ANNUAL REPORT FOR

Contract No. FA9550-06-1-0476
July 1, 2007 – June 30, 2008

Submitted by

Harold Schobert, Principal Investigator

Prepared by

Bruce Beaver
André Boehman
Caroline Clifford
Dominic Santavicca
Robert Santoro
Harold Schobert
Geoffrey Wilson

AFRL-SR-AR-TR-09-0048

REPORT DOCUMENTATION PAGE

OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)* 07/01/2008	**2. REPORT TYPE** Annual Progress Report	**3. DATES COVERED** *(From - To)* 07/01/2007 - 06/30/2008

4. TITLE AND SUBTITLE
(U) Advanced Thermally Stable Coal-Based Jet Fuels

5a. CONTRACT NUMBER

5b. GRANT NUMBER
FA9550-06-1-0476

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Dr. Harold Schobert

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
The Pennsylvania State University
EMS Energy Institute
C211 Coal Utilization Laboratory
University Park, PA 16802

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR/NA
875 North Randolph Street
Suite 325, Room 3112
Arlington, VA 22203-1768

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The contract year 7/1/2007-6/30/2008 represented a no-cost extension on the original contract. Work was continued on the use of solvent extraction of coal to produce a material suitable for further hydrotreating to the coal-based JP-8 fuel. This switch to solvent extraction instead of relying on the refined chemical oil used previously is in full agreement with recomm fuendations provided by RAND. Exploratory work was begun to evaluate the possible production of nuclear graphite from the by-products of co-coking. This would allow use of distillation residua rather than decant oil as feed to the coker, again in agreement with RAND's recommendations. A very solid hypothesis was developed, indicating that the mechanisms of oxidative deposit formation in diesel and jet fuels are the same. This has been backed up with experimental evidence. Work was conducted to compare measurements of the flame response function made in a laboratory-scale lean direct injection combustor operating on Jet-A fuel and a coal-derived JP-8 fuel. The flame response function is determined from phase-synchronized measurements of the fuel flow rate modulation and the resulting fluctuation of the flame's rate of heat release. Completion of this work will await the next pilot-scale run of producing coal-derived JP-8.

15. SUBJECT TERMS
jet fuel, coal, hydrotreating, JP-8, oxidative deposits, flame response functions

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			Julian M. Tishkoff
Unclassified	Unclassified	Unclassified	UL	13	**19b. TELEPHONE NUMBER** *(Include area code)* 703-696-8478

TABLE OF CONTENTS

Introduction

This is the annual project report for Contract No. FA9550-06-1-0476, ending June 30, 2008. The contract year July 1, 2007 to June 30, 2008 represented a no-cost extension on the original contract. Running in parallel to this present contract was a second one, Contract No FA9550-07-1-0451, for which a no-cost extension has been approved through June 30, 2009. A separate annual report will be provided for that parallel contract. However, the reader should recognize that the performance of the work on the two parallel contracts was done by the same people and group leaders. There will be some inevitable overlap between the two reports.

Summary of research progress and results

For many years the work on this contract and its predecessor has been divided into the three broad areas of fuel production, fuel stabilization, and fuel combustion. That subdivision will be followed here, to show the flow of work from the initial production of coal-based jet fuel to studies on enhancing its stability and then to its combustion. During the actual performance of the work there is a continual interchange of samples and data among these areas, as well as multiple feedback loops.

Fuel production

Research continues on the so-called co-coking process, in which finely pulverized coal is blended with the feed to a delayed coker, producing coker liquids that would be hydrocracked and hydrotreated to the jet fuel range, and a coke by-product. Recognizing the Air Force's interest in alternative fuels that have a low carbon footprint, we have had on-going discussions with parties interested in the possibility of coupling an alternative fuels plant with a nuclear power plant, such that the waste heat from the nuclear side would provide the necessary process heat to drive the various alternative fuel production and refining processes. The successful integration of these concepts would reduce the carbon footprint of the overall facility, since the CO_2 emissions from all of the various fired process heaters would be eliminated at once. Furthermore, the hydrogen needed for the downstream upgrading of coker liquids could be produced by electrolysis with power from the nuclear plant, reducing the carbon footprint even further by eliminating the requirement for a coal gasification unit to supply hydrogen. Ever since the inception of the co-coking process at Penn State, we have recognized that if the by-product coke could be marketed as a premium carbon material, i.e., above the market price for fuel coke, then credits for the by-product sales could offset at least some of the costs of downstream upgrading of the coker liquids. Taking these various factors into consideration, we have begun to examine the potential for converting the by-product coke into nuclear graphite, which could then go "across the fence" to the nuclear facility. Since nuclear graphite needs to be isotropic, that also means that the coker feed could be a distillation residuum (resid) and is not required to be a decant oil. Thus we envision the following:

- Substantially reduced carbon footprint, from elimination of fired process heaters and a coal gasification facility for hydrogen production;

- By-product credits for sale or internal use of nuclear graphite;
- Elimination of the need for decant oil as a coker feed, in compliance with recommendations made by RAND in 2007; and
- Substantially reduced costs for the final fuel product.

Feed materials were obtained for a pilot-scale run of the co-coking process at Intertek-PARC, Harmarville, PA. A 725 kg (1600 lb) sample of coal fines from the Jameson cell press was obtained from A.T. Massey's Marfork Cleaning Plant in Raleigh County, WV. This new coal sample was cleaned using best available technology to as low a level of ash yield as possible. It was found that the vibratory screening system similar to the system that used in the past was effective in de-sliming this effluent with the result of increased tonnage that would report to the higher value metallurgical coal tonnage instead of steam coal. Their equipment and screening technique was designed for a larger particle size (>270 mesh, 53 µm) that did not attempt to eliminate the size fraction above 150 µm as we had done in our earlier work. Thus, the plan was to wet screen the new Marfork coal using our Model K vibratory screen by Derrick Corporation using the 270 mesh screen that would best approximate the operation of the Derrick Stacker Sizer being used commercially. The cleaning process has resulted in about 195 kg (430 lbs) of 1.1% moisture, 2.3% ash yield coal, having a higher inertinite maceral content, lower thermoplastic properties and larger particle size distribution than our earlier Marfork (El-187) product.

Nuclear graphite is isotropic rather than anisotropic graphite (produced from needle coke) of other typical graphitic materials. The co-coke precursor for nuclear graphite will be produced with low-sulfur vacuum residuum and Marfork coal. Small-scale microautoclave reactions will be done initially to determine the range of conditions to best generate the precursor coke for nuclear graphite, followed by reproducing the best runs using the our larger coking unit to produce enough coke for extensive evaluation. Feeds will be characterized using proximate and ultimate analyses, simulated distillation gas chromatography (SIMDIS GC), API gravity, and viscosity. Cokes will be characterized by proximate and ultimate analyses, optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), temperature programmed oxidation (TPO), and possibly Raman spectroscopy. The main progress to date is in obtaining feed materials from refineries.

Our previous work on formulating a coal-based jet fuel of high thermal stability used the strategy of hydrotreating refined chemical oil blended with light cycle oil. We recognized about six years ago that supplies of refined chemical oil are limited and likely will never increase in the United States; therefore there is a need to produce a "refined-chemical-oil-like" material from coal using some process that does not require the metallurgical coke ovens from which refined chemical oil itself is produced. Our conclusions drawn in the 2002 time frame were substantiated about five years later in a review conducted by RAND. The strategy that we have developed for making the chemical equivalent of refined chemical oil by some other process is to use solvent extraction of coal.

Research over the past year focused on scale-up to a 1-L stirred autoclave. One of the major challenges has been the separation of the solid and liquid products at a larger scale. A filter that could be heated and pressurized was added to separate the products, and feed was mixed and injected into the reactor as the unit was stirring to prevent coal settling and plugging of the reactor. Initially the filtration step was very slow (several hours), so a settler was added before the filter to remove the majority of the solids before going through the filter. Reaction conditions were the same as previous work, with the solvent to coal ratio kept at 5:1. Conversion data for all the coals were much lower than expected (highest ≈44%). Extractions using light cycle oil and decant oil solvents had the highest conversions.

Larger-scale work on fuel production is done on subcontract to Intertek-PARC, in Harmarville, PA. Their main task is the production of nominally 5,000 gallons of coal-based jet fuel. Originally, the intent was to produce a fuel of high thermal (pyrolytic) stability, i.e., JP-900. However, based on discussions and advice from our colleagues at the Air Force Research Laboratory, the focus of this work was shifted to produce instead a coal-based drop-in replacement for JP-8. Work on achieving that goal is on-going at Intertek-PARC, and is summarized in the 2008 annual report for Contract No. FA9550-07-1-0451.

Fuel stability

It is our view that the soot propensity (i.e. smoke point) of a fuel can be rationalized when a current understanding of the chemistry involved in incompatibility/instability in refining operations is melded with our current understanding of the chemistry involved in the degradation of JP-8 and other fuels. In modern fighter aircraft, while the fuel is circulated throughout the aircraft as a heat sink it undergoes thermal oxidative degradation prior to combustion. Briefly, it is proposed that thermal stressing the fuel converts certain indigenous fuel polar aromatic compounds (i.e. phenols, indoles and carbazoles, etc.) into soluble macromolecular oxidatively reactive species (SMORS). We have used literature procedures for the isolation of SMORS, and a special type of high molecular weight SMORS, an extraction induced precipitate (EIP), to test the following hypothesis: the formation of high molecular SMORS can increase both thermal oxidative deposit formation and fuel soot propensity (i.e. smoke point).

On balance all of the data that we have obtained from microautoclave stressing tests suggest that there are correlations between fuel polar compounds, stressed fuel EIP mass, and mean jet fuel thermal oxidative deposit formation. All of these observations are consistent with the hypothesis that the chemistry of thermal oxidative deposit formation, in both jet and diesel fuels, are similar. In addition, the low-pressure reactor method has been accepted as the method of choice for the U.S. Navy for estimating the long-term storage stability of diesel fuels. Therefore, it is likely that the chemistry of oxidative fuel deposit formation over a wide temperature range, from ambient storage through 550°C, is similar in both jet and diesel fuels.

On a practical level, we have found determination of stressed fuel EIP mass to be a very fast and convenient method for assessing fuel thermal oxidative stability. We suggest that this methodology may prove useful in refineries for assessing the oxidative stability likely achieved upon blending various refinery streams. Testing of this methodology is being conducted. The results of this work will be presented in the 2008 annual report for Contract No. FA9550-07-1-0451.

Fuel combustion

The objective of the research conducted under this task was to compare measurements of the flame response function made in a laboratory-scale lean direct injection (LDI) combustor operating on Jet-A fuel and a coal-derived JP-8 fuel. The flame response function relates the modulation in the fuel flow rate to the resulting modulation in the flame's rate of heat release and is expressed in terms of the gain and phase as a function of frequency. Knowledge of the flame response function for a given injector and fuel-type and its dependence on operating conditions is critical to the successful development of an active combustion control system for suppressing combustion oscillations. Since the flame response function is dependent on the details of the unsteady liquid injection, atomization, vaporization, mixing and combustion processes, it is very sensitive to the fuel's physical and chemical properties.

The flame response study is being conducted in the optically-accessible, laboratory-scale LDI combustor test rig shown in Fig. 1, which was constructed during this past year. Also shown in the bottom left corner of Fig. 1 is the rotary valve that was also developed during the past year to provide fuel flow rate modulation at frequencies as high as 500 Hz.

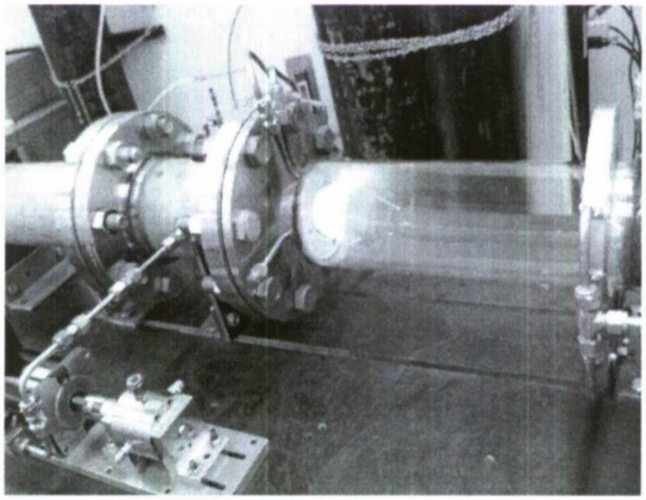

Figure 1. Photograph of optically-accessible laboratory-scale LDI combustor.

The flame response function is determined from phase-synchronized measurements of the fuel flow rate modulation and the resulting fluctuation of the flame's rate of heat release. In addition to developing the LDI combustor and the rotary valve discussed above, a major focus of this past year's research has been on the development of techniques for making these measurements.

In order to measure the time-varying fuel flow rate into the combustor a two-microphone technique has been developed during the past year which uses pressure measurements made at two locations upstream of the injector and a 1-D acoustic analysis to predict the time varying pressure immediately upstream of the injector orifice. This measurement together with the combustor pressure gives the pressure drop across the injector as a function of time. Assuming quasi-steady state flow in the injector, a steady flow injector calibration can be used to determine the time-varying fuel flow rate. To date this technique has been shown to be capable of predicting the injector pressure within an accuracy of a few percent for the case of gaseous fuels. Tests with liquid fuels are currently being conducted.

The time-varying heat release rate is measured using a chemiluminescence-based technique. The natural chemiluminescence from steady lean premixed flames has been shown in numerous studies to be a function of the fuel-type, reactant temperature, equivalence ratio, and the overall rate of fuel consumption. Thus for a fixed fuel, reactant temperature and equivalence ratio, the overall chemiluminescence emission can be used to measure the overall rate of heat release. During this past year the applicability of this technique for measuring the time varying rate of heat release in an LDI combustor operating on Jet A fuel with fuel flow rate modulation was investigated.

Figure 2 shows the chemiluminescence spectra measured in the LDI combustor operating on Jet-A fuel over a range of fuel-lean equivalence ratios. The dominant features of the chemiluminescence spectra are the peak near 430 nm which is due to CH* chemiluminescence and the peak near 309 nm which is due to the OH* chemiluminescence. The broad peak on which the OH* and CH* spectra sit is due to CO_2* chemiluminescence.

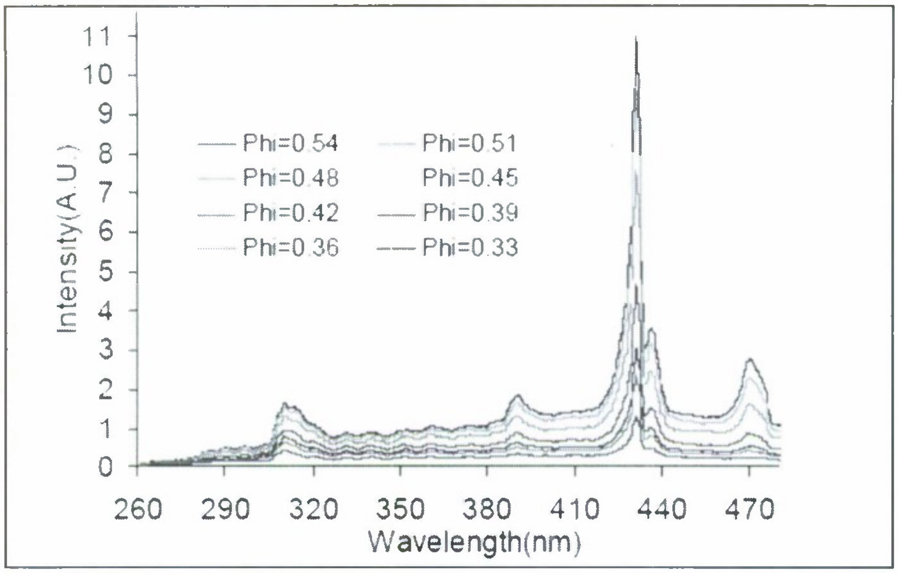

Figure 2. Chemiluminescence spectra from the LDI combustor operating on Jet-A at an air flow rate of 80 SCFM and an inlet temperature of 423 K.

The OH* and the CH* chemiluminescence intensity can be determined by first subtracting the background CO_2* chemiluminescence and then integrating over the respective peaks. Figure 3 is a plot of the OH* chemiluminescence intensity versus equivalence ratio for different air flow rates and a fixed inlet temperature of 398 K. Along any of these curves the air flow rate is constant, therefore increasing the equivalence ratio is equivalent to increasing the fuel flow rate. This is what occurs when performing the forced response measurcments, i.e., the air flow rate is fixed and the fuel flow rate fluctuates. However, unlike the results shown in Fig.3, which were taken in a steady flame, when performing the forced response measurements the fuel flow rate will be fluctuating at frequencies as high as 500 Hz. Therefore an important next step in the development of this technique is to assess the potential effects of the flame's unsteadiness under forced conditions.

Chemiluminescence measurements have not been performed with the coal-derived JP-8 fuel because it is not yet available. It is expected that the coal-derived JP-8 fuel will be available within a month, at which time the chemiluminescence measurements will be repeated with this fuel, after which the flame response measurements will be carried out using both Jet-A fuel and the coal-derived JP-8 fuel.

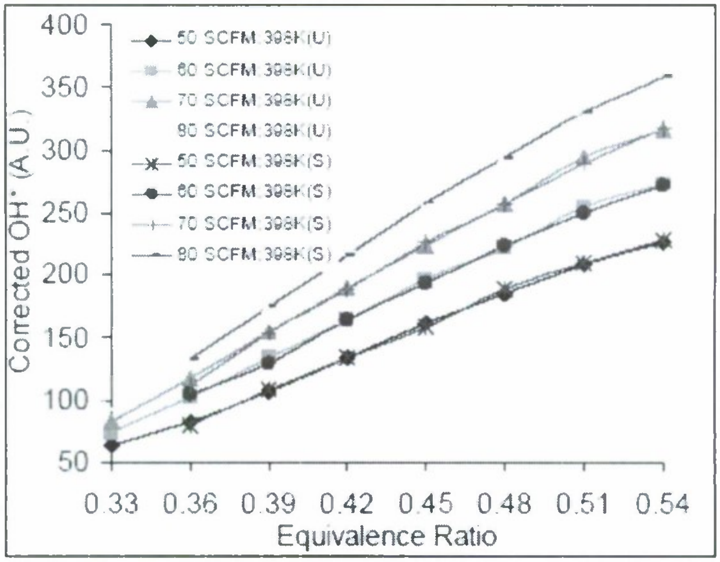

Figure 3. Corrected OH* chemiluminescence intensity versus equivalence ratio for fixed air flow rate with Jet-A fuel and an inlet temperature of 398K.

Personnel

Faculty

Maria Sobkowiak
Domenic Santavicca
Vince Zello
Sibtosh Pal
Harold Schobert
Andre Boehman
Robert Santoro
Bryan Quay
Ronald Wincek
Parvana Aksoy
Nicolas Bouvet
Stephen Kirby
Seong-young Lee
Anne Mouis
Josefa Griffith
Maria Escallon
Bei Wang
Ronald Wasco
Gareth Mitchell
Caroline Clifford
Omer Gul
Scott Berkhous
Jingwen Zhang
Shaoqing Wang

Staff

John Raiser
Carol Brantner
Larry Schaaf
Larry Horner
Mary Newby
Virginia Smith
Glenn Decker
Bradley Maben

Students

Daesik Kim
Hyung Ju Lee
Hee Je Seong
Kyu Tae Kim
Tongxun Yi
Gagan Gothaniya
Dirk VanEssendelft
Arvind Venugopal Menon
Brian Jones
Venkata Pradeep Indrakanti
Sidonie Guiadem
Mhlwazi Solomon Nyathi

Publications

Escallón, M.M. and H.H. Schobert. *Liquids and Premium Cokes from theCo-coking Process.* Proceedings, 12th Coal Indaba, Fossil Fuel Foundation. CD-ROM publication, 6 pages, 2007.

Griffith, J.M. and H.H. Schobert. *Solvent Extraction of Bituminous Coal using Light Cycle Oil: A Method to Obtain Coal Liquids for use in a Refinery.* Proceedings, 11th Coal Indaba, Fossil Fuel Foundation. CD-ROM publication, 4 pages, 2007.

Clifford, C.B., H.H. Schobert, M. Escallón, and J. Griffith. *Effects of Coal Rank and Reaction Conditions on Production of Two-ring Compounds for Coal-based Jet Fuel.* Proceedings, 2007 International Conference on Coal Science, Paper 6D5 (CD-ROM publication), 9 pages.

Aksoy, P., S.H. Figueroa, and H.H. Schobert. *Chemical Activation of Petroleum Coke and Coke Produced from Co-coking of Decant Oil and Coal.* Proceedings, 2007 International Conference on Coal Science, Paper 10B4 (CD-ROM publication), 9 pages.

Escallón, M.M., J. Griffith, C.B. Clifford, and H.H. Schobert. *Co-processing of Bituminous Coal with Petroleum Solvents: Determination of Solubility Parameters*. Proceedings, 2007 International Conference on Coal Science, Paper 2P54 (CD-ROM publication), 8 pages.

Clifford, C.E.B. and H.H. Schobert. *Development of Coal-based Jet Fuel*. American Chemical Society Division of Fuel Chemistry Preprints, vol. 52, pp. 403-404, 2007.

Clifford, C.E.B., O. Gül, J.M. Griffith, P. Aksoy, G.D. Mitchell, M.M. Escallon, U. Suriyapraphadilok, and H.H. Schobert. *Integrating Coal-to-Liquid Processes into Refinery Processes*. American Chemical Society Division of Fuel Chemistry Preprints, vol. 52, pp. 408-411, 2007.

Gül, O., L.R. Rudnick, and H.H. Schobert. *Effect of the Reaction Temperature and Fuel Treatment on the Deposit Formation of Jet Fuels*. Energy and Fuels, vol. 22, pp. 433-439, 2008.

Clifford, C.E.B. and H.H. Schobert. *Production of Coal-based Fuels and Value-added Products: Coal to Liquids using Petroleum Refinery Streams*. Energia,, vol. 19, no. 1, pp. 1-4, 2008.

Balster, L.M., E. Corporan, M.J. DeWitt, J.T. Edwards, J.S. Ervin, J.L. Graham, S.Y. Lee, S. Pal, D.K. Phelps, L.R. Rudnick, R.J. Santoro, H.H. Schobert, L.M. Shafer, R.C. Striebich, Z.J. West, G.R. Wilson, R. Woodward, and S. Zabarnick. *Development of an Advanced, Thermally Stable, Coal-based Jet Fuel*. Fuel Processing Technology, vol. 89, pp. 364-378, 2008.

Aksoy, P., S.H. Figueroa, and H.H. Schobert. *Physical and Chemical Activation of Petroleum Coke and Coke Produced from Co-coking of Decant Oil and Coal*. American Chemical Society Division of Fuel Chemistry Preprints, vol. 53, pp. 470-471, 2008.

Beaver, B. D.; Burgess-Clifford, C.; Sobkowiak, M.; Wei,Y.; Fedek M. *Energy Fuels*, **2007**, 21, 987-91.

Sobkowiak, M.; Burgess-Clifford, C.; Beaver, B. D ., *Energy Fuels*, **2007,** 21, 982-86.

Presentations

Caroline Burgess Clifford, Josefa Griffith, Ömer Gül, Parvana Gafarova Aksoy, André Boehman, Bruce Miller, Gareth Mitchell, Chunshan Song, Harold Schobert, and Geoffrey Wilson, "Production of coal-based fuels and value-added products: Processes using coal and coal liquids with petroleum refining solvents," AIChE National Meeting, Houston TX, April, 2007.

Caroline Burgess Clifford, Josefa Griffith, Ömer Gül, Parvana Gafarova Aksoy, Gareth Mitchell, "Production of coal-based fuels and value-added products: coal to liquids using petroleum refining solvents," 32nd International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, FL, June, 2007.

Caroline Burgess Clifford, Harold H. Schobert, Maria Escallón, Josefa Griffith, "Effects of coal rank and reaction conditions on production of two-ring compounds for coal-based jet fuel," 2007 International Conference on Coal Science and Technology, Nottingham, England, August, 2007.

Maria Escallón, Josefa Griffith, Caroline Burgess Clifford, Harold H. Schobert, "Co-processing of bituminous coal with petroleum solvents: Determination of solubility parameters," 2007 International Conference on Coal Science and Technology, Nottingham, England, August, 2007.

Caroline Burgess Clifford, Ömer Gül, Josefa Griffith, Parvana Aksoy, Gary Mitchell, Maria Escallon, Utaiporn (Yui) Suriapraphadilok, Harold Schobert, "Integrating Coal-to-Liquid Processes Into Refinery Processes," Boston MA, 234th National Meeting & Exposition, *ACS Division of Fuel Chemistry Preprints*, **52** (2), 2007.

Caroline E. Burgess Clifford, Harold H. Schobert, "Development of coal-based jet fuel," Boston MA, 234th National Meeting & Exposition, *ACS Division of Fuel Chemistry Preprints*, **52** (2), 2007.

Caroline Burgess Clifford, "Coal-based jet fuel," Military Energy & Fuels Conference AIE/TTC, Las Vegas, NV, October, 2007.

Inventions

None this reporting period.

Significant Interactions

On an as-requested basis, briefings are provided for Congressman John P. Murtha and his staff.

Continual discussions with Mr. Bonne Posma, President and CEO of Liquid Fuels, Inc., Fort Myers, Florida, in regard to the coupling of nuclear power plants with alternative liquid fuel plants. It is understood (although *no Penn State personnel were involved*) that Mr. Posma has briefed members of the Kentucky Energy Cabinet and of the Florida congressional delegation on this concept.

Collaborative work with Prof. Dolf Bruinsma, School of Chemical and Mineral Engineering, Potchefstroom, South Africa is proceeding on the solvent extraction of coals to produce extracts that could be hydrotreated to high yields of thermally stable jet fuels. *No AFOSR funding is used for this collaboration*, but the results could validate the use of solvent extraction on the AFOSR project.

Preliminary discussions have been held with Sasol R&D, Sasolburg, South Africa, and in particular the Fuel Chemistry group, for possible collaborative work comparing the Penn State coal-based fuel with Sasol's Fischer-Tropsch jet fuel.

A start-up company, Coal Star Industries Inc., Johnstown, PA, has been founded and is seeking investment for the engineering design for a 5,000 to 10,000 barrel per day demonstration plant for production of coal-based jet fuel.