

**ANNUAL PROJECT REPORT  
AS OF DECEMBER 2004**

**1. PROJECT SPONSOR:**

Applied Sciences, Inc.  
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**2. PROJECT MANAGER**

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**3. OCDO GRANT NO. CDO/D-99-14**

**4. PROJECT UPDATE:  
FINAL REPORT: X**

5. **PROJECT TITLE:** "Fly Ash Enhanced Carbon Nanofiber-Reinforced High Strength Cement"

6. **PROJECT TERM:** January 2, 2001 to December 31, 2004

**7. BUDGET:**

CO-SPONSORS NAME	COST SHARE
OCDO	\$ 738,098.00
ASI	\$ 826,898.00
OSU	\$ 109,286.00
<b>TOTAL PROJECT COST:</b>	<b>\$1,674,282.00</b>

## ABSTRACT

### **9. OVERVIEW OF PROJECT & OBJECTIVES:**

This project seeks to utilize gasified coal to produce value-added materials suitable for reinforcement of infrastructure material. For example, coal is currently used as a source of fly ash reinforcement. In addition, gasified coal can be used to produce carbon nanofibers, in a process that is essentially similar to that used to produce carbon black. Carbon nanofibers are highly ordered submicroscopic hollow carbon tubes, which exhibit very good mechanical properties.

The presence of sulfur in the coal feedstock is particularly valuable because sulfur is used as a catalyst to promote nanofiber growth. In other words, sulfur is an asset rather than a liability for this process. Moreover, the effluent from the process is rich in hydrogen, while poor in carbon, nitrogen and especially sulfur, raising the possibility that environmentally clean power generation can be combined with materials synthesis.

Nanofiber reinforced cement offers unique capabilities. Because of the high strength and nanoscopic scale of the reinforcement, high strength cementitious composites can be anticipated with uniform structure. As a result, a high strength, machinable ceramic-like material can be produced.

### **10. WORK TO DATE & CONCLUSIONS:**

Applied Sciences submitted a no-cost time extension for this contract and the Ohio Coal Development Office approved the extension in December 2003.

#### **Battelle Coal Gasifier**

During the majority of the first quarter of 2004, many modifications and repairs were necessary for the proper operation of the coal gasifier. The modifications included the installation of the U-bend to assist fluid flow and allowing faster heat up of the coal gasifier. Repairs included fixing broken welds at the interface of the start up burner and the downcomer chamber in the gasifier.

In March 2004, ASI conducted two gasification trials. In the first trial, coal was gasified using the partial oxidation method. In the second trial, coal was gasified using the hydrogenation method. Carbon nanofibers were produced from both gasification modes. Coal gas produced during the partial oxidation trial generated carbon nanofiber at 13% of the expected output using natural gas.

Coal gas produced during the hydrogenation trial generated carbon nanofiber at 6% of the expected output using natural gas. The hydrogenation trial was terminated after about 35 minutes of operation due to plugging in the U-bend. Table 1 compares the results for the partial oxidation run, the coal hydrogenation run, and normal production of commercial grade carbon nanofibers.

Table 1. Carbon nanofiber production results for partial oxidation of coal and coal hydrogenation.

Parameter	Carbon nanofibers produced during partial oxidation trial	Carbon nanofibers produced during coal hydrogenation trial	Carbon nanofibers produced during commercial production of PR19
Output, g/hr/tube	40	18	300
Acetone extractables	5.2	>>5	2 to 5
Bulk density, lb/ft <sup>3</sup>	1.03	3.17	0.125
Moisture content, %	1.2	1.8	<1
Fiber versus soot	<5% fiber	<1% fiber	>99
Electrical resistivity, ohm-cm at 13.8 vol. %	64	164	2 to 6
Iron content, ppm	30,777	19,196	<14,000

In October 2004, Applied Sciences attempted to produce vapor grown carbon nanofibers directly inside the Battelle gasifier. The coal gasifier was operated in a partial oxidation manner with air being used to partially oxidize the coals. Growth of the carbon nanofibers was attempted in the riser gasifier section of the coal gasifier. Vapor phase catalysts (ammonia and iron pentacarbonyl) were added to the riser gasifier downstream from the air-coal mixing point to allow the coal to start to partially oxidize. The riser gasifier was operated in the temperature region where carbon nanofibers are commercially produced. Samples of the sludge collected in the scrubber, scrubber liquid and fabric filter were analyzed for the presence of carbon nanofibers. No vapor grown carbon nanofibers were detected in any of the three types of samples collected. Evaluation of the operating conditions for the riser gasifier indicated a very large concentration of nitrogen gas (from the air used to gasify the coal) and this nitrogen is known to dilute coal gas to the point of producing a gas mixture that is not conducive to production of carbon nanofibers.

Given the large amount of resources required for each gasification trial, it was recommended that Applied Sciences conduct a series of carbon nanofiber optimization trials in research scale reactors using a simulated coal gas.

## Simulated Coal Gas

Gas compositions simulating various coal gasses were used to conduct optimization tests on growing carbon nanofibers from several different coal gasification technologies. The simulated coal gasses and their associated gasification technology are shown below in Table 2.

Table 2. Typical Compositions of Synthesis Gases Produced Steam Reforming of Hydrocarbons and from Coal Gasifiers, volume percents

	Coal Gasification			
	Lurgi Gasifier	Koppers-Totzek	Winkler	Wabash River Raw Gas
Hydrogen	38.0	36.7	41.8	26.0
Carbon monoxide	20.2	55.8	33.3	45.0
Carbon dioxide	28.6	6.2	20.5	14.0
Methane & other HC's	12.4	0.0	3.0	2.0
Hydrogen Sulfide	0.5	0.3	0.0	1.3
Nitrogen and other gases	0.3	1.0	1.4	4.0
Water vapor				8.0
Water vapor	100.0	100.0	100.0	100.3

Attempts were made to produce carbon nanofibers in coal gas mixtures that were produced to simulate four types of common coal gas – Lurgi gasifier, Winkler gasifier, Koppers-Totzek gasifier, and the Wabash River gasifier. Simulated coal gasses from these coal gasifiers were used along with the gas phase catalysts used by Applied Sciences, Inc. and Pyrograf Products, Inc. to commercially produced carbon nanofibers. The data is contained below in Table 3 along with the results of the carbon nanofiber carbon nanofiber. Table 4 presents the results of laboratory scale carbon nanofiber production using simulated coal gas compositions. Results demonstrate feasibility of producing carbon nanofibers from a variety of coal gas compositions. Actual yields were lower than expected considering the low expected yields based on thermodynamic considerations. However, no attempt was made to optimize yields for the various coal gasses; additional research in this area is required.

Table 3. Composition of coal gases used in chemical engineering studies and bench scale simulated coal gas studies

	Coal Gasification Process Simulated			
	Lurgi Gasifier	Koppers-Totzek (Eastman)	Winkler	Wabash River
Hydrogen	38.0%	36.7%	41.8%	26.0%
Carbon monoxide	20.2%	55.8%	33.3%	45.0%
Carbon dioxide	28.6%	6.2%	20.5%	14.0%
Methane	12.4%	0.0%	3.0%	2.0%
Hydrogen Sulfide	0.5%	0.3%	0.0%	1.3%

Nitrogen & other gases	0.3%	1.0%	1.4%	4.0%
Water vapor				8.0%
Totals	100.0%	100.0%	100.0%	100.3%

Table 4. Results of VGCF production trials using synthetic blends of coal gases

	Reactor Average Temperature, °C	Exhaust Average Temperature, °C	Fiber made (gm)	Actual Yields, %	Maximum theoretical yields regardless of temperature, %
PR-19 Control	941	402	31.0	68.2%	93.7%
Lurgi Trial #1	972	425	1.3	4.2%	10.7%
Lurgi Trial #2	416	248	0.3	1.0%	10.7%
Lurgi Trial #3	613	296	0.2	0.6%	10.7%
Lurgi Trial #4	801	347	0.3	1.0%	10.7%
Winkler #1	808	379	0.4	1.4%	9.2%
Winkler #2	956	432	0.0	0.0%	9.2%
Winkler #3	948	424	0.1	0.3%	9.2%
Koppers – Totzek #1	636	310	0.3	1.0%	10.6%
Koppers –Totzek #2	965	431	0.9	2.9%	10.6%
Wabash River #1	627	324	0.5	1.0%	10.3%
Wabash River #2	964	411	1.1	3.6%	10.3%

A series of scanning electron micrographs were generated for the carbon nanofibers produced from the simulated coal gases. Figures 20 through 24 show typical carbon fibers from commercial carbon nanofiber production (PR19) and from the coal gas compositions tested.

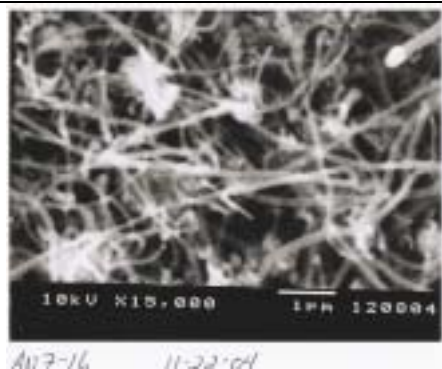


Figure 1. SEM photograph of commercial carbon nanofibers (PR19)  
 Microscopist notes: very good rating for soot – 2 out of 10 level

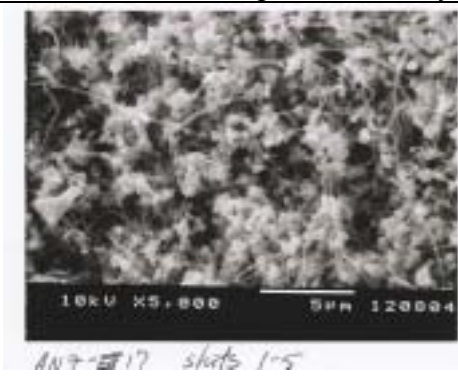


Figure 2. SEM photograph of carbon nanofibers from Lurgi coal gas  
 Microscopist notes: very good rating for soot – 9 out of 10 level; soot everywhere

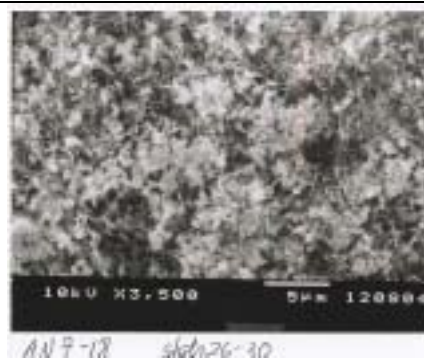


Figure 3. SEM photograph of carbon nanofibers from Winkler coal gas  
 Microscopist notes: very good rating for soot – 8 out of 10 level; soot and clumps



Figure 4. SEM photograph of carbon nanofibers from Koppers-Totzek (Eastman) coal gas  
 Microscopist notes: very good rating for soot – 2 out of 10 level

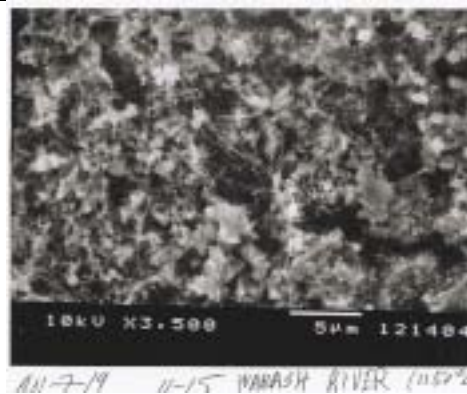


Figure 5. SEM photograph of carbon nanofibers from Wabash River coal gas  
 Microscopist notes: very good rating for soot – 2 out of 10 level

The yields obtained from the carbon nanofiber production trials were considerable lower than the theoretical calculations and the company's previous research on simulated coal gases generated in the Battelle coal gasifier would have indicated. Subsequent to the trials with Lurgi, Winkler, Koppers-Totzek, and Wabash River coal gases, ASI conducted a series of studies to attempt to understand the fundamental impacts of coal gas constituents on carbon nanofiber production. The detailed results of the studies will be in the proprietary version of the final report.

### **Conceptual Design for Large scale Coal Gasifier for Commercial CNF Production**

ASI started the development of a conceptual design for a coal gasifier for use in supplying coal gas for carbon nanofiber production. During recent discussions with Don Bonk of the US Department of Energy, it was learned that the smallest sized coal gasifier that should be built to achieve an effective demonstration of the technology would feed 500 to 750 pounds per hour of coal. This is similar in size to the fluidized bed coal combustor being used at the Cedar Lane Farms in Wooster, Ohio. Any gasifier smaller than 500 pounds per hour is difficult to control and just about as costly as a 500 to 750 pound per hour unit. The gasifier size would support a carbon nanofiber production capacity of about 1 million pounds per year. The details of this work will be in the proprietary version of the final report.

#### **11. PLANS FOR COMING YEAR:**

The plan for 2005 is to generate the final report.

#### **12. HIGHLIGHTS/ACCOMPLISHMENTS:**

- Carbon nanofiber was generated from coal gas generated on the Battelle gasifier under the partial oxidation mode.
- Carbon nanofiber was generated from coal gas generated on the Battelle gasifier under the hydrogenation mode.
- Carbon nanofiber, albeit at low yields, was generated from simulated coal gas replicating four commercial coal gasification methods.

Significant progress has been made on the conceptual design for large-scale coal gasifier for commercial CNF production.

#### **13. ARTICLES/PRESENTATIONS:**

1. "Co-Production of Power and Carbon Nanofibers from Gasified Ohio High Sulfur Coal', Presentation to the Lima, Ohio Rotary Club for the City's Business Leadership, April 2004, Thomas W. Hughes.
2. "Carbon Nanofiber Synthesis from Gasified Coal, American Waste Management Association (AWMA), Indianapolis, Indiana Convention Center, June 2004, David J. Burton.

3. "Carbon Nanofibers Synthesis from High Sulfur Coal", Pittsburgh Coal Conference, Osaka, Japan, September 2004, Takashi Yanagisawa, GSI Creos Corporation, Japan and Max L. Lake.
4. "Overview of Research and Development Programs for Vapor Grown Carbon Nanofibers", Vapor Grown Carbon Nanofiber Materials and Applications Workshop, National Composites Center, September 2004, Thomas W. Hughes.