**EXPLORATION OF COAL-BASED PITCH PRECURSORS
FOR ULTRA-HIGH THERMAL CONDUCTIVITY
GRAPHITE FIBERS**

FINAL REPORT

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SUMMARY

The primary goal of the project was to explore the utility of coal-based pitch precursors for use in ultra high thermal conductivity carbon (graphite) fibers and it was to be determined through analytical and bench-scale studies in a three year program. From experience in the graphite electrode business, it was well established that coal-based pitches tend to form more highly crystalline graphite, and they tend to do so at lower temperatures. Since the funding was limited to year 1 effort of the 3 year program, the goal was only partially achieved.

The coal-based pitches can form large domain mesophase in spite of high Nitrogen and Oxygen contents. The mesophase reactivity test performed on one of the variants of coal-based pitch (D084) showed that it was not a good candidate for carbon fiber processing. Optimization of WVU's isotropic pitch process is required to tailor the pitch for carbon fiber processing. The hetero atoms in the coal pitch need to be reduced to improve mesophase formation.

TABLE OF CONTENTS

SUMMARY	ii
I. INTRODUCTION AND BACKGROUND	1
II. TASK DESCRIPTION.....	2
Task 1 Technology Review and Preliminary Precursor Specifications	2
III. STATEMENT OF WORK	2
Task 1 Technology Review and Preliminary Precursor Specifications	2
IV. DELIVERABLES.....	3
Year 1 Deliverables.....	3
V. MAJOR MILESTONES.....	3
Year 1 Milestones	3
VI. EXPERIMENTAL PROCEDURES	3
VII. DISCUSSION OF RESULTS.....	4
Technical Literature Review.....	4
Technical Review Meeting with WVU	4
Non Fuel Use of Coal Strategy	4
General Analytical Review	4
Product Characteristics.....	5
VIII. CONCLUSIONS	6
IX. RECOMMENDATIONS FOR FUTURE WORK.....	6
X. ACKNOWLEDGMENTS.....	6
XI. REFERENCES	6
Table 1 Experimental Methods Used or Referred.....	3

I. INTRODUCTION AND BACKGROUND

The preparation of high-performance carbon (graphite) fibers requires a mesophase pitch precursor. Traditionally, in the USA, this has been derived from a petroleum precursor. The various grades of pitch-based carbon fibers produced by Amoco Performance Products, Inc. (APPI) are currently made from petroleum-derived pitch. Coal-based precursors can also be used to produce pitch-based carbon fibers. Overseas suppliers have, in fact, developed high-performance fibers from coal derived precursors. Since the United States has an abundant supply of coal, utilizing coal-based precursors for producing carbon fibers (a non fuel use of coal) might reduce our dependency on foreign oil. APPI's goal is to explore coal-based pitch precursor's utility for use in ultra-high thermal conductivity carbon (graphite) fibers.

Carbon fibers were produced from coal-based precursor during the initial pioneering fiber work at APPI, and they were shown to be comparable to the ones produced from petroleum pitch. Coal-based precursors have a great deal to offer. Foremost among these is the fact that pitches which are coal-derived are generally better graphite formers than pitches from petroleum. From experience in the graphite electrode business, it is well established that coal-based pitches tend to form more highly crystalline graphite, and they tend to do so at lower temperatures. Roger Bacon et al.⁽¹⁾ looked at the feasibility of using various pitches as matrix materials in Carbon-Carbon composites under a DARPA program on Carbon-Carbon Materials. The X-ray crystallographic parameters (L_c , C_o , and L_a) were used as measures of relative graphitizability. The data on graphitizability by heat treating pitches at the same (very high) temperature indicated that one of the coal-based precursors had the highest $L_c(002)$, $L_a(100)$ and $L_c(004)$ among the various precursors studied including petroleum and chemically derived pitches. The $C_o(004)$ and 112 widths for certain coal-based precursors were among the lowest. These parameters indicate superior graphitizability of coal-based precursors.

II. TASK DESCRIPTION

The task description for year 1 effort of the three year program is given below since it was only funded.

Task 1. Technology Review and Preliminary Precursor Specifications

The technical literature on coal-based pitches developed by West Virginia University (WVU) will be reviewed in detail. Several discussions with WVU professors will occur to exchange product requirements. The preliminary product specifications will be established by participating in a technical review meeting with WVU. Once this is complete, a sample of coal-based pitch precursor will be obtained and a general analytical review will be performed. The precursor sample will be tested for softening point, ash level, toluene and pyridine extractables, coking value, elemental composition, molecular weight distribution by gel permeation chromatography, proton NMR, and hot-stage microscopy.

Some of the findings of this investigation and future strategy will be discussed by participating in the Non Fuel Use of Coal Strategy Planning meetings. This task will be completed by preparing a document providing direction to WVU for product characteristics required for fiber-grade pitch products.

III. STATEMENT OF WORK

The statement of work for year 1 effort of the three year program is given below since it was only funded.

Task 1. Technology Review and Preliminary Precursor Specifications

- 1.1 Review technical literature on Coal Based Pitches developed by West Virginia University.
- 1.2 Technical Review Meeting with WVU to exchange product requirements and establish preliminary product specifications.
- 1.3 Obtain sample of coal based pitch precursor and perform a general analytical review.
- 1.4 Attend Non Fuel Use of Coal Strategy Planning Meetings.
- 1.5 Prepare a document providing direction to WVU for product characteristics required for fiber grade pitch products.

IV. DELIVERABLES

The deliverables for year 1 effort of the three year program are given below since it was only funded.

Year 1 Deliverables

Task 1 will be completed in year 1. The deliverables will include required Progress Reports for the DOE and a final report due 90 days after completion of the effort.

V. MAJOR MILESTONES

The major milestones for year 1 effort of the three year program are given below since it was only funded.

Year 1 Milestones

AMOCO-3-1 Review of WVU's Reports on Coal Based Pitches - 12/31/95

AMOCO-3-2 Analytical Testing and Evaluation of Coal Based Pitch - 3/31/96

AMOCO -3-3 Summary Report providing direction to WVU - 9/30/96

VI. EXPERIMENTAL PROCEDURES

The experimental procedures used or referred to in this work are either APPI's proprietary methods or methods carried out outside of APPI. These methods are listed in Table I.

Table I
Experimental Methods Used or Referred

Characterization	Method
Softening Point	Alpharetta SJP No. 046
Ash Level	Alpharetta SJP No. GEN 10008
Toluene and Pyridine Extractables	Alpharetta SJP No. 048
Coking Value (Modified Conradson Carbon)	Alpharetta SJP No. 049
Elemental Composition	Done by Quantitative Technologies Inc.
Molecular Weight Distribution by GPC	Alpharetta SJP (Number not assigned)
Proton NMR	Done by UCAR Carbon Company, Inc.
Hot-stage Microscopy	Done by UCAR Carbon Company, Inc.
Mesophase Reactivity Test	Alpharetta SJP No. 043
Thermogravimetric Analysis (TGA)	Done by UCAR Carbon Company, Inc.
Mesophase Domain Size	Done by UCAR Carbon Company, Inc.
Density	Done by UCAR Carbon Company, Inc.

VII. DISCUSSION OF RESULTS

Technical Literature Review

The technical literature on coal-based pitches developed by West Virginia University (WVU) were reviewed in detail. Some recently published reports by WVU and UCAR, data generated by other coal consortium members like KOPPERS and FMI, and publications by Fuller et al. related to characterization of coal-based pitches were also reviewed. Monthly and quarterly reports by West Virginia University (WVU) were reviewed to keep in touch with the research activities on coal-based pitch. The hydrogenated pitches appear to be in the right softening point range. The sulfur contents are in the right range but the nitrogen and oxygen contents are higher. The sulfur contents will depend upon the sulfur content of the coals used and low sulfur coals should be used from carbon fiber precursor point of view. Milestone Amoco-3-1 was completed on schedule (12/31/95). Final reports were received from the Coal Products Consortium (CPC) members UCAR Carbon Company, Inc., Aluminum Company of America, Fiber Materials, Inc. and KOPPERS Industries Inc. and by E. Loren Fuller, Jr. at the University of Tennessee. They were briefly reviewed.

Technical Review Meeting with WVU

A meeting was attended on 23rd October, 1995 at WVU to exchange product requirements and establish preliminary product specifications. The hydrogenated pitches had the right preliminary characteristics. UCAR presented analytical data and some of the variants tested produced large domain mesophase in spite of high nitrogen and oxygen contents which was encouraging.

Non Fuel Use of Coal Strategy

Meetings were attended on 12th and 13th December, 1995 at WVU to discuss and plan future strategy regarding Non Fuel Use of Coal. Recent data on coal-based pitches were presented by the coal consortium members. Amoco made a presentation regarding why coal-based pitches may be good carbon fiber precursors and the process of evaluating them at bench-scale. Most of this work was not carried out since the funds were not authorized for year 2 and 3 of the program.

Memorandums from Dr. Caulton L. Irwin of National Research Center for Coal and Energy (NRCCE) related to Coal Products Consortium (CPC) workshop at Fossil Energy Materials Conference, meeting with DOE's office of Industrial Technologies (OIT), workshop on carbon products and heavy vehicles and recent activities and future plans of interest to CPC were reviewed. There is a fall meeting of the CPC members on November 19-20. Due to lack of future funding on this program, new sources are being explored by CPC.

General Analytical Review

The properties of isotropic pitches D076⁽²⁾ and D084 were compared with APPI's current carbon fiber precursor (hence referred to as APPI's pitch). Since sufficient quantity of pitch D076 was not available, pitch D084 was prepared by West Virginia University (WVU) in essentially the same manner as pitch D076. Pitch D076 differed from APPI's pitch in several properties. The

TI, N, O, TGA yield and mesophase domain size were higher in the case of pitch D076 but the Mettler S.P., M_n , S and C/H ratio were lower. The density and MCC values were comparable. Pitch D084 had significantly higher S.P. than pitch D076 and consequently higher TI than pitch D076. The density was only slightly higher in case of pitch D084.

In spite of high Nitrogen and Oxygen contents, pitch D076 produced a much higher domain mesophase and it was inferred that the oxygen seems to be bonded in a structure where it cannot participate in crosslinking. Hence a mesophase reactivity test was carried out on pitch D084. The S.P. of the mesophase pitch produced in the experiment was lower than standard mesophase and the pitch had two phases (an isotropic-rich phase and a mesophase-rich phase). The reaction time was also lower than normal and the mesophase reactivity was higher than that observed for APPI's pitch. The mesophase content was significantly lower than what would have been expected from APPI's pitch. These data suggest that pitch D084 is not a good candidate for carbon fiber processing and that further optimization of WVU's isotropic pitch process and /or of APPI's mesophasing process may be necessary to obtain a pure mesophase pitch at a low enough softening point so that it is spinnable. Milestone Amoco-3-2 was completed on schedule (3/31/96).

Product Characteristics

A summary report (in a letter form) providing direction to WVU with respect to coal-based pitch development (as it relates to high thermal conductivity graphite fibers) was submitted to Prof. John Zondlo of WVU. This was part of milestone Amoco-3-3 and was completed on schedule (9/30/96). Analytical testing was carried out on the WVU coal pitch D084 and the mesophase (BCR#11) produced from it. Some testing was also done on APPI's pitch for comparative purposes. The tests carried out were ash, elemental analyses, coking value or Modified Conradson Carbon (MCC), Molecular Weight Distribution by Gel Permeation Chromatography (GPC), proton NMR, Toluene Insolubles (TI) and Pyridine Insolubles (PI). There was not enough sample left for softening point. The WVU value was 112.3 °C.

The ash testing show low levels of ash in the coal pitch and its mesophase compared to APPI's pitch. This is expected since the coal-based pitch has been produced by solvent extraction. The elemental analyses showed interesting results. The coal-based pitch had higher nitrogen and oxygen but lower sulfur and carbon than APPI's pitch. The hydrogen contents were comparable. The carbon content of the coal pitch-based mesophase was higher while the hydrogen and oxygen contents were lower than the coal pitch. The nitrogen and the sulfur contents were comparable to the coal pitch. When the coal pitch had produced large domain mesophase, it was inferred that the oxygen is bonded in a structure where it cannot participate in crosslinking. The mesophase reactivity test showed that the high nitrogen and oxygen containing coal pitch formed inferior mesophase. The high nitrogen and oxygen contents of the mesophase from the coal pitch indicate that the hetero atoms are interfering in the mesophase formation.

The proton NMR results showed that coal pitch D084 had higher aliphatic hydrogen content than APPI's pitch resulting from the hydrogenation of aromatic rings during the coal pitch preparation. The GPC results showed that the coal pitch had a lower proportion of larger molecules and more small molecules than APPI's pitch. The TI of the coal pitch were significantly higher than APPI's pitch. The PI were very low and comparable with the quinoline insolubles of APPI's pitch.

The MCC of the coal pitch was higher than APPI's pitch in spite of the lower softening point of the coal pitch. The TI, PI and MCC values of the mesophase pitch (BCR#11) produced from the coal pitch were comparable with APPI's mesophase pitches in spite of the lower mesophase content of BCR # 11.

VIII. CONCLUSIONS

1. The coal-based pitches can form large domain mesophase in spite of high Nitrogen and Oxygen contents.
2. Coal-based pitch D084 was not a good candidate for carbon fiber processing.

IX. RECOMMENDATIONS FOR FUTURE WORK

1. Optimization of WVU's isotropic pitch process is required to tailor the pitch for carbon fiber processing.
2. The hetero atoms in the coal pitch need to be reduced to improve mesophase formation.

X. ACKNOWLEDGMENTS

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XI. REFERENCES

1. R. Bacon, L.C. Nelson, L.S. Singer, D.A. Schulz, G. Wagoner, I.C. Lewis, R.T. Lewis, S.L. Strong, B.W. Rosen, B.J. Sullivan, "Spacecraft Applications for Carbon-Carbon -- Basic Research Effort", Final Report, June, 1989.
2. I.C. Lewis, R.T. Lewis and H.K. Mayer, "Coal Precursors for Production of Carbon and Graphite Products - Final Report", Subcontract 62X-SR928C, WBS Element UCAR-3, April 8, 1996.

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