Low Cost Carbon Fibers from Coal-Based Precursors

Final Report

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April 15, 2002

Contract #1667-MER-DOE-40350

DOE #DE-FC26-98F740350

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TABLE OF CONTENTS

List of Graphic Materials

ABSTRACT

The program objective is to demonstrate commercial viability of using coal tar pitch (CTP) as a precursor to produce low-cost carbon fibers. A commercial demonstration spinning system with a 100 hole spinneret was constructed that provided trouble free spinning of CTP. This included a take-up system that utilized a graphite cylinder, which permitted stabilizing as well as pyrolizing the fiber on the graphite cylinder. The processing of commercial CTP to provide a suitable spinning pitch was scaled-up to 10 Kg capacity. An isotropic pitch from West Virginia University (WVU) and both isotropic and mesophase pitches prepared on this program were spun in the multi-hole spinneret system that demonstrated operability. The strengths of the produced fibers, isotropic and anisotropic was up to 2.2 GPa. This phase of the program demonstrated that quality fiber in small tows can be produced from CTP that provides initial demonstration of commercial viability.

Introduction

During the first year program, calendar 1999, it was demonstrated commercial source coal tar pitch could be purified by solvent extraction, control oxidized with air and/or oxide chemical additions, thermal treated and spun into isotropic fibers, which could be pyrolized without oxidation/stabilization and without fiber fusion. The fiber strengths were in the 1.3 GPa range.

In the second year, calendar 2000, all processing steps were further improved that resulted in producing carbon fibers with strengths up to 3.8 GPa when heat treated to 1200°C and up to 4.2 GPa when heat treated to 1800°C. These strengths are greater than carbon fibers derived from petroleum-based pitch and equivalent to commodity fibers produced from petroleum based polyacrylonitrile (PAN). The coal tar pitch was also 80% converted to mesophase and anisotropic fibers were demonstrated. Fiber spinning in a 25-hole spinneret bead was demonstrated as well as microwaves heating of the fibers.

A goal of this fiber program is to utilize a domestic source coal tar pitch (CTP) as a precursor to produce low cost carbon fibers for use in transportation and a plethora of other applications. The automotive industry has stated that a carbon fiber price of $5.00/lb in continuous form and $3.50/lb in discontinuous form is required for large-scale utilization. If carbon fiber is fully utilized throughout automobile, over 50% weight savings is possible, which translates to substantial fuel savings and pollution reduction. Carbon fibers from petroleum stock that produces the PAN fiber precursor is quite a mature process whose cost has bottomed at approximately $10/lb. If CTP based processing can meet the transportation industry cost goal, a paradigm in carbon fiber production will have been established. The objective of this program is to demonstrate such a paradigm is indeed possible. The goal/objective of the third year was to demonstrate a 100-hole spinneret system could be built to establish the commercial potential of the CTP process, which could be operated to project the cost of fiber production.

Executive Summary

Carbon Fibers have become a commodity for wide and diverse applications but have not penetrated transportation to any major extent because of high cost. All carbon fibers are made from petroleum precursors of polyacrylonitrile (PAN) or petroleum pitch. The cost of these carbon fibers have bottomed at approximately $10/lb. The transportation sector and a variety of other applications require continuous carbon fibers at less than $5.00/lb and discontinuous at less than $3.50/lb. This CPCPC program has demonstrated that coal tar pitch (CTP) or pitch extracted directly from coal provides a low cost precursor to produce carbon fibers with properties equivalent to those produced from the petroleum precursor. CTP purification and the development of additives have resulted in the ability to spin fiber that do not require stabalization/oxidation to prevent fusion prior to heat treatment. Processing has been scaled-up that demonstrates producing small tows and provides a basis for predicting that coal base carbon fibers can be produced for the transportation cost goal. This program has demonstrated it is commercially feasible to produce coal base carbon fiber at low cost and is in the process of continued and expanded commercial demonstration.

RESULTS OF WORK DURING YEAR 2001

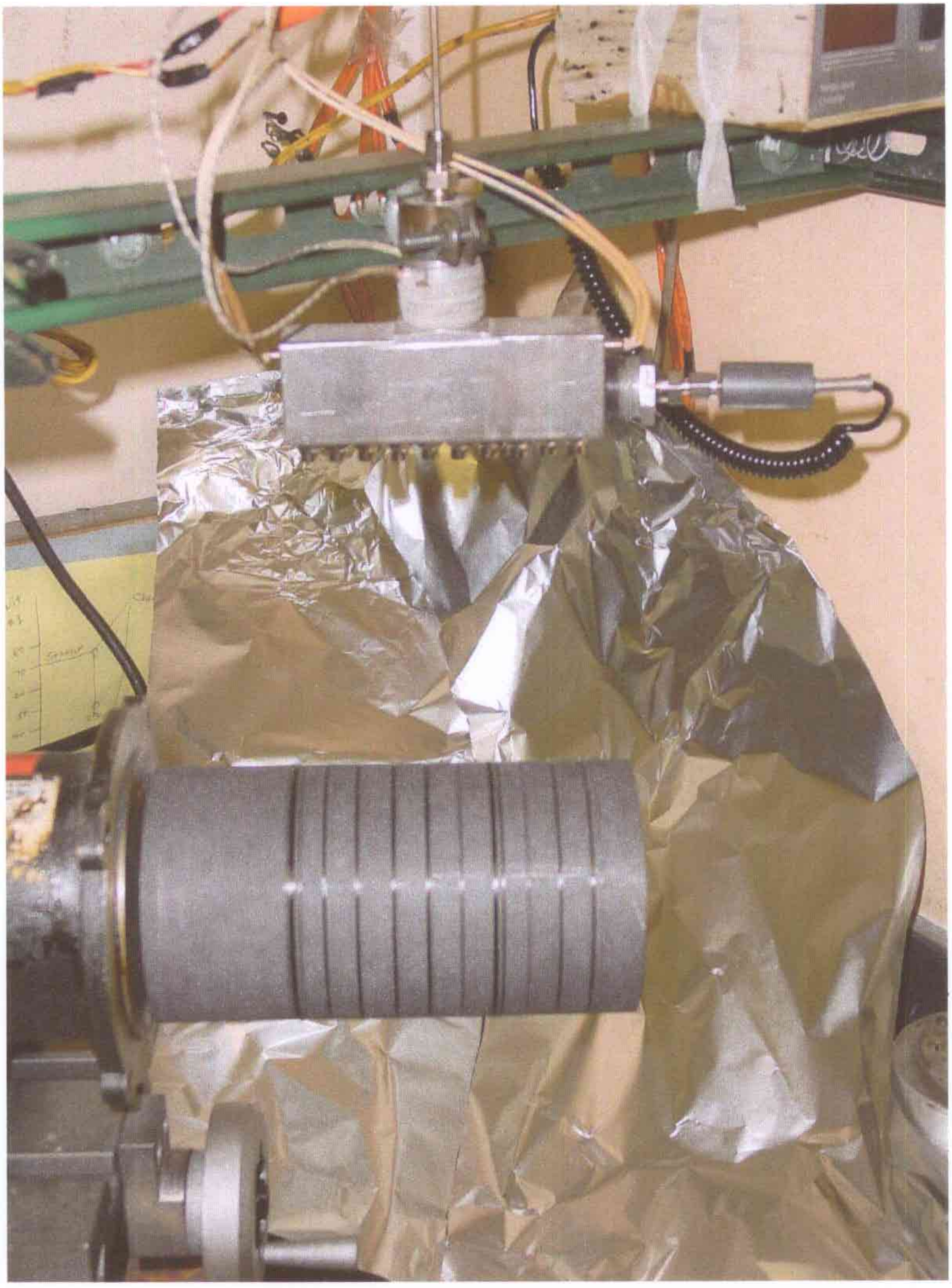
In order to commercially demonstrate the bench scale demonstrated CTP fiber processing system, three major units must be scaled-up. These are the CTP purification and processing to produce the pitch precursor suitable for spinning, the 100-hole spinneret system and the fiber take up system. An adjunct to these three units is the heat treatment to produce the final carbon fiber.

The first unit of purifying and processing the as received CTP has been scaled from about 50 grams processing to 10 kg. During 2001 it is now possible to process up to 10 kg of as received pitch, which provides an adequate supply of pitch for spinning and demonstrates it is possible to scale-up and maintain the quality of fibers. This scale of processing 10 kg of pitch provides more pitch than necessary for fibers investigations which allows the CTP to be investigated for other applications including foam and as a binder for C-C composites for general applications, as well as anodes for lithium-ion batteries. Thus, the scale-up in this fiber program provides the opportunity to utilize the low cost domestic source CTP for other applications.

A well functioning fiber take-up system is required to demonstrate the purified pitch and spinneret system can function to produce low cost fiber. The take-up system was build around a milling machine table linked to a speedometer-regulated drive. The linear advancement is capable of 0.1 mm per revolution that permits winding fibers side by side or as a tow, also side by side. The take-up spool is a polished graphite cylinder mounted on a Teflon cylinder attached to the melting table. The smooth polished graphite cylinder prevents any surface damage to the green spun fiber. The graphite take-up cylinder permits stabilizing the fiber while wound on the graphite cylinder, as well as pyrolysis/heat treating of the fiber to its final temperature. This is somewhat common practice in fiber processing. The take-up system showing columns of spun tows is shown in Figure 1.

Critical to spinning good fibers with the desired diameter of approximately 10 μ, which is the industry standard, is temperature control in the pitch reservoir, proper filtering of the pitch and attenuation or stretching of the green fiber in the 2-3 mm distance of the spinneret hole before the spun fiber hardens. In the second year effort,

Figure 1: Fiber Take-Up System



temperature uniformity was a major problem, i.e. either too low, non-uniform or over heating and coking the pitch. The reservoir system was revamped to achieve uniform temperature control and assure trouble free spinning.

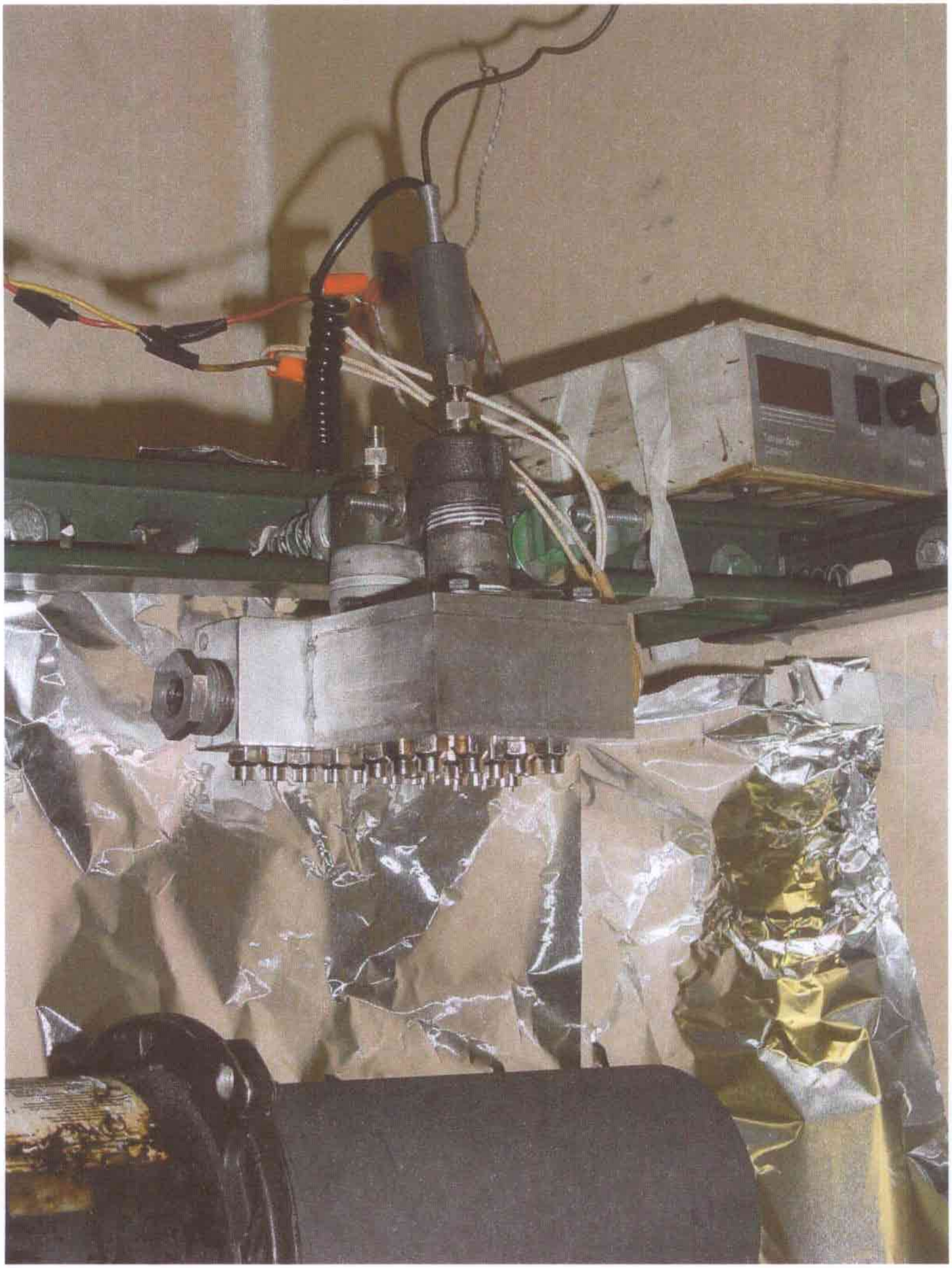
To define the proper spinneret hole size, hypodermic needle heads were initially used in various sizes and the length of the needle varied to aid in defining the attenuation of the fiber as it exited the spinneret hole before hardening. An example of these spinneret needle heads is shown in Figure 2. The needle id varied from 0.050 inches up to 0.090 inches and length of the needle varied from zero to 1 mm long. In fiber spinning trials, a spinneret hole size greater than approximately 0.075 would not produce the desired fiber size of approximately 10 μ. The length of the needle of 0.05 up to 1 mm produced desirable attenuation that achieved fiber diameter, as well as enhanced strength of the final heat treated fiber. These parameters define the 100 hole spinneret head, which consists of 0.05 inch hole sizes that are recessed in the steel head by at least 0.05 mm, but no more than 1 mm.

The reservoir heating system was revamped which included internal heaters, as well as external band heaters with a proportional controller to independently control each set of heaters. For the internal heater, the controlling thermal couple was attached to the surface of the heater to prevent overheating and coking the pitch immediately in contact with the heater surface. This heating system proved to work very well and maintain the bulk pitch in the reservoir within plus or minus 1°C. This degree of temperature control provides the capability of maintaining close control on the spinning parameters.

With a well performing spinning system, it is possible to define the properties in the CTP and spinning parameters to provide high strength fibers that demonstrate the commercial viability of the process.

Pitch supplied from West Virginia University was investigated to demonstrate spinning from the multi-hole spinneret head. The pitch was isotropic with a softening point of approximately 205°C. It was possible to spin the fiber at 220°C, but difficult to stabilize due to the low softening point. The fiber strength was relatively low in the range of 250 to 516 MPa. MER performed further processing of the pitch to increase its softening point, which yielded higher strength fibers in the range of 312 to 2045 MPa. Three batches were spun and the results reported in WVU Final Report DE-FC26-

Figure 2: Spinneret Trials to Define Spinneret Hole Size



98FT40350. The conclusion for this report is that the multi-head spinneret system functioned successfully and the isotropic pitch supplied by WVU could be successfully spun into a coal-based carbon fiber with reasonable properties.

The commercial source coal tar pitch (CTP) was processed in the 10 kg treatment system and used for spinning in the commercial demonstration spinning system described above. The strength of batch one's fiber ranged from 880 to 2.2 GPa, which is considered exceptional for isotropic fibers. The modulus of the isotropic carbon fiber was 29 GPa. If high modulus is desired in the fiber, a mesophase pitch precursor is required. MER converted the CTP to about 80% mesophase and demonstrated spinning fibers in the multi-hole spinneret system. The fibers produced from mesophase are anisotropic whose properties are very dependant on final heat treatment temperature. Heating to the same low temperature of 1200°C for the isotropic fibers, the mesophase pitch fibers had strengths in the 1.7 – 2.3 GPa range.

CONCLUSION

The conclusion of the 2001 year investigation is a fully integrated system which has been demonstrated that provides the capability to commercially demonstrate the CTP fiber processing and establish a basis to project cost of fiber production.