needed by Koppers was made, the laboratory in 317 suffered a major setback. The heater controller on the heater bands that surrounded the 5 gallon reactor in the hood of room 317 remained on overnight. This caused the steel autoclave sidewalls to creep and deform. The 5 gallon autoclave was no longer able to function. Because the Carbon Products group still had some contractual commitments

to make de-ashed extract, we resorted to using the 10 gallon autoclave that was housed in the bunker building below the Engineering science building. Since the procedure using the 5 gallon reactor system worked so well it was decided to duplicate the same reaction procedure in the 10 gallon system. So the same reactor system that existed in room 317 was employed in the bunker. The system consisted of a reactor that drained into a flash tank that was opened to an expansion/evaporation tank. When cooled, the extract in the flash tank was drained into a 55 gallon barrel. The 10 gallon reactor is located on the mezzanine level of the bunker so loading it was somewhat problematic. The top of the reactor is equipped with a port through which a fluid mixture could be loaded into the reactor. About 8 gallons of reaction mixture was hoisted up to the reactor on the mezzanine in a 20 gallon vessel. The vessel had a drain port through which its contents could be emptied though the lid of the reactor. The reactor could then be sealed and the material in the unit could be heated to reaction temperature while being continuously stirred.

After maintaining the mixture at temperature for one hour a valve at the bottom of the reactor was opened and the system drained into a flash tank. A valve on top of the flash tank was opened and a ¹/₂" tube carried any volatiles to the 120 gallon expansion tank. There was a water cooled condenser attached to the top of the tank to condense the volatiles. This aided in the condensation of the volatiles which prevented over pressurization of the expansion tank. When the liquid in the flash tank cooled to the temperature at which it could be handled, a valve on the bottom was opened and the fluid was drained into a receiving 55 gallon drum. This procedure was run repeatedly until the

55 gallon drum was filled. When it was filled the barrel and its contents were moved to the centrifuge system that was still housed in room 317 where it could be centrifuged.

Before the material could be centrifuged it had to be heated so it flowed. This was done with flexible band heaters. Because the barrels have diameters that are 20 inches it takes a significant amount of time for the heat to penetrate so that the contents are uniformly heated. During this process the extract becomes thinner and then became thicker. This anomalous behavior caused the belief that the system might be polymerizing. This effect was controlled by not heating the extract beyond 70°C before centrifugation. At that temperature some of the materials in the extract seemed to coalesce to a thick gel. During centrifugation this material was separated from the lighter more fluid material and collected on the walls of the bowl of the centrifuge. As a result the typical ash of the tails in the centrifuge was only about 20%. Although the centrate was effectively de-ashed the loss of so much material in the centrifuge was a matter of major concern.

The other process components needed to evaluate a mass balance over the process did not exist. There was no unit to distill the de-ashed centrate and make pitch and additional liquid volatiles. There was no unit to coke the pitch and collect addition liquid volatiles. It was felt that the condensed volatiles from the coking system and distillation system would be needed to effectively recycle the solvent as required by the process. To get a complete mass closure "cradle to grave" these units would have to be designed and constructed from concept and tested to evaluate the results.

CHAPTER II: BACKGROUND

2.1 Introduction

The documentation contained in the Background chapter was first described in the dissertation of Barbara E. Bennett "The Effect of Calcination Conditions on the Graphitizability of Novel Synthetic and Coal-Derived Cokes" (B. E. Bennett 2000), the thesis of Brian Wayne Bland "Design, Construction, and Evaluation of Coal Extraction Pilot Plant to Manufacture Coal Based Carbon Pitch" (Bland 2000), the thesis of Kevin Whiteman "The Design, Construction and "Optimization" of a Binder Pitch Refining Unit" (Whiteman 2005), and the thesis of Manoj Katakdaunde "Performance Study in the Hydrotreatment of Coal with Coal-Derived Solvents" (Katakdaunde 2004). This portion of the dissertation is a compilation of information gathered from these four documents. This dissertation is a combination and advancement of information previously gained through past research of these four individuals.

2.2 Coal

Coal is a term given to widespread and greatly differing natural rocks that consist primarily of organic material mixed with inorganic materials. Coal can be defined as a compact stratified mass of lithified plant material. This plant material has been modified chemically to varying degrees, and interspersed with smaller amounts of inorganic materials (Francis 1954). The plant material builds up and partially decomposes in the absence of oxygen to form a mixture of organic and significant inorganic mineral matter. The mineral matter is then compressed to form a heterogeneous carbonaceous rock of organic origin. Coal varies from region to region and era to era. Coal is a mixture of material that is formed from diverse ingredients then subject to heat and pressure to produce a visibly heterogeneous product seen below. The ingredients are composed of trees, ferns, rushes, lyco-pods, and several thousand-plant species that have been identified in coal beds. Plant remains of similar types have been found in all types (ranks) of coal, but the relative amounts vary considerably. Therefore, the composition of coal varies considerably.



Figure 10: Example of Raw Coal

2.2.1 Formation of Coal

Coal is formed from the collection of plant debris under the correct conditions. This formation usually takes place in a swamp or shallow lake where the debris accumulates and partially decomposes to a material called peat. The peat then becomes lithified in what is termed the "coalification" process. The coalification process shown in the figure below is a progressive change in the plant debris as it is transformed from peat to lignite and then through the higher ranks of coals to anthracite. The degree of coalification generally determines the rank of the coal. This process is not a series of straightforward chemical changes; rather, it is a metamorphosis. The metamorphosis of the plant debris not only relies on time but also temperature and pressure, as is shown in Figure 11. The major influences in the coalification process are believed to be the resulting heat and pressure developed because of the overlying sedimentary cover or overburden. Under the correct conditions, oxygen and hydrogen are progressively eliminated. The ultimate final product contains about 90% by weight carbon, i.e., anthracite (Speight 1983).



Figure 11: Schematic Representation of Coalification Process (Speight 1983).

2.2.2 Classifications of Coal

As described earlier, coal is actually a generic term given to widespread and greatly differing natural rocks that consist primarily of organic material mixed inorganic materials. Coal ranges from a soft, moist, brownish material to a very hard, glossy, black solid. With the wide span of compositions and properties, there is a need to have some standard way of describing and classifying coal. The traditional procedure of characterizing coal relies on the following three types of analysis (Schobert 1987).

1) Proximate Analysis: The first method of examining coal is used to evaluate its fuel potential. This method of coal analysis was developed as a simple means for classifying coal by determining the product distribution from coal during heating under standard conditions. Proximate analysis of coal is expressed in terms of the following four constituents:

A) Moisture- Moisture or water is lost upon heating coal to 105°C

B) Volatile matter- The gases and vapors driven off during pyrolysis. (i.e. heating to 800°C in the absence of oxygen).

C) Fixed Carbon- The carbon remaining as the nonvolatile fraction of the pyrolysed coal.

D) Ash- The mineral matter or .ash. that is left after complete combustion of coal, or by heating to 750°C, in the presence of oxygen.

Results from proximate analysis confirm the observation of great variability among coals. The moisture content in coals ranges from nearly zero to almost 70%. The volatile matter ranges from 5% to 60%. The ash content varies from 1% to 35%. And fixed carbon ranges from 20% to 85%. Proximate analysis is relatively quick and easy to perform and is useful in making experimental predictions of the behavior of coal and classification type. 2) <u>Heating Value</u>: This analysis determines the amount of energy that can be obtained by burning the coal, and is termed as the heating value or calorific value of coal. This value is usually reported in BTU/lb.

3) <u>Ultimate Analyses</u>: This analysis is done using IR spectroscopy or the following set of analytical procedures to determine the elemental composition of coal in terms of the weight percentages of carbon, hydrogen, nitrogen, oxygen, and sulfur.

Reacting the coal and separating the materials produced determine the compositions of these elements. (1) Carbon and hydrogen: Burning the coal and collecting the resulting carbon dioxide and water in chemicals that can absorb them is used to measure the carbon and hydrogen. These chemicals are weighed to determine the weight gain and calculate the amount of carbon and hydrogen consumed. (2) Sulfur: One of the common methods to determine the sulfur is to convert it to sodium sulfate, which can then be converted to barium sulfate. The Barium sulfate is collected dried and weighted. (3) Nitrogen: Nitrogen is converted to ammonia, which is then absorbed in a known amount of acid. The difference in the acid is used calculate the amount of ammonia made during the experiment. (4) Oxygen: There is no simple analytical method for determining the amount of oxygen. The most commonly used method today involves bombarding the coal with neutrons to convert the oxygen to unstable isotope of nitrogen (nitrogen-16). The nitrogen-16 rapidly decays emitting beta (β) and gamma (γ) rays, which can be detected and counted. The table below shows the average ultimate analysis of different classifications of coals.

Table 1: Classification Profile Chart

				Average Analysis-moisture and ash-free					
			Volatile				Heating		
			Matter	Hydrogen	Carbon	Oxygen	Value		
Class		Group	(%)	(wt.%)	(wt.%)	(wt.%)	(kJ/kg) ^a	\mathbf{C}/\mathbf{H}	(C+H)/O
I. Anthracite	1	Meta-anthracite	1.8	2.0	94.4	2.0	34425	46.0	50.8
	2	Anthracite	5.2	2.9	91.0	2.3	35000	33.6	42.4
	3	Semianthracite	9.9	3.9	91.0	2.8	35725	23.4	31.3
II. Bituminous	1	Low volatile bituminous coal	19.1	4.7	89.9	2.6	36260	19.2	37.5
	2	Medium-volatile bituminous coa	al 26.9	5.2	88.4	4.2	35925	16.9	25.1
	3	High-volatile A bituminous coal	38.8	5.5	83.0	7.3	34655	15.0	13.8
	4	High-volatile B bituminous coal	43.6	5.6	80.7	10.8	33330	14.4	8.1
	5	High-volatile C bituminous coal	44.6	4.4	77.7	13.5	31910	14.2	6.2
III. Subbituminous	1	Subbituminous A coal	44.7	5.3	76.0	16.4	30680	14.3	5.0
	2	Subbituminous C coal	42.7	5.2	76.1	16.6	30400	14.7	5.0
	3	Subbituminous B coal	44.2	5.1	73.9	19.2	29050	14.6	4.2
IV. Lignite	1	Lignite A	46.7	4.9	71.2	21.9	28305	14.5	3.6
	2	Lignite B	-	-	-	-	-	-	-

^a To Convert kJ/kg to Btu/lb, divide by 2.326

Source: (Hensel 1981)

2.2.3 Rank of Coal

Coal may seem to be a homogeneous substance, but it is not. Like the vegetation from which it was formed, coals composition varies greatly from one region to another. The can even vary from one seem to the next. The vast variety and complexity of the properties and composition of coal made it necessary to develop a procedure to classify it. The classification of some of these properties was necessary for the selection of a standard way to rank or classify different coals for research. Many coal properties and numerous items of commercial description have been proposed as a basis for categorizing coal. The most common of these is "rank", which is a measure of the degree of coalification that the organic plant sediment has reached in its metamorphosis from peat to near graphite-like material. Changes in the metamorphosing coal can be generalized as follows (Smith, Flecher and Pugmire 1994):

- a) moisture content decreases, rapidly in the early stages, slowly in the later stages
- b) carbon content increases while oxygen content decreases
- c) hydrogen content changes little until late stages of coalification where it decreases rapidly
- d) volatile matter generally decreases
- e) calorific value increases, levels off, then drops off slightly

A set of labels for different kinds of coal could help separate coals into classifications having roughly similar properties. For coal in the United States, the classification is made on the basis of rank, and the names of the coal ranks are labels that provide some information about the coal. The rank of coal indicates the extent of the geological maturity of the coal, the carbon content, the volatile matter, and the heating value. In the United States the American Society for Testing and Materials (ASTM) developed the system that is currently used for classification of coal by ranks.

Classification of coal by rank is specified from knowledge of the proximate analysis and calorific value of a coal. Rank is not necessarily directly related to the carbon content of coal or any other specific coal structure. There are four main ranks of coal. These ranks are further broken done into groups to classify the coal. The ASTM Designation D 388-84 (1984), as seen in the table below, is the standard specification for the classification of coal by rank in North America. In this system the higher rank coals are specified by the percentage of fixed carbon from the proximate analysis on a dry, ashfree basis. Lower rank coals contain less than 69% fixed carbon, and are classified by their calorific value on a moist basis. Agglomerating characteristics of coals are used to distinguish between groups, such as between sub-bituminous A and high volatile C bituminous (ASTM 1984).

Table 2: ASTM Standard Classification of Coal by Rank

			Fixed Carbon		Volatile Matter		Caloric Value		
			Limits (%)		Limits (%)		Limits (Btu/lb) ^b		
			(dry mineral-matter		(dry mineral-matter		(moist ^e ,mineral-matter		Agglomerating
			-free basis)		(dry me basis)		-free basis)		Characteristics
Class		Group	>	<	>	<	>	<	
I. Anthracite	1	Meta-anthracite	98	-	-	2	-	-	Nonagglomerating
	2	Anthracite	92	98	2	8	-	-	
	3	Semianthracite ^d	86	92	8	14	-	-	
II. Bituminous	1	Low volatile bituminous coal	78	86	14	22	-	-	Commonly
	2	Medium-volatile bituminous coa	al 69	78	22	31	-	-	Agglomerating ^f
	3	High-volatile A bituminous coal	-	69	31	-	14000 ^e	-	
	4	High-volatile B bituminous coal	-	-	-	-	13000	14000	
	5	High-volatile C bituminous coal	g _	-	-	-	11500	13000	
			-	-	-	-	10500	11500	Agglomerating
III. Subbituminou	us 1	Subbituminous A coal ^g	-	-	-	-	10500	11500	Nonagglomerating
	2	Subbituminous C coal	-	-	-	-	9500	10500	
	3	Subbituminous B coal	-	-	-	-	8300	9500	
IV. Lignite	1	Lignite A	-	-	-	-	6300	8300	Nonagglomerating
	2	Lignite B	-	-	-	-	-	6300	

- ^a This classification applies to coals composed mainly of vitrinite; coals rich in liptinite or inertinite do not fit into this classification system.
- ^b Standard units for ASTM classification for calorific value are Btu/lb. To convert to SI units of kJ/kg, multiply Btu/lb by 2.326.
- ^c Moist refers to coal containing its natural inherent moisture but not including visible water on the surface of the coal.
- ^d If agglomerating, classify in low-volatile group of the bituminous class.
- ^e Coals having 69% or more fixed carbon on a dry, mineral-matter-free basis are classified according to fixed carbon only, regardless of calorific value.

- ^f It is recognized that there may be nonagglomerating varieties in these groups of bituminous class, and that there are notable exceptions in the high-volatile C bituminous group.
- ^g Agglomerating coals in the range 10,500-11,500 Btu/lb are classed as high-volatile C bituminous coal.

2.2.4 Petrography: The Components of Coal

Coal petrography is a visual examination of coal revealing basic chemical and physical properties of its constituents. These visual observations are performed with a microscopic or simply with the naked eye. Microscopic visual observations reveal what are called macerals. Macerals are organic substances derived from plant tissue, cell contents, and animal remains that were incorporated into sedimentary strata, and then altered physically and chemically by natural processes (Gorbaty, Larsen and Wender 1982).

The macerals in coal tend to be aromatic in nature. The carbon content of coal can be classified as aromatic, hydroaromatic, or aliphatic. The aromaticity of coal increases with rank with 40-50% for sub-bituminous coal, and over 90% for anthracite (Larsen 1978). In a typical bituminous coal, 65% to 75% of the total carbon is aromatic, 15% to 25% is hydroaromatic and 5% to 10% is aliphatic.

Bands of material called lithotypes are able to be seen with the naked eye running through samples of bituminous coal. Coal lithotypes arise from different conditions that existed during the coalification process of the coal. Coal contains the following four types of these bands (Schobert 1987):

 Vitrain - a glossy black material that breaks in a circular pattern (called conchoidal fracture) similar to the way glass breaks when chipped;

- 2) Clarain a glossy black material that breaks horizontally;
- 3) Durain -.a dull black material having a granular appearance;
- 4) Fusain -.a material that resembles charcoal.

Lithotypes are composed of macerals, which can be distinguished under a microscope. The three main macerals groups are vitrinite, exinite, and inertinite. Vitrinite is derived from variously decomposed woody tissues. Exinite is derived from spores and pollen coats, cuticles, resins, and other fatty secretions. Inertinites are derived mainly from partial carbonization of various plant tissues in the peat stage.

2.2.5 Organic Component of Coal

The organic matrix of the coal consists mainly of carbon with a smaller amount of hydrogen, oxygen, nitrogen, and sulfur. Coal is actually an aggregate of microscopically distinguishable, physical distinctive, and chemically different macerals and minerals (Gorbaty, Larsen and Wender 1982).

The organic materials in coal are derived mainly from plant remains that have undergone various degrees of decompositions in the peat swamps and various degrees of chemical and biochemical alteration after burial (Meyers 1982). These organic components are composed of large polymer like carbonaceous molecules seen in the figure below (Wiser 1975). The physical and chemical properties of these molecular structures determine the coal properties (Gorbaty, Larsen and Wender 1982).



Figure 12: High-Volatile Bituminous Coal Model Showing the Functional Groups

The major chemical functional groups identified in the coal include hydroxyls, carbonyls, aliphatic bridges, heterocyclic ring units, and aromatic ring units (Larsen 1978). A typical bituminous coal consists of clusters of aromatic and hydroaromatic carbon rings. The following figure shows the major heteroatom functional group types found in coal. Oxygen occurs predominately as phenolic or etheric groups with fewer amounts of carboxylic acids or esters. Sulfur has about the same heteroatom functional groups as oxygen in coal although sulfoxides are not as well defined. Nitrogen occurs predominately as pyridine or pyrolic type rings (Larsen 1978).



Figure 13: Heteroatom Functionalities in Coal

2.2.6 Inorganic Component of Coal

The inorganic matter normally found in coal consists mainly of the minerals deposited with the coal when it was formed. The inorganic minerals are different from ash. The ash is the inorganic oxides that are left after complete combustion of the coal. This inorganic or mineral matter is derived from several sources: transported and deposited by water or air, direct precipitation from solution, precipitation by organic metabolism, etc. The mineral matter deposited in the coal is mainly in the form of aluminosilicates or clay, carbonates, sulfide ores, oxide ores, quartz, and phosphates (Speight 1983). The mineral content of coal can be as high as 35%. The minerals are usually present in the coal as layers or bands (Meyers 1982). These bands or layers are caused by sedimentation of inorganic substance between layers of organic matter. When

the coal is burned these minerals are oxidized to form ferric oxide, calcium oxide, magnesium oxide, sulfur oxide, etc. These oxides are the main constituents of the coal ash.

2.2.7 Inorganic and Organic Sulfur Contained in Coal

Of the eighty elements found in coal, the one beside carbon having the most significant effect on coal use is sulfur. When the sulfur in coal is burned, it produces sulfur oxides that are felt to produce acid rain. The chemistry of the production of the sulfur oxides has been extensively studied. The sulfur in coal has prompted the spending of billions of dollars on equipment and processes to capture the sulfur oxides or to reduce the sulfur content of the coal before it is burned. All coals contain some degree of sulfur. The amount ranges from 0.1% to 10% by weight (Eliot 1978). The average in most coal samples ranges from 1% to 4% by weight. Traditionally the sulfur in coal can be classified as either inorganic or organic. The inorganic sulfur is further broken down into pyritic sulfur and sulfate sulfur as follows:

1) Organic sulfur is a part of the molecular composition of the coal itself.

2) Pyritic sulfur occurs in the mineral pyrite and some related minerals.

3) Sulfate sulfur is mostly iron sulfates.

Organic sulfur, which cannot be removed by physical separation, comprises from 30% to 70 % of the total sulfur contained in coal. Generally, the organic sulfur to total sulfur ratio is the highest for low sulfur coals and decreases as the total sulfur content increases (Eliot 1978). In most bituminous coals, the majority of the sulfur is pyritic sulfur (Schobert 1987).

Pyritic sulfur is sulfur bonded with iron. It is commonly referred to as fool's gold. It occurs in coal as discrete crystals but also as microscopic particles is coal. It is a dense mineral with a specific gravity of around 5.0. This is a specific gravity much higher than coal which has a maximum specific gravity of 1.8. Pyrite content of a coal can be reduced significantly by size reduction and subsequent specific gravity separation. This is a common practice in coal cleaning plants once the coal has been mined. In most coals, sulfur in the form of sulfate is only a small fraction of the total sulfur (less than 0.05%). The sulfate is normally an oxidation product, which is water-soluble and can easily be removed. The problem with sulfate is that it is also soluble in most solvents.

2.2.8 Carbon product precursors

One of the major emphases of research at WVU was to produce carbon product precursors. Carbon products refer to materials such as pitches, cokes, and graphite that are produced on a commercial scale and are used in the metals winning industries. Because these play an important role in the WVU process it is imperative that a discussion which defines carbon materials and their precursors, their chemistries and properties is appropriate.

2.3 A Review of Carbon Materials and Carbon Science

2.3.1 Carbon

Carbon is the most versatile and widely studied element known to man. This is evidenced by the fact that organic chemistry is an entire branch of chemistry and is devoted solely to the study of carbon-containing compounds. Carbon is unique in that it possesses an electron configuration which allows single, double, and triple bonds to be formed. Carbon can bond with itself as well as with most other elements. Carbon also possesses the ability to form cyclic and aromatic compounds which are very stable, planar, monocyclic compounds composed of alternating single and double bonds (Carey and Sundberg 1990). Carbon exhibits unsurpassed versatility both as a compound constituent and in its elemental form. Elemental carbon can be found in nature in either amorphous or crystalline forms. Exotic carbon-carbon molecular structures have also been synthesized in laboratories.

2.3.2 Amorphous Carbon

An amorphous carbon or material, by definition, is simply a material which does not possess long-range atomic order (Callister 1994). These materials should not be confused with polycrystalline carbonaceous materials which are composed of small crystallites congregated together, irrespective of crystallite orientation. There are many different types of amorphous carbon materials and different methods of obtaining an amorphous carbon structure.

Organic chars are a simple example of an amorphous carbon, the most notable of which is charcoal. The chars are obtained from the devolatilization of complex organic materials or biomass composed of large, high molecular weight molecules. The amorphous char is obtained by heat-treating the organic material under a non-oxidizing atmosphere to drive off low-molecular-weight compounds. The result is a highly porous solid where the complex polymeric carbon skeleton is left relatively intact (Marsh 1989).

2.3.3 Crystalline Carbon

Carbon is an element which exhibits polymorphism, which means carbon has more than one distinct crystal structure (Callister 1994). Carbon can be found in nature in either of two distinctly different crystalline forms or allotropes—diamond or graphite. Diamond has only one, well-defined, crystalline structure while graphite has two primary crystalline configurations—a hexagonally stacked crystal configuration and a rhombohedrally stacked crystal configuration.

2.3.3.1 Diamond

Diamond consists of a three dimensional network of carbon atoms arranged in a tetrahedral formation seen in Figure 14. Each carbon atom is bonded covalently to four neighboring carbon atoms in an sp³ configuration. At room temperature and pressures below 60 kbar, this particular carbon allotrope is thermodynamically metastable. At pressures above 60 kbar it is stable (Köchling, McEnaney and Rozploch, et al. 1982).

The locked three-dimensional molecular structure of diamond results in unsurpassed stability and makes diamond one of the hardest materials known to man. The electrons are also very tightly bound and therefore diamond exhibits a low electrical conductivity. Diamond also possesses an unusually high thermal conductivity for a nonmetal and is optically transparent (Callister 1994).



Figure 14: The crystal structure of diamond (Marsh 1989).

Diamond is prized by mankind both for its beauty and its utility. Diamonds have been used in jewelry and for decorative purposes for centuries. The demand for highquality diamonds by man for aesthetic reasons has resulted in a limited availability and increased cost for diamonds. Thus, the use of diamond in industry has, in the past, been limited to specialized applications.

Diamond is used in industry and valued for its hardness. It is used extensively in abrasives and cutting tools. Despite the exceptional mechanical and physical properties of diamond, its use in industry is still somewhat limited because natural diamonds are prohibitively expensive and suitable (cost-effective) methods of synthesizing diamond have only recently been commercialized (Callister 1994).

2.3.3.2 Graphite

Graphite consists of layer upon layer of two-dimensional, connected, six-member carbon rings. An individual sheet of carbon within the lamellar structure is called a graphene sheet or layer (Charlier, Gonze and Michenaud 1994). The graphene layers can either be stacked in a hexagonal or rhombohedral formation. The hexagonal arrangement occurs when the graphene layers are arranged in an alternating ABAB fashion as shown in Figure 15. This type of hexagonal stacking is also sometimes referred to as the Bernal crystal structure (Charlier, Gonze and Michenaud 1994). The rhombohedral formation consists of graphene layers stacked in a repeating ABCABC fashion as shown in Figure 16 (Marsh 1989).



Figure 15: Graphite Crystal Structure With Hexagonal Stacking Arrangement

Both graphite allotropes are highly anisotropic because the molecular structure and thus the properties of the material vary depending on the orientation of the crystal with respect to the graphene planes. The single carbon atoms within a graphene sheet are bonded covalently with one another in the sp^2 arrangement (trigonal bonding) while bonding between graphene sheets is primarily attributed to van der Waals forces.



Figure 16: Graphite Crystal Structure with Rhombohedral Stacking Arrangement

The sp² bonding between the atoms within a graphene sheet implies both sigma and pi bonding. The delocalized pi electrons between the graphene sheets results in high electrical and thermal conductivity in the direction parallel to the graphene planes. Pi bonding and thus delocalized electrons are not present in the direction perpendicular to the graphene sheet and thus the conductivity is significantly less in that direction. The thermal and electrical conductivities in the direction perpendicular to the graphene planes are two orders of magnitude less than the conductivities in the direction parallel to the graphene planes (Thomas 1993). Values determined experimentally for the thermal conductivity of graphite measured parallel to the graphene planes achieve a maximum of 28 W/cm-K at 80 K (-193 °C) while the thermal conductivity measured perpendicular to the graphene planes achieves a maximum of only 0.2 W/cm-K at 75 K (-198 °C) (Kelly 1969). The electrical resistivity, which is the inverse of electrical conductivity, of graphite at 25 °C parallel to the graphene planes was measured to be only 3.9 x 10⁻⁵ Ω -cm while the electrical resistivity perpendicular to the graphene planes was found to be 1 x $10^{-2} \Omega$ -cm (Kinoshita 1988).

Another distinctive aspect inherent to graphite due to its anisotropic nature is there are large differences in the coefficient of thermal expansion (CTE) in the direction parallel to the graphene planes versus the direction perpendicular to the graphene planes. In the perpendicular direction of the graphene planes, the CTE is a function only of temperature and is constant at about 28 μ m/m/°C (Orac and Chang 1991). In the parallel direction of the graphene planes, the CTE is low and variable as shown in Figure 17.



Figure 17: Effect of Temperature on the CTE (a) of the Graphite Crystal Parallel to the Graphene Planes (Orac and Chang 1991)

Graphite and graphitic materials rarely consist of only one crystal configuration, and often, the graphitic material is comprised of both graphite allotropes along with pseudo-graphitic material. The weak van der Waals forces in the direction perpendicular to the graphene planes allow sliding of the graphene layers across one another. Often, the graphene layers will not be aligned properly in either crystalline configuration because the layers have slipped axially out of position. The graphitic material formed when the graphene layers are rotated and translated out of their crystalline position is called turbostratic graphite (Charlier, Gonze and Michenaud 1994). Natural graphite usually consists of no more than 5% to 15% of rhombohedral crystal structure mixed with the Bernal form along with disordered or turbostratic graphite (Charlier, Gonze and Michenaud 1994).

Graphite possesses many desirable properties. Graphite is relatively inert in a non-oxidizing environment. In addition to high electrical and thermal conductivity, graphite exhibits high thermal shock resistance, excellent high temperature strength, high sublimation temperature, and a low modulus of elasticity (Callister 1994). Graphite is among the few materials whose strength increases with increasing temperature. Carbon and graphitic artifacts experience increasing strength with increasing temperature up to about 2500 °C, as shown in Figure 18 (Mantell 1979).



Figure 18: Increase in Graphite Strength as a Function of Temperature (Mantell 1979)

Graphite and graphitic materials have many different industrial applications. Graphite and graphitic materials are very advantageous as structural materials for hightemperature applications due to their increased strength at high temperatures. The high conductivity of graphite is exploited for use in electrodes in metal production. Graphite is used extensively as a lubricant (the weak van der Waals forces perpendicular to the graphene planes allow sliding of the graphene layers across one another and thus result in a lubricating effect). The properties of graphite allow for a seemingly endless number of applications.

Graphite, unlike diamond, can be easily synthesized. Presently, there are two main methods by which graphite or a graphitizable precursor material can be manufactured—a high-temperature process and a low-temperature process. In the hightemperature process, graphite is formed by chemical vapor deposition (CVD) of cracked light hydrocarbons at temperatures exceeding 2100 K (1827 °C) (Marsh 1989). The graphite produced is referred to as pyrolytic graphite (Köchling, McEnaney and Rozploch, et al. 1982). This CVD procedure can also be broken into two separate steps. The material is then further heat-treated to above 2500 K (2227 °C) to promote graphitization.

In the low-temperature production of graphite, high-molecular weight organic materials, known as pitches, are first carbonized (or heat-treated) to temperatures generally below 500 °C. The resultant material—known as coke—is then further heat-treated to promote graphitization (Marsh 1989). The low-temperature graphite production scheme will be discussed further in subsequent sections.

2.3.4 Non-Graphitizable Versus Graphitizable Carbonaceous Materials

Most synthetic graphite and graphitic-based materials are formed by the carbonization and subsequent high-temperature heat-treatment of high-molecular-weight organic materials. However, it is important to note that not all organic materials can be used as graphite precursors. Therefore, carbonaceous materials are divided into two categories—non-graphitizable and graphitizable.

Non-graphitizable materials are defined as those materials in which the carbon cannot be rearranged into a crystalline graphite matrix merely by high-temperature heat-treatment up to 3300 K (\sim 3000 °C) under atmospheric or lower pressure conditions (Köchling, McEnaney and Rozploch, et al. 1982). Graphitizable materials are defined as those materials which can be converted to graphite by heat-treatment to high temperatures—up to 3000 °C.

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2.3.3.1 Non-Graphitizable Carbon

Non-graphitizable carbon materials are generally comprised of high-molecular weight polymeric species where the carbon skeleton is rigid and locked into place (sometimes due to cross-linking) and cannot rearrange itself into a continuous planar polycyclic structure. Heat treatment results in the loss of small-molecular-weight molecules and perhaps even additional cross-linking. The result is an amorphous carbonaceous char where the carbon skeleton has maintained much of its original configuration. Wood and similar organic materials are examples of non-graphitizable carbonaceous materials which result in char upon heat treatment. Certain non-fusing coals (anthracite) and complex polymers are also non-graphitizable (Marsh 1989).

2.3.3.2 Graphitizable Carbon

Graphitizable carbon materials are comprised mostly of high-molecular-weight molecules constructed primarily of connected cyclic and/or aromatic rings. These carbonaceous materials are called pitches. Heat-treating these materials results in the material becoming fluid. Heat allows the large polycyclic-ring molecules to flow and reorient themselves into stacked layers as shown in Figure 19 (Mochida, Fujimoto and Oyama 1994) while further ring formation occurs. Continued heating results in synthetic graphite as shown in Figure 20 (Marsh 1989).


Figure 19: Model of the Lamellar Structure In a Pre-Graphitic Carbon (Mochida, Fujimoto and Oyama

1994)



Figure 20: Model for the Production of Synthetic Graphite from a Graphitizable Carbon (Marsh 1989).

2.4 Pitches

Graphitizable carbonaceous materials comprised of high-molecular-weight molecules constructed primarily of connected cyclic, heterocyclic (cyclic molecules containing heteroatoms), and aromatic rings are generically referred to as pitches. These substances are derived from organic precursors and are generally solid at room temperature. These materials also exhibit a broad softening range instead of a welldefined melting temperature (Köchling, McEnaney and Rozploch, et al. 1982). This softening range is dependent upon the amount of volatile material in the pitch. Softening point refers to the temperature above which the pitch can freely flow. Some pitches are synthesized from polycyclic and polyaromatic organics such as naphthalene, while other pitches are obtained from petroleum resids or derived from coal (Marsh 1989).

Pitches can be derived from either petroleum or coal. Pitches are hydrocarbon materials that exhibit softening characteristics above ambient temperature, prior to devolatilization. That is, pitch is solid at ambient temperature and undergoes a phase change as it is heated. Pitches typically do not have a true melting temperature, since they are often comprised of many chemical species. Thus, raw coal is not considered to be a pitch because coal usually devolatizes before it softens. Although "tar" is sometimes used interchangeably with "pitch," in general, "tar" refers to a hydrocarbon material prior to distillation, and the "pitch" is the remainder after lighter, lower-boiling-point chemicals have been distilled off.

Metallurgical coke ovens produce metallurgical grade coke by devolatilizing coal at high temperatures. The volatile chemicals are condensed as coal tar, which is collected and sent to a distillation plant. The lower boiling point liquids are distilled into different

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fractions, leaving behind a pitch. This pitch can be tailored into different grades such as binder pitch or impregnation pitch.



Figure 21: Metallurgical coke oven schematic showing coal tar pitch recovery. Courtesy of Koppers Industries.

Likewise, petroleum pitch is obtained as the bottoms or heavier molecules from petroleum distillation. Petroleum pitch quality varies widely depending on the source of crude petroleum and the type of refining techniques used. Some petroleum pitches are of sufficiently high quality that they can be blended with coal tar pitch to be used as binder pitch or impregnation pitch. Other petroleum pitch can be used as a precursor for different types of coke.

As discussed in the preceding analysis, there are two main sources of feedstock for carbon products used in metals smelting industries:

a. *Coal tar pitch* is obtained as a condensable byproduct from metallurgical coke ovens. It is used as the primary source of binder pitch, although in recent years petroleum pitch is being used as an extender or blending agent. b. *Petroleum pitch*, obtained at the bottoms from petroleum refining processes is used to produce virtually 100% of the anode coke and needle coke used in the metals smelting industries. The anode coke is used to produce Hall-Heroult anodes for the aluminum industry, and needle coke is used mainly for electrodes incorporated in arc furnaces. Petroleum pitch can also be used as an extender for binder pitch and impregnation pitch.

Both feedstocks are in short supply, and their future viability is in question. The supply of binder pitch in the United States has been steadily decreasing over the past decades. One of the main reasons is it a commodity business with small profit margins. In addition, there is an environmental burden created by coking coal to create metcoke, which has decreased the attractiveness of producing metcoke and consequently the coal tar byproduct. If new coke ovens are built in the US, they will likely combust nearly all of the volatiles to produce energy, with excess energy being used to produce electricity (referred to as a "non-recovery metcoke oven"). Thus these newer ovens will not offset losses in coal tar production elsewhere.

2.4.1 Synthetic Pitches

Synthetic pitches are generally produced by condensing or polymerizing cyclic or aromatic compounds. One of the most widely used synthetic pitches is the Mitsubishi AR pitch. This pitch is produced by polymerizing naphthalene using an acid catalyst (Mitsubishi Gas Company). The pitch is 100 % anisotropic and is relatively homogeneous compared to most petroleum and coal-derived pitches. This pitch has virtually no heteroatomics present (Mitsubishi Gas Company).

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2.4.2 Petroleum Pitches

Petroleum pitches are obtained as by-products of petroleum refineries. The highmolecular-weight resids found at the bottom of the distillation tower or from a cracking process are the source of petroleum pitches. The heavy resids can be upgraded into pitch by thermal treatment, vacuum or steam stripping, oxidation, simple distillation or a combination of the above (Marsh 1989). Petroleum-derived pitches are composed primarily of aromatic and alkyl-substituted aromatic hydrocarbons (Köchling, McEnaney and Müller, et al. 1985).

2.4.3 Coal-Tar Pitches

Coal-tar pitches have historically been obtained as a by-product of metallurgical coke ovens. High-molecular-weight organic materials, referred to as tar, are volatilized during carbonization (or heat-treatment) of coal under an inert atmosphere. Coal-tar pitch is obtained from the coal-tar residue by distillation and heat-treatment processes (Marsh 1989). The pitch material consists of a mixture of predominantly cyclic, aromatic, and heterocyclic organic molecules (Köchling, McEnaney and Müller, et al. 1985).

2.4.4 Coal-Derived Pitches

Pitches have also been obtained from coal by alternative means. Coal-derived pitches can be obtained by direct extraction of coal with a suitable solvent or from extraction of heat-treated, hydrogenated coal residue with an appropriate solvent (Machnikowski and Wajzer, Calcination and Graphitization Behaviour of Cokes From QI-Free Coal-Derived Pitches 1994). Pitches have also been used which are merely fractions of the solvent-refined parent pitch (Swietlik, Jasienko and Wolski 1993).

Coal-derived pitches can be quite different from classical coal-tar pitches. Coalderived pitches obtained from the extraction of hydrogenated coals have many benefits over simple coal-tar pitches. The yield of pitch-like material will be considerably higher because the complicated macromolecules are somewhat broken down into smaller molecules that can be solubilized (Bennett 1995). The level of heteroatomics is also significantly less (Machnikowski, Petryniak, et al. 1991).

2.5 Carbonization, Mesophase Growth, and Coke Formation

Pitch is the starting material for synthesizing graphite and graphitic materials from a graphitizable precursor. However, during the entire production scheme, there are many physical and chemical transformations which occur in the material. The first step in graphite production is referred to as carbonization or green coking. In this process, pitch is (slowly) heated under in a non-oxidizing or inert atmosphere.

The application of heat results in the pitch softening and then becoming fluid. This fluidity is necessary for production of high-quality (highly-anisotropic) graphite. The fluidity allows mobilization and realignment of the large planar or discotic (disk-like) molecules. The heating also results in dehydrogenation and devolatilization while promoting cyclization. As the carbonization temperature exceeds about 660 K (387 °C), the large discotic molecules tend to agglomerate in spherical groupings called mesophase (Marsh 1989). The discotic molecules tend to position themselves into a lamellar stacking arrangement within the sphere. The spherical shape of the groupings is adopted to obtain a minimum surface energy (Marsh 1989). Large discotic molecules, called mesogens, which have not yet been incorporated into the mesophase can also be found

within the isotropic pitch matrix. Figure 22 depicts mesophase spheres and mesogens in an isotropic pitch matrix during carbonization.



Figure 22: Mesogens and Mesophase Spheres In an Isotropic Pitch Matrix During Carbonization (Marsh 1989)

As the carbonization process continues, mesogen molecules within the isotropic pitch matrix become incorporated into the mesophase and smaller mesophase spheres that come into contact with one another coalesce to form a single large mesophase sphere. For some pitches, this process can continue until the entire material is transformed into continuous mesophase. An increase in viscosity accompanies the mesophase growth and consequently the viscosity of the carbonizing system increases steadily as reaction time and temperature increases. As the carbonization temperature approaches 500 °C (the actual temperature or range is dependent on the pitch used), the pitch begins to solidify into a carbonaceous material called coke (Marsh 1989).

During mesophase development and coalescence, the orientation of the lamellar structure within the mesophase often becomes distorted. The lamellar structure becomes bent and twisted as depicted in Figure 23. This is often the result of the coalescence of mesophase spherules where the lamellae within the coalescing spherules are oriented in different directions. Figure 24 shows a simple representation of the coalescence of mesophase spheres (Brooks and Taylor 1968).

Many factors are very influential during the carbonization step. Heating rate, parent pitch, system pressure, and pitch agitation (as well as many other factors) are very important and greatly effect mesophase formation and coalescence—thus affecting the subsequent synthetic graphite (Marsh 1989). The heating rate is probably the most influential factor affecting mesophase formation for a given pitch. In order for mesophase to form to any great extent, the isotropic pitch must possess sufficient fluidity to allow the large planar molecules to reorient and align. Thus, the lower the viscosity of the pitch, the more fluid the matrix and the more mobility allowed the mesophase and mesogens. However, since heating promotes devolatilization and cyclization, as time/temperature increases, the platelets increase in size. Hence, the viscosity of the material increases and the mesophase and mesogen mobility drops significantly. Since mobility is therefore limited, more time is necessary to perfect the molecular alignment.



Figure 23: Lamelliform Structure of Coalesced Mesophase Derived from the Optical Texture (Marsh 1989)



Figure 24: Simplified Representation of Mesophase Sphere Coalescence (Brooks and Taylor 1968)

Figure 25 shows a qualitative relationship between carbonization temperature and the viscosity of pitch (Marsh 1989). The bottom curve demonstrates the relationship for a more-homogeneous, highly-aromatic, synthetic, parent pitch while the top curve

demonstrates the relationship for typical natural pitches. Both systems exhibit a softening phase accompanied by a decrease in viscosity (PQ and AB) until a minimum viscosity is achieved. After a period of minimum viscosity (QR and BC), the viscosity of the pitches begins to increase as mesophase is formed; viscosity continues to increase (RS and DE) as mesophase development proceeds until such time as the material solidifies. Systems where the viscosity-temperature profile matches that of the bottom curve tend to result in large anisotropic regions or domains while systems where the viscosity-temperature profile matches that of the systems where the viscosity-temperature profile matches that of the top curve tend to result in a collective of smaller anisotropic domains arranged into a mosaic (Marsh 1989).



Figure 25: Pitch Viscosity as a Function of Carbonization Temperature (Marsh, 1989)

The parent pitch dictates, to a large extent, the characteristics of the graphitic material produced. The reactivity of the pitch during mesophase development is a function of the chemical composition of the pitch; some pitches contain high concentrations of heteroatoms which tend to promote cross-linking and thus inhibit mesophase development (Marsh 1989). Some pitches are very viscous and mesophase development and coalescence is inhibited due to the lack of mobility of the mesophase and mesogens.

The mesophase islets may not even be able to obtain a spherical configuration because of insufficient mobility (Marsh 1989).

System pressure and pitch agitation are also rather influential factors affecting pitch carbonization. System pressure is important mainly because increased pressure inhibits devolatilization (Marsh 1989). Pitch agitation is influential because it tends to affect mesophase coalescence and development by altering the pitch rheology (Marsh 1989). Agitation by gas flow tends to affect devolitization (Loustalet, Oberlin and Moreau 1994). Overall, there are numerous factors affecting mesophase development and their relationships are very difficult to quantify accurately and independently.

Mesophase and mesophase growth has been an area of intense study and thus methods of characterizing the material and process have been developed. The material is often characterized based upon its optical properties (appearance of mesophase islets within the isotropic pitch matrix,) as observed through an optical microscope with polarized light. Table 3 lists one system of broad classifications for mesophase based on the size, orientation, and general shape of the mesophase islets.

2.5.1 Coke and Graphite Characterization

The solid carbonaceous material obtained after pitch carbonization is referred to as coke. There are different classifications of coke depending upon the pitch precursor, maximum carbonization temperature, and the quality (or degree of anisotropy) of the coke.

Binder Phase	Width (in Microns)	Length (L) to Width (W) Relation
Isotropic	0.0	None
Incipient (anisotropic)	0.5	L = W
Circular (anisotropic)		
Fine circular	0.5 - 1.0	L = W
Medium circular	1.0 - 1.5	L = W
Coarse circular	1.5 - 2.0	$L \leq 2W$
Lenticular (anisotropic)		
Fine lenticular	1.0 - 3.0	$L \ge 2W,L < 4W$
Medium lenticular	3.0 - 8.0	L > 2W, L < 4W
Coarse lenticular	8.0 - 12.0	$L>2W,L\leq 4W$
Ribbon (anisotropic)		
Fine ribbon	2.0 - 12.0	L > 4W
Medium ribbon	12.0 - 25.0	L > 4W
Coarse ribbon	25.0 +	L > 4W

 Table 3: Classification of Mesophase Based Upon Optical Properties (Gray and DeVanney 1986)

The following are some terms associated with each. Petroleum coke is the coke obtained after the carbonization of petroleum pitch. Coal-derived pitch coke or coal-tar pitch coke is the coke obtained after carbonizing a coal-tar pitch or constituent fractions of a coal-tar pitch (Köchling, McEnaney and Neumann, et al. 1983). Green coke or raw coke is defined as the coke obtained after the carbonization of pitch to temperatures below 900 K (~627 °C); the mass fraction of volatile matter remaining in this coke is generally between 16 and 20 % (Köchling, McEnaney and Neumann, et al. 1983). Calcined coke is the coke produced after heat-treating green coke to about 1600 K (~1327 °C). Typical

calcined coke has a mass fraction of hydrogen of less than 0.1 % (Marsh 1989). Needle coke, which derives its name because of its physical appearance, is a coke consisting of long bundles of anisotropic material, all oriented in the same general direction (Mochida, Fujimoto and Oyama 1994).

Cokes generally consist of groupings of anisotropic, pre-graphitic carbon arranged into a three-dimensional mosaic. This results in the subsequent synthetic graphite or graphitic material being polycrystalline. Cokes are characterized by the size, shape, and orientation of the anisotropic, pre-graphitic regions within the mosaic. Similarly, graphitic materials are characterized by the size, shape, and orientation of the individual graphite crystallites, called grains, within the bulk material (Callister 1994). The size and shape of the anisotropic regions or grains is determined by observing the optical texture of the sample under an optical microscope. When a sample is mounted, polished, and then viewed under polarized light, the anisotropic regions appear as isochromatic regions (Marsh 1989). Table 4 lists the classifications and nomenclature for coke based upon its optical texture.

2.5.2 Calcination

Calcination is an intermediate heat-treatment step between the coke formation process and the graphitization procedure. The calcination step is also sometimes referred to as a first bake. Essentially, calcination is the process of heat-treating a green coke to about 1600 K (\sim 1327 °C) (Marsh 1989) to remove moisture, reduce the volatile material content, and improve the physical properties of the material.

Name	Abbreviation	Description
Isotropic	Ι	No optical activity
Very fine-grained mosaics	VMF	$< 0.5 \ \mu m$ in diameter
Fine-grained mosaics	Mf	$< 1.5 > 0.5 \ \mu m$ in diameter
Medium-grained mosaics	Mc	$<$ 10.0 $>$ 5.0 μm in diameter
Supra mosaics	SM	Mosaics of anisotropic carbon orientated in the same direction to give a mosaic area of isochromatic color.
Medium-flow anisotropy elongated	MFA	$<$ 30 μm in length; $<$ 5 μm in width
Coarse-flow anisotropy elongated	CF	< 60 > 30 µm in length; < 10 > 5 µm in width
Acicular flow domain anisotropy	AFD	$>$ 60 μm in length; $<$ 5 μm in width
Flow domain anisotropy elongated	FD	$>60~\mu m$ in length; $>10~\mu m$ in width
Small domains, isochromatic	SD	$<60>10~\mu m$ in diameter
Domains, \sim isometric	D	$> 60 \ \mu m$ in diameter

 Table 4: Coke Classifications and Nomenclature Based Upon Optical Texture (Marsh 1989)

The calcination step is very important for anisotropic material production because many chemical and physical transformations occur within the coke that will affect the resultant graphitic material properties and ultimately the usefulness of the material. One of the major occurrences is the expulsion of hydrogen and heteroatomics from the material. Nitrogen and oxygen are expelled at around 1000 °C and hydrogen is expelled by around 1200 °C (Spain 1981). Figure 26 shows a simplified outline of the carbonization and graphitization process.

Although Figure 26 might suggest that there are discrete temperatures at which certain species are removed, this is not so. Figure 27 shows the hydrogen content and density of a petroleum coke and a coal-tar pitch coke as a function of calcining temperature (Wallouch and Fair 1980). Figure 28 shows the hydrogen and heteroatomic content of two different coal-derived cokes as a function of heat treatment temperature (Machnikowski and Wajzer 1994).



Figure 26: Outline of the Carbonization and Graphitization Process (Spain 1981)



Figure 27: Hydrogen Content and Density for Petroleum and Coal-Tar Pitch Coke Versus Calcining Temperature (Wallouch and Fair 1980)

Calcination is also believed to be a critical step in refining the crystal structure of the pregraphitic material. During calcination, the amorphous material begins the transformation to a highly-ordered crystalline state. Removal of heteroatomics and residual hydrogen facilitates graphene plane alignment (altering the interplanar spacing) and crystal growth. The quality of the calcined coke and subsequent graphitic material is believed to be a strong function of the calcination temperature and heating rate (Brandt 1986). The ultimate calcination temperature dictates the level of impurities (heteroatomics and hydrogen) remaining to inhibit crystallization. Heating rate is believed to be influential because the rate of gas expulsion has an effect on the molecular rearrangements within the coke (Politis, Nazem and Chang 1991), implying molecular reorganization by diffusion. The effects of the calcination conditions upon the material's physical properties and crystallinity will be discussed in further detail in the following section.



Figure 28: Hydrogen and Heteroatomic Content Versus Heat Treatment Temperature (HTT) for Two Coal-Derived Cokes (Machnikowski and Wajzer 1994)

During calcination, initial releases of hydrogen and heteroatomics result in coke shrinkage and an increase in material density (Wallouch and Fair 1980). Accordingly, the porosity of the resultant coke also changes. Both the porosity and coke density are, to a large extent, a function of the rate of degasification and rate of coke contraction (Wallouch and Fair 1980).

There are changes that occur along with and because of the expulsion of heteroatomics. Heteroatomic release coincides with a material density change and a destructive physical process known as puffing. Puffing is defined as an irreversible volumetric expansion of a carbonaceous material during heat treatment between 1650 and 2700 K (1377 and 2427 °C). Puffing is caused by the rapid expulsion of heteroatomics (and especially sulfur) in the form of volatile species (Fujimoto, Yamada, et al. 1986). Puffing results in a decrease in the bulk density, strength, and electrical and thermal conductivity of the synthetic graphite produced and also often results in crack formation (Fujimoto, Yamada, et al. 1986). Puffing can be inhibited, or at least strongly diminished, by heating the material very slowly, by heating isothermally to temperatures just insufficient for puffing, or by addition of puffing inhibitors (suitable metals or metal compounds) to the carbon material to be heat-treated (Fujimoto, Yamada, et al. 1986).

Although the puffing phenomenon is generally associated with the graphitization procedure, an analogous phenomena occurs during the calcination procedure for many coal-derived cokes. Puffing in coal-based cokes has been attributed more to nitrogen expulsion than to sulfur expulsion (Machnikowski and Wajzer 1994). Nitrogen is removed by thermolysis at lower temperatures than sulfur and a significant amount of nitrogen is released during the calcination process (Machnikowski and Wajzer 1994). Figure 29 shows the kinetics of nitrogen and sulfur removal for two coal-derived cokes (Machnikowski and Wajzer 1994). It should be noted that the nature and extent of nitrogen removal is quite dependent upon the type of coke studied. Certain coal-derived needle cokes have been shown not to expel nitrogen until higher temperatures (above \sim 1400 °C) (Fujimoto et al., 1989).



Figure 29: Change in Nitrogen and Sulfur Content With Heat Treatment Temperature (HTT) for Two Different Coal-Derived Cokes (Machnikowski and Wajzer 1994)

2.5.3 Heat-Treatment Effects on Calcined Cokes

Disagreement exists as to what effect calcination has on the structure of coke and ultimately the graphite made from that coke. The effects of calcination conditions (both heating rate and ultimate temperature) have been studied extensively for petroleum derived cokes and to a much lesser extent for coal-tar and coal-derived cokes. This is mainly because petroleum pitches generally produce cokes of a more anisotropic nature than do coal-tar pitches and the highly anisotropic needle cokes are more desirable (mainly for their use in electrodes) than the isotropic graphitic materials (Mochida, Fujimoto and Oyama 1994). Most of the studies generally focused on higher (above 1300 °C) final calcination temperatures and the effects of lower calcination temperatures were not studied as thoroughly. Heat treatments in the 500 °C to 1200 °C temperature

range are presently being perceived to be more influential than earlier thought (Heintz 1995), (Politis, Nazem and Chang 1991).

Practically all researchers emphasize the importance of calcination heat treatment conditions on final coke properties but there is a great deal of disparity as to the degree of the effect. (Machnikowski and Wajzer 1994) studied the calcination and graphitization behavior of cokes produced from coal-derived pitches and reported that increasing the heating rate from 5 to 100 °C per minute in the 500 to 850 °C temperature range had negligible impact on the calcined coke properties. Recently (Heintz 1995) reviewed the effect of calcination rate on petroleum coke properties, prompted by recent work of (Bui, Perron and Read 1993) making similar claims that calcination rates up to 100 °C per minute have little, if any, effect on calcined petroleum coke properties. Earlier work by Rhedey tended to dispute this statement and Rhedey originally asserted that heating rates in excess of 50 °C per minute in the 600-900 °C temperature range resulted in surface accessible porosity increases and pore distribution changes. Later, Rhedey altered his assertion to say that heating rates in excess of 100 °C per minute had deleterious effects on the coke properties. Rhedey reported that these heating rate limitations were found to be valid for petroleum cokes of all qualities—premium, regular, and isotropic.

Heintz (1995) performed tests using a slow heating rate (5.3 °C per minute) and a fast heating rate (80 °C per minute) to determine if heating rates slightly above Rhedey's originally proposed 50 °C per minute could be used without destructive consequences. It was found, however, that the faster heating rate was deleterious to coke quality. The faster calcination rate produced coke particles with lower real density indicating that the coke particles had puffed during the fast calcination rate—all other conditions being

equal. Calcination rates in excess of 50 °C per minute were not recommended by Heintz (1995)for either premium or regular quality cokes.

Akhmetov and related researchers (1986), (1983) have also published several papers on coke calcining processes and calcination heating effects. The research recommends even slower calcination heating rates of 2 to 30 °C per minute for optimum quality. In addition, the studies suggest that cooling rate has little to no effect on coke properties and that real density is almost independent of particle size.

Kocaefe et al. (1995) performed tests to determine the effects of heating rate and coke type on green coking pyrolysis to 1200 °C. The coke structure was found to be strongly affected by heating rate and temperature. The apparent porosity increased slightly with increasing heating rate while the real density and crystallite size decreased. The apparent density was not influenced by heating rate. The real and apparent density, apparent porosity, and crystallite size increased as temperature increased.

Kocaefe et al. (1995) noted several literature sources recommending that crystallite size be used as the parameter for quality control because it was previously considered that crystallite size was a function of temperature only for a particular coke type. Crystallite size was thought to be affected very slightly by heating rate and holding time while porosity and density are affected to a greater extent. The results of their study show, however, that crystallite size is affected significantly by the heating rate and holding time as well as temperature. Legin-Kolar and Ugarkovic (1993) also studied the influence of petroleum feedstock composition and high-temperature calcination/graphitization heat treatments on resulting microstructure and noted that microstructural properties were a function of heating rate as well as final temperature.

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Politis, Nazem, and Chang (1991) attempted to do a systematic study of the calcining process by varying different parameters and noting the subsequent effect on coke properties. The effect of particle size, heating rate, final calcining temperature, cooling rate, and heating and cooling atmosphere on product quality were noted. The multiregressional analysis determined that both the coke crystallite size and interlayer spacing were a function only of the final calcining temperature and the heating rate. The effect of heating rate was attributed to gas expulsion and its effect on molecular rearrangements within the crystal structure. Hence, the faster the heating rate, the larger the d-spacing and the lower the crystallite size. Porosity was found to be a function of heating rate (again because fast gas expulsion leads to higher porosity) and the heating atmosphere. Oxidation increases porosity and deteriorates product quality. Their primary conclusion was that the heating rate between 450 and 800 °C was the most important process parameter controlling most of the calcined coke properties.

The effects of calcination heating on coke puffing have been studied by Fujimoto et al. (1989). It was noted that puffing of individual coke particles has been observed for particles as small as 100 μ m in diameter during calcination. The extent of puffing for smaller particles is not as dramatic as puffing for larger coke pieces. Similar phenomena were observed by Brandtzæg and Øye (1985). The intraparticle puffing phenomena was clearly observable by x-ray diffraction because of crystalline deterioration resulting from puffing induced lattice expansion.

Fisher and Perruchoud (1985) studied the influence of coke calcining parameters on petroleum coke quality. They assert that all physical and chemical properties of petroleum cokes are determined by purity, structure, and porosity and that structure and porosity are decisively influenced by calcining. Their research supports the claims of the previous researcher S. S. Jones to say that cokes with significantly different volatile contents (quality and quantity), microstructure, and/or impurity levels should be calcined differently. From their study, they note that the structure, specific electrical resistance, thermal conductivity, and real density are strongly correlated. They note that during calcination of green coke, the crystallite size increases significantly with increasing temperature but that the influence of residence time on crystallite size is smaller.

2.5.4 Graphitization

Graphitization is defined as a solid state transformation of thermodynamically unstable, non-graphitic carbon into graphite by thermal activation (Marsh 1989). The degree of graphitization depends upon the maximum temperature of the heat treatment and the time allowed for annealing. Graphitization is usually performed by heating cokes to temperatures above 2500 K (~2227 $^{\circ}$ C) (Marsh 1989).

The graphitization process results largely in the transition of turbostratic graphite into crystalline graphite. The graphitization process dramatically alters the properties of the material—and particularly the solid state properties. Before graphitization, the large discotic carbon planes are misaligned with respect to neighboring planes and the distance between the carbon planes is greater than for crystalline graphite. At pressures below about 130 kbar, heating results in the solid state diffusion of the carbon plates into the thermodynamically preferred, hexagonally-stacked, graphite crystal structure (Fischbach 1971).

During this transformation, which is predominated by solid state diffusion, there are several chemical processes occurring simultaneously. The remaining hydrogen and

heteroatomics are eliminated by thermolysis—as well as most other trace impurities such as metals (Fujimoto, Mochida, et al. 1989). Nitrogen removal from coal-tar cokes is virtually complete by about 2000 °C (Fujimoto, Yamada, et al. 1986). Sulfur removal from coal-tar cokes occurs generally between 1500 and 2200 °C (Fujimoto et al., 1989). Removal of metals generally occurs above 2000 °C (Fujimoto, Yamada, et al. 1986).

For pre-graphitic carbons containing few contaminants (metals and heteroatoms), the rate of graphitization is not very influential upon the final graphitic material. However, as heteroatom and contaminant concentrations increases, the rate of graphitization becomes more important due to the puffing phenomena—as described previously (Fujimoto, Mochida, et al. 1989).

The interlayer spacing between the graphene planes, or d-spacing, is a commonly used measure of the level of intracrystallite perfection obtained by a graphitic material after graphitization (Spain 1981). The closer the d-spacing value is to the value for graphite, the more highly oriented the planes are within the crystal. This parameter is determined by x-ray diffraction. The graphene interlayer spacing is on the order of 3.44 Å for a turbostratic carbon material compared to a value of 3.354 Å for a graphite crystal. Thus, the degree of graphitization (G) for a carbonaceous material is often determined by x-ray diffraction) to the values for a turbostratic carbon and a graphite crystal as shown below in equation 2.1 (Spain, 1981).

 $G = (d_{max} - d_{actual}) / (d_{max} - d_{min}) (2.1)$

where: d_{max} = value for the graphene interlayer spacing for turbostratic carbon (~3.44 Å) d_{min} = value for the graphene interlayer spacing for graphite crystal (3.354 Å) d_{actual} = measured value for the graphene interlayer spacing in Å

The level of perfection obtained by a graphitic material is both a function of the maximum heat-treatment temperature and the length of time at that temperature. Figure 30 shows the relationship between the unit-cell height (twice the d-spacing value) and the total heat treatment time at different temperatures for a petroleum coke.

Graphitization also promotes crystallite growth—both parallel and perpendicular to the graphene planes. The turbostratic graphene layers align in the thermodynamically preferred orientation and this results in dramatic increases in three-dimensional ordering. The effective width of the crystallites in the direction parallel to the graphene planes is referred to as La and the effective thickness of the stack of graphene sheets in the crystallite is referred to as Lc. Further discussion of these parameters (including methods of measurement) will be presented later.



Figure 30: Unit-Cell Height as a Function of the Total Heat Treatment Time for Different Temperatures (Fischbach 1971)

One of the most notable changes resulting from graphitization is the materials transition from being an effective thermal insulator into being a very good thermal conductor. By heating the graphite precursor from 1000 °C to 3000 °C, the thermal conductivity of the material increases nearly two orders of magnitude (Kelly 1969). Electrical conductivity also exhibits a large increase after graphitization.

2.6 Commercial Coal Liquefaction Processes

Commercial liquefaction technologies involve hydrogenating coal in a solvent slurry under elevated temperatures and hydrogen pressures (370-480 °C and 1500-4000 psig). High temperatures are required to crack the coal thermally and produce reactive fragments while high hydrogen pressures are required to cap these sites with hydrogen. Depending on the reaction conditions lower molecular weight gases and liquids are formed and recovered from the remaining solid material. Three major commercial liquefaction technologies are discussed below.

2.6.1 H-Coal Process

The H-Coal process was developed by Hydrocarbon Research Inc. (now Hydrocarbon Technologies Inc., a subsidiary of Headwaters Inc.) to convert high-sulfur coal into boiler fuels and synthetic crude oil. This process utilized a catalytic ebullated-bed reactor, in which the reaction mixture is recycled upward through the reactor to maintain the catalyst in a fluidized state. The process used crushed (60 mesh) coal slurried with recycled oil, pressurized to 3000 psig and mixed with compressed hydrogen. The mixture was then preheated and fed to the ebullated-bed catalytic reactor that operated between 340-370 °C. The gas product after separation into light hydrocarbons, ammonia and hydrogen sulfide, is mostly hydrogen, which is recompressed and combined with fresh coal-oil

slurry. The liquid-solid mixture is separated in a flash separator to recover light and heavy hydrocarbons. The remaining solids and heavy oil are processed in a hydrocyclone and a vacuum distillation column. The process requires between 14000-20000 scf of hydrogen for every ton of coal, depending on the type of oil product desired. A portion of the hydrogen needed is produced in the process itself, while make-up hydrogen is required. The conversion of coal to liquid and gas products for this process is about 90 %.

2.6.2 Solvent Refined Coal (SRC) Process.

The SRC process is a non-catalytic process that converts high ash and high sulfur coal into gas, liquid, and/or solid fuels. The product from the process is a solid, carbonaceous material that contains less than 1 % sulfur and 0.2 % ash. Pulverized coal mixed with process-derived solvent combines with gaseous hydrogen at 425-455 °C and 1030 psig. The product gases are processed to recover hydrogen which is recycled to the process. The slurry from the separator is processed in a filtration unit to recover a high molecular weight solvent which is then recycled and mixed with fresh raw coal. As mentioned earlier this principle of the SRC is used in the current research to study the process-derived solvent as a hydrogen donor. The final solid product contains very low amounts of sulfur and ash. The schematic of the process is shown in the figure below.



Figure 31: Schematic Sketch of the Typical SRC Process.

2.6.3 Exxon Donor Solvent (EDS) Process

The EDS process was developed by Exxon to produce liquid products from a wide range of coals. This is a non-catalytic process which recycles tetralin solvent, with a separate solvent rehydrogenation step. Crushed coal is slurried with recycled tetralin and mixed with recycled hydrogen at 425-465 °C and 1500-2000 psig. The products are separated into three fractions: light hydrocarbons, a naphtha fraction and heavy distillate. The heavy distillate is processed in a vacuum distillation column to yield jet fuel and heating oil. A portion of the heavy distillate between 205-455 °C boiling range is hydrotreated and recycled to form the slurry feed with fresh coal. The remaining bottoms product can be converted to heavy oil using a process called flexicoking. One of the unique features of the EDS process is the ability to adjust the recycled hydrogen donor solvent based on the characteristics of the raw coal feed. The quality of the solvent can be adjusted by controlling the reaction in the hydrotreatment step. By tailoring the donor solvent to match the feed coal, the liquid products can be optimized.

2.6.4 Liquefaction Solvents

Industrial processes involving coal-derived solvents as liquefaction solvents generally isolate process-derived recovered solvents, which can be recycled back to the process, thereby minimizing the addition of fresh solvent. The chemical composition of these recycle solvents controls the overall behavior of the coal liquefaction process.

Each class of chemical compounds found in industrial recycle solvents has been shown to have relative merits. The components to be considered include H-donors, H-shuttlers and H-abstractors. They have influence on the rate and extent of coal dissolution, coal conversion, hydrogen consumption, product distribution, and the ability to regenerate solvents. In the SRC process no commercial catalyst is employed and only the intrinsic mineral matter entering with the coal acts as a catalyst for coal liquid upgrading and/or maintenance of proper solvent quality. Thus, the SRC process is essentially similar to the work undertaken in this research, the only difference being it was continuous. An external catalyst is not necessary for dissolution, since the coal is often substantially dissolved through interaction with the solvent by the time the coal exits the reactor. The nature of the process and the selectivity to the various products are primarily governed by the composition of the recycle solvent.

Coal conversion can be envisioned to occur in three stages: dissolution of the coal; defunctionalization of the coal and hydrogen-transfer; and rehydrogenation of the solvent. In each of these stages, the nature of the solvent can affect the rates of reaction and the distribution of the products. In the dissolution stage, because of high temperature, the highly crosslinked structure of coal fragments into radicals, which in the presence of H-donors are capped into stable species. In the absence of hydrogen-donor solvents, the original radicals or the smaller soluble species may recondense to form char or coke. The solvent governs product selectivity by controlling the path taken by the intermediate radicals. When a bond cleaves, at least three different pathways are available for product formation: H-abstraction, rearrangement and elimination, and addition to aromatics. The availability of H-donors will determine the preferred path. The specific chemical properties of interest in recycle solvents are:

a. *Hydrogen-donor capacity of the solvent* – hydrogen donors are believed to be important in the defunctionalization of the dissolved coal and the prevention of char formation. The principle sources of hydrogen appear to be partially hydrogenated aromatic hydrocarbons: tetralin and its homologs, partially hydrogenated pyrene, phenanthrene, and other polycyclic aromatic compounds.

b. *Physical solubilization of coal products* – effective solvents for coal solubilization must contain polar compounds. Assuming the concept of specific solubility parameters applies, then the good solvents should contain such components as polyaromatics, phenols, pyridines, aromatic ethers, and quinolines and their derivatives.

c. *Hydrogen transfer capability (H-shuttling)* – hydrogen transfer is another mechanism for dissolving coal, whereby hydrogen may be supplied from the coal itself or from the SRC to cap off radicals and form smaller soluble species. Reports by Neavel indicate that naphthalene can dissolve 80 % of a vitrinite-rich bituminous coal at short contact times and at temperatures over 750 °F. It was proposed that this dissolution was the result of the shuttling of hydrogen from one position in the coal to another. Naphthalene

acts as an H-acceptor and the resultant free radical formed by the addition of an H-atom act as an H-donor. A reaction of this type is even more probable for phenanthrene or pyrene since they are better H-acceptors than naphthalene. The structures which can contribute to good shuttling properties within recycle solvents are: Naphthalene and its alkyl derivatives, phenanthrene and its alkyl derivatives, heterocyclic polyaromatics etc. This effect is explained in more detail in the later section.

d. *Chemical structures associated with char formation* – recycled solvents may contain compounds which are prone to or which can promote char formation. Heavy phenols and highly aromatic compounds are some of these compounds.

2.6.5 Catalytic Effects of Mineral Matter in Coal

Intrinsic mineral matter can be used to catalyze coal conversion reactions. For example, catalytic activity has been ascribed to the presence of pyrite (FeS₂) or the reduced form of pyrite, pyrrhotite. Although potentially useful, catalysis is also potentially detrimental of polymerization is also catalyzed.

In a recent study on the hydrogenation of a high-vitrinite Indian coal (North Assam) in the absence of a solvent, the catalytic effect of mineral matter was studied by characterizing the coal ash and by adding specific minerals. The best correlation to activity was found using (organic plus pyritic) sulfur. Other materials - iron, titanium and kaolinite (the prevalent clay) - also correlated with coal conversion to benzene- soluble products. Iron pyrite was suspected to be the active form of iron but conversion also increased with the addition of sulfur or titanium hydroxide.

In another study Whitehurst et al. proved that pyrite addition increased the pyridine solubility of four German coals. Samples of a coal enriched in mineral matter were more

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extensively converted. These reactions were carried out in methyl naphthalene at 752 °F under 3000 psi of hydrogen for 2 hours. These studies indicate the effect of iron pyrite on the solvent-solvent interactions that occur during the liquefaction of coal. These results showed that the rate of solvent-solvent hydrogen transfer reactions occurred at a higher rate in the presence of coal containing pyrite than in solvent-solvent reactions alone.

A different approach to study the effect of mineral matter in coal is to selectively remove the mineral matter content without altering the organic composition of the coal before reaction. The mineral matter present in coal can be selectively removed depending on the type of pretreatment. After the pretreatment of these coals to remove the ash content, the coal conversion dropped with lower ash content (see the Figure 32) and the hydrogen consumption dropped with lower ash content signifying that some catalytic activity can be attributed to the presence of pyrite. The coal in this study was Wyodak-Anderson coal containing relatively little pyrite but catalysis of hydrogen gas reactions did respond to total ash content. Such behavior would indicate that even ion-exchangeable iron may have catalytic properties.

In summary there are clearly effects of coal mineral matter on the progress of liquefaction. Mineral matter catalyzed hydrogen gas consumption and other reactions of coal and its products. It also aids in solvent rehydrogenation but its activity is low. Acid demineralization, especially for sub-bituminous coal, increases coal reactivity but decreases conversions and SRC yields at long coal conversion times because of increases in both regressive and forward reactions.

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Figure 32: Wyodak Coal Conversion vs. Ash Content.

2.6.6 Effect of Hydrogen Pressure on Coal Solubility

The presence of a hydrogen atmosphere can greatly benefit the production of soluble coal increasing the product yield. Molecular hydrogen at high pressure could donate hydrogen and stabilize the coal free radicals in one of two ways: (1) directly donate hydrogen to the free radical or (2) transfer hydrogen to the donor solvent, which can then be transferred to the coal particle. Yen et al. showed that when tetralin is used as a donor solvent, the yield of benzene insolubles under a nitrogen atmosphere was 25.3%. When the atmosphere was changed to hydrogen, the yield of benzene insolubles decreased to 13.8% indicating more conversion to benzene solubles. Tomic and Schobert also observed an increase in the amount of conversion when a hydrogen atmosphere is used instead of an inert atmosphere during liquefaction without solvents or catalysts. This increase in conversion is believed to occur as hydrogen reduced the amount of retrograde reactions at high temperature.

There also has been some work on the exact source of the hydrogen during the liquefaction reactions. This hydrogen can come from a variety of sources: the solvent, gaseous hydrogen, or from the coal itself. The most efficient source is the hydroaromatics in the solvent but if such materials are limited in concentration, hydrogen gas or coal become the dominant sources. Whitehurst et. al. have shown that even at short times hydrogen gas can be the dominant source of hydrogen for low rank coals where the demand for hydrogen is largest.

These liquefaction reactions are also sensitive to H-donors, hydrogen gas and H-shuttlers. The rate of coal dissolution is proportional to the concentration of hydroaromatics in synthetic recycle solvents. Whitehurst et al. found the conversion of Illinois #6 coal at 3 minutes in a series of solvents with varying tetralin concentrations increases with the tetralin content in the solvent. This simple relationship is somewhat complicated by hydrogen donation from other sources such as hydrogen gas or the coal itself. It has been proved that low rank coals can give increased yields at short times by application of hydrogen pressure. For higher rank coals (bituminous) hydrogen donation from gas phase is small. It is suggested that bituminous coals are efficient sources of hydrogen because a high proportion of the mass is plastic or mobile at liquefaction temperatures.

The donation of hydrogen from hydroaromatic structures in coal can be assisted by certain highly condensed aromatic molecules in the solvent. Such molecules are not net donors of hydrogen but can rapidly equilibrate with hydroaromatics in the coal and can thus "shuttle" hydrogen from one region of the coal to another. The following figure shows a group of solvents of limited H-donor capacity, containing naphthalene and phenanthrene homologs, where the amount of coal becoming soluble in 4 minutes is

proportional to the concentration of polycondensed aromatic compounds in the solvent. It is noteworthy that a good shuttling solvent can even induce higher solubility than a solvent containing 40 % tetralin. So, bituminous coals can give the highest yields and require little hydrogen, but the presence of either good hydrogen donors or hydrogen shuttlers is necessary for high conversion. Sub-bituminous or lower rank coals can give high yields of soluble material but at a slower rate.

2.6.7 Temperature Effects upon Coal Liquefaction Reactions

Increasing the temperature of the reaction during coal liquefaction increases all reaction This includes rates of coal dissolution, heteroatom rejection, hydrogen rates. consumption, gas formation and charring. The effects of increasing temperature on conversion for bituminous coals have been found to be small at short contact times. With sub-bituminous coals, for which the rates of dissolution are considerably slower than for bituminous coals, raising the temperature may be desirable for dissolving coal. With one sub-bituminous coal (Wyodak Anderson) increasing the temperature to 820, 840, 850, and 860 °F gave increasing conversion at short times. The net effect of increasing the temperature of reaction in long contact time coal conversion is to decrease the SRC yield and increase the yield of light hydrocarbons. This is true either with or without hydrogen donors in the solvent. The products of high temperature conversion also contain lower concentrations of highly polar fractions and are therefore more soluble in hydrocarbons, which is why even though the SRC yield might decrease, the overall conversion is increased due to good solubility of the SRC and the increased light hydrocarbons content in the extracting hydrocarbons.

2.6.8 Williams, Landel, and Ferry Viscosity Model

The Williams-Landel-Ferry (WLF) equation evolved from an empirical relationship describing viscosity dependence on temperature. The WLF expression can be related to fundamental principles. Beginning with Eyring's rate theories, Doolittle entailed thermodynamic principles to describe viscosity changes based on free volume concepts. Cohen and Turnball further developed Doolittle's free volume model into a useable equation. Later, Williams, Landel, and Ferry developed and incorporated the Doolittle equation into their own free volume expression, which became known as the WLF equation. This involved establishing a relationship with the activation energy of the material and the thermal energy introduced into the material. The activation energy can be related to the free volume in the sample and a reference temperature; i.e.,

$$\log \mu = \log \mu_r - \frac{C_{1,r}(T - T_r)}{C_{2,r} + T - T_r}$$

where μ_r is the viscosity at the reference temperature, T_r , and $C_{1,r}$ and $C_{2,r}$ are constants dependent upon the choice of reference temperature.

The WLF equation was employed by Nazem and Lewis for the rheological characterization of mesophase-containing pitches. Their method established a shift factor, A_T , which is the ratio of relaxation times for the pitch at a measured temperature and the reference temperature. Because of its thermodynamic significance, the glass transition temperature (T_g) is often used for the reference temperature in the WLF equation. This is because the free volume changes rapidly at the glass transition temperature in most pitch materials. When plotted against a temperature, the shift factor places the viscosities measured at different temperatures onto one line of a constant slope. They showed that the shift factor could be represented by the relationship:
$$\log A_T = \log\left(\frac{\mu T_r}{\mu_r T}\right) .$$

The following equation is simply rearranged into a slope-intercept form. This was done by the logarithmic of the reference viscosity (log μ_r) being transferred to the left side of the below equation resulting in:

$$\log \frac{\mu}{\mu_r} = -k(T-T_r)$$

where

$$k = \frac{C_{1,r}}{C_{2,r} + T - T_r}$$

The difference in the logarithmic of the temperature and reference temperature $[\log (T - T_r)]$ was added to both sides of the below equation. After rearranging and collecting variables, the equation is now in slope-intercept form (y = mx + b) as shown in the following equation.

$$\log A_T = \log \left(\frac{\mu T_r}{\mu_r T}\right) = -k(T - T_r) + \log \frac{T_r}{T}$$

.

These equations are widely used to predict the viscosity behavior of both isotropic and mesophasic pitches. Remarkably, the WLF relationship holds for pitches that range from nearly isotropic to essentially crystalline in nature.



Figure 33: Plot of (T – Tr) vs. Log AT for a Range of Mesophase-Containing Pitches

2.6.9 Van Krevelen Analysis

A graphical method for studying the chemical changes that occur during the coalification process was developed in 1950 by D.W. Van Krevelen. This method, consists of graphing the atomic hydrogen-to-carbon ratio versus the atomic oxygen-to-carbon ratio of organic materials. Depending on the slope and direction of these trends, the atomic ratios can indicate whether decarboxylation, dehydration, and dehydrogenation reactions are present.



Figure 34: H/C versus O/C Diagram

For example, Van Krevelen analyzed the elemental composition of a wide range of coals that varied in rank. He examined lignites, bituminous coals, and anthracites. He also included coal antecedents in his analysis: wood, cellulose, and lignin. Van Krevelen suggested that the process of coalification is associated first with little change in hydrogen content but with large decreases in oxygen content. Decreases in hydrogen content occur prevalently during the latter stages of coal maturation.

To explain the chemical progression from low rank to high rank coal, Van Krevelen proposed that decarboxylation reactions take place upon going from lignite (V) to low rank bituminous coal (VI). Dehydration occurs predominantly proceeding from low rank bituminous (VI) to high rank bituminous coal (VIII). The final stage of coalification, the transformation of high rank bituminous coal (VIII) into anthracite (X), entails demethanation.

The use of the Van Krevelen plots can be extended to explain the mechanisms occurring during the thermal-chemical treatment of other bituminous materials. Joseph and Oberlin studied the effects of air oxidizing various carbonaceous materials at different temperatures and time. They postulated that two parts are associated with oxidation. The first part involves a rapid release of hydrogen, after which oxygen content increases slowly, as shown in Figure 35. Joseph and Oberlin also noted that the slopes of the oxidation paths were distinctly different and depend upon the elemental composition of the starting material. They pointed out as well that all of the materials studied tend to reach the same plateau at an O/C atomic ratio of about 0.5.



Figure 35: Van Krevelen Diagrams Showing Oxidation Paths of Various Organic Materials.

Generally, elemental analysis is performed to obtain the C, H, N, and S weight percentages, and oxygen is determined by difference. It is best to determine oxygen directly, as was done by Joseph and Oberlin, since there are errors associated with the determination of each element. This means that finding the determination of each element. This means that finding the percent oxygen by difference does not necessarily measure the content of oxygen accurately in many instances. A separate or direct measure of oxygen content is preferred to ensure that the C, H, S, N, and O contents are indeed accurate and that all five elements add up to 100 percent, in order to make the Van Krevelen plots reliable

CHAPTER III: EXPERIMENTAL DESIGN AND CONSTRUCTION

3.1 Introduction

The Experimental Design and Construction chapter is a discussion of the design concepts, all of the preparation for the construction of the systems, and the actual construction of the processes. It begins with the external de-ashing process in Stoystown, PA followed by the improvements to the efficiency of the internal de-ashing or centrifugation process. The chapter then proceeds to the design and construction of the combined reaction and centrifugation system. The cleaned, de-ashed centrate produced is transported from the bunker laboratory to the laboratory in Room 317 of the Engineering Research Building. The discussion then proceeds through the design and construction of the vacuum distillation system and finally the design and construction of the coking system housed in this laboratory.

3.2 The Stoystown External De-ashing Process

3.2.1 The Original External De-ashing System

The original external de-ashing system was designed to analyze the ability to reclaim the coal from gob waste using a detergent solution. Gob waste fines are a complicated composite material. Frequently the particles are a mixture of good coal, heavy rock ash, and clays. The clays are enriched in the cleaning plants and are discarded with the fine

coal particles and rock ash. The clays act as glue to combine the coal and rock ash together as a composite so that the coal particles cannot be separated from the rock ash by gravity methods without first dispersing the clays. Once the clays were dispersed, the coal and rock ash composite would decompose and separation by gravity methods was possible. The company, Coal Innovations LLC, built the original de-ashing system in Stoystown, Pa next to a 2.5 million ton gob pile (Figure 36).

The gob material at this facility was typically 56% ash. The original clay dispersion mixture included an anionic detergent, a nonionic detergent, a defoaming agent, and urea. The original test unit was a square tank of about 400 gallons. It had an aerator in the bottom. In the initial experiments 350 gallons of water were mixed with the detergents and 350 lbs of coal gob were added. The tank was agitated with an external paddle stirrer. The slurry was pumped from a sump in the bottom of the tank through a density differentiating cyclone. The underflow contained the heavy ash rich material while the coal and clays exited the top flow of the cyclone. The top flow was then run through vibrating screen and the coal particles, that are much larger than the clays, were captured. The underflow from the cyclone went back into the tank for reprocessing. The particles that were collected from the screen were very low in ash, approximately 6.5%. However, only a hand full of material collected from the 350 lbs of gob fed to the system. It became apparent that the system only demonstrates the potential that could exist, but was not practical.



Figure 36: Original testing system for the external de-ashing of coal.

3.2.2 Review of the External De-ashing Objectives

The primary objective will be to evaluate the ability of the Stoystown process to remove clay from the Australian coal prior to the liquefaction reaction. The Australian coal contains roughly 24% ash by weight, most of which is clay ash. To accomplish this objective, several secondary objectives must be met. These objectives include:

- 1) To redesign the external ash removal testing system (or Product Development Unit) and test it to determine if it is capable of producing reliable and repeatable results.
- To develop a laboratory to perform proximate analysis testing of the PDU samples, bench scale testing of various detergent blends, and consistent detergent preparation for the PDU.
- 3) Determine if the use of external ash removal for the Australian coals should be pursued.

This process was developed to clean gob. In this initial process step the composite gob was decomposed to a combination of coal and heavy rock ash as the clays were dispersed by the detergent. Thus the product of this dispersion step is a mixture of coal and ash. The application was extrapolated to Australian sub-bituminous coal, which was rich in ash; however the ash was primarily clay. It was hypothesized that the clays would be dispersed and the product would be cleaned coal. Instead of explaining the effort to clean coal it is important to review the situation developed to disperse the clays from gob.

3.2.3 External De-ashing Design Concepts

The entire process will have to be redesigned to have the ability of producing reliable and repeatable results. The original system consists of the mixing tank where the contents and therefore the control variables are continually changing. It was difficult to analyze how the detergent solution was affecting the removal of ash from the coal as the conditions were continually changing. A much better design for the testing system would be a closed batch process unit where the entire contents of the mixing tank were processed to liberate the clays from the coal and suspend them in the solution. Then the entire contents of the mixing tank can be processed through a separation system where the coal and hard rock ash are removed from the slurry. The final step was to remove the clay and other fine particles from the detergent solution. This step is critical because it is necessary to determine the conditions of the detergent solution at the end of the process. It had to be analyzed to determine how much can be recycled and reused in the mixing tank. The conditions also needed to be known to determine if further processing was necessary before the detergent solution can be returned to the environment.

3.2.3.1 The Mixing Tank

The purpose of the mixing tank will be to agitate the slurry which consists of the detergent solution containing the suspended dirty gob. In order to achieve reliable and consistent testing results it was necessary to redesign the mixing tank to process the entire amount of coal consistently. The redesign prevented material from settling out of solution. Furthermore, the agitation needed to be turbulent. Collisions between the coal containing composite particles suspended in the detergent solution mechanically broke them apart and increased the amount of clay liberated from the coal.

In the original system there are several deficiencies with the mixing tank. The first and most obvious was the shape of the mixing tank seen in the picture below. This square tank with a flat bottom shown in Figure 37 was replaced with a circular tank and a conical bottom. With the original shape of the tank, much of the coal would settle out into the corners of the tank due to eddy currents at the sharp corners. These currents caused_much of the coal to settle out and never be exposed to the actual process. The coal rich particles would sit in the corners of the tank and experience little agitation and collisions.



Figure 37: Mixing tank for the original Stoystown testing system during operation.

Another aspect of the original mixing tank was that the slurry was being aerated during operation. The idea behind the aeration was that it supplied additional agitation to the mixing tank. Several problems resulted from the aeration. First the specific gravity of the detergent solution was decreased by the addition of the air. With a lowered specific gravity, more of the heavy gob waste settled out of solution and thus was able to avoid being processed. Aeration also caused foaming within the mixing tank. Frequently the slurry in the mixing tank would foam and the contents overflowed, spilling out onto the floor. Once this occurred all of the results from the test were unreliable. Mass balance was no longer possible and the results could only be an estimate for the amount of coal recovered at the end. Therefore, aeration had to be eliminated and the agitation for the new testing system will be generated from other sources.

The new mixing tank was cylindrical with a conical bottom. It had the same type of paddle agitator to mix the slurry in the radial direction. Directly under the cone was an isolation valve followed by the transfer pump. Once the entire amount of coal was added to the mixing tank, the valve below the cone was opened to the transfer pump that diverted the flow back into the tank. The recirculation of the pump pulls material from the bottom and recycles it back to the top of the tank and also to an inlet on the side of the tank. This allows for mixing of the tank from top to bottom as well as creating turbulence within the tank. This provides the type of agitation that is desired to increase the rate of collisions between the gob particles.

3.2.3.2 Recovering the Cleaned Coal

One of the traditional methods of separating coal particles from liquid incorporates the use of cyclones. However, the separation by cyclones is complex with many different variables. Their operation is based on empirical models without rigorous definitions. Many of the control variables for the mixing tank would affect the operation of the cyclone making it more difficult to analyze the effects of the detergent solution in the mixing tank. These variables would include the flow rates of the slurry leaving the mixing tank and entering the cyclone, the particle size of the coal in the mixing tank, and the specific gravity of the slurry or the amount of coal particles in the detergent solution. The goal of altering the control variables for the mixing tank will be to determine how these different conditions along with the detergent blend affects the ability of the process to liberate the clay and suspend it in solution. Even though cyclones are traditionally used for separation, they are not the best option to achieve the objectives for this testing system.

The goal of the mixing step is to liberate the clay and suspend it in the solution. Therefore, the best method to determine the effectiveness of the detergent solution and the process of agitation is to separate the disseminated gob particles with a vibrating mesh screen. Clay particles are very small, less than 300 mesh. They remain with the detergent solution and pass through any mesh screen larger than 300 mesh. Cleaned coal (disseminated gob particles) proceeded along the top of the screen to be collected in a container at the end.

3.2.3.3 Removing the Clay From the Detergent Solution

As stated earlier it is necessary to remove the clay and other fine particles from the detergent solution in order to analyze both the ability to reuse the detergents as well as the conditions of the liquid that would be returned to the environment. The only way to remove such fine particles efficiently is through centrifugation. After the liquid containing the fine particles, "clay", passes through the separation screen, it is pumped through a scroll type centrifuge that separates the fine particles from the liquid material. The solid cake of fine particles will be collected and analyzed for ash%. The liquid will be sent to a holding tank. From the holding tank the liquid can either be pumped back into the mixing tank or simply drained once a sample is retrieved. In addition, a portion of the detergent solution can be sent back to the mixing tank with fresh solution added to make up the difference.

3.2.3.4 Development of the Analytical Laboratory

In order to analyze the effectiveness of the process with respect to removing ash from the coal, it is necessary to perform a proximate analysis or partial proximate analysis on the coal. The process can be analyzed by observing the reduction in ash percent between the raw coal and the cleaned coal. The ash% of the centrifuge tails should also be determined to analyze the amount of fine coal particles passing through the separation screen. The problem was that sending the samples out to be analyzed at local laboratories had a return time of 3 to 5 business days. This means the results of a testing run would

not be known for as long as a week. It would be desirable to have the information needed to make changes to the operating conditions faster. Therefore, an on-site analytical lab was developed to determine the ash percent of samples taken. The results could then be obtained within 24 hours of the completion of the test. Changes to the operating conditions can be made in a much more timely manner.

In addition to determining the ash percent of the samples, the analytical laboratory will perform bench scale testing to determine the effectiveness of different detergent blends. The final testing of the blend needed to be done on the larger scale testing system. However, the bench scale testing can guide the mixture of detergent blends and reduce the total number of test needed from the PDU. The final duty of the analytical lab was to prepare the concentrated detergents that were added to the PDU. In the original testing procedure, the detergents were added to the mixing tank using a measuring cup designed for the kitchen. The amount of detergents added was on the scale of tens of milliliters per 200 gallons of water. Therefore, small changes in the amount added could have large effects on the results. The laboratory will make up the detergent blend in a one gallon container prior to the test run. Once the mixing tank is filled with water, the surfactant blend can simply be poured in.

3.3 Internal De-ashing: Centrifugation

3.3.1 The Original Centrifuge System

The centrifuge system employed with the previous liquefaction process was housed in the room 317 laboratory of the Engineering Research Building. The centrifuge process was able to sufficiently reduce the ash% in the extract so the centrate could meet commercial

standards. The blended product was used to make graphite electrodes by GrafTech. These electrodes passed commercial testing. But to accomplish this ash reduction, the 55 gallon drum of extract produced by the reaction system had to be processed several times until enough ash was removed. The centrifugation system uses a batch type centrifuge that accumulates the ash and other materials removed from the extract along the inner wall of the rotating turbine inside of the centrifuge housing. As the turbine fills, the rotational radius decreases which in turn decrease the ash removal efficiency. Once the turbine fills completely, no further material can be removed. At this point the centrifuge process has to be stopped and the turbine removed and cleaned out.

Each time that the tails were removed from the centrifuge turbine, the ash percent of the contents was only about 20% by weight. Eighty percent of the tails was un-dissolved coal or agglomerated product. Losing so much of the product not only means that there will be less de-ashed centrate available for further processing, it also meant that this large amount of waste material has to be disposed of. The deposal of the centrifuge tails would be a major expense for commercial operation. These factors concerning the low ash percent in the centrifuge tails rendered the whole process economically infeasible. Additionally, every time the drum of material had to be reprocessed, the viscosity of the centrate increased making it more difficult and less efficient to process. It was believed that the increase in viscosity would further lower the efficiency of the centrifuge process. An increase in viscosity of the centrate impedes the movement of small ash particles towards the wall of the centrifuge. This is particularly true when the density of the ash material is close to the density of the centrate fluid. It was hypothesized that a

polymerization reaction within the centrate fluid could be reduced by keeping the temperature of the centrifugation system less than 70°C.

To achieve the objective of improving the overall efficiency of the internal ash removal process, a greater ash% by weight had to be concentrated in the centrifuge tails. If the ash% contained in the centrifuge tails was increased, the majority of the existing deficiencies would be improved. Less product was lost as waste from the centrifuge process. Less hazardous waste had to be disposed of in the form of the centrifuge tails. And finally, every time the process is stopped to empty the centrifuge turbine, more ash was removed from the material. Therefore the extract required fewer processing runs which prevented further increases in viscosity. The remainder of the Internal De-ashing section will discuss the steps required for increasing the ash% by weight in the centrifuge tails.

3.3.2 Review of Objects for Internal Ash Removal

The primary objective is to increase the efficiency of the centrifugation process by increasing the ash% by weight in the centrifuge tails. To accomplish this object, several secondary objectives were investigated. These secondary objectives were:

- 1) To determine the cause for the increase in viscosity of the extract and centrate during heating and processing of the material.
- To develop and construct a Proof of Concept system to test and verify any new concepts that can improve the efficiency of the process.
- 3) To incorporate any viable internal ash removal concepts into the new production system

3.3.3 Viscosity of the Extract

The extract produced in the digestion process was collected in a 55 gallon drum. Since it is impractical to move hot drums of material, the drum and its contents were permitted to The drum was then transported to Room 317 to be cool to room temperature. centrifuged. When the material cooled to room temperature, it became more and more viscous and most times would solidify to a rubber-like state. Before the drum contents could be centrifuged it had to be reheated. As heat was applied to the drum using flexible ban heaters, the material would become thinner and less viscous. Because of the larger radius of the drum there is a significant heat gradient from the walls of the drum to the center of the drum. The extract would begin to liquefy along the drum wall closest to the heating source. However, as the heating time progressed and the material was heated to higher temperatures, it seemed to get thicker and more viscous. This was especially true when the extract was heated and centrifuged, cooled, and then reheated for the next centrifuge process. These observations seemed to indicate that the increase in viscosity was due to a polymerization reaction. This theory, in turn limited the temperature at which the centrifuge process could be operated. Therefore, the centrifugation process in Room 317 operated at a maximum temperature of approximately 70°C. The viscosity of the extract at this temperature was measured to be 625 cp. The material had a consistency of honey at room temperature.

3.3.3.1 Testing the Theory of a Polymerization Reaction

The efficiency and ash removal ability of the centrifuge process is tied directly to the viscosity of the material. The lower the viscosity, the lower the force of gravity needed to separate the solid ash material from the liquid extract. In addition, the Spinner II

centrifuge operates with increased RPMs and therefore an increased gravitation force as the flow rate through the centrifuge increases. Lower viscosity allowed for a higher flow rate through the system using the existing equipment. So the largest factor in increasing the efficiency of the centrifuge process was to identify the temperature at which the material has the lowest viscosity. However, if the material was polymerizing above a given temperature, processing the material under these conditions would ultimately decrease the de-ashing efficiency. So the first step was to determine if a polymerization reaction is actually taking place.

After the centrifuge process was performed and the system cooled, some of the tails produced were gathered and put in a beaker. The beaker, with its contents, was then placed in an oven at 110°C. At this temperature the tails became fluid. If the non-ash material contained in the tails had polymerized, one would not expect the polymer to soften again as polymerization reactions are not reversible. At this point, it was safe to assume that the polymerization reaction did not occur below 80° C, which was the processing temperature when the tails were produced. So, the next step was to determine if the polymerization reaction was actually occurring at any temperature, and if so what temperature it would occur.

The viscosity of the extract was measured as a function of temperature using a Brookfield viscometer Model 106. At 135°C the viscosity of the extract dropped to about 25 cp. The extract was then cooled to room temperature and the viscosity versus temperature test was repeated. If a polymerization reaction had indeed occurred, the viscosity of the extract would be higher than 25 cp when the repeated test reached 135° C. But once again, the viscosity was 25 cp at 135° C. The measurement of viscosity versus

temperature repeated itself a third time, so it was decided that the extract was not polymerizing and could then be centrifuged at higher temperatures with no ill effects. This would reduce the viscosity of the extract during the centrifuge process, thus theoretically increasing the efficiency by producing a higher ash% in the centrifuge tails. But the question still remained, why does the material become thicker and more viscous as the heating time increases?

3.3.3.2 The Loss of Light Volatiles from the Material

Once it was determined that no polymerization reaction occurred, the next logical assumption was that the lighter volatile material was boiled off and lost from the system leaving behind the thicker more viscous material. There were three main observations that lead to this assumption. The first was the odor detected every time that the material was heated. The next observation was the practice of adding the condensed liquid volatiles from the reaction process to the drum of extract to "cut" or "water down" the extract. The addition of these condensed volatiles dramatically reduced the viscosity of the extract. The final observation was the presence of naphthalene crystals on the inside surface of the drum above the level of the material after the drum was heated.

The distinct odor of volatile coal vapors was present in the 317 laboratory every time the centrifuge process was operating. This was especially true during the heating of the 55 gallon drum of material to the processing temperature. The heating bands wrapped around the drum reached temperatures of over 200°C. They were set to a high temperature to allow the heat to penetrate the drum; otherwise it would take several days for the center of the drum to reach the proper temperature. A significant temperature gradient existed within the material. Along the inside wall of the drum the temperatures

were much higher during the heating phase that could evaporate off the light volatiles. When the bulk temperature begins to increase over 70°C for the centrifuge process, the lighter volatiles including benzene, toluene, and xylene begin to escape from the extract into the vapor phase. The current centrifuge system is not designed to capture light hydrocarbons that have vaporized from the extract. So as the heating time and temperature for the drum increases, the lighter volatiles escape into the vapor phase and in turn are lost from the system. This is also why the practice of adding light volatiles collected from the reaction process only had temporary benefits.

The condensed light volatiles obtained in the reaction process are added back into the drum of material and the viscosity is indeed reduced. However, these are the volatiles that would be boiled off during the heating phase. This explains why the viscosity is reduced initially but then gradually increases as the same volatiles that were added begin to boil off. The final observation also supports the assumption that volatile materials are being boiled off. After the centrifuge process is performed and the drum is inspected, the inside surfaces are covered with naphthalene crystals. These crystals are not present prior to heating the drum. Naphthalene, along with other light volatiles, escapes the material while it is at an elevated temperature. As it contacts the inside walls and cover of the drum which is cooler than the extract temperature, it solidifies on the wall. The crystals are retained in the process. However, the system is not sealed and the volatiles that do not condense along the cooler inside surface of the drum escape into the atmosphere and are lost from the material.

In order to test the assumption a drum of extract was weighed and then equipped with the centrifuge and heating bands just as if centrifuge process was beginning. The drum was

heated up to the temperature at which the process starts. However, instead of running the process, the drum was allowed to cool back to room temperature. The drum was once again heated to the temperature of the centrifuge process and then allowed to cool back to room temperature. This heating and cooling of the drum was repeated a third time. Then, the heating bands and centrifuge were removed and the drum reweighed. Over 6% of the original weight had been lost. With no other action other than heating the drum, the assumption that the light volatiles were boiled off and lost from the material was proven. This not only affects the viscosity and, therefore the efficiency in the centrifuge process, it also greatly affects the mass balance numbers for the process as a whole.

If the system was sealed, or the ability of the materials in the system to escape to the environment was eliminated, then the centrifuge system could be heated to higher temperatures to reduce the viscosity. No loss of light volatiles would occur and the viscosity of the extract could be controlled by temperature with no negative effects. An ash separation could occur with more efficiency and mass balance could be obtained. Furthermore, retention of the valuable light volatile material would be accomplished. The next step was to examine the rest of the centrifuge process to determine where the other deficiencies lay. From this information, along with the proven assumption that the loss of light volatiles increases the viscosity, a proof of concept system was designed and constructed to determine if the centrifuge process efficiency can actually be increased. This was determined by running the proof of concept system and analyzing the centrifuge tails for a higher ash% by weight.

3.3.4 **Proof of Concept Testing System**

3.3.4.1 The Diaphragm Pump

The remaining obstacle to heating the extract to higher temperatures is the diaphragm pump. This pump is the driving force behind the flow of the material through the centrifuge and ultimately the rotational speed of the centrifuge. The diaphragms within the pump are made of a flexible polymer material that can handle temperatures up to 100° C. At 100° C, the viscosity was still too great to efficiently separate the ash from the extract. Another drawback of the diaphragm pump is that it produces a pulsatile flow similar to the beating of a heart. The inconsistent flow of material leads to an inconsistent rotational speed of the centrifuge. So a small "thumper" tank designed to absorb some of the effects of the pulses was installed between the pump and the centrifuge. But even with the thumper tank, the rotational speed of the centrifuge still pulsed. Not only is it inefficient to operate the centrifuge with a pulse type flow, it is also difficult to reproduce the experiment given an inconsistent rotational speed.

3.3.4.2 Design Concepts

The use of a gear pump to drive the centrifuge was eliminated in the original system due to two factors. First, it was believed that the high viscosity and particulate property of the extract would render the use of a gear pump to be impractical. It would not be able to supply the necessary flow rate to drive the rotation of the centrifuge. The second factor is that a gear pump requires a positive head pressure to operate effectively. Due to the design of the original system, the gear pump would have to draw the material up into the pump from the drum situated beneath it. In order for a gear pump to be feasible in this application, the 55 gallon drum would have to be elevated above the gear pump itself. Because of these two factors, the diaphragm pump was chosen for the original system. But seeing that the diaphragm pump cannot handle temperatures of over 100° C, the use of a gear pump must be re-examined. If the temperature is heated high enough so the extract will flow more easily with a much lower viscosity, then the lower viscosity of the extract would enable a gear pump to force the fluid through the system at high enough velocity to drive the centrifuge. A gear pump has a high thermal tolerance so it would also permit the extract be heated so that the viscosity of the extract could be lowered to around 10 centipoise. However, a gear pump requires a head pressure so a new centrifuge system would have to be designed in which the extract would not have to be drawn up out of the drum.

As was stated earlier the goal of the changes for the centrifuge system is to increase the ash percent in the centrifuge tails. The centrifuge system was able to reduce the ash percent in the centrate to less than 1%. However, in order to accomplish this, the material had to be run through the centrifuge system many times. The enhanced gravity was not great enough for the ash material to be removed for a single pass. That would require a much more expensive scroll type centrifuge suitable for a continuous process. So the system re-circulated the extract from the drum, through the centrifuge were ash and other material was removed, and finally back into the drum where the recirculation loop would begin again. Once the centrifuge turbine filled up with material, the process had to be stopped. The centrifuge was disassembled and the tails removed. Due to the scale of system and high costs of motor driven centrifuges, the concept of circulating

material through the bowl type centrifuge will be maintained for the proof of concept system.

With no budget from Quantex for the construction and operation of the proof of concept system of Figure 38, it was necessary to use equipment that the carbon products group already possessed. This would not produce an optimized process. It would be a temporary system that would only be run a few times in order to prove whether the concepts could increase the efficiency of the centrifugation process.



Figure 38: Diagram of the Proof of Concept centrifuge testing system.

This proof of concept system will be very similar to the existing system. It is only meant to determine what changes will be made in the new production system. The 55 gallon drum of extract with the centrifuge mounted to the lid will remain. The extract will be circulated through the centrifuge for a specific time just as the process is currently operated. The diaphragm pump will be replaced with a gear pump and the gear pump located below the level of the extract to provide positive pressure to the pump. The biggest obstacle to overcome will be locating a gear pump that can be used to test these concepts. After the gear pump is located below the centrifuge, a drain will be necessary, so the centrate would not clog the piping as it cooled after the run.

3.3.4.3 **Proof of Concept System Construction Preparation**

Several gear pumps were available from the pilot plant on the mezzanine of the NRCCE. Of the three gear pumps available, none of them produced a flow that operated in the optimal range for the Spinner II centrifuge. Also, it had been some time since any of the gear pumps had been operated. There was no telling what operating condition they were in or if they would operate at all. The gear pump that produced the highest flow rate with the motor available was T - 104 from the pilot plant (Bland 2000). The gear pump seen in Figure 39 was model A.D-25 manufactured by the Tuthill Corporation.



Figure 39: Gear pump as it was found in the NRCCE Pilot Plant

Initially the gear pump was locked up and would not turn, even with a pipe wrench. The input and output of the gear pump were 1 1/2 inch NPT threaded connections. A 90° elbow was connected to the input side and the output capped. The pump gears were then

filled with NMP in order to dissolve any material inside the gears that were locking it up. After the NMP was added the input was also capped. After 24 hours the output cap was removed and there is an attempt to turn the gears of the pump. Once again the pump did not rotate. So the output cap was replaced, the pump filled with NMP, and heating tape wrapped around the pump. It was allowed to sit under heat for another 24 hours. Then the output cap was once again removed and there was an attempt to turn the gears of the pump. This time the pump did rotate slightly with a good bit of effort. So the pump was then once again filled with NMP and left to heat overnight. Once again the pump turned, this time with less effort. This action of heating the pump with NMP was repeated a third and fourth time. After the addition cleanings the pump spun rather easily and it was ready to use for the proof of concept system.

Although this gear pump produced the highest flow rate, it only produced about half of the optimal flow for the centrifuge. So the construction of the proof of concept system will be to eliminate any flow restrictions between the pump and the centrifuge. Even though the testing system will not be operating at optimal conditions, the hope is that the system will still show improvements in centrifuge efficiency at the lower flow rate.

In order to provide a positive pressure on the gear pump, the 55 gallon drum containing the extract will need a bung hole on the side wall on the bottom section. The Carbon Products Group had several drums with such an opening. One of which was nearly empty. This drum was emptied completely and cleaned out. The side bung hole cap was removed. The 2" opening was reduced down to $1 \frac{1}{2}$ " and then fitted with a ball valve to isolate the gear pump from the drum. The extract to be tested was heated and transferred into the empty drum using the diaphragm pump from the existing centrifuge system. The

drum lid equipped with the centrifuge was fitted with a new drum lid gasket and installed. The opening on the lid for the diaphragm pump take-up line was sealed. Therefore, when the bell housing of the centrifuge is installed, the system should now be isolated from the environment and have the ability to contain the light volatiles that will escape the extract at the higher temperature.

3.3.4.4 Proof of Concept Testing System Construction

To produce the highest possible flow rate with the available gear pump, it would be necessary to minimize pressure losses between the gear pump in the centrifuge. The input and output of the gear pump are NPT threaded 11/2" male connections. But the input to the centrifuge has a diameter of 1 inch. To reduce the pressure loss in the piping, the diameter will remain at 1.5 inches and will be reduced down to 1 inch just before entering the centrifuge. The proof of concept system would also be constructed using the shortest route the piping from the gear pump output to the centrifuge. The gear pump output piping would immediately turn in the vertical direction to elevate the extract up to the level of the centrifuge using a wye fitting followed by an additional 45° elbow. Two more 45° elbows would be installed at the top of the vertical piping to direct the flow to the input of the centrifuge. This design will allow for the least amount of pressure drop from the output of the gear pump to the centrifuge, thus providing the greatest amount of flow rate for the available equipment. A thermocouple was installed near the input of the centrifuge to monitor the operation temperature of the system. The same flexible heating bands were installed around the drum along will a high temperature ceramic heater also recovered from the NRCCE pilot plant. The heating bands will be used to heat the extract to the higher operation temperatures. The plumbing along with the gear pump

will be wrapped will heating tape and insulated to maintain the temperature as the material proceeds to the centrifuge.



Figure 40: Gear pump after it was prepared for operation.

3.3.4.5 Experimental Procedure for the Proof of Concept System

The first step in operating the proof of concept testing system was to heat the drum of extract, the gear pump, and the circulation piping. With the isolation valve connected to the side of the drum closed, the heating bands wrapped around the drum were turned on. As the temperature of the extract increased, the heating tape wrapped around the plumbing and gear pump were also turned on. The temperature of the piping and gear pump could be monitored and controlled prior to running the system by using the installed thermocouple. Once the extract is heated to the appropriate temperature, the isolation valve was opened and the heated liquid extract allowed to flow to the gear pump. The gear pump was then turned on at a low speed. Once the gear pump was

operating, the speed of the pump was increased to its maximum by adjusting the flywheel connected to the motor. The extract was circulated through the centrifuge for several hours at elevated temperature.

When the process was complete the drum of extract was isolated from the gear pump by closing the isolation valve. The heating bands surrounding the drum of extract were turned off and the heating tape around the piping and gear pump was reduced. The drain valve connected to the output of the gear pump was opened and the material left in the piping was drained and collected as a sample. A smaller sample was collected and sent to the analytical laboratory for proximate analysis. The heating tape on the piping remained on at a low temperature to allow as much of the residual material in the lines to drain. Once the centrifuge cooled to a temperature where was able to be handled, the turbine was removed. The centrifuge tails were collected and maintained as a sample. A smaller sample was collected and sent to the analytical laboratory for proximate analysis and particularly to obtain the ash%.

3.3.4.6 Results and Conclusions of the Proof of Concept System

The proof of concept system was only run a few times but was able to verify the theory that centrifuging at a higher temperature can increase the de-ashing efficiency. When the centrifuge tails were analyzed, it was found that the ash percent was greater than 20% by weight. This was roughly the same ash% that was obtained in the original centrifuge system. However, the system was operated at a greatly reduced flow rate. With an appropriate flow rate for the centrifuge, or a centrifuge that is sized correctly for the gear pump, the ash% in the tails can be increased. In addition to the analysis of the centrifuge

tails, the centrate was also analyzed. The volatile% was consistent with the retention of the light volatiles during processing. After the system was run, the drum of centrate was reweighed. This weight was added to the weight of the centrifuge tails and the centrate drained from the plumbing. The final mass was about 1% less than the original mass of the drum prior to operation.

The proof of concept system was successful in showing that processing at higher temperatures will increase the efficiency of the centrifuge process. It proves that a gear pump could be used to drive the rotational the centrifuge. Finally, it also showed that a proper design can maintain the volatiles previously lost during the heating and processing of the extract.

3.4 The Reaction and Centrifugation Process

In the previous sections of this chapter, two methods of ash removal were investigated and discussed. The first method, external de-ashing, involved ash removal directly from the coal prior to the liquefaction reaction using a detergent solution to separate and disperse the clays. The second method, internal de-ashing, involved increasing the efficiency and overall effectiveness of the ash removal process after the coal has been liquefied. The external de-ashing did prove to be effective. It did reduce the ash% down to approximately 9.0% by weight. The internal de-ashing method had already proven successful in reducing the ash% of the centrate low enough for the products to pass commercial grade testing. With the Brookfield viscosity testing and the testing of the proof of concept centrifuge system with the gear pump, it was shown that the efficiency of the ash removal after liquefaction can be increased. And the de-ashing procedure by centrifugation could be financially viable. So, the research proceeded with the internal

de-ashing as the preferred method with a new design incorporated directly into the coal reaction process. The external de-ashing was no longer pursued, although it can be investigated in the future for potential cost savings with different coals used in the liquefaction process. Coal Innovations will pursue this effort without input from this research.

The goal of this section is to discuss the design and construction of the updated digestion reaction process including the new design of the centrifugation process. The section will be presented as a series of steps. In the first step, the previous reaction operation is discussed followed by the primary objective and secondary objectives for the new process. Step 2 describes the design concepts for the new process and each of the unit operations in the new process. These include sub headings described as step 2a, 2b, 2c etc. for each component in the system. Step 3 discusses the general preparations for construction. This is subdivided to include specific preparations for each component in the system. It includes, step 3a, preparation of the bunker facility; step 3b, collecting and refurbishing old equipment that will be used in the new system; step 3c, setting up to cut and thread the plumbing; and step 3d, repairs to the existing reactor. The remaining items in step 3 discuss the alterations to some of the equipment from a locale machine shop and the cleaning and refurbishing of used equipment to accomplish the design objectives. Finally, step 4 is a detailed discussion of the construction of the system. This step is subdivided into items 4a, 4b, 4c, etc. describing the construction and design of each unit operation.

3.4.1 Reaction Process Introduction

3.4.1.1 Step 1a: A Review of the Previous Bunker Operation

In the original bunker process in room 317, a specific quantity of crushed coal was blended with a specific quantity of coal tar distillate (CTD). The total mixture nearly filled a 55 gallon barrel. The mixture was stirred to assure homogeneity. However, homogeneity was only an assumption because after standing for a period of time the coal and other solids did settle to the bottom of the barrel. The barrel was placed on a floor scale and a quantity of the blend was pumped into the reactor. The barrel was weighed after the material had been pumped to get an accurate starting weight. The reactor was heated to 425°C and the mixture was permitted to react for a period of about one hour. After the reaction was complete, the mixture was emptied from the reactor into the holding tank where it was allowed to partially cool before being emptied by gravity into a 55 gallon drum. This process was repeated until the original quantity of material was completely reacted and the products nearly filled the 55 gallon collection barrel. At this point, the barrel was heated and centrifuged multiple times until the ash% was lowered to the desired level. It is important to appreciate that the original bunker operated in 55 gallon quantities. The purpose of this operation was not to get mass balance but to provide a large quantity of centrate to be sent to Koppers Industry for further processing to pitch that would be used to make graphite electrodes for commercial testing. Because of this, the accuracy needed for mass balance, in both measurement and procedure, were not followed.

3.4.1.2 <u>Step 1b</u>: Review of Research Objectives

The primary objective for the new reaction process was to design and construct a system that performs a single batch process for the digestion reaction and ash removal of lower rank coal that achieves mass closure from the raw materials through the moisture, condensed reaction volatiles, centrate, centrifuge tails, and non-condensable gases.

The following is the list of secondary objectives that were accomplished to produce the new coal digestion and centrifugation process so that the liquefaction technology can be evaluated for commercialization:

- 1) To construct and operate the reaction process to achieve mass closure from the combining of the raw material to the collection of all products from the process.
- To design and construct a new process that combines the digestion reaction process and an ash removal process that is redesigned to increase the efficiency of internal de-ashing of the extract.
- 3) To construct and operate the updated reaction process to produce a high quality centrate suitable for further processing in the vacuum distillation system along with products from the moisture collection system and the volatile collection system.
- 4) To construct and operate the reaction process to minimize or eliminate all of the safety hazards that occur prior to operation, during operation, and during the collection of the products.
- 5) To construct the bunker process with the ability to test control variables by altering the operation conditions and obtaining well representative samples for further evaluation from the analytical laboratory.

3.4.2 <u>Step 2</u>: Process Design Concepts

The first item, and possibly the most important, for the design concepts of the new reaction and centrifugation system, is Quantex did not authorize a budget to further

advance their technology. Quantex did purchase the lower flow rate "Spinner II" centrifuge for the new process after the proof of concept centrifuge system, which also had no budget, proved successful. Although there was a plethora of used equipment that could be refurbished owned by the Carbon Product program, a project of this magnitude could not be completed without additional supplies, equipment, and fabrication of specialty equipment. The only option would be to use the funds available in Dr. Stiller's overhead account with the hope that Quantex would replenish them. If this process could not be successfully designed, constructed, and operated with no budget, then the technology that Quantex had already paid to license would remain worthless and the funds would probably not be replenished. Therefore, economics will play a large role in building this process. The amount of funds ultimately spent to complete this part of the research amounted to just over \$12,000, which was an amazing accomplishment. A detailed list of the equipment purchased to complete this portion of the research is available in Appendix A.

The focus of this research is to design and construct a new reaction process where accurate mass balance can be obtained. This involves significant changes and alterations in both the equipment and procedures. The discussion follows a top down procedure so the work for the new process will follow the same order. First, the question of sample preparation is discussed. It has already been implied that the sample consistency in the original system must be improved as the coal seemed to settle to bottom of the loading drum and no two samples were identical. Second, the transfer method from a 55 gallon drum into the reactor also creates errors and a new loading process will be considered.

The next step in the process is the operation of the reactor. Some aspects of this step must be examined to accomplish the objectives. How are the reaction conditions controlled to produce consistent and repeatable results? What happens to the moisture that enters the system with the coal? How are the vapor volatiles produced during the reaction handled and collected? How will the reactor be drained given the extreme operating conditions? The new reaction and centrifugation system must be designed with all these questions in mind. Another crucial aspect is how can all of this be done safely? Once the reaction is complete, the process will proceed to the ash removal step.

The process of upgrading the reaction and centrifugation systems is divided into unit operations. Each of the unit operations can best be considered as separate entities and the entire system is the accumulation of the unit operations.

3.4.2.1 Step 2a: Design Concepts for the Loading System

First consider loading of the reactor. A decision had to be made as to what mechanism would be used to fill the reactor. In the original system, a large sample of the raw materials was prepared as a slurry and batches pumped into the reactor. It was felt that the samples probably were not homogenous, so no two samples were the same. To insure such similarity, it would be better to prepare smaller individual samples. Each individual sample could be weighed and loaded into the reactor for that particular run. Thus, all of the samples would be as nearly identical as possible. The raw materials to be fed into the reactor are ground coal, CTD, and a proton donor liquid. The single important condition for feeding the reactor is that an accurate weight of each of the components can be obtained. At this stage of the research the loading of the reactor was not yet well defined. The slurry could either have been pumped into the reactor or mixed in a transport vessel and hoisted up to load the reactor. With either of these two loading concepts, it

was of the utmost importance to transfer all of the material weighed into the reactor. This was the first step in obtaining mass closure for the system and being able to identify where all of the material goes.

The only consideration in determining which of these two loading concepts was implemented in the new bunker process was which one would give the best mass balance numbers at the beginning of the process. The material loaded into the reactor was a slurry that varied in viscosity as the temperature changes. So, the inside of any container, pump, or length of piping collected trace amounts of the slurry. This is slurry that had been accounted for in the weighed inputs, yet not transferred into the reactor. For example, the raw materials could be weighed and loaded into a vessel connected to a pump. The raw materials mixed in the tank until they are homogeneous and then pumped from the ground floor up into the reactor through the connection on the lid. After the loading process has been complete, the lines can be drained out and any of the slurry material collected and weighed for mass balance numbers. However, there will still be trace amounts left in the piping, the pump, and the mixing vessel. The only way to determine how much material has collected inside of this system would be to disassemble and weigh each piece before operation and then disassemble and weigh each piece after operation. The increase in the amount of weight would be the material that was weighed and added to the mixing tank but was not loaded into the reactor. Unless the system was disassembled and reassembled every time the reactor is loaded this amount of material would not be considered in the mass balance of the reaction system.

Similarly, with the transport vessel, the weight can be measured and recorded before any of the raw materials are loaded. The raw materials can then be added directly into the vessel and agitated until they are homogeneous. The transport vessel can then be hoisted to the second floor

and connected to the lid of the reactor. The isolation valves can be opened and the slurry allowed to drain into the reactor through the lid. Once this step is complete the transport vessel can be detached from the reactor and reweighed. Therefore, all of the raw materials that were weighed and loaded into the transport vessel can be accounted for. The exact weight of material loaded into the reactor will be known.

Although it would be easier from a procedural standpoint to load the reactor by pumping the slurry and not accounting for the amounts materials left in the piping, the bunker process would start out with mass balance numbers that were less accurate. Since one of the primary objectives of this research is to obtain accurate mass balance numbers, the use of the transport vessel to load the reactor was the obvious choice for this application.

3.4.2.2 Step 2b: Design Concepts for the Reactor

Before the reactor was put back into operation, the pressure transducer was disassembled and inspected and the tubing replaced. In addition, some repairs to the temperature controller including replacement of solid-state relays also had to be performed before the reactor can once again operate properly and safely. Operating with the damaged relays allowed for operation of the reactor heating elements, but disabled the overprotection circuit which would stop the reactor heater bands when optimum temperature was obtained.

The heating bands, along with all of the electrical connections, would be disassembled, cleaned, and inspected to ensure proper connections. Once the reactor resumed operation it was loaded, sealed, and the heating bands turned on. The temperature increased at a given rate, up to the maximum temperature, and was held for a given amount of time. The rate of increase in temperature and the hold time was controlled by the reactor temperature controller. In addition,
the pressure inside the reactor was monitored using the existing pressure transducer that is installed. The data collected during the run was the temperature, pressure, and time so the conditions can be duplicated for multiple runs.

The reactor pressure abatement system is the next item that was addressed from the original bunker system. Pressures will typically increase to over 800 psig in the reactor at its hold temperature. It will be necessary to vent the pressure so the reaction system can be evaluated at mild conditions. In the new system the one-quarter inch stainless steel tubing was replaced with three-quarter inch piping exiting the reactor which expands to one inch piping in order to prevent the possibility of clogging in the vapor line. This also reduced the tremendous velocity of the volatile vapors as they traveled down such a small diameter tubing at such high pressures. The vapors then continued through a large shell and tube heat exchanger and into the 120 gallon expansion tank. The 120 gallon expansion tank greatly lowered the pressure, which was contained in the two gallon vapor volume of the reactor (PV = P'V'). In addition, a high pressure stainless steel tube from the rupture disk connected to the lid of the reactor was connected directly to the 120 gallon expansion tank as a secondary safety precaution.

3.4.2.3 <u>Step 2c</u>: Design Concepts for the Moisture Collection System

It was stated earlier that the CTD produced by the process would be recycled to liquefy the next round of coal. However, with the current estimated mass balance results from the old process there was a deficiency of 16% by weight. This means that each new round of digestion reactions would require additional CTD to sustain the reactions. CTD was consumed instead of produced. This was also referred to as a showstopper, as the process could never be commercially viable. But, is this 16% by weight an accurate number even with the estimated mass balance? What happens to the weight of moisture in the coal that is loaded into the reactor? As CTD is recycled back into the process without the moisture being removed, the moisture would continue to build up in the process and become a greater percentage of the CTD makeup.

The moisture collection system is a brand-new concept developed for the new reaction process during the course of this research. It previously did not exist in any form in any of the liquefaction processes in the past. The idea for the moisture collection system was a two-stage heating of the reactor. Once the slurry was loaded into the reactor and the reactor sealed, the temperature was increased to about 140° C. This is the temperature at which water vaporizes at the pressure inside of the reactor. Once this temperature was achieved, the vapor vent valve was opened and the vapor moisture allowed to flow into the moisture collection tank, which was connected to a water-cooled condenser. This caused a drop in pressure in the reactor and the vent valve was closed. The temperature remained constant at 140° C and the reactor continued to be vented to the moisture tank until the pressure was no longer rising. It was then assumed that all of the water and light volatiles that vaporize at temperatures below 105° C, at atmospheric pressure, will be removed from the reactor and collected as a liquid in the moisture tank.

In addition to preventing the accumulation of water in the CTD, there are several other benefits to the moisture removal system. Water in any system will act as a heat sink. It would require a great deal more energy to raise the contents of the reactor to the hold temperature if the moisture is still present. This will be a great cost savings for the process. Furthermore, in many parts of the world, water is a valuable resource, especially in very arid regions. After the water and other light volatiles are removed from the system, they can be further processed to produce clean, potable water. This also greatly improves the value of this process and is a great step forward in making it economically feasible. Without the removal of the moisture before the digestion reaction, this process would not be economically feasible and never reach commercialization.

3.4.2.4 Step 2d: Design Concepts for the Flash Tank

Several improvements were made to the flash tank (Figure 41) in the new system, or the blow down tank, as it was referred to in the old bunker system. First, proper placement for the flash tank had to be decided upon. In the first bunker system, the vessel was placed in a more horizontal position underneath the reactor show below.



Figure 41: Placement and set-up of the blow down tank in the original bunker reaction process.

As can be seen from the picture, the flash tank was not the ideal system for collecting material entering at a high velocity over 400°C and several hundred pounds of pressure. It is connected to the reactor using a flexible hose that was not rated for these conditions. The use of the flexible braded metal hose at extreme conditions was a great safety risk and had to be replaced. Furthermore, it was not securely fastened and was able to move around. In addition to the drop in pressure when the extract exits the reactors and enters the flash tank, more volatiles would escape the extract into the vapor phase. This tank

was also connected to a 120 gallon collection tank using quarter inch stainless steel tubing. As is the case with the reactor vapor lines, this presents a clogging problem as well as a safety concern with such small diameter tubing to transport the vapors. This was not the ideal set up to obtain mass balance for the system. As the material cooled it tended to solidify to a rubber-like material. This coated the large surface area inside of the tank as it was horizontally lying on its side.

In the second iteration of the bunker process, the orientation of the flash tank was changed to a vertical position. In that orientation the tank could be securely fastened to the 4 inch I-beam directly in front of the reactor. It was then stable when the extract was forced from the reactor into the flash tank using the remaining volatile pressure in the reactor. It could also be directly hard-piped, employing the use of flanges or unions and, thereby eliminating the use of the flexible metal hose. It emptied to the centrifuge system more efficiently, thanks to the threaded opening at the very bottom of the flash tank when oriented vertically. An isolation valve was installed at this threaded opening to contain the extract in the flash tank as it cooled to the operating temperature of the centrifuge system.

Several of the additional threaded openings were used. Directly below the 1 inch opening at the center of the tank that received the extract from the reactor, was another 1 inch opening. Here, a thermocouple was installed, which read the temperature of the extract as it cooled in the flash tank. On the side of the tank, near the bottom, was a 2 inch threaded opening. A threaded cap was installed there that could be removed to visually inspect the tank for standard maintenance and to help determine any problems that may occur. On the same side of the tank, closer to the top, was a second large

opening. Here, a 1.5 inch piping exits the flash tank and carry the vapor volatiles from the extract to the volatile collection system. The large diameter piping was used in place of the quarter inch tubing that was previously used to carry the volatiles from the flash tank. A pressure gauge was placed at the top of the flash tank. If access pressure did build in the tank, it would determine whether a clog had occurred somewhere in the vapor lines.

3.4.2.5 <u>Step 2e</u>: Design Concepts for the Volatile Collection System

The primary feature of the volatile collection system was of the large 120 gallon vessel referred to as the expansion tank. Like the flash tank, it was oriented vertically. The primary reason for this was to save floor space on the ground floor of the reactor room in the bunker. There are other advantages to this orientation. When the vapors are condensed to a liquid they will settle at the bottom of the tank. Setting the tank vertically will give the smallest amount of surface area available for any of the heavier volatiles to collect and remain in the system. The expansion tank will have one primary input which was the volatile vapors vented from the reactor and the flash tank. They will enter the very top of the expansion tank immediately after passing through a large single pass shell and tube heat exchanger. This heat exchanger has cold water and condenses some of the volatiles to a liquid as they pass through and collect in the bottom of the expansion tank. This heat exchange will continually remove energy from the system condensing more of the vapors.

Vapor molecules occupy about 1000 times the volume that liquid molecules do. So, in addition to the increased volume to reduce the pressure, vapors condensing into liquids also assist in reducing the high pressure being released from the reactor. As the vapors

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condense in the heat exchanger and also inside of the expansion tank, when contacted with its colder surface area, the pressure drop in this area will pull more vapors towards the colder surfaces. The idea is that all of the condensable volatiles produced in the reaction will condense and collect in the expansion tank. The liquids were drained out of the expansion tank through the opening at the bottom. After they are collected and weighed they were combined with the condensed volatiles produced in the distillation and coking steps to be used as CTD in the next round of reactions. The weight of liquids was also one of the products used in the mass balance calculations.

The expansion tank is present to collect all the condensable materials. The idea is to collect all of the condensable volatiles that are produced in the process for mass balance purposes. There were trace amounts of non-condensable gases in the vapor stream. The design of this process did not include the ability to collect or measure these non-condensable gases. It was outside of the scope of this project. However, these non-condensable gases must be dealt with. They cannot simply be expelled from the process into the environment.

3.4.2.6 <u>Step 2f</u>: Design Concepts for the Centrifuge System

The first problem in designing a new centrifuge system is to produce the appropriate flow rate for optimum centrifuge operation. The existing Tuthill gear pump costs over \$8000 when purchased new. This does not include the motor, the gear reducer, or the stand. However, spinner II which makes the bowl type centrifuge is does make smaller centrifuges that require a lesser flow rate to operate optimally. The smaller centrifuge also has a smaller capacity to contain the centrifuge tails. So in order to prevent the inefficient operation of having to reheat and reprocess the extract, smaller amounts will need to be processed. Ideally, the amount of extract processed should be sized for a single operation of the centrifuge process.



Figure 42: Flow rate parameters for the centrifuge purchased for the new production system provided by Spinner II

Smaller batches could be processed; therefore the smaller centrifuge can be used. Spinner II makes the model 600HD centrifuge that was used in the original system and also the proof of concept system. It also makes smaller models. The 400HD model is nearly identical to the 600HD model with the only difference being tails capacity and the required flow rate. Since this model requires about half of the flow rate, it was properly sized to operate in the optimal range for the existing gear pump. With the flow rate of the current gear pump, the centrifuge rotates at roughly 4000 RPMs. The rotational speed was estimated using Figure 42. This should concentrate the ash percent in the tails and increase the overall efficiency of the centrifuge process. Spinner II renamed their models. So, model 400HD for the new process is now model 3400 display in Figure 43. But, it is the same piece of equipment.



Figure 43: The model 3400 Spinner II centrifuge that will installed in the new reaction and centrifugation system.

The next problem arises from the higher operating temperatures and the reduction in viscosity. As the extract viscosity is reduced to increase the efficiency of the de-ashing, the force of gravity causes the ash to settle out within the heated drum and collect at the bottom. The proof of concept system drew extract from the side of the drum into the gear pump and pumped it back up to the centrifuge. This opening on the drum is several inches from the bottom. Any ash material that settled out below this level would not be processed in the system. In the previous procedures for the centrifuge process, the drums were not completely emptied after centrifugation. This material at the bottom of the drum of the ash material and was not included in the mass balance

calculations. There are two ways to solve this problem. The first would be to agitate the extract during processing. This would reduce the amount of solid materials including the ash to settle to the bottom. The other option would be to change the containment vessel for the extract. If smaller batches are processed due to the smaller size of the centrifuge, a different extract containment vessel can be used. A tank with the output to the gear pump at the lowest point can be employed rather than a drum. Therefore, any solid material that settled out to the bottom would be the sent directly to the centrifuge to be processed.

It had also been determined that the repeated heating of the 55 gallon drum of centrate was the largest factor in the loss of volatiles from the material. The proof of concept system did show that a sealed system can retain the volatiles that were previously lost. However, the extract still had to be transported from the bunker facility to the 317 laboratory. Once there it had to be reheated which required about 24 hours. Although most of the volatiles were maintained in the material, it was still an inefficient method for de-ashing the extract.

In the reaction process, the extract is drained from the reactor at a temperature of over 400°C into a holding tank where the temperature was reduced to around 200°C where it could be more safely transferred to the 55 gallon drum. The most efficient method for de-ashing this extract would be to drain the contents of the holding tank directly into a stationary vessel. The stationary vessel would have the centrifuge mounted on the top of the tank and the gear pump connected to the lowest point of the tank. The extract would not have to be reheated for the centrifuge process. The de-ashing can be accomplished in the same facility as the reaction. This would also allow for the centrifuge with a smaller

capacity to contain the tails from processing batches of no more than 8 gallons at a time. In addition, all of the extract in the tank is processed and can be evaluated as a whole to test the new de-ashing system. After the de-ashing process is complete, it can then be loaded into a drum for transport to the laboratory in room 317.

3.4.2.7 <u>Step 2g</u>: Design Concepts for the Volatile Scrubbing System

The odors produced by the reaction process simply would not be accepted on the campus. Therefore, the vapor stream containing the non-condensable gases had to be scrubbed before it was sent to the environment. These non-condensable gases consist mainly of hydrogen sulfide and other materials. In order to handle these vapors, an alkali scrubber was designed and constructed. The idea was to build a packed scrubbing tower made of a material that will not corrode in the alkali solution such as PVC. The tower will consist of an 8 inch to 10 inch diameter PVC pipe with as large of a height that the bunker will accommodate to provide the greatest surface area. It was packed with a large surface area packing elevated above the alkali solution reservoir. The non-condensable gases enter the tower beneath the level of the solution. It will bubble through the liquid and then up through the packing. The alkali solution was pumped to the top of the tower and sprayed in through a showerhead to coat the surface area of the packing. The flow of the liquid and vapor was countercurrent. The scrubbed, non-condensable gases, which now consist mainly of nitrogen, will then exit the side of the tower near the top. They continue through piping to the vent stack were they are exhausted from the building.

These are the design concepts for each of the unit operations for the new reaction and centrifugation process as a whole. Once the process was constructed using these design concepts and the proper procedure put into place, all of the objectives for the bunker

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process were achieved. Mass closure from the raw material through the moisture, condensed volatiles, centrate, centrifuge tails, and non-condensable gases was realized. The digestion and centrifuge steps were combined into one process which will operate safely and produce a quality centrate, which was further processed in the vacuum distillation system. Finally, a new reaction system will have the ability to alter control variables for testing purposes.

3.4.3 <u>Step 3</u>: Bunker Construction Preparation

3.4.3.1 Step 3a: Preparation of the Bunker Facility

Before construction of the new process began several tasks had to be completed. First, the old process had to be completely disassembled and removed. The only thing that would remain was the reactor with the heating bands and temperature controller along with the transducer to record the pressure. The reactor itself would be completely stripped of all the fittings and cleaned. Any of the fittings along with the rupture disk that could be salvaged would be cleaned and replaced. All of the wiring and leads for the reactor heating bands were also checked along with the condition of the thermocouple and agitator.

In order to complete the work needed to construct the new process, the garage area of the bunker had to be available. This space had been occupied by the Mechanical Engineering department but had not been used for construction or experimentation in some time. It was currently used as storage for parts of previous experiments and equipment that was no longer in use. Also, the Civil Engineering department was storing containers full of concrete from past experiments on the cement patio behind the building. It was a major accomplishment to gain access to these areas for the use of the

new bunker process. Without this space, the construct would not have been possible. Neither would the ongoing maintenance of operating the process.

The second item that needed addressed was the low budget that we were operating under. The new centrifuge sized for the gear pump had already been purchased. Also, a 120 gallon vertical tank had also been purchased to be used for the expansion tank. However, the rest of the equipment would either have to be refurbished from old carbon products experiments or purchased with the limited funds available in Dr. Stiller's overhead account. As mentioned earlier, Quantex provided no funds to advance their technology other than purchasing the centrifuge. The responsibility of enhancing the coal liquefaction technology to the point of commercialization fell entirely on the Carbon Products research group at WVU. So the process of going through the old carbon products experiments, particularly the pilot plant on the mezzanine of the NRCCE, had begun. The idea was to locate and identify any equipment, including piping and fittings, which could be salvaged and refurbished to be used in the new bunker process. This would allow the limited budget to purchase any equipment that was not available or could not be modified for use.

The construction of this new bunker process posed many problems. The main problem, or the overall problem in constructing this new process, was the limited space available in the bunker reactor room (Figure 44). How can all of the equipment fit in the space available and still provide the necessary room for personnel to maneuver, collect samples, and operate the system? So, the first step in this construction project was to disassemble and remove the old system, down to the reactor. The next step was to generate a diagram of the footprints of the reactor room and the space that is available. Next was to identify the equipment that needed to be in a specific location and what equipment or unit operations could be moved. For example, the reactor was in a stationary position on the second floor of the reactor room. Once the old system is removed, the only other fixed pieces of equipment that will remain are the vent stack, which leads out of the building to the atmosphere, and ladder to access the second floor.



Figure 44: Empty first floor of the reactor room after the old bunker system was removed.

Each unit operation will also have its specific problems with construction. These problems are due to the limited space, the availability of refurbished or used equipment, the necessity to meet the objectives laid out for experimentation, and the limited monetary funds available. The unique problems of building each unit operation were explored in more detail throughout the construction section or Step 4. One key point to remember is that the original design concept is not "set in stone". This is an original process with unique problems to overcome for the liquefaction of coal. Given the limited space and resources available, the design concepts must have the ability to be altered as the construction progresses. Also, the reactor loading process, which was critical for obtaining mass balance along with consistent reactor inputs, had yet to be designed. Dimension of the bunker facility are shown in Figure 46 with the reactor room in greater detail in Figure 45.



Figure 45: First floor layout of the reactor room with the possible placement of some of the equipment.

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upper reactor compactment

Figure 46: Layout of the entire bunker facility.

3.4.3.2 Step 3b: Preparation of Plumbing Requirements and Used Fittings

There was no shortage of used fittings and valves that were property of the Carbon Products program. The only problem is that every used fittings and valve was caked with some form of liquefied coal or other material and had to be thoroughly cleaned, inspected, and possibly repaired. It was a major effort to clean all the threads so they could be properly sealed in the new system without leaking. Each one required a combination of wire brushes, rags, NMP, light volatile hydrocarbons, heat, and anything else that could be found to clean these pieces. But, with the exception of more specialized fittings, just about everything that was needed was available without using the limited funds available in the budget. Some of the used fittings collected are shown in Figures 47 and 48 while Figure 49 shows pieces after they had been cleaned and are ready to be installed.



Figure 47: Used fittings removed from previous Carbon Products experiments before they have been cleaned.



Figure 48: Used valves from Previous Carbon Products experiments before they have been cleaned and refurbished.



Figure 49: Used valves and fittings ready to be installed in the new reaction and centrifugation system.

3.4.3.3 <u>Step 3c</u>: Plumbing the equipment and Setting up the pipe cutter and threader

In order for all of the equipment to fit together properly and capture all of the volatiles, specific lengths of pipe must be cut and threaded. Alternatively, the various sections of pipe could be measured, cut, and welded together. Either option would be expensive and time consuming for any pipe or section of pipe that was needed. Thus, a system had to be set up in the bunker to cut and thread the pipe as it was being installed.

Plumbing the equipment together with the resources available was a very difficult task, especially when dealing with the high temperatures and pressures of the coal liquefaction and centrifugation process. If there were funds available in the budget, flanges could have been purchased and contractors would have been hired to weld the pipe together at specific lengths for the equipment to fit properly. Alternatively, Swaglok fittings and steel tubing could be purchased so that the system could easily and securely be plumbed together. Seeing that neither these options were feasible, the equipment had to be plumbed together by cutting and threading stock diameter piping to the required lengths.

The motor driven pipe threader and cutter seen below was borrowed from the Chemical Engineering machine shop and temporarily moved to the bunker during construction.



Figure 50: Motor driven pipe cutter and threader used to construct the reaction system.

As stated earlier, most of the fittings were readily available as refurbished fittings from old Carbon Products experiments. Just about all of the fittings and piping in the new reaction system would have a diameter of 3/4", one inch, or 1 ½ inches. Thus, 20 foot sections of stock carbon steel piping were purchased at each of these diameters for plumbing the equipment together. In addition to the increased cost, stainless steel could not be cut and threaded using this machine because the cutting heads were not the right material to thread such a hard metal. For the application of the reaction system, flanges and gaskets would be the preferred method of connecting the piping together. However, flanges were not available and would be expensive to purchase. There were many unions available from old experiments. Therefore, unions were used to connect the piping together. For each of the three diameter piping sizes, various lengths of pipe nipples were ordered. The pipe nipples were available in half inch incremental lengths. Therefore, small adjustments could be made between fittings so that the plumbing will provide a tight and secure fit. This is necessary to contain all of the materials at the extreme conditions. Without this type secure fit for the plumbing of the equipment, mass balance could not be obtained and the process could not be safely operated.

One method of allowing for error in plumbing a system together is the use of flexible hoses. However, due to the high temperatures and extreme pressures of this process, flexible hoses are not an option. This is more of a safety concern than anything. If this process cannot be operated safely, it will not be operated at all. It was common for more than one piece of piping to be cut and threaded in order to obtain the exact fit needed for the plumbing. Also, slight adjustments in the mounting and placement of equipment would have to be designed into the construction process for this tight fit to be accomplished.

3.4.3.4 <u>Step 3d</u>: Construction Preparation for the Reactor

3.4.3.4.1 <u>Step 3d1</u>: Repairs and Upgrades to the Reactor

Given the state of the old process, it was stripped down to the reactor and rebuilt from there. The reactor output piping, including the valves and flex hose leading to the 40 gallon tank, was disconnected and removed. The fitting on the bottom of the reactor for the outlet piping was a specialized fitting. It was threaded for one inch NPT piping. However, as the pipe was threaded into the fitting, it narrowed similar to a Swaglok fitting. This allowed for a good seal to the reactor using NPT threads even at the extreme temperatures and pressures that the reactor was operated. These threads were cleaned out using a soft wire brush and NMP but the fitting itself was not removed. The fitting had not leaked even at more extreme conditions that the system was operated under. So there was no need to remove the fitting to inspect it further unless it began leaking in the future.



Figure 51: Condition of the reactor prior to construction of the new system.

The connections on the lid of the reactor were specialized threads. The threads were MHP fitted and had to be ordered from PPI (Pressure Products Industries), the company that designed and built the reactor. One fitting connected to the lid of the reactor was an MHP thread to 1 inch NPT. This connection had been used to load the reactor. Because it was the largest opening on the reactor lid, it will continue to be used to load the reactor. This is for the purpose of mass balance which would most easily allow transfer of material from the transport vessel into the reactor. The other connections for the lid were three-quarter inch MHP threaded. But, the only fittings that were available were plugs for these openings or fittings suitable to connect quarter inch Swagelok fittings. Three of these fittings were connected to the lid. One was for the tubing leading to the pressure transducer, the second was for nitrogen input into the reactor, and the third was the exiting vapor line to vent the reactor. In order to increase the vapor line size to three-quarter inch, a specialized fitting was ordered from the company. The condition of the reactor when construction began is shown in Figure 52 and Figure 53.



Figure 52: State of the connections on the reactor lid at the beginning of construction.



Figure 53: The tubing connected to the reactor lid prior to construction.

The remaining fittings were removed from the reactor lid along with the 1 inch fitting to load the reactor and the $\frac{1}{2}$ " threaded opening that connected to the rupture disk. All of the quarter inch stainless steel tubing with Swaglok fittings was removed along with the cooling water tubing for the reactor agitator. The next step would be to clean the reactor of all of the material that has collected on the lid and sides of the reactor. Because of the high reactor temperatures, this buildup of volatile material is a safety hazard. The threads for the reactor lid were easy to clean because sealant had not been used. The MHP connections are actually a metal to metal seal that is machined to a precise fit. The threads only act to hold the metal to metal connection together.

The next step was to check the condition of the thermocouple, the thermocouple wiring, and the pressure transducer. The quarter inch tubing connecting the pressure transducer to the reactor was replaced. The nitrogen input tubing had to be altered to house a manual pressure gauge so the pressure transducer can be checked during operation. Once the reactor lid fittings had been cleaned (Figure 54) and the new three-quarter inch MHP to NPT fitting had been ordered and received, the reactor lid fittings were all reinstalled.



Figure 54: Condition of the reactor lid after cleaning and upgrades.

3.4.3.4.2 <u>Step 3d2</u>: Repairs and Inspection of the reactor heating and temperature control system

During operation of the original bunker process, a terminal block failure occurred that was a result of chronic thermal expansion and contracting, which allowed one of the three 480vac phases to open and not make connection. Operating with only two phases caused an operational voltage imbalance in the three phase supply voltage for the reactor. This allowed the voltage to back pass when the terminal block failure occurred and thereby blew the two protection solid state relays. Isolation of the circuit and ohm checks verified that two high-voltage solid state relays had failed in a shorted mode. This allowed for operation of the reactor heating elements, but disabled the overprotection circuit, which would stop the reactor heater bands when optimum temperature was obtained. Two replacement high voltage solid state relays that the system requires are Omega brand, model number SSRL660DC50. The damaged solid state relays were removed from the reactor temperature controller and replaced with the new solid state relays (Figures 55 and 56). This restored proper operation of the reactor temperature controller.



Figure 55: The disassembled reactor temperature controller.



Figure 56: The new solid state relays installed in the temperature controller.

The second item that was addressed with the heating system for the reactor was the leads. After all the material had been cleaned from the lid and sides of the reactor, it was possible that some of the material had seeped down inside the covering for the wire leads of the heating bands. This could cause damage to the heating bands or could possibly short out and cause a spark. Due to the presence of explosive vapors in the process, these boxes were taken apart and the leads checked to make sure they were in proper working order. All of the leads were in proper working order and the boxes, seen in Figure 57, were put back together. Once again, due to the extreme conditions that this process operates, safety was considered at every step along the experimental design and construction.



Figure 57: Boxes covering the wire leads for the reactor heating bands.

3.4.3.5 <u>Step 3e</u>: Construction Preparation for the Loading System

The vessels that are commercially available would not meet the requirements that were laid out in the design concept for the transport vessel. The transport vessel began as a standard 13 gallon carbon steel tank that had brackets to mount in the horizontal or vertical positions. The vessel was sent to the local machine shop to have the necessary fabrications for proper operation. The commercially available vessels consist of a piece of the sheet metal of a standard width that is welded to create a cylinder opened at the top and bottom with a predetermined diameter. Rounded caps are then welded to the top and bottom openings of the cylinder and the threaded opening are welded into place.

With eight gallons of raw materials loaded into the transport vessel, the 13 gallon tank would hold all of the raw materials and provide the additional volume to agitate the slurry. A ten gallon tank would only leave two gallons of volume above the liquid level. This would make it possible for the agitation of the slurry to splash material onto the top of the transport vessel. This material would likely collect of the top of the vessel and not be loaded into the reactor. Therefore, the weight would not be accounted for in the mass balance numbers. Below is a picture of the transport vessel after it had returned from the machine shop.



Figure 58: Fabricated transport vessel to ensure proper transfer of raw materials in the reactor.

Three alterations were made to the vessel at the machine shop. First and foremost, the rounded bottom was removed and replaced with a cone that is 45^o from horizontal. This

allows the slurry to more easily drain from the transport vessel into the reactor. The second alteration was an eye bolt that was welded into the threaded opening at the top of the vessel on the oppose side as the cone. The eyebolt was installed to connect to the hoist. At the same side as the eyebolt at the top of the transport vessel, two large openings were added. Two 3 inch holes were cut at the top of the vessel with three inch threaded nipples welded to the openings. One side was fitted with a removal three inch threaded cap for loading the raw materials into the transport vessel. The second large opening at the top of the vessel was fitted with an agitator connected to an electrical drill to agitate the slurry.

3.4.3.6 <u>Step 3f</u>: Construction Preparation for the Moisture Collection System

The moisture collection tank will only act as a receiving vessel. Therefore, a standard "off the shelf" vessel can be used. A 13 gallon tank was mounted to the 4 inch I-beam above the flash tank. Two pieces of unistrut were cut to secure the tank around the I-beam in the vertical position. The other item needed for the moisture collection system is a condenser. A shell and tube heat exchanger that was used in the old bunker system was used as the condenser for the moisture collection tank (Figure 59). The tube side consists of U-tubes. The cooling water can flow through the U-tube and act as a cool finger in the moisture collection system. The old fittings and piping was stripped from the heat exchanger. Both the tube side, shell side, and all of the connections were cleaned and prepared for operation.



Figure 59: Refurbished heat exchanger to be used as the moisture collection system condenser.

3.4.3.7 <u>Step 3g</u>: Construction Preparation for the Flash Tank

Once the 40 gallon tank was remove from the old system it needed to be cleaned out of the material from the earlier bunker operation. Light volatiles were loaded into the tank and the openings were temporarily sealed. Heating bands were wrapped around the tank and turned on overnight to dissolve any material on the inside walls. The next day the heating bands were turned off and the volatiles drained from the tank. With the inside of the tank cleaned, the next step was preparing to mount it in the vertical position in front of the reactor.

The legs for the 40 gallon tank are wider than the I-beam. So, for the tank to be securely fastened, two braces were fabricated using quarter inch thick and 2 inch wide carbon steel stock to fit around the I-beam. The braces shown in Figure 60 will then connect to pieces of unistrut cut and fastened across the legs of the tank. With the braces able to move vertically along the I-beam and the connection to the unistrut pieces able to move in the horizontal direction, the extract input for the flash tank will have the ability to line up

exactly with the output piping from the reactor. This will ensure a proper fit and prevent leakage of the volatiles when draining the reactor.



Figure 60: Fabricated braces and attached unistrut pieces to mount the flash tank.

3.4.3.8 <u>Step 3h</u>: Construction Preparation for the Volatile Collection System

The volatile collection system consists of a standard 120 gallon tank with a stand at one end to orient it in the vertical direction. Mounted directly above the tank was a heat exchanger that will condense the heated volatile vapors. The only other components of the volatile collection system are the fittings, valves, and all of the vapor piping. A large, single-pass shell and tube heat exchanger was located in the old NRCCE pilot plant (Figures 61 and 62). This shell and tube heat exchanger is ideal for the application of the primary vapor condenser before entering the large expansion tank. The openings for the tube side are large at 1 $\frac{1}{2}$ ". The tubes in the tube bundle are also a large diameter, at three quarters of an inch. The large diameter tubes in the tube bundle are important to eliminate any clogging in the condenser. The reason clogging in the condenser is a major concern is because the heavier volatiles material will condense to a solid rubberlike form. It will most likely condense and collect on the first cold surface that it encounters, which would be the inside of the tube bundle of the condenser. Another advantage to this condenser is the length. At around three feet in length, it provides a large surface area for heat transfer, between the hot volatile vapors and the cooling water on the shell side.



Figure 61: The large heat exchanger from the pilot plant that was used as the volatile condenser.



Figure 62: View of the large diameter tubes in the tube bundle of the volatile condenser.

Once the condenser was removed from the pilot plant, all of the fittings were removed and the threaded connections cleaned. While inspecting the tubes, it was found that they had been stuffed full with steel wool in order to increase the surface area. Leaving the steel wool in the tubes would surely cause the condenser to clog. So using long forceps the steel wool was completely removed from each of the tubes. The tube side of the heat exchanger was capped at one end, filled with water, and stood upright. Fifty psig of nitrogen pressure was applied to the shell side. No bubbles were observed on the tube side filled with water. Therefore, it was determined that the tube side was isolated from the shell side and the piece of equipment could be used for the desired application without having to re-weld any of the tubes. This piece of equipment was now ready to be used in the new reaction and centrifugation system.

3.4.3.9 Step 3i: Construction Preparation for the Centrifuge System

3.4.3.9.1 <u>Step 3i1</u>: Centrifuge system equipment alterations

Quantex was able to continually benefit financially from high quality equipment owned by the Carbon Products program that was in used in previous experiments but was still in great condition. A 24 gallon tank with horizontal mounts was available. In order for this tank to be used as the centrifuge tank, several alterations were required. First, legs had to be installed to orient the tank in the vertical direction. These legs also had to elevate the tank high enough off the ground to accommodate the isolation valve, tee to the gear pump, drain valve, and the clearance for a one gallon can to collect any residual centrate for mass balance.



Figure 63: The centrifuge tank after the alterations had been made.

The second alternation made to the tank was the addition of a four inch diameter threaded nipple to replace the one inch threaded opening at the top on the tank. This four inch opening is necessary to connect to the four inch opening at the bottom of the centrifuge that allows the cleaned, de-ashed centrate to return back into the centrifuge tank for further processing through the system.

The centrifuge itself sat at the top of the centrifuge tank which was elevated roughly six feet off the ground. It is crucial for the centrifuge and therefore the centrifuge tank to be level and stable. Any vibration or "wobbling" of the centrifuge will decrease the rotation speed and therefore, the efficiency of the centrifuge. So the bottom of each leg of the centrifuge tank is fitted with a treaded, height adjustable foot seen in Figure 64. This will not only help to level the centrifuge given the inconsistent floor of the reactor room, but will slightly adjust the height of the tank to allow for a proper fit of the plumbing from the flash tank and prevent any loss of material.



Figure 64: Height adjustable feet on the legs of the centrifuge tank.

The gear pump stand also had to be elevated for the plumbing from the centrifuge tank to fit together properly (Figure 65). Each of the feet of the gear pump stand were also

treaded for fine adjustments to be made for the plumbing to properly seal without losing any material to the environment.



Figure 65: Height adjustable feet installed on the gear pump stand.

3.4.3.9.2 Step 3i2: Volatile Condenser Preparation

The heat exchanger to condense the volatiles vaporized in the centrifuge process was an interesting piece of equipment. It was a custom-made heat exchanger. It consisted of a 1 $\frac{1}{2}$ " threaded stainless steel piping with a 4 inch stainless steel piping around it. 4 inch diameter circular stainless steel plates with 1 $\frac{1}{2}$ " openings drilled in the center were welded to the ends of the larger diameter pipe. The smaller diameter pipe, which was a few inches longer on either end, was passed through the center opening of the steel plates. This pipe was then welded into place creating a single pass, one tube, heat exchanger displayed in Figure 66. Into the side of the 4 inch pipe, $\frac{3}{4}$ " holes were drilled and stainless steel 90° elbows welded over the holes. This was the input and output flows for the shell side of the heat exchanger. However, it appeared that neither side was water cooled in its previous application. Both the tube side and the shell side need to be

thoroughly cleaned out. But first all of the fittings were removed and the threads cleaned. The heat exchanger was filled with NMP and heated overnight to dissolve any material inside. It was then drained and flushed several times with water. This, along with refurbished volatile condenser and moisture condenser, was a tremendous budget savings because of the high cost of heat exchangers.



Figure 66: The single tube heat exchanger that was used as the centrifuge tank condenser.

The single tube heat exchanger allowed for an updated design of the centrifuge process. In the original design concept, the flash tank would be emptied using gravity into the centrifuge tank. After the transfer had taken place, the centrifuge tank would be isolated and any of the vapors that built up would be further condensed using a condenser connected to the opening on the opposite side of the centrifuge tank. A standard shell and tube condenser could not be connected to the centrifuge tank along the transfer piping from the flash tank. The extract would solidify and clog in the small diameter tubes of a standard heat exchanger tube bundle. However, with this large diameter single tube exchanger, the extract from the flash tank can be transferred directly through the heat exchanger into the centrifuge tank. This simplifies the process. In addition, any light volatiles that are retained in the system were condensed on the cold walls of the exchanger. If any solid volatiles, like naphlathene, where to collect and begin clogging the line, they would be flushed out by the next transfer of hot extract through the piping. Therefore, this heat exchanger was connected directly above the input piping from the flash tank to the centrifuge tank.

3.4.3.10 Step 3j: Construction Preparation for the Volatile Scrubbing System

The first step in preparing the volatile scrubbing system is to identify the location of the scrubber and install the frame to hold the scrubber. It makes sense to install the scrubbing tower next to the bunker vent stack. The frame was built using unistrut with a pair of six foot long pieces attached directly to the concrete wall of the reactor room (Figure 67). The scrubbing tower was attached to these vertical pieces using metal strapping. A horizontal base will elevate the bottom of the scrubber about 8 inches above the ground. This clearance will allow for the drain valve to flush and refill the caustic solution when it becomes fouled. Luckily, the Carbon Products group already had a small circulation pump and motor constructed mainly out of plastic, which does not corrode in the alkali solution.


Figure 67: Stand constructed for the scrubbing tower.

The next step was to purchase the 10 inch diameter PVC piping along with the 10 inch top and bottom caps which are impervious to the alkali environment for the scrubbing tower. The smaller diameter vapor PVC piping and circulation PVC piping along with all of the other fittings were purchased. Holes must then be drilled into the sides of the tower at the top and bottom and in the center of each of the end caps. For the alkali solution piping, the drilled holes were threaded and then sealed with an epoxy material (Figure 68). For the vapor lines, pre-threaded fittings were inserted into the holes drilled in the tower. These fittings were also sealed to the walls of the scrubbing tower with the same epoxy material.



Figure 68: Top of the scrubbing tower with the sealed vapor output connection.

The packing material was elevated above the level of the alkali solution reservoir. So a perforated drain cover was filled with additional drilled holes and attached to a 2' long 4" diameter PVC pipe section. The bottom was beveled to allow the solution to be properly drained from the scrubbing tower when it needed to be replaced. The drain cover fit snuggly inside of the tower and supported the packing above it. The top cap was equipped with a fitting that could attach piping from the top and bottom. This would let the circulation piping extend through the cap to the shower head for dispersion of the alkali solution across the packing.



Figure 69: The packing support stand and top cap of the scrubbing tower.

Now that the preparation of bunker reactor room, the repairs to the reactor and heating system, the fabrication of the specialized equipment, and the refurbishing of the used equipment has been completed, the construction of the bunker process is now possible.

3.4.4 <u>Step 4</u>: Bunker Process Construction

3.4.4.1 <u>Step 4a</u>: Process Construction of the Loading System

After the transport vessel was fabricated, an isolation value and a connection to the reactor had to be installed. A 1 inch ball value seen in Figure 70 was chosen for the isolation value because when opened it has no restrictions for the slurry to solidify and clog the plumbing. The value for the transport vessel was connected directly under the bottom of the cone followed by a 45° elbow and the second half of the union connected to the lid of the reactor.



Figure 70: Raw material loading valve on the lid of the reactor.

The transport vessel had two 3 inch diameter ports cut into it. One of the 3" openings at the top of the vessel was fitted with a removable threaded cap. This opening was used to load the raw materials in the vessel. The other 3" opening was fitted with an agitator that extended down into the cone and was connected to a handheld electric drill. The agitator will serve two functions. First to mix raw materials added into the transport vessel to ensure homogeneous slurry. The second function was to agitate the slurry as the vessel is hoisted and connect to the reactor. The agitation will prevent the coal particles from settling out of solution which could collect above the isolation valve and cause the transfer to the reactor to be more difficult.

The final step in the construction of the loading system was to provide a method to control the temperature of the slurry. So the vessel along with the plumbing was wrapped with heating tape equipped with a controller. The entire transport vessel was then covered in insulation (Figure 71) to prevent any heat lost to the environment and also to eliminate personnel contact with the hot surface during the loading step in the procedure.



Figure 71: Insulated transport vessel ready for operation.

3.4.4.2 <u>Step 4b</u>: Process Construction of the Moisture Collection System

Collecting the moisture was a new concept for the reaction system and the overall liquefaction process. It had never previously been attempted in the WVU liquefaction process and was conceived during the construction of the bunker system. The first step in the construction of the moisture collection system is the mounting and location of the 13 gallon moisture tank. It was mounted to the same I-beam in front of the reactor that the flash tank is mounted to, only slight above the flash tank and facing away from the right side of the beam (Figure 72). But the moisture tank's precise location and the exact fitting of the plumbing is not as crucial. This is because the pressure of the moisture removal step will never reach above 50 - 60 psig which is low enough to be handled with a flexible braided metal hose.



Figure 72: The moisture and tank and moisture condenser mounted to the I-beam above the flash tank.

The shell side of the U-tube heat exchanger is connected to the side of the moisture tank through the 1 ¹/₂" threaded port. In the picture below, the vapor line enters the moisture tank first and then the vapors condense after they contact the water cooled tubes of the condenser. However, the vapor input to the moisture tank was ultimately changed to enter into the top opening of the shell side of the condenser so that the vapors would contact the cold U-tubes on their way to the collection tank. An isolation valve is installed on the bottom opening of the moisture tank to drain the product after the experiment has completed. The weight of the condenser was not easily supported by having only the connection to the moisture tank. So a brace was installed from the grated floor of the second story up to the bracket at the bottom of the condenser. Then the cooling water input was attached to one side of the U-tubes while the cooling water output was attached to the other side. Finally, a nitrogen input was connected to the moisture collection tank. A nitrogen supply was connected to every tank and vessel in

the reaction and centrifugation process to provide inert conditions if required. All of the openings that are not being used were plugged and sealed.



Figure 73: The installed moisture tank and moisture condenser.

3.4.4.3 Step 4c: Process Construction of the Flash Tank

The flash tank can be considered the "middle of the system" and is the one piece of equipment connected to just about all the others. The flash tank is connected to the reactor, the 120 gallon expansion tank, as well as the centrifuge system. The next step was placing the flash tank with a major emphasis placed on connecting the flash tank to all of the other equipment. The most difficult plumbing connecting to make in the entire process was connecting the reactor output piping to the flash tank. One way to minimize the difficulty in transport is to reduce the length of piping from the reactor output to the flash tank input. With a shorter length of piping between the two pieces of equipment, it is also a safety and mass balance benefit with less threaded connections. Less threaded connections would mean less opportunity for high-pressure vapors to escape the system.

It would also minimize the risk of losing valuable volatiles from the process which would affect the quality of samples and mass balance numbers. Furthermore, due to the high temperature and pressure of the extract entering the flash tank, it was securely mounted and held in place to the 4 inch I-beam in front of the reactor. It was necessary to secure the tank in place before connecting the flash tank to the other pieces of equipment to maintain a tight fit in the plumbing for containment of the volatiles and extract.

The product of the reactor was a mixture of gases, liquids, and solids that did not dissolve. At the end of the reaction, the content of the reactor was over 400°C and about 400 psig. Before the contents of the reactor are emptied into a flash tank, the reactor was depressurized through the large shell and tube condenser and into the 120 gallon expansion tank, plumbing that is also connected to the vapor line of the flash tank. When the reactor reaches a moderate pressure, the content of the reactor was fed by gravity and the pressure remaining the reactor into the 40 gallon flash tank. The flash tank will also be vented to the expansion tank through a large diameter vapor line that will facilitate the depressurization of the system and carry the volatiles liberated from the decrease in pressure through to the volatile collection system. The hot mixture of solids and liquids was held in the flash tank until the monitored temperature drops to a level that is suitable for to the centrifuge process to begin the internal de-ashing process. Because the flash tank deals with high pressure, it was securely fixed to the 4 inch I-beam using steel brackets. Therefore, the vessel cannot be used to get accurate weights for mass balance. The mass balance weights for the extract will have to be attained after centrifugation by combining the weights of the centrate and centrifuge tails.

With the extreme temperatures and pressures of the extract when it leaves the reactor, the outlet piping was plumbed using 316 stainless steel. In addition, to reduce the force exerted on the piping when the reactor is drained under pressure, two 45° elbows was used instead of one 90° elbow. With the location of the reactor output fixed and the 4 inch I-beam located directly in front of the reactor, the length of piping between the two pieces of equipment was very short. With a short amount of heavy-duty piping, there was very little room for give. This makes the pipe fitting extremely difficult and will require a high level of accuracy in order to ensure a tight fit. So a good deal of attention had been given to mounting the flash tank with the ability to insure a tight fit to the reactor output piping. Because of the fabricated brackets and the unistrut pieces attached to the legs of the flash tank, it now has several degrees of freedom that were used, as the heavy duty piping from the reactor is connected.

The first step in the process was to attach the isolation valve to the output of the reactor. Immediately below the reactor one half of the union was connected which would connect to the rest of the piping. Next, the flash tank was hoisted into place and connected loosely to the I-beam. It still had the ability to move vertically up and down, horizontally left and right, and slightly forward and backward. At this point a short pipe section with one half of a union was connected to the extract input for the flash tank. The remaining section of pipe which would include the pair of 45° elbows was assembled using the vice in the workshop that was set up in bunker garage area. All of the connections were made using high temperature sealant. Once the remaining pipe section was fabricated, it was brought up to the reactor and loosely tightened into place. The flash tank was then secured more firmly to the beam but still was able to move slightly in all directions.

transfer piping from the reactor to the flash tank was then securely tightened down (Figures 74 and 75). Once the piping was in place and securely tightened, the remaining connections to secure the flash tank were also securely tightened down. At this point the reactor was securely plumbed to the flash tank which was securely attached to the I-beam.



Figure 74: The reactor outlet plumbing securely attached to the flask tank.

Although the plumbing was heavy duty stainless steel and securely fit, the unions could not remained sealed when the reactor was drained do to the level of thermal expansion. So, shortly after the process was put into operation, the reactor outlet plumbing was disassembled and the unions replaced with stainless steel flanges sealed using spiral wound gaskets. Also, a second isolation valve was installed in the horizontal section of the piping. The purpose of this second valve was to act as a backup for the first isolation valve. If the first valve failed or began to leak even slightly, the reactor would not have the ability to maintain the high internal pressure. The second isolation valve would allow the experiments to continue until the process was shut down for standard maintenance. The same procedure to securely attach the plumbing was followed and the plumbing was securely attached. The flange bolts are checked and tightened after each run. They will periodically loosen due to the thermal expansion.

The final step to installing the flash tank was to attach all of the fittings for plumbing to the other equipment and sealing all of the openings that are not being used. Directly under the flash tank a 1 inch ball valve was installed. This is to isolate the extract from the centrifuge system and allow it to cool to the proper temperature. The next step is to attach a 1.5 inch isolation valve to the top port facing the expansion tank. From this valve the vapor line for the flash tank to the volatile collection system was plumbed. The other large opening on that side of the tank was sealed with removable plug. This will act as a viewport to visually inspect the inside of the flash tank when needed or during standard maintenance. The side of the flash tank that faces the reactor has two additional 1 inch threaded openings. The one at the bottom will hold a thermocouple that will read the temperature of the extract as it cools. The second opening was an input for nitrogen into the tank. Due to the hazardous nature of the volatiles, each piece of equipment will have a nitrogen input installed. The final addition to the flash tank was a pressure gauge attached to the top. This was used as a secondary pressure check for the pressure transducer after the reactor has been drained. Now that the flash tank is securely placed and all of the fittings attached, construction of the volatile collection system can begin.



Figure 75: Original reactor outlet plumbing before the flanges were installed.

3.4.4.4 <u>Step 4d</u>: Process Construction for the Volatile Collection System

It had previously been decided that the large 120 gallon expansion tank would be placed on the right side of the bunker reactor room near the viewport from the office. One of the overall goals was to keep the distance of vapor piping as short as possible to reduce vapor condensation and build up in the vapor lines. So this is the only location for the expansion tank that did not interfere with the spacing of the other equipment. The centrifuge system would be gravity fed from the flash tank. Therefore, it was located directly under the flash tank and reactor. With the expansion tank placed against the wall of the reactor room, it allows for the transport vessel to be moved into place so it can be hoisted up to the reactor. As stated in the design concepts, the large shell and tube heat exchanger will be mounted directly above the expansion tank (Figure 76 and Figure 77).



Figure 76: Expansion tank set in place with the volatile condenser mounted to the top.



Figure 77: Top of the volatile condenser extending to the second floor of the reaction room.

Due to the height of the expansion tank with the large condenser mounted on top, a section of the floor grating had to be cut out in order for the top of the condenser to pass

through to the second floor. Immediately above the condenser, an isolation valve was installed and above the isolation valve was a wye fitting. The top opening of the wye fitting will connect to the vapor piping directly from the reactor. The other opening of the fitting entering at a 45° angle was connected to the vapor output of the flash tank. As much of the vapor piping as possible was at a 45° angle. The idea was to eliminate lengths of pipe in the vapor system that is horizontal. If any condensation occurs in the vapor piping is a 45° angle, it will tend to collect and sit in the piping. If the vapor piping is a 45° angle, it will tend to proceed down the slope towards the expansion tank where it can be collected. The major consideration for attaching the vapor line from the flash tank is to ensure that the height is correct. The expansion tank is not securely fixed to the floor; therefore, it has the ability to move with two degrees of freedom as long as the height is exact. Once the $1\frac{1}{2}$ inch vapor line is connected, then the volatile collection system was set in place and the rest of the vapor piping can be connected from the reactor to the moisture tank and volatile collection system (Figure 78).



Figure 78: The vapor piping connecting the flash tank to the volatile collection system.

The vapor piping coming directly from the reactor was sent to two different locations: the moisture collection system and the volatile collection system (Figures 79 and 81). The vapor piping was initially isolated from the reactor using a three-quarter inch ball valve seen in the picture below. But due to the extreme conditions the seals in this ball valve did not last more than three runs and the reactor would no longer hold pressure. It was replaced with a Swagelok SS-8UK gate valve of Figure 80 that is rated for high temperature, high pressure, volatile material, and high velocity. Once again this is an expensive valve that was available from previous carbon products experiments. Once this valve was installed it worked as intended and there were no additional problems with the reactor vapor isolation. There were also other advantages. The main one being that the flow of vapor exiting the reactor could be more precisely controlled using the gate valve as opposed to a ball valve.



Figure 79: Reactor vapor piping with original isolation valve.



Figure 80: Swagelok SS-8UK valve to replace the original reactor vapor valve.

Immediately after the isolation valve the vapor line is a split to divert the flow to the moisture collection system or to the volatile collection system. In the picture below, the valve with the yellow handle isolates the moisture collection system while the valve with the blue handle isolates the volatile collection system. During the initial heating step of the reactor when the moisture is driven off, the blue handle valve is closed in the yellow valve is opened. Once the conditions are met the reactor isolation valve is opened and the moisture is allowed to flow into the moisture collection system. Once the moisture is driven off, the blue handle valve is opened. The remaining vapor piping from the split to the large shell and tube condenser of the volatile

collection system has been increased from a diameter of three-quarter inches exiting the reactor up to 1 inch.



Figure 81: Isolation valves for the moisture and volatile collection systems.

After the valve to divert the flow between the two systems, the vapor piping has a short horizontal run followed by a 45° section of piping shown in Figure 82 that proceeds down to the volatile condenser. Before entering the condenser the piping is connected to another isolation valve that sits above the wye fitting on top of the condenser. With all of the valves in place, each of the unit operations can be combined to work together or can be closed to isolate different parts of the process. This will allow different areas of the system to be pressure tested. It also allows for different sections be isolated, removed, inspected, and repaired if needed.



Figure 82: Vapor piping from the reactor and the flash tank to volatile condenser.

The rupture disk for the reactor shown in Figure 83 was removed, disassembled, and inspected. All of the pieces were cleaned. All of the plumbing was sealed using a high temperature, graphite based sealant and reconnected to the reactor lid. For safety purposes, to take advantage of the large volume of the expansion tank, the plumbing after the rupture disk proceeded directed to the expansion tank.



Figure 83: Rupture disk connected to the lid of the reactor.

3.4.4.5 <u>Step 4e</u>: Process Construction of the Centrifuge System

The first steps in the construction of the centrifuge system was placing the centrifuge tank, connecting the input of the centrifuge tank to the flash tank output, attaching the centrifuge itself, and making sure that the centrifuge is level. The overall goal of these steps were to ensure a tight fit with the plumbing so there is no loss of material and to make sure that the centrifuge is level and operates properly at high rotational speeds.

To transfer the viscous extract from the flash tank to the centrifuge tank, it would be ideal to enter directly into the top of the centrifuge tank to avoid any elbows that would restrict the flow of extract. However, this is not possible because the centrifuge itself sits atop of the tank. The next best option was to connect a pipe vertically from the bottom of the flash tank into the top of the single tube condenser before making one 90° turn and entering the side of the expansion tank. The extract is transferred at the proper temperature with the addition of the force of gravity through large diameter piping. So, clogging in the line during the extract transfer should not be a problem. To prevent any condensation or solidifying of the extract as it is transferred, the water to the heat exchanger will not be turned until the transfer is complete.

The centrifuge was connected to the 4 inch threaded opening at the top of the centrifuge tank. Next the single tube heat exchanger was connected to the 1.5 inch opening on the side of the centrifuge tank near the top. Then a predetermined length of pipe was cut and threaded. One side was attached to the drain valve of the flash tank output while the other side was attached to the centrifuge condenser. Both ends were connected using unions. The adjustable feet of the centrifuge tank were placed on rubber floor mats to absorb vibrations in the system and increase the coefficient of friction of the feet with the

cement floor. The feet were adjusted slightly to level the centrifuge and ensure proper fit of the piping. The centrifuge tank along with the centrifuge itself and condenser are now securely plumbed into position as can be seen in Figures 84 and 85. The centrifuge is level and stable on top of the centrifuge tank. The next step was to connect the gear pump and circulation piping which is shown in Figures 86 and 87.



Figure 84: The centrifuge and tank secure and plumbed into the process.



Figure 85: The plumbing connecting the flash tank and centrifuge system.

An isolation valve was placed immediately under the bottom opening of the centrifuge tank. If the extract did not have the proper temperature or conditions, it would not be allowed to proceed to the gear pump and possibly clog the piping or the pump itself. In addition, it the temperature were too high, it could damage the bearings in the centrifuge. After the isolation valve a tee was installed. The horizontal opening of the tee proceeded to the input of the gear pump while the bottom opening of the tee was fitted with another valve. This bottom valve was installed to drain any residual centrate from the lines to be weighed for mass balance and added back into the total weight of centrate. To the output of the gear pump, a wye fitting was attached. The horizontal opening of the wye was immediately reduced from 1.5 inches down to three quarters of an inch followed by an isolation valve. This piping would later be equipped with a drain valve and connected to a braided flexible metal hose used to send the final centrate product into a 16 gallon storage drum. The 45° opening of the wye was connected to another 45° elbow and then to an isolation valve. After the valve the 1½ inch piping proceeded vertically upward to another series of 45° angles which oriented the flow in the horizontal direction to enter the centrifuge.



Figure 86: Centrifuge tank plumbed to the gear pump.



Figure 87: The complete centrifuge system with the gear pump and circulation plumbing installed.

The construction of the system was performed in a way to reduce any restrictions in the flow of the centrate. Since the rotational speed of the centrifuge, and therefore the ash removing ability of the centrifuge, is based upon the flow of material through the system, the greater the flow rate the higher the efficiency of the ash removal system. This is the reason why 45° angles were installed in the circulation line after the gear pump as opposed 90° angles. Also the piping diameter remained at 1½ inches which was the diameter of the input and output of the gear pump until immediately before entering the centrifuge. The diameter is then reduced down to one inch which is the size of the centrifuge input. Now that the structure is complete a few additional items must be installed in order for proper operation of the centrifuge system.

It is imperative that the temperature be monitored throughout the operation of the centrifuge process. The thermocouple was installed in the centrifuge tank in the opening seen in the picture above. This will provide a temperature reading for the material contained in the centrifuge tank. A second thermocouple was installed in the circulation piping immediately before entering the centrifuge. This is the temperature that was controlled to the desired level determined by the Brookfield viscosity tests. In order to control and maintain the temperature in the system, ceramic heating bands were wrapped around the centrifuge tank. All of the circulation piping along with the gear pump was wrapped with heat tape. A heating mantle was placed on the rounded bottom of the centrifuge tank to prevent any of the material from solidifying on the inside walls at the bottom of the tank. Finally, the tank, the centrifuge, all of the piping, and the gear pump were insulated to prevent any heat loss. By controlling the levels of the ceramic heating bands around the centrifuge tank and the heat tape wrapped around the circulation piping, the desired termine tank and the material form solidifying on the circulation piping.

3.4.4.6 <u>Step 4f</u>: Process Construction of the Volatile Scrubbing System

After all of the PDC pieces have been fabricated, the first step in constructing the volatile scrubbing system was assembling the scrubbing tower. First the bottom cap was attached to the large diameter PVC pipe. The ends of the tower pipe were beveled in order for the caps to be installed. Each cap is equipped with a gasket on the inside. Once it is installed it is not possible to remove without cutting it from pipe. The cap was installed using a soapy solution as a lubricant along the pipe wall and a rubber mallet to force the cap into place. Once the bottom cap was in place the next step was dropping the two foot tall platform to support the packing into the tower. Once the platform was in place, the

scrubbing tower was filled with packing until it reached a height of one foot below the shower head. The tower was continually shaken so the packing completely filled the available volume. The final step in assembling the tower was installing the shower head on the inside of the top cap, and then installing the top cap onto the tower. Once the scrubbing tower was assembled it was lifted onto its stand and secured in place using metal straps (Figure 88).



Figure 88: The assembled scrubbing tower placed in the stand.

The vapor input piping was the next item to be installed. It serves two purposes. It received the non-condensable gases from the expansion tank. It also was equipped with a

secondary input with a funnel to load the alkali solution into the tower. But before the solution could be loaded, the drain valve must be attached to the bottom cap and the plumbing to the circulation pump must be installed. The circulation pump output plumbing was installed and connected to the top cap of the tower. Finally, the vapor output piping which carries all of the scrubbed non-condensable gases was installed to the fitting near the top of the tower. This PVC piping proceeded back down towards the floor and entered the ventilation stack to exit the building.



Figure 89: The circulation pump before being plumbed in and the vent stack on the right.

3.5 The Vacuum Distillation Process

3.5.1 Introduction and Review of the Objectives

Before this research began, vacuum distillation of the centrate to produce pitch and volatiles had never been done at West Virginia University. No apparatus existed for this process. The primary objectives for the vacuum distillation section was to design and construct a vacuum distillation system which produces high quality pitch and condensed distillation volatiles while achieving mass closure for the complete process

In addition to the primary objective, several secondary objectives must be accomplished. These secondary objectives are:

- To design and construct a vacuum distillation process that inputs a homogenous sample of de-ashed centrate and produces a quality pitch suitable for further processing the coking system, and distillate that could be recycled as CTD in future experiments.
- To design and construct a process to alter and evaluate the control variables with an extensive ability to monitor process conditions.
- To design and construct a distillation column that is capable of extracting pitch samples at different points during the distillation run without affecting the operation of the experiment.
- 4) To design and construct a condensation system that is capable of extracting condensed volatile samples from specific ranges of distillation conditions.

3.5.2 Vacuum Distillation Design Concepts

One important aspect to consider in the design and construction of the vacuum distillation system is that it is the only system in the overall process which had ample funds supplied by Quantex to advance their technology. The system would still be constructed using any available equipment from the carbon products program. Quantex still would not provide a budget, but did provide the ability to purchase new equipment and have any alterations made to the new and existing equipment. The availability of funds provided an opportunity to design and construct a system that would operate with great consistency. It also provided an opportunity to design and construct a system where all of the necessary information could be extracted from every experimental run. All of the conceived objectives could be accomplished.

The 16 gallon drum of centrate from the bunker process was taken into Room 317 and placed on the floor scale. The centrate was heated and agitated before a predetermined weight is pumped into the distillation column. Once the centrate is in the column, the heat and vacuum system was turned on and the temperature of the centrate gradually increased. A nitrogen sparge is applied, but the pressure is maintained at 28.5 mmHg. The volatiles are driven off and carried to the primary condensation system, along with the nitrogen that is sparged through the column. The volatiles enter the collection pot and proceed up into the shell and tube heat exchanger cooled with water. Most of the volatiles condense and fall back into the collection pot. The nitrogen and any remaining volatiles then follow into the ballast tank which increases the overall volume of the process before proceeding into the freezer condenser, where any remaining volatiles are condensed. The ballast tank serves as a secondary condenser, but more importantly it also serves to maintain the vacuum. The nitrogen then continues through the vacuum pump where it will then leave the system and enter the walk-in hood. Finally, the nitrogen will exit through the hood exhaust.

Due to the vacuum of greater than 28 mmHg and the ability to purchase equipment and supplies, all of the plumbing connections for the vapor line consisted of flanges sealed with spiral wound gaskets. All of the threaded connections after the primary condensation system used a sealant appropriate for vacuum conditions. The sealant can be used without worry of the process leaking due to consistent temperature in this portion of the process. However, the plumbing from the distillation column to the primary

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condensation system will continually be heated during operation and cooled while the process is at rest. Due to thermal expansion, threaded connections with the sealant provided a possibility for leakage of air into the system at the high vacuum conditions. Therefore, the connection between the distillation column and the primary condensation system was welded to prevent any leakage.

3.5.2.1 Design Concepts for the Distillation Loading System

As stated earlier, when the centrate is at room temperature it has the consistency of a solid rubberlike material. From the bunker the centrate is loaded into 16 gallon drums and transported to the laboratory in room 317 of the Engineering Research Building. In order for the centrate to become a liquid able to flow from the loading drum to the distillation column, heat must be added. Loading the distillation column is a delicate practice. Many things must be considered due to the loss of light volatiles, which was discussed in the centrifugation section. The most important item was that it took quite a bit of time for the heat to penetrate all the way to the center of the drum. In order to speed up this process, agitation of the centrate was required. As heat was applied to the outside walls of the drum, the centrate was liquid along the walls yet solid in the center.

Because the drum is not a stationary piece of equipment and several drums were used in transporting the centrate from the bunker to the distillation column, a permanent agitator was not feasible. This also impacted how the drum was loaded at the conclusion of the reaction and centrifugation process. So, a removable agitator was the best option. For this application a paint stirrer attached to an electrical drill was used. The agitator will

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need to be heavy duty to account for the high viscosity of the material until it reaches the proper temperature. Another advantage to an agitator connected to a handheld drill is that it can be moved around inside of the drum. This provides more precise agitation of the centrate as the drum is heated. The agitator however only mixes the contents of the drum in the radial direction. It was observed that higher specific gravity material would tend to settle towards the bottom as the viscosity of the centrate decreased due to the heat added. To homogenize the drum, it also had to be mixed from top to bottom. This agitation could be achieved by removing material from the bottom of the drum through the take up pipe connected to the diaphragm transfer pump. Instead of sending the centrate directly to the column, it was first recycled back into the top of the drum.

3.5.2.2 Design Concepts for the Distillation Column

The first step in the design for the distillation column was to select proper size. It should be able to process an amount of material on the same scale or a similar scale to the reaction and centrifugation process. The reaction process begins by loading about eight gallons of material and it produces roughly 6 gallons of de-ashed centrate. The carbon products program has a three foot tall cylindrical vessel with a flanged lid on top (Figures 90 and 91). The vessel was constructed of 316 stainless steel has a diameter of 9.5 inches and a volume of 12 gallons. It was supported by legs welded to the side of the bottom of the vessel elevating it about one foot off the ground. There is an opening about six inches from the bottom on the side of the vessel. Some alterations had to be made to the vessel, but otherwise it was perfect for the distillation column.



Figure 90: Distillation vessel before any alterations were made.



Figure 91: The inside of the distillation vessel before any additions were made.

There is no agitator in the distillation column. If the heat is supplied from the walls with no agitation there were temperature gradients within the column. One way to agitate the column was to add nitrogen into the bottom and let it bubble up through the liquid material in the bottom of the column. The nitrogen also provided additional benefits agitating the molten pitch. It regulated the vacuum in the column by controlling the flow rate of gases through the system. Another benefit is that it will create a continual flow exiting the distillation column. This flow assisted in carrying the volatile vapors to be condensed in the primary condensation system. Finally, the bubbling of nitrogen through the material orients the molecules as the pitch is produced. This produced higher quality pitches that are more anisotropic in nature.

One additional aspect of the input nitrogen that had to be addressed was the temperature that the nitrogen enters the system. Ideally, the nitrogen should enter the distillation column at the same temperature as the contents of the distillation column. One way this was accomplish was to add the nitrogen from the lid of the distillation column. The flow passed through the lid into an internal tubing system that carried the nitrogen from the top of the distillation column down to the bottom. This internal plumbing consisted of 1/2 inch copper tubing which provided a large heat transfer area for the nitrogen to heat up as it proceeded downward. At the bottom of the column the split nitrogen flow entered a perforated coil where it can be dispersed evenly over the cross section of the distillation column.

The final design concept for the distillation column was the ability to extract pitch samples at various pitch temperature during operation of the process. The product from the distillation column was a higher-quality pitch and condensed liquid volatiles. The nitrogen is just a spectator in the process and will exit the system through the output of the vacuum pump. To determine the transformation of the centrate into pitches with different softening points, each run produced one data point for each of the end products.

However, one experimental run could produce multiple data points if the samples could be extracted at different temperatures. The sample port made use of the opening 6 inches from the bottom of the column. The idea was to extract a well representative pitch sample across the cross section of the column to determine the progress of the distillation process.

3.5.2.3 Design Concepts for the Primary Condensation System

The purpose for the primary condensation system was to condense most, if not all, of the vapor volatiles driven from the material in the distillation column. These volatiles consisted of a mixture of hydrocarbons. Some of the larger molecule hydrocarbons condensed on the first cold surface and solidified to a rubberlike state similar to the extract at room temperature. Therefore, it may present the problem of the system becoming clogged. Even a restriction in the system presented a problem with the vacuum system. The primary condensation system needed to provide a large surface area for these heavier molecules to solidify on. So, the flow leaving the distillation column entered into a containment vessel that had no heat applied and no insulation. The inside walls of this vessel provide the necessary cold surface area for these larger molecule to condense upon. The remainder of the molecules can then proceed through the vessel into a shell and tube heat exchanger where the remaining volatiles can condense. Once condensed, the liquids can drain back into the collection vessel along with the heavier molecules.

The final design concept for the primary condensation system was to have two collection vessels with the condensers in parallel. There are several benefits to having parallel primary condensation systems. First, if one of the condensers becomes clogged, the

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primary condensation system can be switched with minimal interruption to the experiment and the conditions inside the distillation column. Different "cuts" of volatiles can also be obtained. This will coincide with the extraction of pitch samples during operation. When the pitch sample is removed, the primary condensation system can be switched, the liquids collected to that point drained, and the different mixture of volatile vapors can be examined at different points for a single experimental run. This allowed the system to provide all of the information of multiple runs from a single experiment. It also allowed the distillation system to service a second purpose. The volatiles from the other systems could be loaded into the distillation column and separated into different "cuts". Therefore, the system can also act as a simulated distillation unit on a larger scale.

3.5.2.4 Design Concepts for the Ballast Tank

The ballast tank served several purposes. First, it increased the overall volume of the system (PV = P'V'). In a small volume system with vacuum levels around 28 mmHg, small changes can cause substantial variations. Therefore, the primary purpose of this ballast tank was to increase the overall volume of the process by 60 gallons which controlled the vacuum absorbing these minor changes. In addition to the increase in volume, the ballast tank provided a location for a second input of nitrogen. This way the vacuum in the process can be controlled by altering the flow of nitrogen through the vacuum pump without changing the flow of nitrogen through the distillation column. Finally, the ballast tank acted as a secondary condensation system. The flow will enter near the bottom of the ballast tank and exit directly out of the top. With the large surface

area of the inside walls at room temperature, any volatiles that pass through the primary condensation system could possibly be condensed in the ballast tank.

3.5.2.5 Design Concepts for the Freezer Condensation System

It was assumed that most of the volatiles, if not all the volatiles would condense the primary condensation system. Additionally, the ballast tank would act as a secondary condensation system. However, for the purposes of mass balance and to prevent any volatiles from proceeding to the vacuum pump, a low temperature condensation system was employed. In the pilot plant that was located on the mezzanine level of the NRCCE, a vertical freezer unit was converted into a condensation system (Figure 92). The concept of this freezer system was similar to the primary condensation system to where the flow entered into a collection tank that provides a large surface area where volatiles could solidify before entering a condenser. The difference is that the collection tank and condenser were housed inside of the vertical freezer unit that lowered the temperature to negative 13°C. Also, the collection tank and condenser sat on top of a reservoir of ethylene glycol that was also contained in the freezer system. A diaphragm pump drew the chilled ethylene glycol out of the reservoir and pumped it through the tube side of the condenser. The vapor flow entered into the collection tank through the side wall of the freezer unit. The vapors continued vertically upward through the condenser and flowed across the tubes filled with the chilled ethylene glycol before the condenser outlet piping exits back through the side wall of the freezer unit (Bland 2000).



Figure 92: condensation system from the NRCCE pilot plant that was used in the vacuum distillation system.

3.5.2.6 Design Concepts for the Vacuum System

The vacuum in the system was generated exclusively by a Welsh Duo-Seal vacuum pump model 1374. Once again, carbon products had a high quality vacuum pump seen in Figure 93 that was no longer in use. It too was once used in the pilot plant. Although it is a high quality heavy duty vacuum pump, it does not have the ability to vary the rate at which it pulls vacuum. The vacuum must then be controlled by other means. As mentioned earlier, changes in the vacuum can be absorbed by the large volume of the ballast tank. In addition, the nitrogen flow is a second method for maintaining a consistent level of vacuum in the distillation column. Finally, a gate valve was installed on the input of the vacuum pump. This adjustable restriction in the flow also helped to control the vacuum in the system.


Figure 93: Welsh Duo-Seal vacuum pump model 1374 to be used in the vacuum distillation system.

Although some funds where available from Quantex for the design and construction of this system, most of the equipment was supplied through the Carbon Product research group. The only new equipment that was purchase using funds supplied by Quantex were the ballast tank, both of the shell and tube heat exchangers, and the valves and other general parts. All of the design concepts for the vacuum distillation system and procedure had already been developed on a proof of concept vacuum distillation system. This proof of concept vacuum distillation system was built entirely with equipment and labor supplied by the Carbon Products group using university resources. It was also operated, achieved mass balance, and produced high quality pitch using centrate derived from bituminous coal, Australian bronze and gold sub-bituminous coals, Texas lignite coal, and Australian lignite coal all while using university resources.

3.5.3 Vacuum Distillation Construction Preparation

Most of the equipment for the vacuum distillation process was freestanding. The distillation column sits on a stand. The ballast tank that was purchased will also stand vertically. The freezer condensation system is also freestanding and the vacuum pump

rests on the floor. But the primary condensation system must be elevated. The collection vessels and condensers are too heavy to merely connect to the walls of the hood which are not designed to support such a load. Starting with the empty hood, a frame of unistrut was built to hold the primary condensation system. It was also an excellent framework for all the electrical wiring in the process.

In order to plumb all of the equipment together, pipe sections of various lengths are required. Most of this plumbing for the system consisted of 1 inch diameter carbon still piping. As with the bunker process, stock carbon still piping was purchased and the various lengths pipe cut and threaded. So the automatic pipe threader used for the reaction and centrifugation system construction was transported to the third floor of the Engineering Research Building for the construction of the vacuum distillation system.

3.5.3.1 Construction Preparation for the Loading System

The lid for the 16 gallon drum has no openings. To load the column a lid had to be altered with three openings. One opening, directly in the center was simply drilled out at ³/₄ inch. It was the opening for the stirrer connected to an electric drill. To seal this opening and prevent the escape of volatiles, the lid was plugged with a rubber stopper and the stirrer will pass through the center. This allowed for this stirrer to be moved around inside of the drum while preventing the loss of volatiles. The agitation helped to transfer the heat and eliminate the "iceberg" effect when heating the centrate. The second opening was a 1 inch opening along the edge of the lid. Here, the take-up line to the drum. Once again, a rubber stopper was used to prevent the loss of volatiles. The final opening for the lid was a three-quarter inch threaded coupling welded in place on

the opposite side from the take-up line. A union was attached to this opening to connect to the recycle line from the diaphragm pump (Figure 94). This will allow for the vertical mixing of the drum. The take-up line will remove material from the bottom of the drum and it was pumped back through the coupling on top.



Figure 94: Fabricated 16 gallon drum lid for loading the distillation column.

3.5.3.2 Construction Preparation for the Distillation Column

In the previous application of the vessel that was used for the distillation column, heat was supplied using multiple ceramic ban heaters with adjustable temperature controllers (Figure 95). These heating bands are able to produce temperatures of over 300°C. The distillation column will require several zones of heating from the bottom to the top of the vessel with control over the different zones. Therefore, using the same ceramic heating bands was ideal for supplying heat to the distillation column.



Figure 95: Ceramic heating bands with adjustable temperature control surrounding the distillation column.

The column was elevated above the ground by four legs welded to the side of the vessel near the bottom shown in Figure 96. This presented a series of problems. The ceramic heating bands could not be fitted around the bottom of the column, which is the area where the highest temperature should be applied. Because of this fact alone, the existing legs had to be replaced. In addition, the vessel is not elevated high enough off of the ground. When draining the column only a small pan could fit underneath the drain valve. The distillation column was taken to the machine shop to have the legs removed. A new frame (Figure 97) that was connected only to the bottom of the column was fabricated and installed on the distillation column. Another advantage of the new frame was the adjustable legs so the height of the column can be raised to fit the necessary application.



Figure 96: Original stand for the vessel to be used for the distillation column.



Figure 97: The new stand with adjustable legs to support the distillation column.

One of the ceramic heating bands could then be fitted around the bottom of the column. Directly above the top of the first heating band is the opening that protrudes from the side that cannot be removed. This was the only area on the vertical sides of the column that would not be covered with the wrap-around ceramic heating bands. It was the perfect location for the input of additional thermocouples to monitor the temperature. Three holes were drilled and tapped for thermocouple probes which will monitor the temperature at various locations at the bottom of the column. Monitoring the temperature of the vapor phase near the top of the column was accomplished using thermocouples passing through the lid of the column.

The lid of the distillation column has six threaded openings along with the bolt holes to secure the lid to the vessel. The largest opening is $1\frac{1}{2}$ " located in the center of the lid. This opening was used for the vapor output piping leaving the distillation column. There are also four $\frac{1}{4}$ " openings all equally spaced around the larger center opening. The final opening is a hole, just inside the bolt holes, with a bolt welded over the opening. On the inside of the bolt is $\frac{3}{4}$ " threaded NPT.



Figure 98: Original condition of the distillation column lid

The large 1.5 inch opening at the center of the lid and the opening through the bolt did not need to be altered. The threads were not damaged. The four ¹/₄ inch openings may cause a problem. Some of the threads were damaged and would not properly seal. Also, some of the connections required larger openings. Each of these four openings were drilled and tapped for ¹/₂ inch NPT threads. Two of the openings were threaded all the way through the lid. These openings provided the connections for the split nitrogen flow into the distillation column. The openings had to be threaded all the way through because fittings were connected to the underside of the lid and attached to the internal copper tubing of Figure 99.



Figure 99: Coil at the bottom of the copper nitrogen sparge.

In order to obtain well representative sample cross the entire cross-section of the column, Figure 100 shows a tube passed through the opening on the side of the column and extended to the other side. The ½ inch stainless steel tubing passed through a fitting threaded into sample port. The tubing was crimped at one end and perforated to allow the liquid pitch to flow into the sample port and be collected outside of the column. Because of the flow of material, the perforations were spaced closer together the further distance from the sample port opening. An isolation valve was installed on the sample tubing outside of the column



Figure 100: Sample port tubing to extract pitch samples during operation of the system.

3.5.3.3 Construction Preparation for the Primary Condensation System

The primary condensation system consists of two different piece of equipment in parallel, the collection vessel and a standard single pass shell and tube heat exchanger. The collection vessels began as standard 13 gallon carbon steel tanks purchased from McMaster Carr. This is the same model tank used in the bunker for the moisture collection tank and the starting point for the transport vessel. Just like the transport vessel, the vacuum system collection pot contained material with higher viscosity at room temperature. Draining the collection vessel presented a problem. For all of the material to drain properly, the bottom of the tank was removed and replaced with a conical bottom.

Due to the design concepts and layout of the process, the flow ideally entered the collection vessel through a large opening on the front. This opening did not exist, so it would have to be installed. The collection vessel would also be subject to temperature changes which could cause threaded connections to expand and contract. Eventually this could lead to leakage in the process. Therefore, the plumbing of the newly installed input for the volatile vapors and the output at the top of the tank are welded. The connection

on the side of each of the collection vessels which hold the vacuum gauge was also welded. It is important that the connections that hold the vacuum gauges do not leak so accurate vacuum measurements could be recorded.



Figure 101: Volatile collection vessel after the alterations were made.

3.5.3.4 Construction Preparation for the Freezer Condensation System

The major task of preparing the freezer condensation system for operation in the vacuum distillation system was in transporting the unit from the mezzanine level of the NRCCE to the room 317 laboratory. The diaphragm transfer pump, along with the take-up plumbing, were not attached to the system. However, the loading plumbing for loading the ethylene glycol reservoir extended from the top of the freezer unit. This PVC piping had to be cut off in order for the unit to fit through the door of the 317 laboratory. Once in place, this plumbing was reattached.

3.5.4 Vacuum Distillation Process Construction

The two major challenges in the overall construction of the distillation process are the placement of the equipment and plumbing the equipment together. Not only does all the equipment have to fit within the given space, all of the valves that need adjusted and gauges that need read will have to be easily and safely accessible during operation of the process. This can be best illustrated in the photo below. In the corner of the hood between the 60 gallon ballast tank and the primary condensation unit is an open area. It had to remain open in order to access the vacuum pump. This is necessary due to the standard maintenance of draining, flushing, and refilling the vacuum pump oil. So, the plumbing from the primary condensation system leaving the top of the condensers had to remain at a high enough level to access this area before it enters the flange near the bottom of the ballast tank. This level of consideration needed to be given to the placement of each valve and gauge along with all of the plumbing.



Figure 102: Open area above the vacuum pump.



Figure 103: Process construction with the primary plumbing connected.

3.5.4.1 Process Construction for the Distillation Loading System

The construction of the loading system was begun by attaching the diaphragm pump to the unistrut supports. The next step was to plumb the output of the diaphragm pump to the loading port for on the lid of the column. This section of plumbing was connected using a flexible braided metal hose (Figure 104). The advantage to using the flexible hose was that the plumbing did not have to be exact. Also, when the diaphragm pump was started, the flexible hose would "jump" with the beats of the pump. The "jumping" of the hose had a distinct change once the centrate began to flow through it. Next the inlet piping was connected to the diaphragm pump which included a drain valve. The inlet piping extended above the top level of drum as it sits on the scale. The take-up line was connected to the inlet piping using a flexible hose. Next the recycle plumbing from the output of the pump back to the drum was installed along with the drain valve for the output piping. The recycle plumbing was also connected using a flexible metal hose. These flexible hoses along with the ability to move the drum allowed for the connections to be quick and easy.



Figure 104: Installation of the plumbing to load the column.

It is important to drain the inlet and outlet piping for two reasons. The first is to recover any centrate remaining in the lines for mass balance calculations. The weight of centrate loaded is the different between the beginning and end weight of the drum minus the weight drained out of the lines. The second reason it is important to drain the input and output piping is the centrate solidifies to a gel like state at room temperature. If centrate was left in the lines, transfer of the centrate from the drum to the column was much more difficult.

Once all the plumbing is attached, it was all wrapped with heating tape and a thermocouple installed on the recycle line. Prior to loading the system, the heat tape was turned on and the temperature of the piping monitored using the thermocouple. The final step in constructing the loading system was attaching the half inch tubing from the pressurized air available from the fume hood to the diaphragm pump. The pump input was threaded for ¹/₂ inch plumbing. This allowed for maximum airflow to the pump when needed as well as a very low flow rate which could be controlled using the air valve connected to the hood.

3.5.4.2 Process Construction for the Distillation Column

Constructing the distillation column was begun with installing the interior components and securing the lid seen in Figure 105. The gasket was cut from a sheet of grafoil and set in place on the top flange. The nearly three feet long nitrogen sparge is placed inside of the distillation column. The lid was elevated several inches above the top of the column using wooden blocks. The sparge was connected to the fittings on the underside of the lid. Instillation of the sparge was done in this manner to avoid damage as the lid is put into place. The blocks were then removed and the lid set in place. It was firmly bolted to the distillation column. Once the lid was connected, the sample port was installed. The threaded connection for the sample port along with all of the connections on top of the lid were made using a high temperature flexible sealant used to connect parts inside of automobile engines.



Figure 105: Underside of the distillation column lid.



Figure 106: Interior view of the nitrogen sparge and sample port in the distillation column.

One of the thermocouple probes monitored the temperature at the level of the sample port. A second probe entered the column and dropped down to about ¹/₄ inch above the bottom of the column. This allowed the temperature to be monitored for any situation

where the liquid level dropped below the sample port. This was especially important during the secondary function for large-scale simulated distillation of condensed volatiles. A third thermocouple was angled upward and monitored the temperature in the center of the column between the third and fourth ceramic heating bands. The location and orientation of the thermocouple probes could be verified through the large opening in the center of lid before the vapor plumbing was installed.

The opening for the vapor piping was reduced from $1\frac{1}{2}$ " down to 1 inch. This allowed for a large reduction in the surface area of the piping where heat could be lost to the environment and volatile material could condense out of the vapor stream. As stated earlier, the outlet vapor piping was welded together to prevent leakage. It was threaded into place in the center opening of the lid and sealed using the high temperature sealant. The outlet piping consisted of a four-way cross. One leg is connected to the lid and each of the other three legs were connected to flanges. The top flange held a thermocouple that monitored the temperature at the point where the vapors exit the column. It also contained a pressure gauge that could be isolated. The pressure gauge was used to monitor the nitrogen pressure, which was used to drain the pitch from the column. The flange facing the primary condensation system was equipped with an isolation valve and was connected to the primary condensation system. The other leg of the cross was connected to the plumbing of the sample port. This line was used to equalize the pressure between the column and the sample port in order for samples to be obtained without affecting the vacuum within the column.



Figure 107: The connections on the lid of the distillation column before insulation is installed.

The remaining connections on the lid of the distillation column are the four smaller openings threaded for ½ inch NPT plumbing. The connection on the front was plumbed for a thermocouple which extended into the column and monitored the temperature between the fifth and sixth heating bands. This plumbing was also connected to the large vacuum gauge seen in the picture above. This is the primary source to monitor the vacuum conditions within the column. It was also the final thermocouple that was installed on the system. The temperature within the column could then be monitored at five locations: along the bottom of the column, at the level where the sample port is located, the midpoint of the column, the vapor phase between the top two heating bands, and the point that the vapor leaves the column at the beginning of the vapor piping.

There are three remaining connections on the lid of the distillation column. The one towards the back is connected to a vent valve. It was opened for air displacement when the distillation column was loaded. The two openings on the sides were connected to ¹/₄ inch fittings. These are the same openings that have been connected to the nitrogen sparge on the underside of the lid. Directly above the fittings were isolation valves to control the flow of nitrogen supplied from a cylinder.

3.5.4.3 Process Construction for the Primary Condensation System and Vapor Piping

The first step in constructing the primary condensation system was placing the parallel collection vessels seen in Figure 108. They were attached to the unistrut frame and elevated with enough clearance to place a 5 gallon bucket under the drain valve. The unistrut frame was constructed for the horizontal supports for the collection vessels to be adjusted vertically to the correct height. The condensers were then attached to the outputs of the vessels. The top of the condensers were also supported by the unistrut frame. The horizontal supports for the condensers could be adjusted vertically and horizontally. This flexibility of the unistrut frame allowed for the primary condensation system to be properly and securely supported in place.



Figure 108: Collection vessels and condensers supported by the unistrut frame.

As stated earlier, these were the only pieces of equipment that were stationary once set in place. The distillation column, loading drum, ballast tank, freezer condensation system, and vacuum pump all have the ability to be moved along the floor (Figure 109). Once the collection vessels and condensers are in place, the next step was to connect the collection vessel inputs to the distillation column. The prefabricated section of the vapor piping is connected by bolting the flanges together.



Figure 109: Distillation column connected to the primary condensation system.

Now that the primary condensation input was connected, the remaining plumbing for the condensers was completed. A valve was connected to the output of both condensers to isolate one side from the other. A four-way cross fitting was connected to the output of both valves. The fittings provided the necessary openings for the parallel equipment to be recombined before heading to the ballast tank and also equip each side with a thermocouple to monitor the primary condensation system output temperature. Therefore, the conditions of volatile condensation could be monitored in the process and conditions changed if needed.

The cooling water was plumbed from the available water source from the fume hood to the bottom opening on the shell side for each of the condensers (Figure 110). The flow proceeds upward through the condenser and exist the top before heading to the drain. The flow of the cooling water was co-current to the vapor flow instead of the preferred countercurrent flow. The co-current flow was chosen because if there is any disruption in the water supply, the shell side of the condenser would remain full of water allowing the condenser temperature to reach a maximum of only 100°C.



Figure 110: Primary condenser with all of the plumbing connected.

The thermocouples that monitor the input temperature to the primary condensation system were connected to the side of the collection vessel. The tip of the thermocouple was located directly in the flow of vapor to accurately monitor the input temperatures. The drain valves, which are rated for high vacuum, are installed underneath the cones of each of the collection vessels. Then the nitrogen input was installed on the front opening. The nitrogen was supplied from a second nitrogen cylinder so it did not alter the flow to the distillation column during operation. The vacuum gauges were installed and plugs sealed into the openings not being used on both the collection vessels and condensers. The final step was to wrap the vapor line with heating tape and insulate it to maintain temperature and prevent condensation prior to entering the collection vessel.



Figure 111: The completed primary condensation system.

3.5.4.4 Process Construction for the Ballast Tank

The ballast tank shown in Figure 112 was set in place on top of the bricks cemented together for stability. This allowed for ground clearance for the drain valve underneath the tank to be installed and a small sample container placed underneath. A 2 inch diameter tee was connected to the opening on the side of the ballast tank near the bottom. The vertical opening was connected to the piping from the primary condensation system. The horizontal opening was used as an inspection port for the tank. It was sealed with a threaded plug during operation. A large vacuum gauge was connected to the opening on the front of the tank near the top. The nitrogen input was connected to the opening on the

backside of the tank. This nitrogen was also supplied from the second nitrogen cylinder and was used to control the level of vacuum in the process by controlling the amount nitrogen sent to the vacuum pump. An isolation valve was connected to the opening on the top of the tank. This valve was later connected to the input of the freezer condensation system. The final step was to install the plumbing from the primary condensation system to the ballast tank. This plumbing was cut and threaded to size and equipped with flanges before being installed.



Figure 112: The ballast tank set in place.

3.5.4.5 Process Construction for the Freezer Condensation System

Some of the PVC circulation plumbing and the diaphragm pump to circulate the ethylene glycol were missing from the freezer condensation system. A diaphragm pump was placed on top of the freezer and secured using brackets. The air supply was connected to the available pressurized air from the fume hood. The missing PVC plumbing was installed and the circulation system was ready for operation (Figure 113). The only

remaining task was to connect the plumbing from the isolation valve exiting the ballast tank to the vapor input for the freezer unit. This piping was also cut to size and threaded. It was supported using a brace connected to the wall of the hood.



Figure 113: Diaphragm pump and plumbing to circulate the chilled ethylene glycol through the freezer condenser.

3.5.4.6 Process Construction for the Vacuum System

The gate valve to control the restriction in the flow to the vacuum pump was installed on the outlet piping of the freezer unit. After the gate valve the plumbing was connected to the vacuum pump using a flexible metal hose. This was to dampen the vibrations from the pump. Due to the weight of the gate valve and the vibrations from the pump, this section of piping was also supported using a brace connected the wall of the hood.

The output plumbing for the vacuum pump extended several feet vertically, which can be seen in Figure 114. The piping was split into two parallel arms that expand to 2 inches in diameter to provide a larger volume. The high vacuum level forces the vacuum pump oil up into the outlet piping. The greater the flow of molecules into the vacuum pump the greater the force lifting the vacuum pump oil into the outlet piping. The additional volume allows for the system to be evacuated at a faster rate and prevents the pump oil from overflowing. At the top of the arm on the front was a funnel for loading pump oil. It was isolated with a valve which could be opened to provide additional volume. The back arm was equipped with a muffler on the top to restrict the oil from escaping the plumbing.



Figure 114: Vacuum pump with outlet plumbing completed and ready for operation.



Figure 115: The vacuum distillation system ready for operation after the vacuum testing.

3.6 The Coking Process

3.6.1 Coking Process Introduction and Objectives

The final step in the overall process is the production of coke and condensed volatiles from the pitch and centrifuge tails produced in the vacuum distillation process and centrifuge. This step is necessary to recover the remaining volatiles to analyze the overall liquid volatiles recovery for mass balance. It is also necessary to determine if quality, value added cokes can be produced from non-caking coals after processing through the reaction and distillation steps of the process. The primary research objective for the coking process section is to design and construct a coking system capable of producing quality coke from pitch created from non-caking coals and condensed coking volatiles with an acceptable level of mass closure considering the non-condensable gases produced.

The largest problem that will need to be addressed in the design of the coking system will be the removal of the coke from the vessel after the experiment. In standard coking operations the solid carbonaceous material bonds to the wall of the steel vessel as it is produced. Traditionally there are two ways to remove the coke. The first way is to use a jackhammer and remove the coke by force. A hammer and chisel can be employed and the coke physically chipped out of the vessel if a jackhammer is not available. The second method which is used by commercial production operations is cutting the coke from the metal surface using a high pressure water knife. The high expense of this water knife is the deciding factor when determining the scale of commercial coking facilities. For the system that will be constructed to be operated with any degree of time efficiency, a better method for removing the coke will have to be realized.

To design and construct an entire coking process that can be used to coke both pitch and centrifuge tails. The unit will have several parts. A basic coker, a condensing system to recover the volatiles released during cooking. A recovery system so the condensed volatiles and coke can be easily handled. The secondary objectives of this section are listed below.

 To design and construct a process that produces condensed liquid coking volatiles and determine if commercial quality coke could be produced from the pitch of non-caking liquefied coal.

- To test a new method of removing solid coke from the coking vessel where the product was produced.
- 3) To design and construct a coking process that achieves a reasonably high mass closure considering the process was not design to collect and weigh the amounts of noncondensable gases produced.
- To design and construct a coking system that not only processes pitch but also processes centrifuge tails to recover the remaining volatiles.

3.6.2 Coking Design Concepts

The coking process will be constructed in two adjacent hoods in the room 317 laboratory of the Engineering Research Building. The process will be performed at atmospheric pressure, however the system could also permit coking to be done under pressures as high as 50 psig as well as coking under vacuum. Pitch will be loaded into a vessel then lid securely fastened. Heat will be applied evenly to the vessel to a maximum temperatures reaching about 600°C. As the temperature is increased more volatiles are driven off the material. A chemical change occurs as the pitch is transformed into coke while the additional volatiles and non-condensable gases are released. Nitrogen is continually fed into the coker to create a non-oxidizing environment. The volatiles and other gases leave the coker along with the nitrogen supplied. They will enter the condensation system to condense and collect the volatiles. The stream leaving the condensation system will contain nitrogen, the lower boiling point volatiles that did not condense, and non-condensable gases including hydrogen. This stream will be sent to the off gas system to extract the remaining volatiles and handle the other gases. Due to the production of non-

condensable gases, it is assumed that mass closure of less than 1% attained in the reaction process and distillation process will not be obtained in the coking process. However the mass balance should be over 90%.

3.6.2.1 Design Considerations for the Coking Vessel and Vapor Piping

The first design consideration is to identify an appropriate coking vessel within the carbon product group. This vessel should have a capacity that would match the production for the preceding operations. From another past experiment, the carbon products program used vessel that was constructed of a thick wall pipe nine inches in diameter. The pipe formed a cylindrical vessel by standing vertically on a blind flange welded to the bottom. A standard flange was welded to the top bolted to another blind flange for a lid. Similar to the distillation vessel lid, this blind flange lid had a large opening in the center with several other smaller openings around. One of the openings was equipped with a quarter inch Swaglok fitting that had been welded in place. The connections for the vapor piping outlet and other plumbing connected to lid will be welded to prevent leakage of explosive vapors. The other advantage to using this vessel is that it fits inside of a potter's kiln, also owned by carbon products group.

3.6.2.2 Design Considerations for the Coker Heating System

The potter's kiln in the carbon products group is a Paragon kiln capable of temperatures of over 1000°C (Figure 116). The kiln is equipped with a model DTC1000 controller which controls the temperature, ramp rate of the temperature, and hold times inside the kiln. The kiln was heavily used and would require some repairs to the heating coils before it will be able to be put into use.



Figure 116: Paragon kiln to be used to heat the coking vessel.

3.6.2.3 Design Considerations for the Condensation System

The nature of the condensed volatiles that will be recovered in the coking process are similar to those recovered and the distillation process. The volatiles will be a mixture of different hydrocarbons consisting of lighter small molecules and heavier larger molecules. The larger molecules will solidify to a gel like state at room temperature causing a clogging concern in the vapor piping and condensation system. The vapor stream will first enter into the coking collection vessel to provide a cool surface area for the heavier volatile materials to collect before entering the small diameter tubing of the condenser. After the vapor stream enters the coking collection vessel that will proceed vertically upward through a shell and tube heat exchanger before exiting the condensation system.

3.6.2.4 Design Considerations for the Off Gas System

The off gas system will consist of a large tank followed by plumbing to ensure that a clog in the system has not occurred and also to expel the explosive off gases from the system and out through the fume hood exhaust. The standing, 60 gallon tank will act as a secondary condensation system. Just as with the ballast tank for the vacuum distillation system, the flow will enter near the bottom and exit directly out of the top. With the large surface area of the inside walls of the tank at room temperature, any volatiles that pass through the primary condensation system may condense in the standing tank. If the system is converted to a coker that operates under pressure, or if it is converted into a delayed coker, then the large standing tank will greatly increase the volume of the system and act as a ballast tank to absorb changes in the pressure.

3.6.3 Coking Process Construction Preparation

To minimize the opportunity of material solidifying in the vapor line and presenting clogging problems, the length of connecting piping will be as short as possible. The coking vessel inside of the kiln will be located in the hood on the right and the vapor piping will have to pass through the window into the next hood before entering the condensation system. This is because the large hood in the room 317 laboratory is employed by the distillation system and the remaining hoods are not large enough to accommodate all of the equipment. The coking vessel will be elevated (Figure 117) to shorten the length of the vapor piping by placing the kiln on a stand on a moveable cart. The cart will be to move the kiln and coker in and out of place so it can be loaded and unloaded for operation.



Figure 117: Stand to raise the kiln to the proper height.

A frame constructed of unistrut will be installed and secured to the wall of the second hood to support the collection vessel and condenser. Feet were connected to a pair of nine foot long pieces of the unistrut. They were set into place with two horizontal cross braces that the collection vessel will be attached to. The braces can be moved up or down to adjust the height of the collection vessel. A third horizontal brace is extended several inches from the wall to secure the top of the condenser.

3.6.3.1 Construction Preparation for the Coking Vessel and Vapor Piping

The first step in preparing the coking vessel for operation is to have the inside of the vessel chrome plated to assist in coke removal (Figure 118). The plunger of Figure 119 which lifts the coke out of the vessel will have to be fabricated and then chrome plated. The fabrication of the plunger will be simple. It will be a round steel plate about 1/2" thick that will have a diameter slightly less of the inside radius of the vessel to provide a snug fit. In the center of the plate a Rod will be connected with a eyehole at the top. This allows for the plunger to be hoisted out of the coking vessel along with the coke that was produced.



Figure 118: Coking vessel after the inside has been chrome plated.



Figure 119: Plunger after fabrication and chrome plating.

Due to the high temperature inside of the kiln, the connections on the lid will be welded to avoid the leakage of explosive vapors into the hot kiln (Figure 120). The 1.5 inch opening will have a pipe and flange welded into place. A $\frac{3}{4}$ inch pipe and flange will also be welded in place on the lid which will hold a thermocouple that passes through the lid and monitors the temperature inside of the coking vessel. The $\frac{3}{4}$ " plumbing is also connected to a pressure gauge to monitor the pressure in the coking vessel and ensure that the system is not clogged. An isolated vent line is also connected to vent the system directly to the fume hood exhaust if needed.



Figure 120: The fabricated lid for the coking vessel.

3.6.3.2 Construction Preparation for the Heating Kiln

When placed inside of the kiln, the coking vessel is taller than the height of the kiln and protrudes above the level that the insulating lid would be placed to enclose the area of

heating. There is currently no budget to purchase a new heating kiln and there is actually a benefit to the protrusion. The lid for the coking vessel can be securely bolted in place without having to lift the vessel out of the kiln. If the vessel fit down into the kiln, the bolts on the underside of the top flange could not be gripped and tightened.



Figure 121: Coking vessel sitting inside the kiln.

To solve the problem of closing the kiln, insulating bricks shown in the picture below are placed around the top rim of the kiln. This extends the height above the level of the coking vessel which will now be able to enclose the coking vessel and contain the heat. However, the problem still remains with the plumbing that will need to pass through the lid. To correct this problem the lid will be cut in half with notches removed for the vapor plumbing as well as the plumbing with the pressure gauge and thermocouple connected to it.


Figure 122: Coking vessel enclosed in the kiln using insulating bricks.

3.6.3.3 Construction Preparation Condensation System:

A single-pass shell and tube heat exchange which had been used in a previous apparatus in the Carbon Products program was available. The shell side was clean but the tube side was coated with a tar like material. The tube side was filled with light cleaning volatiles and heat was applied overnight. The cleaning volatiles were drained and the tube side of the heat exchanger was clean and ready to be used as a condenser in the coking process. The end caps were removed and the gaskets replaced and the outside of the condenser was painted black.



Figure 123: Shell and tube heat exchanger from a previous Carbon Products experiment.



Figure 124: Fabricated collection vessel very similar to the coking system collection vessel.

Pictured above is one of the finished collection pots for the distillation system. The fabricated collection pot for the coking system will be nearly identical. The conical section connected to the bottom is identical. It was the first step in altering the 13 gallon standard tank purchased from McMaster-Carr. The three tanks were taken to the machine

shop and all three had the same conical bottom installed. The only difference between the collection vessels for the two systems is the input of the volatile vapors. The coking vapors will enter the collection vessel from the side instead of the front. On the side of the vessel there is already an available 1.5" threaded opening so one does not have to be installed. There will be no permanently installed plumbing for a gauge on the coking collection vessel. This location will be used for the vapor input. Instead of a tee fitting for the vapor input, a four-way cross fitting will be welded into place. The opening on the top as well as the opening on the side of the four-way cross will have 1.5" flanges welded in place. The bottom opening will have a valve welded in place to assist in remove any volatile material that has solidified in the vapor plumbing. The top flange will connect to the vapor plumbing from the coking vessel after it has passed through the hood window. The flange on the horizontal opening will be blind flanged and used as a viewport to inspect the inside of the collection vessel and cleanout the vapor plumbing if needed.

3.6.3.4 Construction Preparation for the Off Gas System

A large vertically standing tank with a volume of 60 gallons was available from a previous experiment in the carbon products program and will be used in the off gas system (Figure 125). When inspected it was found that the bottom was full of material. The drain valve at the bottom of the tank was opened but the tank would not drain, even after heated was applied overnight and the tank pressurized. The tank was drained through an opening on the side and the drain valve removed. The inside of the tank was cleaned out with NMP. The wear on the outside of the tank was easily noticeable. Just like the shell and tube heat exchanger that will be used in the condensation system, the

standing tank will be painted black. Similar to the ballast tank for the distillation, it will have to be elevated using bricks in order to install a drain valve and allow for a small container to be placed underneath.



Figure 125: 60 gallon tank that will be used as the standing tank in the off gas system.

3.6.4 Coking Process Construction

3.6.4.1 Process Construction of the Coking Vessel and Vapor Piping

Before the nitrogen enters the top of the coking vessel, it will travel through tubing wound around the body of the kiln to heat the nitrogen. It is especially important that the nitrogen is heated because of the location on the lid of the coker where is enters. It enters near the thermocouple which could cause inconsistent temperature readings inside of the vessel. More importantly, it enters near the vapor output. The addition of cool nitrogen at this point would condense some the volatiles and cause a reflux effect rather than carrying the volatiles to the condensation system where they will be condensed. The nitrogen tubing is 1/4" copper tubing which provides high heat transfer. The tubing was filled with water and capped before it was wound around the vessel to prevent the tubing from becoming kinked.



Figure 126: Copper tubing wound around the body of the coking vessel turned upside down.

The Coker turned right side up and placed in the kiln with the nitrogen tubing. The lid was installed and the vapor piping connected to the flange. Because the Coker and kiln were placed on a moveable cart it had freedom of movement in two directions but could not be adjusted vertically. So the vapor piping had to be connected to install the collection vessel at the correct height in the adjacent hood.



Figure 127: Coking Vessel installed in the kiln and connected to the outlet vapor piping.

3.6.4.2 Process Construction of the Condensation System

First, the coking collection vessel will be attached to the horizontal braces of the unistrut frame. The height is not an issue in this hood so it will not have to be lowered so a five gallon bucket can fit underneath to collect the condensed volatiles. The main concern for the height of the collection vessel will be to minimize the length of the vapor piping from the coking vessel. To secure the collection vessel in place, the height will be adjusted to seal the flanges between the vapor piping and collection vessel input. A thermocouple will be installed on the opening on the front of the tank. The tip of the thermocouple will be positioned directly in the flow of the input vapor stream to monitor the temperature entering the collection vessel.

Next step was to connect the condenser (Figure 128). It was first connected to the collection vessel using flanges and sealed using a spiral wound gasket. The third horizontal brace the extended several inches from the wall was connected to the top brackets of the condenser to secure it in place. On the output of the condenser is a 2" threaded opening where a 2" tee fitting was installed. The horizontal opening of the tee was reduced to one inch and an isolation valve installed followed by a flange to connect the plumbing to the off gas system. The vertical opening of the tee will be plugged and fitted with a thermocouple to the monitor the temperature at the output of the condenser. The plug and thermocouple can be removed and the tee used to view the conditions on the tube side of the condenser and determine if they are clog has occurred. If a clog did occur in the tubes of the condenser or the flow was restricted, the condenser can be wrapped with heating tape and the volatiles melted out. The material in the tube will drip out of the condenser tubes back into the collection vessel. If needed, the ¹/₄" diameter tubes can be clean out with a rod.



Figure 128: Constructed condensation system and standing tank set in place and elevated off the ground using bricks.

3.6.4.3 Process Construction for the Off Gas System

The main piece of equipment for the off gas system is the standing 60 gallon tank. Its primary function in this application will be to act as a secondary condenser. However it can also be used as a ballast tank in the future if the coking process is run under pressure. The tank will act as a condenser for the volatiles remaining in the off gas system by providing a large room temperature surface areas on the inside walls of the tank. The plumbing for the vapor stream leaving the condenser will enter the standing tank through the large 2" opening on the side of the tank near the bottom. The gases will precede vertically upward and exit the tank through the top opening.

From the top opening, plumbing will be installed to divert the flow to three different locations. The first location will be directly towards the back of the hood. Tubing will

be installed so that the plumbing output is situated directly at the intake for the hood exhaust. The second and third locations will be located in the next hood which contains the coking vessel. Similar to the first location, the second location will be plumbed directly to the exhaust of that hood. This allows for the non-condensable gases produced in the process to be split between the two hood so one exhaust is not overwhelmed. The third location will proceed through a copper sparging tube and be submerged in a water bath. The use of the sparge is to ensure that the gases are proceeding all the way through the end of the system and there's no clog.



Figure 129: Standing tank for the off gas system set in place. On top is the plumbing to the hood exhaust.

CHAPTER IV: EXPERIMENTAL PROCEDURES

4.1 Introduction

The Experimental Procedures chapter is a discussion of the operation for the each of the systems that have been designed and constructed. It begins with the external de-ashing system in Stoystown, PA and the procedure used for the experiments to test the ability to remove the clay from the sub-bituminous Australian Bronze coal. The discussion then moves to the coal liquefaction process and explains the procedure for the reaction and centrifugation of coal in the system that was designed and constructed in the laboratory located in the bunker facility. The cleaned, de-ashed centrate is collected in a 16 gallon drum and transported to the laboratory in Room 317 of the Engineering Research Building where the drum of centrate is placed on a scale and the weight recorded. The procedure for processing the centrate into pitch and condensed volatiles is then discussed using the vacuum distillation system that has been designed and constructed. Finally, the procedure to operate the coking system to produce coke and additional condensed volatiles is explained completing the experimental procedure for the overall coal liquefaction process.

4.2 The External De-ashing Process

4.2.1 Operating the Product Development Unit:

The process begins with an empty mixing tank. The valve underneath the cone is closed and about 200 gallons of water is fed into the mixing tank. Once the tank is full, the concentrated detergent solution is added and the paddle stirrer is turned on. The tank is allowed to mix for several minutes to disperse the detergent solution in the water. Then the coal is added to the belt feeder shown in Figure 130 and carried up to the top of the tank. It drops into the mixing tank and is suspended in solution due to the agitation.



Figure 130: Belt feeder to load coal into the mixing tank.

Once the total amount of coal is in the tank, the valve below the cone is opened and the recirculation pump turned on. The flow from the pump is diverted back into the mixing tank. This along with the paddle stirrer creates the agitation conditions for particle collisions in the mixing tank. The mixing tank (Figures 131 and 132) is agitated between 5 and 30 minutes. Once this time is reached, the outlet valve above the pump is partially opened sending the slurry to the separation screen. In order to maintain the agitation while the mixing tank is emptied, a portion of the flow from the transfer pump is sent back to the mixing tank until the level drops into the cone of the tank.



Figure 131: The product development unit mixing tank.



Figure 132: cone, isolation valve and transfer pump underneath the mixing tank.

Once the mixing time is reached and the flow diverted to the separation step, it enters the top of the vibrating 250 mesh screen displayed in Figure 133. The coal particles are collected on top of the screen and proceed to the shoot at the end while the liquids containing the clay and other fine particles pass through the screen and are collected in a tank underneath. Given the mesh size of the screens used, the liquid has a tendency to

blind across the top. This means that the liquid proceeds across the top layer of the screen along with the coal particles and does not fall through. In order to prevent this problem the output valve from the pump is adjusted to lower the flow rate across the screen. At the proper flow rate the screens they will not blind and the liquid will pass through.



Figure 133: Vibrating mesh screen to separate the cleaned coal and rock ash from the detergent solution and clay.

When the entire contents of the mixing tank are processed through the vibrating screen, the liquid in the collection tank underneath is pumped to the centrifuge (Figure 134). A circulation pump is placed in the tank in order to prevent the clays and other fine materials from settling out of solution. The detergent solution with and fine particles are pumped to the centrifuge where the solid particles are removed in the form of a centrifuge cake. The liquids are sent to the collection tank where they will either be transferred back into the mixing tank for further processing or drained to the environment.



Figure 134: Centrifuge to remove the clay and fine particles from the detergent solution.

4.2.2 Operation of the Analytical Laboratory

Samples are taken from each experiment of the testing process to be analyzed in the analytical laboratory. The samples are taken from the raw coal added into the mixing tank, the cleaned coal removed by the vibrating screens, the centrifuge tails, and a sample taken from the detergent solution after it has left centrifuge. This liquid sample will be processed separately from the other samples. The three samples of solid material are taken in the pans, then weighed, and placed in a standard kitchen oven at 105 °C. Once the materials are dried, they are reweighed and the moisture percent for each sample is recorded. Smaller samples of about one gram are then taken from the larger dried samples and placed in crucibles. The crucibles are weighed and then placed inside of a horizontal kiln seen in Figure 135. The kiln is heated to 750°C in an oxidizing environment. After several hours, the crucibles are removed and placed in a desiccator and allowed to cool. Once the samples or cool they are weighed and the ash% recorded.



Figure 135: Kiln and exhaust hood in the analytical laboratory to determine ash% of the samples.

The liquid samples are collected in 250 ml containers, weighted, and placed in the bucket centrifuge in the figure below. The clay and fine solid particles are separated from the detergent solution. The fine solid particles are then dried and to determine the amount of solids remaining in detergent solution. One gram of the dried material is then placed in a crucible and the ash% determined along with the other samples.



Figure 136: Bucket centrifuge with the one gallon containers of the concentrated detergent solution on top.

4.3 The Reaction and Centrifugation Process

4.3.1 Bunker Process Operation Overview

The process begins with loading the raw materials into the transport vessel. The transport vessel is placed on a scale and the desired weight of CTD is added. The stirrer is turned on and the pre-weighed coal and additive are added. The weight of the CTD, coal, and additive are all recorded. Once loaded, it is hoisted from its stand up to the second floor above the reactor. The transport vessel is connected to the loading port and the raw materials gravity fed into the reactor. It is then disconnected from the loading port and the reactor is sealed. The transport vessel is then reweighed and the weight recorded. The reactor is then heated to 130 °C where the moisture has a vapor pressure of 50 psig. The moisture vapors are then vented and condensed in the moisture collection system. The reactor is once again sealed and heated to the temperature of the digestion reaction and held there for 30 minutes to one hour. When the volatile pressure increases above a certain point, the vapors are vented to the volatile collection system where they are condensed.

When the reaction hold time is complete, most of the volatiles are vented to the volatile collection system. The remaining volatile pressure will assist the transfer of the extract from the reactor into the flash tank. As the extract cools in the flash tank, additional volatiles escape the liquid and are condensed in the volatile collection system. Once the proper temperature is reached, the extract is drained into the centrifuge tank. It is circulated using the gear pump through the centrifuge where ash is removed before draining back into the centrifuge tank. This process repeats itself for 30 minutes to one hour depending on the starting ash% of the extract. Once the ash is removed and the

process is complete, the centrate is pumped into a 16 gallon drum. The drum is weighed and the weight of centrate produced is recorded. When the 16 gallon drum is filled, it will be transported to the laboratory in Room 317 of the Engineering Research Building (ERB). There the centrate will be loaded into the vacuum distillation system for further processing.



Figure 137: The Process Flow Diagram for the reaction and centrifugation system.

After the expansion tank cools to near room temperature, the non-condensable gases are vented to the volatile scrubbing system and then exhausted from the building through the vent stack. The condensed moisture and volatiles are drained from their collection systems and weighed for mass balance. The turbine inside of the centrifuge is removed and weighed. The difference between this weight and the starting weight of the turbine is recorded for the weight of the centrifuge tails produced. The accumulated centrifuge tails are removed and the turbine cleaned for further operation.

4.3.2 Loading the Reactor

The loading process begins by placing the transport vessel supported by the stand on to the scale. The transport vessel and the stand are weighed recorded for mass balance. Therefore the initial weight of the transport vessel is known before any of the raw materials are loaded. The heating tape for the transport vessel is turned on to its predetermined level and the three inch threaded cap at the top is removed. CTD from a well mixed 55 gallon drum is pumped into the transport vessel at a controlled rate using a diaphragm pump. The diaphragm pump is air powered and is controlled using a needle valve, so the amount of CTD transferred can be precise. Once the amount of CTD is loaded into the transport vessel the diaphragm pump is stopped and the agitator inside the transport vessel is turned on. A control sample of the CTD is taken and sent to the analytical laboratory for analysis. The pre-weighed sample of coal is slowly poured into the transport vessel so that it mixes with the CTD. Finally with the agitator still running, a weighted sample of the additive is poured into the transport vessel and a three inch loading port sealed. The final weight of the transport vessel containing the raw materials to be loaded into the reactor is recorded.



Figure 138: Position of the transport vessel above the reactor while the reactor is loaded.

The transport vessel and stand are then moved to the position between the gear pump and the expansion tank. The cable for the hoist is connected to the eyebolt on top of the transport vessel which is then hoisted up to the second floor above the reactor. The bottom plumbing for the transport vessel is then connected to the loading port of the reactor in Figure 138. The vapor output valve for the reactor is opened so that pressure does not build up while the raw materials are being transferred into the reactor. The drain valve for the transport vessel and the isolation valve on the reactor lid are both opened and the slurry of raw material drains into the reactor. The three inch cap is removed and a visual inspection performed to ensure that the transport vessel has completely emptied. At this point both of the valves for the reactor and transport vessel are closed and the plumbing disconnected. The transport vessel is then lowered back down onto the stand and reweighed for mass balance measurements. The vapor valve for the reactor is closed, 10 psig of nitrogen pressure is added to the reactor and the agitator is turned on.

4.3.3 Venting the Moisture

In the next phase of the Bunker procedure the heating bands for the reactor are turned on. The temperature is gradually increased to about 130° C to 140° C. At this point the pressure inside of the reactor is between 40 and 50 psig which is the vapor pressure of the moisture at that temperature. At this point the temperature inside of the reactor is held constant. The valve on the vapor line to the moisture tank is opened and the valve to the expansion tank is closed. The vapor valve on the reactor is opened and the vapors are allowed to flow to the moisture collection system seen in Figure 139. When the pressure falls to 0 psig, the vapor valve is then closed with the temperature held constant. Once the pressure again rises to around 30 to 40 psig, the vapor valve is once again opened and the vapors are collection system. When the pressure ceases to rise in the reactor, the temperature is once again increased. The valve to the moisture collection system is closed and the valve to the valve



Figure 139: The moisture collection system.

4.3.4 Controlling the Reaction Pressure

As the temperature increases in the reactor more volatiles were forced into the vapor phase. In addition the rise in temperature causes the pressure to increase in the reactor. When the pressure reaches 500 psig or a lower predetermined pressure, the vapor valve for the reactor is opened and the volatiles allowed to flow through the large condenser and into the expansion tank. Once the pressure drops to between 200 and 400 psig, the vapor valve is once again closed. This step is repeated each time the pressure in the reactor reaches the maximum pressure set point for that particular experiment.

4.3.5 Draining the Reactor into the Flash Tank

After the contents of the reactor are held at the soak temperature of about 400°C for 30 to 60 minutes, the heat supplied to the reactor is turned off. The vapor valve is opened and the volatile pressure vented through the condenser and into the expansion tank. The pressure is reduced in the reactor until it reaches around 150 psig and vapor valve is then closed. The valves for the flash tank are all checked to ensure that they are in the proper position. The drain valve for the reactor is then opened remotely using a cable and pulley system. The remaining 150 psig of volatile pressure forces the extract from the reactor into the flash tank. The system is quickly depressurized as the remaining volatile pressure is expanded to the large volume of the volatile collection system and flash tank. Also, the vapor volatiles are condensing in the large shell and tube condenser and expansion tank.

4.3.6 Cooling the Extract and Draining the Flash Tank

The ceramic heating bands surrounding the centrifuge tank as well as the heat tape wrapped around the circulation piping and gear pump are turned on when the reactor is drained to the flash tank. The extract remains in the flash tank as the temperature decreases. Volatiles continue to escape the extract and are collected in the expansion tank through the condenser. At this point the valves for the centrifuge system will all be checked. The drain valve underneath the tank is closed and the vent valve connected to the expansion tank is opened. This vent valve allows for the volume of air inside of the centrifuge tank to be displaced for easier transfer of the extract into the centrifuge tank. Once the extract is cooled to the operating temperature of the centrifuge system, about 140°C, the flash tank drain valve is also opened remotely using a cable and pulley system. The extract is transferred by gravity into the centrifuge tank.

4.3.7 The Centrifugation Process

Once the extract is in the centrifuge tank, the temperature is checked to ensure that the material has the proper viscosity for operation. All of the valves on the circulation piping are checked along with the drain valves underneath the centrifuge tank. The isolation valve connected to the centrifuge tank is then opened and the heated extract allowed to flow to the gear pump. The gear pump is turned on at a low speed initially. The speed of the gear pump is then increased using the fly wheel on the back of the motor until it reaches its maximum rotational speed. The material travels through the gear pump, up through the circulation piping, and into the centrifuge. Inside of the bowl-type centrifuge the solid materials are forced to the outer wall of the centrifuge turbine due to the tank. The material is recycled through the centrifuge numerous times throughout the process during the 30 to 60 minute processing time. Once the process is complete the speed of the gear pump is reduced and the gear pump stopped.

4.3.8 Scrubbing the Non-Condensable Gases

Once the temperature inside of the expansion tank has dropped to near room temperature, it is assumed that all of the vapors that are condensable have condensed in the expansion tank. The remaining pressure in the system is in the form of non-condensable gases. All of the valves are then checked on the volatile scrubbing system. The scrubbing tower circulation pump is turned on and alkali solution pumped through the shower head at the top of the tower. At this point the output vapor valve from the expansion tank is slightly opened and the pressure slowly bled off to the volatile scrubbing system. The vapor pressure of the system slowly drops until it reaches atmospheric pressure. At this point the vapor output valve for the expansion tank is closed and the circulation pump for the alkali solution of the scrubbing system turned off.

4.3.9 Collecting and Weighing the Products for Mass Balance

The remaining products of the process are now collected and weighed. The moisture tank drain valve is opened and the water and other light volatiles are collected and weighed. A sample is taken and sent to the analytical laboratory for analysis. The condensed volatiles are drained from the expansion tank. The liquids are weighed and a sample taken to the analytical laboratory for further analysis. The condensed liquids from the expansion tank will be combined with the volatiles collected from the distillation process and the coking process. These condensed volatiles will be the recycled CTD for the next round of bunker process runs using the same coal.

4.3.10 Weighing the Centrifuge Tails and Cleaning the Turbine

The final product of the process that needs to be removed and recorded is the tails collected in the centrifuge turbine. All of the tails are contained in the centrifuge turbine

as can be seen in Figure 140. The clean empty turbine was weighed before being placed in the centrifuge housing prior to the process. When it has had time to cool sufficiently, the centrifuge is opened up and the turbine removed. The turbine is weighed and the difference in weight recorded. This difference in weight is the weight of centrifuge tails collected during the ash removal process. The turbine is placed on a fabricated stand to disassemble it and remove the tails. It is opened up and a sample of the centrifuge tails taken to the analytical laboratory for evaluation. Most of the tails are removed from the turbine and collected in a one gallon container. These tails will be further processed in the coking system to recover the remaining volatiles. The residual material remaining on the inside of the turbine will be cleaned out by placing it in a heated bath of light cleaning liquids. Once the centrifuge turbine is clean, it is ready to be weighed and place back into the centrifuge body for the next bunker run.



Figure 140: Centrifuge turbine with the tails collected during the process.

4.3.11 Collecting and Weighting the Centrate

Nitrogen pressure is applied to the centrifuge input piping forcing the remainder of the centrate through the centrifuge and back into the tank leaving only the tails in the centrifuge turbine. The valve after the gear pump on the circulation piping is then closed and the valve to the collection drum is opened. The gear pump is once again turned on at a low speed and the contents of the system pumped into a 16 gallon collection drum which had been weighed prior to receiving the centrate.

Containers are then placed underneath the drain valve for the centrifuge tank as well as underneath the drain valve on the gear pump output. Any residual centrate remaining in the plumbing is allowed to drip into the pre-weighed containers. A sample of the centrate is taken and sent to the analytical laboratory for analysis. The centrate is also weighed after the process is complete and recorded for mass balance purposes. The material from the drain valves is added back into the collection drum or maintained as a sample of the centrate.

4.4 The Vacuum Distillation Process



Figure 141: Process Flow Diagram for the Vacuum Distillation Process

4.4.1 Loading the Distillation Column:

Once the material is homogenized in the 16 gallon transport drum, the loading valve to the distillation column can be opened and the material transferred into column. The drum sitting on top of the scale will have already been weighed before the transfer process had started. The desired amount of weight transferred will be subtracted and the scale set to the final weight. Because the diaphragm pump (Figures 142 and 143) is air driven, it can be precisely controlled so that small pulses of material are sent to the distillation column at a controlled rate. By controlling the air flow to the diaphragm pump the transfer of material can be controlled and the proper amount transferred.



Figure 142: The drum of centrate connected to the loading system.



Figure 143: The diaphragm pump connected to the distillation column.

4.4.2 Evacuation of the System

The first step in evacuating the system will be closing all of the valves from the distillation column output to the end of the process including the gate valve. The level of the vacuum pump oil is checked and additional oil added if necessary. The vacuum pump is turned on and the gate valve cracked open. The system is evacuated slowly. If too much flow is to the vacuum pump, the oil will flood up through the output piping and overflow. When the pressure begins to decrease in the freezer condenser, the valve to the ballast tank is cracked open. When the pressure equalizes the valve is fully opened and the input valve to the ballast tank input valve is opened. Next, the valve above the condenser is cracked opened. Once the pressure equalizes the valve is fully open. Then the valve to the distillation column is opened as little as possible. Once again, as the pressure equalizes, the valve is fully opened. The gate is opened as much as possible and the pressure in the entire system is allowed to decrease to the desired point.

4.4.3 Heating the Distillation Column

At the desired level of vacuum, around 28 mmHg, the nitrogen to this sparge is turned on in the system adjusted to maintain the desired vacuum pressure. Then all of the heating bands around the distillation column were turned on. The column is separated into three separate the heating zones: the bottom zone, the middle zone, and the top zone. The temperature for each zone is controlled using two heating bands. The temperature in the column is gradually increased at about 4-5°C per minute while maintaining the desired difference between the temperature of the liquid in the bottom and the vapors leaving the column. This difference in temperature controls the reflux of the volatile materials in the distillation column and therefore the properties of the condensed volatiles and pitch produced.



Figure 144: The distillation column.



Figure 145: The valves, gauges, and thermocouples connected to the top of the distillation column.

4.4.4 Draining the Distillation Column

When the system reaches the temperature for the desired softening point of the pitch, the process is complete. The outlet valve to the distillation column is closed and the nitrogen begins to pressurize the column. The gate valve to the vacuum pump is fully closed and the vacuum pump turned off. Once the distillation column reaches several pounds per square inch of positive pressure, the nitrogen sparge is turned off. A five gallon container is placed underneath the column on scissor platforms and lifted into place. The drain valve for the column is slightly opened and the pitch allowed to empty slowly into the container. The drain valve output passes through an opening in the fabricated lid of the five gallon container. This prevents the volatiles from escaping the molten pitch as the distillation column is drained. It is important to not drain the pitch to quickly due to the loss of volatiles, even the lid for the container. Additional nitrogen pressure is added to

the column if the pressure drops into the vacuum range as the pitch is removed. The drain valve is closed once the column is empty.

4.4.5 Pressurizing the Rest of the System and Draining the Volatiles

The nitrogen flow is once again turned on and the output valve for the primary condensation system closed. The output valve for the distillation column is cracked open and the systems allowed equalized. The nitrogen pressurizes the system to the output of the condenser. It is added through the distillation column in order to transfer any remaining volatiles to the condensation system. The system is not pressurized with air due to the fact that it contains explosive vapors at elevated temperatures. Several pounds of nitrogen pressure are supplied before the nitrogen flow is stopped. The condensed volatiles in the collection vessel are drained into a 5 gallon bucket. The drain valves for the column and collection vessel are left open for all of the material to drip out. All of the product will be collected, weighed, and analyzed for mass balance. Samples will be sent to the analytical laboratory for further analysis. The ballast tank and freezer condensation system are allowed to remain under vacuum to reduce the evacuation time for the next experimental run. If there is a discrepancy is the mass balance number, the ballast and freezer unit will be pressurized, drained, and inspected.

4.5 The Coking Process



Figure 146: Process Flow Diagram for the Coking process

4.5.1 Loading the Coking Vessel

The process begins with a clean and empty coking vessel. The lid for the kiln and the insulation bricks are removed from the kiln to access the coking vessel. The lid for the vessel has been removed. The next step will be to lower the plunger into the coking vessel. The next step is to be to dump the pieces of solid pitch that have been previously weighed into the coking vessel (Figure 147). This weight of pitch is the starting weight for the coking process mass balance calculations. Once the vessel is loaded, the gasket is inspected and inserted into the notch of the top flange. After several uses or if it has sustained damage, the gasket will be discarded and a new Grafoil gasket cut. The gasket shown in Figure 148 is set in place so the lid bolted to the top of the vessel.



Figure 147: Pitch produced in the distillation column loaded into the coking vessel.



Figure 148: Gasket for the coking vessel lid cut from a sheet of Grafoil.

4.5.2 Connecting the Coking Vessel to the System

The kiln and coker are wheeled into place so the vapor piping flanges are lined up. The flanges for the vapor piping and are connected and sealed using spiral wound gaskets to ensure a secure fit and prevent the escape of the explosive vapors (Figure 149). The plumbing which holds the thermocouple and pressure gauge is also bolted to the lid and sealed using a spiral wound gasket. The nitrogen tubing would around the coking vessel

has two openings. The input opening is connected to the nitrogen cylinder and the other opening is connected to the fitting on top of the coking vessel for the nitrogen input.



Figure 149: The coking vessel loaded and connected to the rest of the system

Before the heat is turned on and the process started, the system must be pressure tested to ensure that it is sealed. It is critical that the explosive vapors do not leak from the system. The nitrogen that is added to the system is turned on. Nitrogen pressure builds up to five psig and the nitrogen feed is then stopped. The system will be allowed to sit for 20 minutes to see if it holds pressure. If the pressure does not hold, the leak must be found and the repaired prior to operation. The next task will be properly insulating the system before operation is began. The insulating breaks are placed around the edge of the kiln. The two halves of the lid are set in place to isolate the kiln and maintain the heat generated. Additional insulation is added to the plumbing and to fill in any gaps or openings that might exist.

4.5.3 Heating the Coking Vessel

The ramp rate, hold temperatures, hold times, and maximum temperature are all programmed prior to starting the heat for the kiln seen in Figure 160. Therefore, no adjustments will need to be made to control the temperature once the experiment is started. Before the heat is turned on, the flow of nitrogen is started through the system. All of the process valves are opened through the 60 gallon standing tank. Until higher temperatures in the coking vessel are attained, the process does not produce a large volume of non-condensable gases. So the two vent valves to the hood exhausts are closed and the gases are diverted through the sparge in the water bath. As the temperature increases, the non-condensable gases are produced at a much higher rate. The odor in the laboratory becomes noticeable. Once to odors are detected the flow will be stopped to the nitrogen to sparge and diverted into the hood exhausts. The flow of nitrogen to the coking vessel is stopped. No oxygen remains in the coking vessel and the gases carries the vapor volatiles from the coker into the primary condensable gases.



Figure 150: Kiln with the heating coils on.

4.5.4 Cooling the Coking Vessel and Draining the Volatiles

Due to the high temperatures of the coking process and large heat mass of the coking vessel, the process of cooling is allowed to last throughout the night. When the hold time at the maximum temperature is complete, the heating coils in the kiln shut off and the process of the cooling the system begins. Several of the insulating bricks that support the lid for the kiln are removed. This permits room temperature air to flow through the kiln and across the outside surface of the coking vessel removing energy from the system in the form of heat. The flow of nitrogen into the coking vessel is turned back on at a higher flow rate. The nitrogen also removes energy in the form of heat. In addition, it carries the volatiles still coming off the coke to the condensation system where they will be recovered. A five gallon bucket is placed under the collection vessel and the liquid coking volatiles drained before they have a chance to cool and the heavier molecule solidity of the inside walls. The volatiles carried to the condensation system by the nitrogen flow condense and drip from the collection vessel into the bucket. When the temperature inside the coker sufficiently drops, the nitrogen flow is reduced and the system left to cool overnight.

4.5.5 Unloading the Coking Vessel

The next morning when the system is cooled, the kiln lid and other insulation is removed. The flanges connected to the lid of the coking vessel are unbolted and the nitrogen tubing is disconnected. The kiln and coking vessel are rolled out of the way. The lid is unbolted and removed from the top flange. With only a little bit of effort, the plunger along with all of the coke is removed from the coking vessel (Figure 151).


Figure 151: Coke easily removed from the chrome plated coking vessel using the plunger.

The insulation is removed from the 1.5 inch blind flange attached to the collection vessel vapor input. The blind flanges is unbolted and removed. The vessel and vapor piping are inspected for the build-up of any solidified volatiles. If necessary, heating bands are wrapped around the collect vessel and the volatiles melted out. The 2" view port on the top of the condenser is opened and the tube side of the condenser inspected. If necessary, the condenser is wrapped with heating tape and any volatiles melted out as can be viewed in Figure 152.



Figure 152: Solidified volatiles removed from the system using heat.

CHAPTER V: RESULTS AND CONCLUSIONS

5.1 Review of the Overall Coal Liquefaction Process Objectives

The overall objective of this research was to analyze the coal liquefaction technology invented at West Virginia University and enhance its potential for commercialization. This was a monumental task given the state of the overall liquefaction system seen in Figure 153 when this research began. It not only included a complete redesign of the existing reaction and centrifugation systems, it required the design of the brand new vacuum distillation and coking systems to complete the process and produce end products. The distillation and coking steps had previously never been done at West Virginia University. The final product of the original process was clean, de-ashed centrate which was sent to Koppers Industries for further processing. The process shown in Figure 154 when this research concluded was able to produce commercial grade pitches (if desired), cokes, liquid water, and sufficient CTD to completely sustain the solvent recycle with addition CTD as a product.

Accomplishing this objective was further complicated by the unwillingness of Quantex to supply adequate funding for the construction of the new systems to further the technology that they licensed from WVU. Therefore, all of the systems were constructed mostly of refurbished equipment that was used in previous Carbon Products experiments.



Figure 153: Block flow diagram of the process licensed by Quantex when the research began



Figure 154: Block flow diagram of the final overall coal liquefaction process invented at West Virginia University

Based on the results of this research and experiments performed on the new systems, Quantex has concluded that the WVU coal liquefaction process is economically viable. They have invested five million dollars into a facility in Westover, WV which will move the technology closer to commercialization. To complete a project with such a large scope, the research was broken down into six primary objectives. Each of the primary objectives was further separated into secondary objectives. The primary objectives with their results were to:

- (1) Investigate how effective the use of detergent solutions are in removing clay ash from the low rank Australian coal prior to the liquefaction reaction in the external de-ashing process.
- The external de-ashing test system was redesigned at the facility in Stoystown, PA. The new Product Development Unit, or PDU, was tested and produced reliable and repeatable results. The de-ashing of the Australian coal was performed and the ash% by weight was reduced from over 24.0% down to 8.8% with a 79% coal recovery.
- (2) Increase the efficiency of the internal de-ashing process by evaluating the current centrifuge process and determining the cause of changes that occur in the material as it is processed from ash rich extract into very low ash% centrate and very high ash% tails.
- The efficiency of the internal the ash in the process was increased by processing the extract at higher temperatures to reduce the viscosity and by employing a gear pump to supply a steady flow to the centrifuge as opposed to the diaphragm pump that produces a pulsatile flow. The increased temperature of the centrifugation process was only feasible after proving that a polymerization reaction was not occurring at these higher temperatures.
- (3) Design and construct a closed system that performs a single batch process for the digestion reaction and ash removal of lower rank coal that achieves mass closure from the raw materials through the moisture, condensed reaction volatiles, centrate, centrifuge tails, and non-condensable gases.

- The reaction section of the process was disassembled and completely redesigned. The new process also includes the internal ash removal with both actions performed in the same batch experiment. The mass closure for the new system has increased to over 99% by weight. The new system processes the low rank coal and the products are moisture and light volatiles, condensed liquid volatiles, ash rich centrifuge tails, non-condensable gases, and the cleaned de-ashed centrate to be processed further in the vacuum distillation and coking system.
- (4) Design and construct a system that performs a single batch process for the vacuum distillation of cleaned de-ashed centrate into quality pitch and condensed liquid distillation volatiles while achieving mass closure from input through products.
- A vacuum distillation system was designed and constructed to process the centrate into pitch and condensed distillation volatiles. This operation had previously been performed at Koppers and had never been done at WVU. The experiments produced reliable and repeatable results with a mass closure of over 99%.
- (5) Design and construct a system that performs a single batch process for the coking of pitch to produce quality coke from non-caking coals and condensed liquid coking volatiles with an acceptable level of mass closure considering the non-condensable gases produced.
- The coking process, which had previously been performed by GrafTech and also had never been done at WVU, was designed and constructed to produce Coke and additional condensed liquid volatiles. The system produced quality Coke from non-caking caking coals of sub-bituminous and lignite ranks. The mass closure is over 90% by weight which is expected considering the production of non-condensable gases.

- (6) Develop the coal liquefaction technology to a level where economic and commercial viability can be determined through a mass closure analysis of the entire process from the raw materials through final products, the determination of whether volatile liquids are produced by the process, and performance of final products when subject to commercial testing.
- The coal liquefaction technology has been developed to a level where economic and commercial viability can be determined. A "cradle to grave" mass closure analysis on the entire process can be performed from the raw materials through each step the process to the end products. All of the material can be accounted for and it can be determined whether volatile liquids are produced or consumed by the process. Final products produced in the coal liquefaction process were subjected to commercial testing.

5.2 The External De-ashing Process

5.2.1 Review of the External De-ashing Objectives

The primary objective for the external de-ashing process was to investigate the effectiveness of detergents in removing clay ash from sub-bituminous Australian coal prior to the liquefaction reaction. This process will be investigated in Stoystown, Pennsylvania where a test system has been constructed and operated to clean and reclaimed gob waste. The purpose for this process is to disperse clays in a detergent solution so the good coal and heavy rock ash can be separated by gravitational means. The reason this process was chosen to evaluate the Australian sub-bituminous coal was it contained over 24% ash by weight made up mostly of clay ash. The redesigned testing system is shown in Figure 155.

5.2.2 Secondary Objectives for the External De-ashing Process

- 1) To redesign the external ash removal testing system (or Product Development Unit) and test it to determine if it is capable of producing reliable and repeatable results.
- The testing system for the external ash removal was completely redesigned. It was constructed and tested numerous times using the coal gob available at the site which was a nearly unlimited supply. With the consistent input of the gob the system was tested and produced reliable and repeatable results.
- To develop a laboratory to perform proximate analysis testing of the PDU samples, bench scale testing of various detergent blends, and consistent detergent preparation for the PDU.
- The analytical laboratory was developed and performed moisture percent and ash percent tests on the samples taken from the PDU. The laboratory was able to quickly produce results and guide future testing on the PDU. Bench scale testing was also performed to determine how effective different detergent blends were in removing and dispersing the clay. The detergent blends were made up prior to the operation of the PDU which allows the concentrations to be standardized.
- 3) Determine if the use of external ash removal for the Australian coals should be pursued.
- Once it was determined that the system produced reliable repeatable results the Australian coal was tested on the PDU. The testing system was able to reduce the ash percent from 24% down to 8.8%. This is still too high to produce quality products from the end of the coal liquefaction process. So internal the ash and will also be pursued.



Figure 155: The testing system (PDU) that was used to determine how effective the use of a detergent solution was in reduce the Ash% for the Australian coal.

5.2.3 External De-ashing Process Results

5.2.3.1 Bench Scale Testing Results

The bench scale testing of different detergent solutions was performed and the analytical laboratory did not yield many usable results. The changes in the results from one concentration to another were very small and within experimental error. The only large changes in the results that were observable were the use of cationic surfactants in the place of anionic surfactants. This showed a significant increase in the amount of ash removed from the samples. This would also make sense because the available water at the plant had a pH of around five. The increase in hydrogen ions would neutralize the negative charge in the anion surfactant. Thus it would seem logical to use cationic surfactant would be more practical for the use of a detergent solution to clean coal with the available water. The available water is acidic in nature.

5.2.3.2 Australian Coal Experimental Results

The external de-ashing process began with Australian sub-bituminous coal with an ash percent of around 24% by weight. After processing through the external ash removal system the ash percent of the coal was reduced to 8.8% by weight. Of the 370.5 pounds of moisture free ash free coal added to the system as an input, 8.9 pounds was not recovered from the products. That means that the mass closure was 97.6% for this experiment. Furthermore, of the weight of moisture free ash free coal input into the process, 79% was recovered as a product with the 8.8% ash.

5.2.4 External De-ashing Conclusions

5.2.4.1 Viability of the Process to De-ash the Australian Coal

The reduction of ash percent from 24% by weight down to 8.8% by weight is a great accomplishment for a coal cleaning process. However the ash percent would have to be further lowered in order to produce quality products that meet commercial standards. Therefore, internal de-ashing after the material has been reacted will still be required. In the previous runs of the coal liquefaction process a 5% ash by weight high volatile bituminous coal was used. This ash percent is 8.8% which is greater than the previous coal used for the internal de-ashing in process. Therefore, even with this reduction in ash percent the efficiency of the internal de-ashing process will still have to be increased in order for the process to be economically viable. The use of the external de-ashing process will not be pursued in removing the ash from the Australian coal prior to the reaction process.

5.2.4.2 Future Development of the Process

Although the external de-ashing process in Stoystown Pennsylvania is not suitable for cleaning the coal to the level needed for liquefaction, it is still a major accomplishment. So the process was developed further to clean coal gob waste as well as other types of coal (Figure 156). The major effort would be in the separation of the coal from the ash using gravity separators such as hydro cyclones and spirals. The process in Stoystown is now operating commercially processing 150 tons of coal or gob per hour and can be viewed in Figure 157.



Figure 156: Final version of the Product Development Unit



Figure 157: Commercial cleaning plant in Stoystown, PA operating at 150 tons per hour.

5.3 The Internal De-ashing Process: Centrifugation

5.3.1 Review of the Internal De-ashing Objectives

The primary objective of the Internal de-ashing process was to increase the efficiency of the centrifugation process by increasing the ash% by weight in the centrifuge tails and to determine what is causing changes to the properties of the extract. To accomplish this object, three secondary objectives also be will be investigated.

5.3.2 Secondary Objectives for the Internal De-ashing Process

- 1) To determine the cause for the increase in viscosity of the extract and centrate during heating and processing of the material.
- It was proven that the increase in viscosity of the extract was not due to a polymerization reaction at higher temperatures, which was the primary reason for low centrifuge processing temperatures in the past. It was determined that the increase in viscosity was

due to the loss of low molecular weight volatiles vaporizing and escaping the system when it was heated.

- To develop and construct a Proof of Concept system to test and verify any new concepts that can improve the efficiency of the process.
- A proof of concept system was designed and constructed that gave us the ability to test the ash removal of the centrifuge at higher temperatures using a constant flow gear pump.
 From the results of the proof of concept testing it was concluded that the efficiency of the centrifugation process can be increased.
- 3) To incorporate any viable internal ash removal concepts into the new production system
- The new ash removal concepts include processing the extract at a higher temperature, designing and constructing a system that will allow for these higher temperatures without the loss of light volatiles, and the use of a gear pump for more consistent flow. In addition the centrifugation will be included as part of the reaction process so that the extract does not have to be reheated after the reaction. Figure 158 and Figure 159 show the centrifuge system in the redesigned reaction process.



Figure 158: Smaller capacity centrifuge to process single batches of extract from the reaction process.



Figure 159: The centrifuge, centrifuge tank, gear pump, and basic plumbing for the new internal de-ashing system.

5.3.3 Internal De-ashing Conclusions

During the centrifugation process, the increase in viscosity was determined to be due to the loss of low molecular weight volatiles from the extended heating time for the drum of extract. It was also determined that the increase in viscosity was not due to a polymerization reaction. With testing of the proof concept system, it was determined that the efficiency of the centrifugation process can indeed be increased by increasing the ash percent in the centrifuge tails. These concepts would be incorporated into the new production process by processing smaller batches and combining it with the reaction process. The extract is drained from the reactor at over 400°C. Given that the materials are the at a temperature high enough for the centrifugation process, the extract will now be centrifuged before it has a chance to cool and solidify. This also allows for single bunker runs to de-ash a single reaction run without the extract being combined with many other runs.

5.4 The Reaction and Centrifugation Process

5.4.1 Review of the Reaction and Centrifugation Objectives

The primary objective for the reaction step was to design and construct a system that performs a single batch process for the digestion reaction and ash removal of lower rank coal that achieves mass closure from the raw materials through the moisture, condensed reaction volatiles, centrate, centrifuge tails, and non-condensable gases (Figure 160 and Figure 161).

5.4.2 Secondary Objectives for the Reaction and Centrifugation Process

- 1) To construct and operate the reaction process to achieve mass closure from the combining of the raw material to the collection of all products from the process.
- The previous coal liquefaction reaction process was disassembled and stripped down to the reactor. A new loading system was employed where all of the raw materials can be accurately weighted before each reaction. Also, all of the products of the reaction process can be collected and weighed after each run to ensure mass closure. The atypical run produced mass closures of about 99% by weight.
- To design and construct a new process that combines the digestion reaction process and an ash removal process that is redesigned to increase the efficiency of internal de-ashing of the extract.
- The two processes of reaction and centrifugation were combined into one combined configuration that performs both tasks. After the reaction is complete the extract is sent to the flash tank until the proper temperature is reached. The extract is then sent to the centrifugation system where the de-ashing is performed without having to re-heat the extract. It is all done with one experimental run before the cleaned de-ashed centrate is collected in a 16 gallon drum to be transported to the room 317 laboratory.
- 3) To construct and operate the updated reaction process to produce a high quality centrate suitable for further processing in the vacuum distillation system along with products from the moisture collection system and the volatile collection system.
- The main product of centrate is of high enough quality with only trace amounts of sulfur and an ash% over below 1.0% to be further processed into pitch and ultimately coke.

- 4) To construct and operate the reaction process to minimize or eliminate all of the safety hazards that occurs prior to operation, during operation, and during the collection of the products.
- The system was constructed with a lack of flexible metal hoses and equipment that is all rated to handle the extreme conditions of the process. It was plumbed with precision to ensure a tight fit where none of the material, particularly explosive vapors, are able to escape from the system. Also the most dangerous parts of draining the hot extract under pressure from the reactor can be done remotely using a cable and pulley system to turn the valves.
- 5) To construct the bunker process with the ability to test control variables by altering the operation conditions and obtaining well representative samples for further evaluation from the analytical laboratory.
- All of the products of the process can be separated, collected, and weighted individually.
 Well representative samples can be gathered from each of the products as well as the raw materials. The new reaction and centrifugation process also have the ability to control variables such as reactor temperature, reaction pressure, rate of increase in temperature, and many other variables.



Figure 160: The 2nd floor of the reaction process.



Figure 161: The reactor, flash tank, and moisture collection system.

5.4.2 Reaction and Centrifugation Process Results

Each reaction and centrifugation experiment began by loading the raw materials into the transport vessel. The first step was loading 42.0 pounds of CTD into the pre-heated transport vessel from a homogenous supply of CTD. The agitator was turned on and 2.5 pounds of additive was supplied along with 15.5 pounds of the coal that was being tested. Process data including mass balance, reactor, and centrifugation data was recorded for

each experiment and can be viewed in Appendix B. There were 13 total runs performed using Bronze coal, 10 using lignite coal, 3 using coal from Manitoba, and 3 using coal from Saskatchewan. The mass balance data for several of the experiments using Bronze coal and lignite coal can be seen in the two tables below.

 Table 5: Product weights for the Reaction process using Australian bronze coal.

Bunker Ou	<mark>tputs (lbs</mark>)						
Centrate	CTD	Moisture	Tails	Total		Mass Lost	and gases produced
45.0	7.5	0.0	6.5	59.0	lbs	1.5	lbs
41.5	15.0	1.0	4.5	62.0	lbs	-1.5	lbs
40.5	9.0	0.0	5.5	55.0	lbs	5.5	lbs
51.0	8.5	0.0	6.5	66.0	lbs	-5.5	lbs
46.5	7.5	0.0	5.0	59.0	lbs	1.5	lbs
44.5	10.0	0.0	6.0	60.5	lbs	0.0	lbs
43.5	10.0	0.0	6.0	59.5	lbs	1.0	lbs
312.5	67.5	1.0	40.0	421.0	lbs	2.5	lbs
73.79%	15.94%	0.24%	9.45%	99.41%		0.59%	

Table 6: Product weights for the Reaction process using Australian lignite coal.

Bunker Ou	<mark>tputs (lbs</mark>)										
Centrate	CTD	Moisture	Tails	Total		Mass Lost and gases produced					
36.0	10.0	0.0	5.5	51.5	lbs	9.0	lbs				
34.5	19.5	6.5	5.5	66.0	lbs	-5.5	lbs				
40.5	13.0	3.5	4.5	61.5	lbs	-1.0	lbs				
35.0	16.0	3.0	3.0	57.0	lbs	3.5	lbs				
146.0	58.5	13.0	18.5	236.0		6.0					
60.33%	24.17%	5.37%	7.64%	97.52%		2.48%					

Seen below in Figure 162 through Figure 165 are the products recovered from the reaction and centrifugation process. The first one is the 16 gallon transport drum filled with de-ashed centrate. It will be taken to the laboratory in Room 317 of the Engineering Research Building. Next is an example of the contents of the moisture collection system.

Water and light violates can be seen in the graduated cylinder. The final two pictures are both examples of the centrifuge tails. The first one contains a high level of volatiles indicating that the centrifuge process was not operated at optimal conditions while the second picture shows an example of ash rich tails processed at the proper conditions.



Figure 162: 16 gallon drum of cleaned de-ashed centrate ready to transport to the Room 317 laboratory.



Figure 163: Product drained from the moisture collection tank. The lower specific gravity volatiles can be seen at the top of the graduated cylinder.



Figure 164: The centrifuge tails inside of the turbine after operation below optimal temperature. A high percentage of volatile material in present.



Figure 165: Centrifuge tails when processed at the correct temperature to produce the desire viscosity.

5.4.3 Reaction and Centrifugation Conclusions

The primary objective for the reaction and centrifugation step of the overall process has been achieved. The system was designed and constructed to perform a single batch process for the digestion reaction and de-ashing of lower ranked coals. Mass closure is obtained to around 99% by weight. Coal, additive, and CTD are weighed and loaded into the system prior to the experiment. The products produced are clean de-ashed centrate, moisture containing light volatiles, condensed liquid volatiles, the ash rich centrifuge tails, and the non-condensable gases.

The results are reliable and repeatable.

5.5 The Vacuum Distillation Process

5.5.1 Review of the Vacuum Distillation Objectives

The primary objective is to Design and construct a system that performs a single batch process for the vacuum distillation of cleaned de-ashed centrate into quality pitch and condensed liquid distillation volatiles while achieving mass closure from input through products.

5.5.2 Secondary Objectives for the Vacuum Distillation Process

- To design and construct a vacuum distillation process that inputs a homogenous sample of de-ashed centrate and produces a quality pitch suitable for further processing the coking system, and distillate that could be recycled as CTD in future experiments.
- The vacuum distillation system inputs a homogenous sample of de-ashed centrate by mixing the heated centrate in both the radial and vertical directions before loading into

the distillation column. The pitch produced was further processed in the coking system and produced quality products.

- To design and construct a process to alter and evaluate the control variables with an extensive ability to monitor process conditions.
- The distillation system has the ability to change and accurately control the vacuum, flow of nitrogen through the column, temperatures at multiple heights inside of the distillation column, and rate at which each of the those temperatures is increased. The temperature is monitored at five points in the distillation column, both of the collection vessels, the outputs of both primary condensers, and the circulation plumbing for the loading system. The vacuum is monitored in the distillation column, both of the collection vessels, the ballast tank, and the freezer collection vessel.
- To design and construct a distillation column that is capable of extracting pitch samples at different points during the distillation run without affecting the operation of the experiment.
- Pitch samples were extracted during operation of the distillation column at various temperatures without affecting the experiment.
- To design and construct a condensation system that is capable of extracting condensed volatile samples from specific ranges of distillation conditions.
- The condensed liquid volatiles were extracted during operation by isolating and pressurizing one side of the primary condensation system. The collection vessel is

drained, the molecules inside evacuated, and the system prepared to put back online with no disruption in the operation of the experiment.

Before this research began, vacuum distillation of the centrate to produce pitch and volatiles had never been done at West Virginia University. No apparatus existed for this process. The primary objectives for the vacuum distillation section is to design and construct a vacuum distillation system which produces high quality pitch and condensed distillation volatiles while achieving mass closure for the complete process. Figures 166 and 167 show the entire vacuum distillation system in room 317 of the Engineering Research Building.



Figure 166: The vacuum distillation process.



Figure 167: The freezer condensation system for the vacuum distillation process.

5.5.3 The Vacuum Distillation Process Results

Process data including mass balance weights, temperatures, and pressures for each vacuum distillation experiment were recorded and can be viewed in Appendix C. There were around 30 total experiments performed using Australian Bronze centrate, Australian

Lignite centrate, and Kingwood centrate derived from bituminous coal. The mass balance data for several of the vacuum distillation experiments using Bronze and lignite centrate can be seen in the two tables below.

Distil	lation Proces	s:					
			Centrate	Pitch	СТД	Product	
			Loaded			Total	
	02/24/11		68.5	30.5	38.0	68.5	lbs
	02/28/11		49.5	30.0	19.5	49.5	lbs
	03/03/11		62.0	25.5	36.5	62.0	lbs
	03/07/11		60.0	35.0	24.5	59.5	lbs
	04/26/11		68.5	34.0	34.0	68.0	lbs
	05/03/11		64.0	26.5	37.5	64.0	lbs
	Total		372.5	181.5	190.0	371.5	lbs
				48.72%	51.01%	99.73%	

 Table 7: Mass balance weights for several of the Distillation experiments using Bronze centrate.

Table 8: Mass balance weights for several of the Distillation experiments using Lignite centrate.

Distillation Pro	cess:				
	Centrate	Pitch	СТД	Product Total	
	courcu			····	
01/28/11	54.5	17.0	37.0	54.0	lbs
02/01/11	54.0	8.0	45.5	53.5	lbs
02/08/11	76.5	14.0	62.5	76.5	lbs
Total	185.0	39.0	145.0	184.0	lbs
		21.08%	78.38%	99.46%	

Figure 168 shows a vacuum distillation experiment showing the top and bottom temperatures of the distillation column along with the temperature of the collection vessel

of the primary condensation system. Two distinct peaks can be seen which indicate two distinct "cuts" of condensed volatiles produced.



Figure 168: The conditions where volatiles escape the material inside of the distillation column.



Figure 169: Pitch produced in the vacuum distillation process.



Figure 170: Condensed volatiles drained from the collection vessel after the first experiment performed in the new system.

5.5.4 Vacuum Distillation Conclusions

The primary objective and all of the secondary objectives were accomplished with the design and construction of the vacuum distillation system. The operation and experimental results even surpassed the expectations for the process. The conditions are easily controlled and altered during the experimental operations. The system typically achieves over 99% mass closure and can produce pitches with any desired softening point by extracting samples at various conditions during the experiment. The system also supplies the ability to visually inspect the equipment when testing any new types of coal to be evaluated.

5.6 The Coking Process

5.6.1 Review of the Coking Objectives

The primary objective for the coking section is to design and construct a system that performs a single batch process for the coking of pitch to produce quality coke from non-caking coals and condensed liquid coking volatiles with an acceptable level of mass closure considering the non-condensable gases produced (Figure 171).

5.6.2 Secondary Objectives for the Coking Process

- To design and construct a process that produces condensed liquid coking volatiles and determine if commercial quality coke could be produced from the pitch of non-caking liquefied coal.
- The coking process has been designed and constructed. It produces condensed coking volatiles and high quality coke from non-caking coals at the end of the overall liquefaction process. The cokes produced form sub-bituminous and lignite coals both passed commercial grade testing.
- To test a new method of removing solid coke from the coking vessel where the product was produced.
- A new method was tested for removing the solid coke from the coking vessel. A plunger was placed under the pitch loaded into the coking vessel. Both the plunger and the inside of the vessel were chrome plated to prevent the coke from adhering to the surfaces. And indeed the coke was able to be removed from the coking vessel by hand with minimal effort.

- 3) To design and construct a coking process that achieves a reasonably high mass closure considering the process was not design to collect and weigh the amounts of noncondensable gases produced.
- The coking process produces commercial grade coke and condensed liquid volatiles while recovering between 90% - 95% of the weight of pitch loaded into the coking vessel.
- To design and construct a coking system that not only processes pitch but also processes centrifuge tails to recover the remaining volatiles.
- The coking system has been operated with centrifuge tails and the remaining volatiles were recovered in the collection vessel.



Figure 171: The complete coking system housed in adjacent hoods in the Room 317 laboratory.

5.6.3 The Coking Process Results

Process data including mass balance weights, temperatures, and pressures for each coking experiment were recorded and can be viewed in Appendix D. The experiments were performed using Australian Bronze pitch, Australian Lignite pitch, and Kingwood pitch derived from bituminous coal. The mass balance data for several of the coking experiments using Bronze and lignite pitch can be seen in the two tables below.

Table 9: Mass balance weights for several of the Coking experiments using Bronze pitch.

Coking Process:								
	Pitch Coke		CTD	Line	Product		Mass Lost and	
	Loaded			Residue	Total		Gases produced	
04/07/11	12.0	6.4	4.6	0.4	11.4	lbs	0.6	lbs
04/13/11	21.1	10.6	8.0	0.7	19.3	lbs	1.8	lbs
Total	33.1	17.0	12.6	1.1	30.7	lbs	2.4	lbs
		51.36%	38.07%	3.41%	92.84%		7.16%	

Table 10: Mass balance weights for several of the Coking experiments using Lignite pitch.

Coking Process:								
	Pitch	Coke	CTD	Line	Product		Mass Lost	and
	Loaded			Residue	Total		Gases produced	
05/10/11	19.0	7.7	8.5	2.0	18.2	lbs	0.8	lbs
		40.53%	44.74%	10.53%	95.79%		4.21%	

In Figure 172 and Figure 173, coking experiments showing the kiln temperature along with the temperature of the collection vessel of the condensation system can be seen. The peak in the collection vessel temperature corresponds to the coking temperature where the volatiles are driven off. The first chart shows a standard coking experiment processing pitch and the second chart shows a coking experiment processing the centrifuge tails. The coke produced from sub-bituminous pitch can be seen in Figures 174 and 175 while coke produced from lignite pitch can be seen in Figures 176 and 177.



Figure 172: Coking experiment show the temperatures of pitch processing.



Figure 173: Coking experiment show the temperatures of centrifuge tails processing.



Figure 174: Sub-bituminous coke produced from Australian bronze coal in the overall WVU coal liquefaction process.



Figure 175: bronze coke easily supporting a five pound load.


Figure 176: Lignite coke produced by the overall liquefaction process. The smooth side of the piece of coke on the left did not adhere to the chrome plated coking vessel wall.



Figure 177: Lignite coke supporting a five pound load.

5.6.4 Coking Conclusions

The primary objective and all of the secondary objectives were accomplished with the design and construction of the coking system. Furthermore, the coking system processed the centrifuge tails without any problems. The conditions are easily controlled and altered during the experimental operations. The system achieves mass closures in the range in the low 90% range and can produce cokes that meet commercial standards.

5.7 Mass Balance Results for the Entire Process

With the completion of all six of the primary objectives, the overall objective of analyzing the coal liquefaction technology invented at West Virginia University was accomplished. The technology was also enhanced for potential of commercialization.

5.7.1 Australian Bronze Coal Overall Mass Balance

Table 11: Overall liquefaction process mass balance based on a one ton input.

Bronze Coal input	Coke Produced	CTD Produced	CTD (including tails)
lbs	lbs	lbs	lbs
2000.0	1441.5	-73.7	147.5

Without including the CTD contained in the tails the system is producing less CTD than it is consuming. But there is about double the percent weight of tails per bunker run of Bronze coal than there is for the lignite coal. Also, for these values it was assumed that 30% of the CTD in the tails is recovered while it is believed that closer to 35% of the tails weight can be recovered. As was the case with the lignite coal, processing the Bronze coal has not been optimized and could also be tailored to produce liquids.

5.7.2 Australian Lignite Coal Overall Mass Balance

 Table 12: Overall liquefaction process mass balance based on a one ton input.

Lignite Coal input	Coke Produced	CTD Produced	CTD (including tails)
lbs	lbs	lbs	lbs
2000.0	1200.0	-145.2	32.3

Without including the CTD contained in the tails, the system is producing less CTD than it is consuming. However, the system conditions have not yet been optimized to produce CTD and the input CTD had only been recycled twice.

5.8 Original Contributions

5.8.1 Reaction and Centrifugation System Contributions

- Reactor loading with the transport vessel to achieve proper mixing of the reactor inputs and mass balance for the loading process
- Process for mixing, combining, and recovering CTD
- Flash tank to allow reactor contents (extract) to cool to the proper temperature and vent volatile pressure for the proper conditions of the centrifugation system
- Moisture tank and moisture condenser to separate the water and low boiling temperature volatiles form the digestion process Patent Filed
- Pressure control of the reactor and collection of the volatiles with vent valve, expansion tank, and expansion tank condenser Patent Filed
- Centrifuge system with recycling gear pump to feed the centrifuge and the proper heating system for the temperature of the centrate
- Alkaline scrubber to absorb the off gases from the reaction process
- Procedure to operate the bunker process to achieve mass balance, well representative samples, and reliable data

• Testing the viscosity/temperature relationship for the materials at different points in the process to set various operating temperatures

5.8.2 Vacuum Distillation System Contributions

- Nitrogen sparge inside of distillation column
- Sample port for pitch extraction
- Centrate mixing and loading system
- Standard Operating Procedure for the distillation process to achieve mass balance, well representative samples, and reliable data

5.8.3 Coking System Contributions

- Coking of sub-bituminous pitch after processing material through the bunker unit into centrate and the distillation unit into pitch
- Coking of lignite pitch after processing material through the bunker unit into centrate and the distillation unit into pitch
- The use of a chrome plated coking vessel to process bituminous coal into coke Patent
 Filed
- The use of a chrome plated coking vessel to process sub-bituminous coal into coke Patent
 Filed
- The use of a chrome plated coking vessel to process lignite coal into coke Patent Filed
- Chrome plated plunger for removal of coke from chrome plated coking vessel Patent Filed

• Procedure for operating the coker to achieve mass balance, well representative samples, and reliable data

5.9 Recommendations

5.9.1 Combining the Three Systems in One Laboratory

Due to the size and electrical requirements of the overall process, the system had to be divided between two separate laboratories. For material handling purposes, it would advantageous for all three of the systems to housed in the same laboratory. Since the conclusion of the research, Quantex has rented a facility in Westover, WV and the system have been moved from the university to the new facility.

5.9.2 Bench scale Laboratory to Optimize the Liquefaction Reaction

With the number of control variables for the coal liquefaction reaction, it is not feasible to optimize the reactor conditions using the existing process. It would be much more efficient to optimize the reactor conditions using a smaller scale and then use the existing system to verify the optimized conditions. A smaller scale reaction laboratory is being designed for the new facility in Westover.

5.9.3 Delayed Coking

The construction of the coker makes it amenable to conversion to a delayed coker if desired. Currently the basic coker structure in supported on a stand that enables access to the bottom. A hole has already been drilled thorough the bottom flange of the coker body, but it is now plugged. This could be the input site for fluid pitches to be coked. That hole is for a ³/₄ inch diameter tube. A piece of tubing that is either wrapped with heating tape or equipped with a heater can be fixed to an elbow that leads into the bottom of the coker

body. A heated reservoir vessel for pitch could be constructed. The hot pitch from this reservoir could be piped into a high temperature /high pressure pump that could push the fluid through the input tubing into the coker body. The pump would have to be a variable rate pump so the flow velocity could be varies as desired. Currently the coker body is placed in a ceramic kiln, however there are separate heating rings that could be added to the kiln. These could be run at various temperatures so that the bottom of the coker body need not be at the coking temperature therefore the fluid could flow into the coker unrestricted by coke. The main body of the coker would be at coking temperature and upper rings could be added that would either be higher than the coking temperature or lower than the coking temperature. The pressurizing system and condensing system will have already been constructed. A design for a delayed coking system is shown is Figure 178 below.



Figure 178: Diagram to convert the process into a delayed coking system.

5.9.4 Continuous Overall Process

The overall process operates as three separate batch systems. A continuous testing system would produce more accurate results for the economic modeling of a commercial process. Quantex has invested five million dollars in the facility in Westover. This will include a continuous testing system that is currently being design by Chemtec based on the results of this research.

5.9.5 Pilot Plant

A larger scale continuous pilot plant should be designed and constructed that is gives a better representation of the economics of the full-scale commercial plant. Quantex has purchase land in Beaumont, TX and a pilot plant is currently being designed by S&B Engineering based on the results of this research.

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APPENDIX A

Equipment Purchased for the Construction of the Reaction System:

<u>Date</u>	<u>Company</u>	Description	<u>Amount</u>
5/4/2010	McMaster-Carr	5 gallon steel storage containers	\$66.14
5/6/2010	Koval bldg&plumbing	PVC pipes and fittings for the scrubber	\$65.58
5/10/2010	McMaster-Carr	gas cyclinder for the bench scale coking apparatus	\$197.51
5/18/2010	McMaster-Carr	1 gallon and 1 quart storage containers for samples and products	\$267.46
5/24/2010	McMaster-Carr	additional 5 gallon steel storage containers	\$96.96
5/25/2010	Koval bldg&plumbing	8 inch diameter PVC piping for the main scrubber body	\$111.96
5/26/2010	Koval bldg&plumbing	1 1/2" PVC fitting for the scrubber	\$16.13
5/26/2010	Koval bldg&plumbing	Additional PVC fittings for the scrubber	\$14.71
6/7/2010	Lowes	Paint and painting supplies, shop towels, and other items for the bunker	\$407.19
6/10/2010	Jaeger Products	Rashing rings for additional surface area inside of the scrubber	\$69.76
6/15/2010	Lowes	Additional paint and painting supplies	\$110.78
6/17/2010	McMaster-Carr	120 gallon expansion tank for volatile collection	\$1,029.24
6/21/2010	Wilson Works, Inc	Minor metal work on the bench scale coking vessel from the machine shop	\$40.00
6/28/2010	Hugharts Supply, Inc.	1 1/2" and 1" untreaded carbon steel piping	\$451.50
6/30/2010	Wilson Works, Inc	Alterations made to the 24 gallon tank so it can be used as the centrifuge tank	\$665.00
7/6/2010	McMaster-Carr	4 transport vessels for reactor loading, 2 large SS ball valves, various SS nipples	\$1,544.11
7/8/2010	McMaster-Carr	1 1/2" nipples for the vapor line and centrifuge system	\$159.50
7/8/2010	McMaster-Carr	one case of latex gloves	\$181.69
7/12/2010	McMaster-Carr	Stainless steel ball valves and pipe nipples	\$704.76
7/13/2010	Hugharts Supply, Inc.	3/4" untreaded carbon steel pipe	\$45.45
7/19/2010	Omega Engineering	Solid state relays for the reactor temperature controller	\$98.00
7/20/2010	McMaster-Carr	1 1/2" ball valves and fitting for the centrifuge system	\$381.72
7/20/2010	Lowes	Rubber matting to reduce equipment vibration and shop towels	\$110.98
7/20/2010	McMaster-Carr	3/4" and 1" pipe nipples and 4 stainless steel ball valves	\$341.33
7/21/2010	McMaster-Carr	Additional fittings and valves	\$143.66
7/23/2010	Milton Roy Company	Specialized high pressure stainless steel fitting for lid on the reactor	\$265.00
7/26/2010	Hugharts Supply, Inc.	PVC pipes and fittings for the cooling water of the condensers	\$60.24
7/26/2010	McMaster-Carr	Stainless steel pipe nipples and wire brushes for equipment cleaning	\$110.64
7/27/2010	Hugharts Supply, Inc.	PVC fittings	\$16.18
7/27/2010	McMaster-Carr	one pipe nipple	\$3.50
7/30/2010	Hugharts Supply, Inc.	PVC pipe and fittings, carbon steel fittings, and several tools for the bunker	\$200.36
8/2/2010	McMaster-Carr	Stainless steel pipe fittings	\$110.85
8/5/2010	Hugharts Supply, Inc.	PVC and carbon steel fittings	\$80.87
8/17/2010	McMaster-Carr	Thermocouples and samples jars	\$276.04
8/20/2010	Lowes	Cables and pullies for remote valve operation	\$97.53
8/19/2010	McMaster-Carr	3/4" and 1" carbon steel pipe unions	\$115.95
8/19/2010	McMaster-Carr	Heating bans and heating tape for the centrifuge system, thermocouple wire	\$813.54
8/21/2010	Lowes	Additional part for the cables and pully system	\$15.59
8/23/2010	McMaster-Carr	Additional valves and pipe nipples	\$261.73
8/24/2010	Advance Auto Parts	gasket material for the gear pump and shop towels	\$36.63
8/24/2010	Hugharts Supply, Inc.	Tread sealant, PVC glue and primer, fittings	\$62.29
8/28/2010	Milton Roy Company	Specialized high pressure stainless steel fitting for lid on the reactor	\$265.00
9/1/2010	McMaster-Carr	High pressure stainless steel fittings, flanges, and nipples for reactor drain piping	\$863.40
9/2/2010	McMaster-Carr	High pressure stainless steel nipples for reactor vent piping	\$170.89
9/2/2010	AP Services, Inc	High temperature tread sealant	\$64.80
9/3/2010	McMaster-Carr	High pressure stainless steel nipples for reactor vent piping	\$50.49
9/3/2010	Swaglock	2 high pressure and high temperature 1" stainless steel ball valves	\$1,253.20
9/7/2010	McMaster-Carr	2 lids for 16 gallon storge drums	\$35.00
		TOTAL	S12.550.84

APPENDIX B

Experimental Results from the Reaction and Centrifugation System:

The first six pages of Appendix B data shows all of the information recorded for a single experiment. Each pair of the remaining pages will provides the process conditions and mass balance weights for an additional experiment. Over 30 experiments were performed on several different coals using the reaction and centrifugation system. The data shown is a well representative sample of the results obtained from the numerous experiments.

Pre	ocess Inf	ormatio	n			
	General Ir	nformation	:			
	Date			January 14, 2011		
	Date samp	ole code		2102011		
	Run numb	er		/C003_06/002A/		
	Raw Mate	rial Inform	ation:			
	Weight of	coal		15.5	lbs	
	Weight of	CTD		42.0	lbs	
	Weight of	additive		3.0	lbs	
	Reactor In	formation	:			
	Agitator s	peed	-	200	RPM	
	Initial nitr	ogen press	ure	10	PSI	
	Moisture	hold temp	erature	130	°C	
	Moisture	hold time		0	min	
	Set tempe	erature		390	°C	
	Temperat	ure hold ti	me	30	min	
	Maximum	pressure		500	PSI	
	Vent pres	sure		400	PSI	
	Centrifuge	e Informati	on:			
	Target ten	nperature		130	∘с	
	Pump Spe	ed		max	rpm	
	Run time	turbine 1		20	min	
	Run time	turbine 2		0	min	
	Nitrogen	clean out p	ressure	50	psi	

Da	ta Form	<u>1</u>				
	Date samp	ole code:		2102011		
	Run numb	er:		/C003_06/	002A/	
Rav	v Material v	weights an	d samples	:		
		_				
	Weight of	coal to be	added		15.5	lbs
	Weight of	coal bucke	et		2.0	lbs
	Total weig	ght (coal ar	nd bucket)		17.5	lbs
	Final coal	bucket we	ight		2.0	lbs
	Weight of	coal			15.5	lbs
	Dull Cool 9	amplo		2102011	10001 021	0020/040
	Pull Coal 3	ampie		2102011	/001_02/	002A7040
	Weight of	CTD to be	added		42.0	lbs
	CTD and lo	oading equ	ip. weight		147.0	lbs
	Final CTD	and equip.	weight		105.0	lbs
	Weight of	CTD			42.0	lbs
		-				
	Pull CTD S	ample		2102011	/C001/002	_01/030
	Weight of	additive to	o be added	1	3.0	lbs
	Additive a	nd contain	ner weight		3.0	lbs
	Final cont	ainer wieg	ht			lbs
	Weight of	Additive			3.0	lbs
	Total load	ed into the	e transport	vessel	60.5	lbs
Rav	v Materials	Loading w	eights:			
	Transport	stand weig	ght		47.0	lbs
	Stand and	empty ves	sel weight	t	105.0	lbs
	Stand and	full vesse	weight		165.5	lbs
	Final stan	d and emp	ty vessel w	veight	105.0	lbs
	Total weig	ght loaded	to the read	tor	60.5	lbs

Pro	duct Weigl	hts and Sar	nples:			
	Centrate v	weights:				
	Initial Cen	trate vess	el weight		61.5	lbs
	Final Cent	rate vesse	l weight		100.5	lbs
	Init tank d	rain can w	eight		0.5	lbs
	Final tank	drain can v	weight		2.0	lbs
	init pump	drain can v	weight		0.5	lbs
	Final pum	p drain car	n weight		2.0	lbs
	Total weig	ght of cent	rate		43.0	lbs
	Pull extra	ct sample		2102011	/C001/002	_01/050
	Pull centra	ate sample	e(s)	2102011	/C001/002	_01/060
	Condense	d Volatiles	51			
	Initial con	tainer wei	ght			lbs
	Final cont	ainer weig	ht		9.0	lbs
	Weight of	condense	d volatiles		9.0	lbs
	Pull volati	les sample	2	2102011	/C001/002	_01/070
	Moisture	Tank:				
	Init moist	ure can we	ight			Ibs
	Final mois	sture can w	reight		0.4	Ibs
	weight of	moisture			0.4	IDS
	Dull moist	uro compl		2102011	10001 1000	01/100
	Pull moist	ure sample	e	2102011	/001/002	_01/100
	Centrifug	e tails weig	thts:			
	Drain pan	weight	<u>,</u>			lbs
	Pan and e	moty turbi	ne		20.0	lbs
	final pan a	and turbine	e weight		25.5	lbs
	Weight of	Tails			5.5	lbs
	Pull Uppe	r Tails sam	ple	2102011	/C001/002	01/090
	Pull Lowe	r Tails sam	ple	2102011	/C001/002	01/100
			-		-	
Tot	al weight o	f the prod	ucts		57.9	lbs
		_				
Diff	ference in v	weight from	m loading		2.6	
		-				

Rea	action Data					
	Date sample co	ode:	2102011			
	Run number:					
	Agitator speed		200	RPM		
	Initial nitrogen	pressure	10	PSI		
	Moisture hold	temperature	130	°C		
	Moisture hold	time	0	min		
	Set temperatu	re	390	°C		
	Temperature h	old time	30	min		
	Maximum pres	sure	500	PSI		
	Vent pressure		400	PSI		
	Time	Time Elasped	Temperature	Pressure	Notes	
	9.30	0	15	20		
	9.35	5	17	20		
	9.40	10	25	20		
	9.45	15	78	20		
	9.50	20	118	30		
	9.55	25	149	50	released moisture@130	
	10.00	30	169	30		
	10.05	35	190	80		
	10.10	40	200	90		
	10.15	45	220	120		
	10.20	50	240	160		
	10.25	55	251	170		
	10.30	60	271	200		
	10.35	65	288	230		
	10.40	70	313	250		
	10.45	75	331	270		
	10.50	80	347	300		
	10.55	85	368	370		
	11.00	90	386	450	released pressure to 150	
	11.05	95	412	250		
	11.10	100	419	360		
	11.15	105	415	450		
	11.20	110	405	500		
	11.25	115	396	520	released pressure	
	11.30	120	389	440		
	11.35	125	373	430		

Centrifuge Data					
	Date sample	code:		2102011	
	Run number:			/C003_06/00	2A/
	Target tempe	erature		130	°C
	Pump Speed			max	rpm
	Run time_tur	rbine 1		20	min
	Run time_tur	rbine 2		0	min
	Nitrogen clea	an out pressu	re	50	psi
	Time	Elapsed	Tank Temp	Cent Temp	
	12.10	0		163.2	
	12.15	5		163.9	
	12.20	10		157	
	12.25	15		153.7	
	12.30	20		149.1	
	12.35	25		146.8	
	12.40	30		149.4	
	12.45	35		149.4	
	12.50	40		149.6	
	12.55	45		150.9	
	1.00	50		152.7	
	1.05	55		153	
	1.10	60		154.3	



Pr	ocess Informati	on		
	General Information	on:		
	Date		October 8, 2010	
	Date sample code		10082010	
	Run number		/C001_02/002A/	
	Raw Material Infor	mation:		
	Weight of coal		15.5	lbs
	Weight of CTD		42.0	lbs
	Weight of additive		3.0	lbs
	Reactor Informatio	<u>n:</u>		
	Agitator speed		200	RPM
	Initial nitrogen pre	ssure	10	PSI
	Moisture hold tem	perature	130	°C
	Moisture hold time	2	0	min
	Set temperature		390	°C
	Temperature hold	time	30	min
	Maximum pressure	2	500	PSI
	Vent pressure		400	PSI
	Centrifuge Informa	tion:		
	Target temperature	2	130	°C
	Pump Speed		max	rpm
	Run time_turbine 1	L	30	min
	Run time_turbine 2	2	0	min
	Nitrogen clean out	pressure	50	psi



Pr	ocess Informat	ion			
	General Informat	ion:			
	Date		October 10, 2010		
	Date sample code	2	10102010		
	Run number		/C004_01/002A/		
	Raw Material Info	rmation:			
	Weight of coal		15.5	lbs	
	Weight of CTD		42.0	lbs	
	Weight of additiv	e	3.0	lbs	
	Reactor Informati	on:			
	Agitator speed		200	RPM	
	Initial nitrogen pr	essure	10	PSI	
	Moisture hold ter	nperature	130	°C	
	Moisture hold tim	ne	0	min	
	Set temperature		390	°C	
	Temperature hold	d time	30	min	
	Maximum pressu	re	500	PSI	
	Vent pressure		400	PSI	
	Centrifuge Inform	nation:			
	Target temperatu	re	130	°C	
	Pump Speed		max	rpm	
	Run time_turbine	1	30	min	
	Run time_turbine	2	0	min	
	Nitrogen clean ou	it pressure	50	psi	



cess information		
General Information:		
Date	November 2, 2010	
Date sample code	11022010	
Run number	/C001_04/002A/	
Raw Material Information:		
Weight of coal	15.5	lbs
Weight of CTD	42.0	lbs
Weight of additive	3.0	lbs
Reactor Information:		
Agitator speed	200	RPM
Initial nitrogen pressure	10	PSI
Moisture hold temperature	130	°C
Moisture hold time	0	min
Set temperature	390	°C
Temperature hold time	30	min
Maximum pressure	500	PSI
Vent pressure	400	PSI
Centrifuge Information:		
Target temperature	130	°C
Pump Speed	max	rpm
Run time_turbine 1	30	min
Run time_turbine 2	0	min
Nitrogen clean out pressure	50	psi



Pre	ocess Inf	ormatio	<u>n</u>			
	General Ir	nformation	<u>:</u>			
	Date			November 4, 2010		
	Date samp	ole code		11042010		
	Run numb	er		/C001_05/002A/		
	Raw Mate	rial Inform	ation:			
	Weight of	coal		15.5	lbs	
	Weight of	CTD		42.0	lbs	
	Weight of	additive		3.0	lbs	
	Reactor In	formation	<u>.</u>			
	Agitator s	peed		200	RPM	
	Initial nitr	ogen press	sure	10	PSI	
	Moisture	hold temp	erature	130	°C	
	Moisture	hold time		0	min	
	Set tempe	erature		390	°C	
	Temperat	ure hold ti	me	30	min	
	Maximum	pressure		500	PSI	
	Vent pres	sure		400	PSI	
	Centrifuge	e Informati	ion:			
	Target ten	nperature		130	°C	
	Pump Spe	ed		max	rpm	
	Run time_	turbine 1		30	min	
	Run time	turbine 2		0	min	
	Nitrogen o	lean out p	ressure	50	psi	



Pr	ocess Inf	ormatio	<u>n</u>			
	General Ir	nformation	<u>:</u>			
	Date			November 9, 2010		
	Date samp	ole code		11092010		
	Run numb	er		/C002_01/002A/		
	Raw Mate	rial Inform	ation:			
	Weight of	coal		15.5	lbs	
	Weight of	CTD		42.0	lbs	
	Weight of	additive		3.0	lbs	
	Reactor In	formation	:			
	Agitator s	peed		200	RPM	
	Initial nitrogen pressure		10	PSI		
	Moisture hold temperature		130	°C		
	Moisture	hold time		0	min	
	Set tempe	rature		390	°C	
	Temperature hold time		30	min		
	Maximum	pressure		500	PSI	
	Vent pres	sure		400	PSI	
	Centrifuge	e Informati	ion:			
	Target ten	nperature		130	°C	
	Pump Speed		max	rpm		
	Run time_	turbine 1		30	min	
	Run time_	turbine 2		0	min	
	Nitrogen o	lean out p	ressure	50	psi	



Process Information						
	General Ir	nformation	<u>:</u>			
	Date			November 11, 2010		
	Date samp	ole code		11112010		
	Run numb	er		/C002_02/002A/		
	Raw Mate	rial Inform	ation:			
	Weight of	coal		15.5	lbs	
	Weight of	CTD		42.0	lbs	
	Weight of	additive		3.0	lbs	
	Reactor In	formation	<u>.</u>			
	Agitator s	peed		200	RPM	
	Initial nitrogen pressure		10	PSI		
	Moisture	hold temp	erature	130	°C	
	Moisture	hold time		0	min	
	Set tempe	erature		390	°C	
	Temperat	ure hold ti	me	30	min	
	Maximum	pressure		500	PSI	
	Vent pres	sure		400	PSI	
	Centrifuge	<u>e Informati</u>	ion:			
	Target ten	nperature		130	°C	
	Pump Spe	ed		max	rpm	
	Run time_	turbine 1		30	min	
	Run time_	turbine 2		0	min	
	Nitrogen o	lean out p	ressure	50	psi	



Process Information						
	General Ir	nformation	<u>:</u>			
	Date			November 30, 2010		
	Date samp	ole code		11302010		
	Run numb	er		/C002_04/002A/		
	Raw Mate	rial Inform	ation:			
	Weight of	coal		15.5	lbs	
	Weight of	CTD		42.0	lbs	
	Weight of	additive		3.0	lbs	
	Reactor In	formation				
	Agitator s	peed		200	RPM	
	Initial nitrogen pressure		10	PSI		
	Moisture	hold temp	erature	130	°C	
	Moisture	hold time		0	min	
	Set tempe	erature		390	°C	
	Temperature hold time		30	min		
	Maximum	pressure		500	PSI	
	Vent pres	sure		400	PSI	
	Centrifuge	e Informati	on:			
	Target ten	nperature		130	°C	
	Pump Speed			max	rpm	
	Run time_	turbine 1		30	min	
	Run time_	turbine 2		0	min	
	Nitrogen o	lean out p	ressure	50	psi	



Process Information						
	General Ir	formation	<u>:</u>			
	Date			December 2, 2010		
	Date samp	ole code		12022010		
	Run numb	er		/C002_05/002A/		
	Raw Mate	rial Inform	ation:			
	Weight of	coal		15.5	lbs	
	Weight of	CTD		42.0	lbs	
	Weight of	additive		3.0	lbs	
	Reactor In	formation				
	Agitator s	peed		200	RPM	
	Initial nitrogen pressure		10	PSI		
	Moisture hold temperature		130	°C		
	Moisture	hold time		0	min	
	Set tempe	rature		390	°C	
	Temperature hold time		30	min		
	Maximum	pressure		500	PSI	
	Vent pres	sure		400	PSI	
	Centrifuge	<u>e Informati</u>	on:			
	Target ten	nperature		130	°C	
	Pump Speed		max	rpm		
	Run time_	turbine 1		30	min	
	Run time_	turbine 2		0	min	
	Nitrogen o	lean out p	ressure	50	psi	



Pro	Process Information					
	General Ir	formation	<u>:</u>			
	Date			December 2, 2010		
	Date samp	ole code		12022010		
	Run numb	er		/C002_06/002B/		
	Raw Mate	rial Inform	ation:			
	Weight of	coal		15.5	lbs	
	Weight of	CTD		42.0	lbs	
	Weight of	additive		3.0	lbs	
	Reactor In	formation				
	Agitator s	peed		200	RPM	
	Initial nitrogen pressure		sure	10	PSI	
	Moisture hold temperatur		erature	130	°C	
	Moisture	hold time		0	min	
	Set tempe	rature		390	°C	
	Temperature hold time		30	min		
	Maximum	pressure		500	PSI	
	Vent pres	sure		400	PSI	
	Centrifuge	e Informati	ion:			
	Target ten	nperature		130	°C	
	Pump Speed			max	rpm	
	Run time_turbine 1			30	min	
	Run time_turbine 2			0	min	
	Nitrogen o	lean out p	ressure	50	psi	


APPENDIX C

Experimental Results from the Vacuum Distillation System:

The first two pages of the Appendix C data shows all of the information recorded for a single experiment. Each one of the remaining pages will provide the process conditions, mass balance weights, and a distillation curve for an additional experiment. Over 30 experiments were performed on centrate derived from several different coals using the vacuum distillation system. The data is a well representative sample of the results obtained from the numerous experiments.

Operator(s): Chris Yur	Total Output 64.2	Samples 0.2	Freezer Liquids 0.0	Volatiles 28.4	Pitch 35.6	entrate Loaded 64.5	Sample ID	COAL NAME: Bronze	UN NUMBER: 090111-20	METHOD:	DATE: 09/01/11		
chick	lbs	lbs	lbs	lbs	lbs	lbs	NON						
	Vacuum Set Point	TOP/BTM Divergence	Data Record Rate	N2 Flowrate	Time at Set Point	Still Set Point	Conditions					Distillation	
	28.5	15	5	15	0	285						Run	
	mm Hg	°	Minutes	PSI	Minutes	°C	NON						
End Time	Start Time		Mass Balance		Yield Volatiles	Yield Pitch	Output						
15:40	10:15		99.53		44.55	55.45							
			%		%	%							

									TOP / BTM				
	Time Elapsed	Temp 1	Temp 2	Temp 3	Still Pressure	Coll. Press	Ballist Pressure	Freezer Pressure	Divergenc e	Temp 4	Temp 5	Temp 6	Temp 7
10:15	0	89	118	129	16.5	15	16	18	39	79	56	22	22
10:20	5	119	125	124	17	20	17	26	43	82	60	22	22
10:25	10	126	127	126	25.5	23.5	25.5	29	6	121	76	28	22
10:30	15	129	130	129	26.5	24	26.5	29	12	118	82	25	23
10:35	20	131	132	131	26.5	24	26.5	29	15	117	84	25	24
10:40	25	133	134	133	27	24	26.5	29	15	119	87	29	22
10:45	30	135	136	135	27	24.5	27	29	15	121	88	29	23
10:50	35	137	138	137	27.5	25	27.5	29	14	124	95	29	23
10:55	40	140	141	140	27.5	25	27.5	29	14	127	103	31	23
11:00	40	145	145	145	27.5	25	27.5	25	14	125	105	22	25
11:00	55	1/19	140	1/19	27.5	25	27.5	29	13	135	121	35	23
11:15	60	151	152	151	28	25	27.5	29	12	130	121	35	23
11:20	65	153	154	153	28	25	27.5	29	11	143	127	37	23
11:25	70	154	155	154	28	25	27.5	29	11	144	130	38	23
11:30	75	155	157	155	28	25	27.5	29	11	146	132	39	23
11:35	80	158	160	158	28	25	28	29	10	150	138	41	23
11:40	85	162	163	162	28	25	28	29	7	156	143	43	24
11:45	90	167	168	167	28.5	25.5	28	29	5	163	151	48	24
11:50	95	172	174	172	28.5	25.5	28	29	6	168	141	56	24
11:55	100	178	179	178	28.5	25.5	28	29	6	173	161	64	24
12:00	105	183	184	182	28.5	25.5	28	29	5	179	154	68	25
12:05	110	185	186	185	28.5	25.5	28	29	4	182	159	75	25
12:10	115	187	188	187	28.5	25.5	28	29	6	182	173	79	25
12:15	120	192	194	192	28.5	25.5	28	29	10	184	1/8	/9	25
12:20	125	198	199	197	28	25	27.5	29.5	12	187	1/8	77	25
12:23	125	204	205	205	27.5	24.5	20.5	29.5	17	100	1/2	66	25
12:30	133	205	210	205	27.5	24.5	26.5	29.5	19	191	165	59	25
12:33	145	222	223	2210	27	24	26.5	29.5	19	204	105	56	25
12:45	150	224	225	224	27	24	26.5	29.5	16	209	197	53	25
12:50	155	224	225	224	27	25	26.5	29	13	212	210	54	25
12:55	160	224	225	224	28	25	27	29.5	9	216	208	62	25
13:00	165	224	225	224	28	25	27.5	29.5	10	215	209	89	25
13:05	170	225	226	225	28.5	25	27.5	29.5	11	215	208	109	26
13:10	175	227	228	226	28.5	25	27.5	29.5	12	216	206	117	26
13:15	180	229	230	228	28.5	25	27.5	29.5	12	218	215	109	26
13:20	185	232	233	231	28.5	25	27.5	29.5	13	220	218	104	26
13:25	190	234	235	235	28.5	25	27.5	29.5	13	222	220	101	26
13:30	195	237	238	237	28.5	25.5	27	29.5	14	224	222	94	26
13:35	200	238	239	238	28.5	25	27	29.5	14	225	221	89	27
13:40	205	239	240	238	28	25	27	29	15	225	218	88	27
13:45	210	241	242	241	28.5	25	27	29.5	15	227	220	87	27
12:55	215	244	245	244	20	25	27	29 5	15	230	224	04 80	27
14.00	225	248	249	248	28	25	27	29	14	235	231	79	27
14:05	230	250	250	249	28	25	27	29.5	13	237	234	78	27
14:10	235	251	252	250	28	25	27	29	14	238	236	79	27
14:15	240	252	252	251	28	25	27	29	13	239	237	82	27
14:20	245	253	254	252	28	25	27	29.5	15	239	238	85	27
14:25	250	254	255	253	28	25	27	29	15	240	238	87	27
14:30	255	255	256	255	28.5	25	27	29	15	241	239	89	27
14:35	260	256	257	255	28.5	25	27	29	15	242	240	91	28
14:40	265	258	259	257	28.5	25	27	29	16	243	241	92	28
14:45	270	259	260	258	28.5	25	27	29	16	244	242	94	28
14:50	275	261	262	259	28.5	25	27	29	18	244	243	94	28
14:55	280	263	263	261	28.5	25	27	29	18	245	244	95	28
15:00	285	264	205	262	28.5	25	27	29	19	240	243	95	28
15:05	230	200	207	203	26.5	25	27	29.5	30	248	240	90	28
15:10	300	267	208	204	29	25	27	29	19	240	240	95	20
15:20	305	265	265	262	29.5	25.5	27.5	29	19	246	236	96	28
15:25	310	265	266	260	28.5	25	26	29	21	245	239	112	28
15:30	315	272	272	258	26	22	23.5	29.5	25	247	220	107	28
15:35	320	279	280	264	27	24	25	26	33	247	197	89	28
15:40	325	283	284	264	26.5	22	24.5	26.5	42	242	187	79	28

















APPENDIX D

Experimental Results from the Coking System:

The first four pages of the Appendix D data shows all of the information recorded for a single coking experiment. The next three pages show all of the data recorded for a single experiment where the centrifuge tails are processed to recover the volatiles. A total of 13 experiments where performed using the coking system. Centrifuge tails along with pitches derived from bituminous, sub-bituminous, and lignite coals where all successfully processed in the coking system.

Operator(s):		Total Output		Line Residue	Volatiles	Coke	Pitch Loaded	Sample ID	COAL NAME: E	DATE:			
Chris Yu		18.4		0.6	7.2	10.6	19.5		Bronze	04/07/11			
chick		lbs		lbs	lbs	sql	lbs	NON					
		Program / Ramp Rate	Pressure Set Point	Data Record Rate	N2 Flowrate	Time at Set Point	Kiln Set Point	Conditions					
		#2	0	5	15	30	500					Coke	
			PSI	Minutes	PSI	Minutes	°C	NON				r Run	
	End Time	Start Time		Mass Balance		Yield Volatiles	Yield Coke	Output					
		9:45		94.36		42.39	57.61						
				%		%	%						

	T :				Coker	
	l ime				Р -	
					י ב	
	a	Kiln	Coker	Cond.	s	Inside
	p	Т	Т	Т	S	T
	S	е	е	е	u	e
	е	n	r	n	r	n
	d	р	р	р	е	p
			. –	. –	-	
9:45	0	19	1/	1/	0	19
9:50	5	32	18	17	0	44
9:55	10	54	25	1/	0	107
10:00	15	/1	38	20	0	1/3
10:05	20	8/	49	20	0	204
10:10	25	112	59	21	0	214
10:15	30	165	/2	20	0	242
10:20	35	194	89	20	0	265
10:25	40	219	107	19	0	281
10:30	45	245	123	18	0	299
10:35	50	268	141	17	0	318
10:40	55	293	158	17	0	340
10:45	60	323	185	17	0	365
10:50	65	333	206	17	0	373
10:55	70	344	227	17	0	383
11:00	75	336	240	17	0	360
11:05	80	336	249	17	0	359
11:10	85	338	261	17	0	356
11:15	90	338	269	17	0	356
11:20	95	340	287	18	0	358
11:25	100	335	302	19	0	387
11:30	105	335	316	18	0	405
11:35	110	336	329	18	0	416
11:40	115	350	339	19	0	416
11:45	120	346	348	19	0	428
11:50	125	350	358	19	0	438
11:55	130	352	368	19	0	446
12:00	135	356	376	19	0	454
12:05	140	360	382	19	0	460
12:10	145	365	383	18	0	465
12:15	150	369	401	19	0	473
12:20	155	373	416	19	0	479

12:25	160	377	428	19	0	485
12:30	165	381	438	19	0	491
12:35	170	385	443	22	0	501
12:40	175	392	451	23	0	511
12:45	180	394	452	23	0	513
12:50	185	394	455	23	0	514
12:55	190	400	460	23	0	519
13:00	195	398	462	23	0	506
13:05	200	410	461	24	0	519
13:10	205	410	465	23	0	524
13:15	210	413	470	24	0	528
13:20	215	416	476	24	0	532
13:25	220	420	481	24	0	535
13:30	225	421	485	24	0	538
13:35	230	425	488	24	0	542
13:40	235	429	492	24	0	546
13:45	240	433	496	24	0	549
13:50	245	437	500	23	0	552
13:55	250	441	504	23	0	555
14:00	255	442	508	22	0	557
14:05	260	439	505	22	0	540
14:10	265	437	503	22	0	528
14:15	270	437	501	22	0	526
14:20	275	436	501	22	0	527
14:25	280	431	501	22	0	529
14:30	285	440	499	21	0	530
14:35	290	441	499	21	0	526
14:40	295	415	495	21	0	525
14:45	300	411	491	21	0	518
14:50	305	441	486	21	0	513
14:55	310	439	487	21	0	513
15:00	315	438	489	21	0	514
15:05	320	440	491	22	0	521
15:10	325	440	492	22	0	520
15:15	330	448	494	22	0	535
15:20	335	452	498	22	0	541
15:25	340	446	498	22	0	519
15:30	345	447	497	22	0	521
15:35	350	448	497	22	0	521
15:40	355	452	497	23	0	524
15:45	360	450	496	23	0	520

	15:50	365	450	496	23	0	519
	15:55	370	449	496	23	0	522
	16:00	375	450	496	23	0	520
	16:05	380	450	496	23	0	522
	16:10	385	450	496	23	0	522
	16:15	390	450	496	23	0	523
	16:20	395	450	496	23	0	523
	16:25	400	455	496	24	0	539
_	16:30	405	462	501	25	0	555
	16:35	410	468	506	25	0	564
	16:40	415	489	510	25	0	563
	16:45	420	479	509	25	0	550
	16:50	425	498	512	25	0	558
	16:55	430	495	515	25	0	576
	17:00	435	497	523	25	0	584
	17:05	440	498	529	25	0	585
	17:10	445	485	527	24	0	536
	17:15	450	473	518	25	0	514
	17:20	455	464	510	24	0	497

Coker Run - Tails Coker Run - Tails Sample ID UOM Conditions UOM Output Sample ID UOM Conditions UOM Conditions UOM Output Sample ID Imme at Set Point 550 °C Yield Tails 66.25 % Coke 6.1 Ibs Time at Set Point 90 Minutes Yield Volatiles 33.76 % Volatiles 3.1 Ibs Point 90 Minutes Yield Volatiles 33.76 % Volatiles 3.1 Ibs Point 90 Minutes Yield Volatiles 33.76 % Line Residue 0.0 Ibs Pressure Set Point 0 PSI Mass Balance 91.23 % Total Output 9.2 Ibs Program / Ramp Rate n/a . Start Tme 11.35 End Time End Time 11.35 End Time M M M M M M M M M M M M M <t< th=""><th></th><th></th><th>N/A</th><th>p Hold Time:</th><th>3rd Ramp</th><th>2 hrs</th><th>2nd Ramp Hold Time:</th><th>440°C</th><th>Hold Time:</th><th>Ramp H</th><th></th></t<>			N/A	p Hold Time:	3rd Ramp	2 hrs	2nd Ramp Hold Time:	440°C	Hold Time:	Ramp H	
Coker Run - Tails Coker Run - Tails Coker Fairs UOM Conditions UOM Output Sample ID VOM Conditions VOM Conditions VOM Output Soct Yield Tails 66.25 % Cocke 6.1 Ibs Time at Set Point 90 Minutes Yield Tails 66.25 % Volatiles 3.1 Ibs Data Record Rate 55 Minutes Yield Volatiles 33.75 % Uine Residue 0.0 Ibs Pressure Set Point 0 PSI Mass Balance 91.23 % Total Output 9.2 Ibs Program / Ramp Rate n/a . Start Time 11.36 Kin			N/A	d Ramp Rate:	a in 3rd	90°C/hr	*2nd Ramp Rate:	190°C/hr	Ramp Rate:	Initial F	
Coker Run - Tails Coker Run - Tails Coker Tails Total NAME: VOM Conditions Vom Vom Sample ID Vom Conditions Vom Vom Vom Vom Vom Vom Vom Vom Vom Volutions <				gasket on lid.	sed graphoil	cted. Re-u	G with N ₂ , no leaks dete	ed to 5 PSI	as pressurize	System wa	10
Operator(s): Chris Yurchick Coker Run - Tails Coker Run - Tails Operator(s): Chris Yurchick											
Coker Run - Tails DATE: 09/23/11 VOM Conditions UM Sample ID VOM Conditions UM Conditions UM Output Pitch Loaded 10.1 Ibs Conditions UM UM Output Vial Tails 66.25 % Volatiles 3.1 Ibs Time at Set Point 90 Minutes Vial Tails 66.25 % Volatiles 3.1 Ibs Data Record Rate 55 Minutes Vial Volatiles 33.75 % Total Output 9.2 Ibs Presure Set Point 0 PSI Mass Balance 91.23 Total Output 9.2 Ibs Pregram / Ramp Rate n/a . End Time 11.35 Volatiles 0.0 Ibs Pregram / Ramp Rate n/a . End Time 11.35 Unite Pregram / Ramp Rate Ind Ind Ind Ind Ind Unite Ibs Pregram / Ramp Rate Ibs									rchick	Chris Yu	Operator(s):
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Coker Run - Tails Coker Run - Tails Coker Run - Tails Coker Run - Tails Conditions UOM Output Conditions UOM Output Output Pitch Loaded 10.1 lbs Conditions UOM Muntes Output Vield Tails 66.25 % Volatiles 3.1 lbs Time at Set Point 90 Minutes Vield Volatiles 33.75 % Volatiles 3.1 lbs Data Record Rate 550 % Mass Balance 91.23 Mass Balance 91.23 Mass Balance 91.23 % Total Output 9.2 lbs Program / Ramp Rate n/a o Start Time Lit.35 Kent Time Lit.35											
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Coker Run - Tails Coker Run - Tails Coker Run - Tails Colspan="4">Conditions Conditions Conditions Conditions Conditions Conditions Conditions Conditions Conditions Colspan="4">Conditions Colspan="4">Colspan= 4"Colspan="4"Colspan= 4"Colspan="4"Colspan="4"Colspan="4"Colspan= 4	11:35	Start Time		,	n/a		Program / Ramp Rate		sql	9.2	Total Output
Coker Run - Tails Conditions Image: Conditions Sample ID UM Conditions UOM Conditions UOM Output Image: Conditions UOM Conditions UOM Output Image: Conditions UOM Conditions Image: Conditions UOM Output Image: Conditions Imag				PSI	0		Pressure Set Point		sql	0.0	Line Residue
Coker Run - Tails Sample ID Volatiles UOM Imat Set Point Imat	ce 91.23 %	Mass Balance		Minutes	თ		Data Record Rate		sql	0.0	reezer Liquids
Coker Run - Tails Sample ID VION Image: Conditions Imag				PSI	15		N2 Flowrate		sql	3.1	Volatiles
Coker Run - Tails DATE: 09/23/11 :OAL NAME: 09/23/11 Bronze Tails I OM I Conditions I I Ibs Kin Set Point 550 °C Yield Tails	es 33.75 %	Yield Volatile		Minutes	90		Time at Set Point		sql	6.1	Coke
Coker Run - Tails DATE: 09/23/11 :OAL NAME: Bronze Tails UOM I Oatricitions I UOM Output	ils 66.25 %	Yield Tai		ô	550		Kiln Set Point		sql	10.1	Pitch Loaded
DATE: 09/23/11 Output Output </td <td></td> <td>Output</td> <td></td> <td>MON</td> <td></td> <td></td> <td>Conditions</td> <td></td> <td>NON</td> <td></td> <td>Sample ID</td>		Output		MON			Conditions		NON		Sample ID
Coker Run - Tails DATE: 09/23/11 OAL NAME: Bronze Tails											
DATE: 09/23/11 Coker Run - Tails									S	Bronze Tai	COAL NAME:
Coker Run - Tails										09/23/11	DATE:
Coker Run - Tails											
Color Dun - Taile											
					Taile	Din	Coker				

	Elasped					Collection	Coker	Ballast	
	Time,	Kiln	Coker	Coker Wall	Cond.	Pot	Pressure,	Pressure,	Visual Smoke
Clock Time	min	Temp, °C	Temp, °C	Temp, °C	Temp, °C	Temp, °C	psig	psig	Check
11:35	0	24	23	22	52	71	0	0	
11:40	5	25	23	24	48	64	0	0	
11:45	10	34	23	47	43	57	0	0	
11:50	15	60	29	113	38	51	0	0	
11:55	20	85	40	128	35	47	0	0	
12:00	25	100	50	134	33	44	0	0	
12:05	30	115	59	143	31	41	0	0	
12:10	35	131	69	154	29	39	0	0	
12:15	40	144	78	160	28	38	0	0	
12:20	45	163	89	181	27	36	0	0	
12:25	50	175	100	191	26	35	0	0	
12:30	55	192	112	204	25	34	0	0	
12:35	60	210	125	222	25	34	0.2	0	
12:40	65	226	139	241	25	33	0.2	0	
12:45	70	241	152	255	24	33	0.2	0	
12:50	75	258	169	272	24	37	0.2	0	
12:55	80	271	182	276	25	32	0.2	0	
13:00	85	288	203	300	23	32	0.2	0	
13:05	90	305	215	316	24	32	0.2	0	
13:10	95	323	235	330	23	32	0.2	0	
13:15	100	338	250	352	23	32	0	0	
13:20	105	356	270	370	23	32	0	0	
13:25	110	368	288	375	23	32	0	0	
13:30	115	388	307	406	23	32	0	0	
13:35	120	403	330	422	23	32	0	0	
13:40	125	417	344	422	23	32	0	0	
13:45	130	426	348	413	23	32	0	0	
13:50	135	442	379	438	23	33	0	0	
13:55	140	436	385	422	23	33	0	0	
14:00	145	441	379	424	23	34	0	0	
14:05	150	433	389	425	23	35	0	0	
14:00	155	433	404	429	23	37	0	0	
14:15	160	437	413	429	23	39	0	0	
14:20	165	430	413	420	23	41	0	0	
14:25	170	456	/22	434	23	41	0	0	VAS
14:20	175	456	420	440	23	40	0	0	yes
14:35	180	400	451	450	23	41	0	0	
14:30	100	472	456	403	23	42	0	0	
14:45	190	400	455	457	23	42	0	0	
14:50	195	470	455	402	23	45	0	0	
14:55	200	472	401	405	23	40	0	0	
15:00	200	472	400	405	23	40	0	0	
15:00	203	472	470	472	25	47	0	0	
15:00	210	472	470	470	25	52	0	0	
15:10	212	401	4/3	4/3	23	50	0	0	
15:15	220	504	4/9	501	23	52	0	0	
15:20	223	523	491	505	23	55	0	0	
15:25	230	522	498	503	23	55	0	0	
15:30	230	530	511	521	23	55	0	0	
10:35	240	552	519	541	23	54	0	0	
15:40	245	551	529	530	23	54	0	0	

15:45	250	547	531	529	23	55	0	0	
15:50	255	548	535	535	23	51	0	0	
15:55	260	547	539	540	23	48	0	0	
16:00	265	549	544	546	23	46	0	0	
16:05	270	551	546	546	23	45	0	0	
16:10	275	552	550	553	23	44	0	0	
16:15	280	554	554	559	23	43	0	0	
16:20	285	551	558	557	23	42	0	0	
16:25	290	551	560	559	23	42	0	0	
16:30	295	551	562	561	23	41	0	0	
16:35	300	551	562	558	23	41	0	0	
16:40	305	552	562	558	23	40	0	0	
16:45	310	552	563	557	23	40	0	0	
16:50	315	547	562	555	23	39	0	0	
16:55	320	549	562	554	23	39	0	0	
17:00	325	547	563	556	23	38	0	0	
17:05	330	549	564	558	23	38	0	0	
17:10	335	549	565	558	23	37	0	0	
17:15	340	551	564	559	23	37	0	0	
17:20	345	551	566	560	23	37	0	0	
17:25	350	551	567	562	23	37	0	0	
17:30	355	549	567	560	23	36	0	0	
17:35	360	551	566	560	23	36	0	0	

