RESEARCH PROJECTS

Generic Structural Characterization and Liquefaction Research (CFFLS)
May 1, 1991 - April 30, 1992

Being generic in nature, this project is fairly broad and has a number of objectives. As with last year’s project, the CAER tasks include providing well-characterized coal samples, and access to liquefaction reactor systems, to UK and other CFFLS researchers.

As in the past, the CAER will continue to collaborate with other CFFLS universities in designing liquefaction experiments. Since the CAER has the largest range of liquefaction reactor types, we will participate in programs for testing novel catalysts, pretreatments, etc. subject to funding limitations. Examples of these collaborations include determining the liquefaction characteristics of bioprocessed coal and cation exchanged lignites.

Liquefaction Pathways (CFFLS)
May 1, 1991 - April 30, 1992

This research will experimentally determine the rate constants and half-lives for the thermolysis of coal related model compounds representing the bridging groups in coal. They will also determine the reaction pathways of individual, and mixtures of, model compounds and the effect of substitution of a number of group types on the reactivity of the bridging linkages.

Another objective is to determine whether the deuterium exchange of methylnaphthalene is a thermal or catalytic reaction, and which structure/position of coal is susceptible to deuterium exchange.

A series of model compounds with functional groups similar to those representing reactive linkages, such as ethers, will be studied using mild conditions. These data will provide the base case for the evaluation of a number of substituents on the linkage reactivity. Model compounds, which are not commercially available or require a radioactive label will be synthesized in-house. Both thermal and catalyzed reactions will be studied.

A series of model compounds with functional groups similar to those found in coal (e.g. ethers,
alkyls, amines, phenols, etc.) will be deuterated (in the presence and absence of coal). The proton and deuterium analysis of each individual compound will provide the data necessary to examine which structure and/or functional groups are more susceptible to hydrogenation during coal liquefaction.

Small Particle Analysis (CFIISL)

May 1, 1991 - April 30, 1992

The objectives of the research project are to extend the laser pyrolysis synthesis technique to the production of controllable size iron oxide ultrafine particles (UFPs) with certain particle diameters; and to study the size and composition-dependence of the physical properties. The effect of ultrafine particle size and composition on the catalytic enhancement of coal liquefaction is also being studied.

The laser approach to the production of UFPs will allow the synthesis of a wide range of transition metal- and rare earth-containing catalysts. The development of active, highly-dispersed, iron based catalysts can provide a means to exploit the high reactivity of low-cost, low-rank coal.

Fischer-Tropsch
(Iron Catalysts)

December 18, 1990 - December 17, 1993

Starting in December of 1990, the coal conversion group began a major research program funded by the DOE to develop an iron based catalyst for Fischer-Tropsch Synthesis (FTS). The objectives are to establish a process, at laboratory scale, for the reproducible preparation of a catalyst of optimum activity. The process will then be scaled up to a semi-technical catalyst preparation plant (100 lb. of catalyst/week) and a cost estimate will be made for the plant and for the catalyst.

The scale-up design will be provided by United Catalysts, Inc. (UCI), a company that manufactures and sells commercial catalysts that are based on iron oxide. UCI and the CAER have had a long-term cooperative program involving catalyst characterization of developmental and commercial catalysts that relates the characterization data to catalyst performance.

Clean Gasoline - Aromatics Removal from Coal Gasoline

September 25, 1990 - September 24, 1992

Current coal liquefaction processes produce a naphtha containing a high fraction of naphthenes. The conversion of this naphtha to gasoline by today's reforming processes means gasoline with a very high aromatics content. However, environmental considerations require the aromatic content of gasolines to be drastically reduced. If coal liquefaction is to advance to a viable commercial process, a way must be found to reform the naphtha to a clean gasoline that will find acceptance in the market place.

This study reforms naphtha at low temperatures. A series of superacid catalysts are being investigated. The initial work concentrated on a catalyst known to isomerize alkanes at low (125-300°C) temperatures and pressures (200-400 psi). Since there are potential problems with the chlorided catalyst, other superacid catalysts will also be investigated.

Advanced Concepts - Direct Liquefaction

November 1, 1991 - October 30, 1993

The purpose of this research is to evaluate at the laboratory scale a number of technological innovations related to the improvement of direct coal liquefaction. Taken together, these innovations constitute an integrated concept which can significantly reduce the cost of direct liquefaction through lowering process capital costs by improvements in process performance.

In general, the process concepts involve “pretreatment”: chemical and physical modifications to the feed materials to the liquefaction process, before their introduction into the liquefaction reactors. CAER and SANDIA will evaluate chemical approaches to allow better control of the initial conversion reactions through (1) the use of CO pretreatment to stabilize the coal, reject oxygen (thereby lowering hydrogen consumption) and inhibit the propensity for regressive reactions (CAER); (2) the introduction of promoted dispersed iron-based catalysts (CAER); and (3) the production of active H-donor distillate solvent fractions (SANDIA), using dewaxed distillate (CONSOL) and fluid coker overhead (CAER/CONSOL) as feedstocks. It is assumed that the level of improvements in the new integrated process will allow the de-asher to be eliminated. The success of the research in developing an integrated process concept will be gauged in part by the results of an economic evaluation (LDP Associates).

Emphasis will be given to low-rank coals. Currently, the low mine mouth coal of these coals
and their ability to produce high quality distillates is offset by the low rate and extent of conversion experienced in larger scale plants. The high oxygen content of these coals also contributes to hydrogen consumption. It is believed that the proposed research can increase the conversion kinetics and conversion level for low rank coals on a process scale to the same extent which has already been achieved in small-scale research.

Rate Enhancement for Catalytic Upgrading of Coal Naphthas

October 1, 1991 - September 30, 1994

The overall objective of this project is to develop catalysts that have a high activity for simultaneous N, S, and O removal from naphtha fractions derived from bituminous and subbituminous coals. Since gasoline, derived from naphthas, accounts for about 50% of today's transportation fuels, the coal liquefaction program is interested in producing environmentally acceptable gasoline feedstocks.

Hydrotreating coal-derived naphtha requires sulfur levels be decreased, along with a concurrent decrease in nitrogen levels. To meet the hydrotreating activity level, new catalysts must be identified that provide a tenfold increase in catalytic activity over that of MoS₂, which is the currently used hydrotreating catalyst. The project is aimed at locating metal sulfides that have a much higher hydrotreating activity than that of MoS₂. The role of the acidic and basic fractions in determining the activity and selectivity for naphtha upgrading to remove S, N, and O will be determined.

Role of Second Component Upon Mercury Penetration Data

July 1, 1991 - June 30, 1992

The objective of this study is to make a comparison of the nitrogen and mercury adsorption techniques used to evaluate the pore structures and surface areas of catalyst support. The addition of a second component to a support alters mercury penetration so that data diverges from that of nitrogen adsorption. We hope to define the causes by which the added component can influence mercury penetration, permitting us to make more reliable comparisons of data for catalysts testing and development.

Catalytic Liquefaction Pathways

July 1, 1991 - June 30, 1992

Liquefaction studies of U.S. high volatile bituminous coals suggest a common thermal liquefaction pathway. This was verified using process conditions selected to obtain the entire range of conversions (20-90%) for a single coal. The data showed that before a significant increase in oil yields, there is a maximum in the asphaltene plus preasphaltenes yield which directly corresponds to the maximum conversion. The objective is to investigate a number of approaches to change the observed pathway so oil yields increase with increasing conversion in the initial stages of coal dissolution. By changing this selectivity, higher yields of oils (i.e., distillates) may be obtained during the early dissolution stage of coal liquefaction.

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Recovery of Fine Coal from Waste Using Advanced Column Flotation

September 1, 1990 - August 31, 1991

The objective of this program was to investigate the applicability of the 'Ken-Flote' column flotation for recovery of fine clean coal from Illinois preparation plants fine refuse streams. The scope of the research program involved optimizing bubble generation and reagent systems to achieve about 90% coal recovery with minimum sulfur and ash content.

The results of the study concluded that using glycol based frother, the Ken-Flote' could recover a clean coal product containing about 5% ash at more than 90% recovery. The results were also confirmed in a pilot scale study conducted using a larger size column. In these tests about 80% of the pyritic sulfur was also removed from the coal.

Dewatering Studies of Fine Clean Coal

September 1, 1990 - August 31, 1992

During the first year of this project, an ultra-fine clean coal was obtained from an Illinois high-sulfur coal waste stream and characterized using the Ken-Flote column.

Bench-scale vacuum dewatering studies were conducted using optimum surface chemical parameters. Structure analysis of the filter cake was also conducted to identify factors which might enhance or retard filtration kinetics or final moisture of the clean coal filter cake. Continuous dewatering tests on fine size clean coal were conducted using a laboratory drum filter, utilizing the optimum filtration conditions identified in previous tasks.

Now, the overall objective is to develop an understanding of fine clean coal dewatering characteristics and use surfactant, metal ions and pH chemistry to develop effective dewatering conditions to lower clean coal moisture content to less than 20% using conventional vacuum dewatering equipment. The project will use statistical design of experiments to determine the optimum operating variables for effective dewatering. Continuous dewatering tests will then be performed using a small laboratory vacuum drum filter. Successful completion of the project will promote the use of newly developed fine and ultra-fine clean coal technologies and establish wide and stable market for regional coals.

Beneficiation Studies of Anthracite

October 1, 1991 - September 30, 1991

The objective of this study is to investigate the beneficiation of Pennsylvania Anthracite using column flotation. The specific goal is to produce a clean anthracite coal containing less than 4% ash, at about 90% recovery.

Successful completion of this project will encourage anthracite producers to use the column technology to produce a premium anthracite product.

Beneficiation Studies of Eastern Oil Shale Using Column Flotation

June 1, 1991 - May 1, 1992

This research aims to determine the column flotation characteristics of Eastern oil shale and to investigate a novel integrated grinding and column flotation technique in a single-stage operation. Specifically, the goals are to remove up to 90% of inorganic minerals and to obtain a high grade (~30 gallons/ton) oil shale product at a 90% oil recovery using minimum grinding energy.

Reconstitution of Fine Coal

July 1, 1991 - June 30, 1992

Various process-chemistry parameters for pelletization of ultra-fine clean coal are being examined. The specific goals of the project are to modify the ultra-fine clean coal surface obtained through column flotation and to minimize the amount of binder to produce a stable pelletized product.

Successful completion will help in the solicitation of funding support for larger scale research and development.

Surface Characterization of Coals

July 1, 1991 - June 30, 1992

The objective of this study is to conduct quantitative studies of the hydrophobicity, chemical functionality and energetic heterogeneity of fine coal surfaces and of their correlations, using novel physical-organic surface research methods and advanced surface analytical techniques. This project will not only advance the understanding of the surface chemistry of coals, but will also likely lead to developing new technologies related to coal beneficiation.

Fine Grinding of Coal

July 1, 1991 - June 30, 1992

The objective of this research project is to develop process parameters to reduce the energy required for ultra-fine grinding of coal. The scope of the project is to study pretreatment of coal with various inorganic and organic
Solvents and grind it in the attrition grinding mill. The amount of energy consumed will be monitored. The work is being partially supported with Title III BOM funds from the Institute for Mining and Mineral Resources (IMMR).

Re-Constitution of Fine Size Clean Coal
July 1, 1991 - June 30, 1992
The objective of this project is to develop process criteria to form pelletized coal from fines using minimum amount of binders.

The scope of the project will involve a study of the adsorption of various surfactants on coal to provide better wetting and hence more compaction and bonding properties. This work is also partially supported with Title III BOM funds from IMMR.

Surface Chemistry Characterization of Pyrite
July 1, 1991 - June 30, 1992
The objective of this project is to conduct studies on the surface reactivity of pyrite using advanced techniques and to correlate the alteration of the coal-pyrite surface with the efficiency of pyrite rejection in coal flotation. The scope involves electrochemical, potentiometric titration, zeta potential and surface analysis studies. The pyrite (mineral and coal) hydrophobicity will be measured by contact angle and stability studies of thin liquid films and froths. This will provide a better understanding of the rejection of pyrite from coal during flotation. The work is partially supported with funds from the U.S. DOE.

Southeast Regional Oxidant Network (SERON): effect of ozone interaction with hydrocarbons on regional atmospheric phenomena
This project has two parts. The first is regional scale modeling, designed to determine regional scale transport and mixing processes to interpret chemical measurements made at sites. This activity should determine the ability of the regional models to simulate the spatial and temporal ozone.

The second endeavor, subregional scale modeling, will evaluate and simulate the role of small scale processes such as cumulus transport, topography and urban heat islands in altering the temporal and spatial distribution of ozone in the Southeastern environment. Small scale topographic simulations are required to interpret these results. Subregional scale models are also required to evaluate the transport into and from urban areas.

Non-Intrusive Measurement of Particle Charge: Dry Coal Cleaning
October 1, 1991 - September 30, 1994
The data obtained from this project will be used to better understand particle charge formation/duration and to define those coal properties that affect electrostatic coal-mineral separation.

Certain coals and ash minerals will be finely ground, triboelectrically charged, and passed through a
high intensity electrical field. The charged particles will be monitored using a two component laser phase doppler particle analyzer. The particle charge will be calculated and charge dissipation rate will be obtained. The influence of gaseous environment and temperature will also be examined.

**Pilot Scale-up of the In-bed Staged Fluidized Bed Process**

July 1, 1991 - June 30, 1992

The objective of this study is to successfully scale-up the In-bed Staged FBC process, currently under development at the CAER. This concept uses sequential reducing and oxidizing zones. Results, obtained from the bench scale in-bed staged reactor study, show promise. Staging of secondary combustion air within the dense phase fluidized bed can increase limestone sorbent conversion by 40% over that obtained from single stage operation. These results indicate NOx emissions can be limited, while sulfur capture is enhanced. However, corrosion in the reducing zone and secondary air distribution may be potential problems with larger scale units. A series of short trial tests with the modified Advanced Combustion System pilot plant to assess engineering problems related to the in-bed staged concept will be pursued. Fluidization dynamics around the reducing/oxidizing zone will also be characterized. INCO, Inc. has expressed interest in participating in the corrosion aspects of this project. Relative corrosion/erosion rates will be analyzed near the steam tube area.

**Thermal Analysis/Mass Spectrometry Cluster**

July 1, 1991 - June 30, 1992

The scope of this project is to provide a thermal analysis - mass spectrometry (TA-MS) capability at the CAER and provide in-house support to a broad range of projects. The instrumentation has been moved to a central location with the view of establishing an analytical cluster. Parts of a Cahn CI1000 pressure balance have also been relocated to the area for possible future development. Potential applications for the TA-MS cluster include gas storage materials, catalysis, and sorbents.

**Porous Solids Characterization Cluster**

July 1, 1991 - June 30, 1992

The scope of this project is to develop and provide gas adsorption and mercury porosimetry expertise and capabilities at the CAER for use in internally and externally funded research. Included in the adsorption capabilities are traditional BET N_2 and CO_2 adsorption and Hg porosimetry. Specific and directed development will include the measurement iodine number, methylene blue and CCl_4 adsorption for the characterization of adsorbent carbons.

**Surface Science Analytical Cluster**

July 1, 1991 - June 30, 1992

This project will provide standard and nonstandard surface specific analytical data for internally and externally funded projects at the CAER. Included in the analytical facilities are x-ray photoelectron spectroscopy (XPS), scanning electron microscopy/energy dispersive spectrometry (SEM/EDS) and scanning tunneling microscopy (STM). The XPS and SEM/EDS are sophisticated instruments requiring dedicated and trained personnel for their efficient use and application. In addition, the STM is new research-grade equipment, the application of which is to be formulated and proven.
Integrated Multistaged Fluidized Bed Retort (KENTORT II)

September 28, 1990 - September 27, 1994

The objective of this research is the development of an efficient and environmentally acceptable retorting technology tailored to the unique processing characteristics of Eastern oil shale. This technology, an integrated multistaged fluidized bed retort, should deliver high oil yields; produce a medium-Btu, hydrogen-rich gas stream; recover sulfur in a usable form; and produce a spent shale with very low residual carbon and sulfur. KENTORT II will produce oil from Eastern shale at lower costs and with less environmental impact than currently available commercial technology.

The overall goal of this technology is to develop economically competitive and environmentally compatible extraction and conversion processes to convert oil shale to liquid fuels and other high value products. The program is directed toward characterizing the chemistry kinetics and emissions related to Eastern and Western oil shale processes.

Geological research indicates that Eastern oil shale is an enormous energy resource of untapped potential. The KENTORT II concept is based on obtaining high oil yields via fluidized bed pyrolysis and recovery of sulfur and residual carbon through an integrated fluidized bed gasification/desulfurization step.

Coolside Waste Management

April 25, 1991 - April 24, 1995

The Coolside Waste Management contract is concerned with research on the environmental impact of landfilling solid waste produced when coal is burned (e.g., storage and leakage of waste) and finding how waste can be used in a positive way (e.g., materials used in concrete and roads). This endeavor includes Consolidation Coal Company and the Kentucky Transportation Commission. Analytical techniques for evaluation of the Coolside materials have been developed at the CAER, the Kentucky Transportation Center, and the UK Department of Chemistry. The project is sponsored by the U.S. DOE Morgantown Energy Technology Center and the Ohio Coal Development Office.

Applied Petrography

July 1, 1991 - June 30, 1992

The Applied Petrography group is involved in a variety of in-house and sponsored projects for beneficiation of coal and oil shale, coal conversion, and resource characterization. In beneficiation research, a project involving the Petrography analysis of oil agglomerated Eastern Kentucky coals will continue with the primary objective of determining how macerals partition between clean coal and tailings streams. Another project will investigate maceral partitioning for several high volatile bituminous coals, anthracite and oil shale during flotation. A third project will investigate dewatering efficiency as measured by image analysis.

In coal conversion, activities associated with developing florescence microscopy capabilities will be continued. Further activities in resid and residue characterization will be conducted in cooperation with Amoco as a Society for Organic Petrology research committee project.

Resource characterization efforts will relate to developing image analysis capabilities in coal petrology. In addition, research on characterization of Kentucky's coal resources is an ongoing activity, particularly with respect to the Fire Clay deposit.

Cooperative Research with the University of Strathclyde

July 1, 1991 - June 30, 1992

This project is a joint venture between the CAER and the University of Strathclyde in Scotland to extend understanding of the pyrolysis and hydrocracking characteristics of shales containing two fundamentally different types of organic matter. The first task is for the Center for Applied Energy Research (CAER) to carry out fluidized bed pyrolysis (3.8 cm reactor) of Turkish Geynuk oil shale which contains an immature Type I kerogen. The second task is for the University of Strathclyde to investigate the effects of dispersed catalysts, hydrogen pressure, and two-stage hydrocracking on the Type II Devonian oil shale of the Eastern U.S. The cooperative arrangement will take the form of travel by CAER personnel to the University of Strathclyde to reciprocate visits already made by University of Strathclyde personnel to the CAER during the past year.

Annual Report and Plan 1991
Conversion of Illinois Coals to Activated Carbons

September 1, 1990 - August 31, 1991

This research evaluated Illinois bituminous coals as feedstocks for commercially competitive activated carbon production. Potentially, this project could open alternative, high added-value markets for these resources. In addition, specific objectives were to ascertain the fate of coal sulfur, and to determine whether coal cleaning can be advantageous.

Six Illinois coals from the Illinois Basin Coal Sample Program, representing broad ranges of ash, and organic and inorganic sulfur content were studied. The synthesis route involved admixing the feedstock with a phosphoric acid solution and heat treating in two stages. The final products were leached to remove excess acid.

A wide range of analytical techniques were applied to characterize the chemical and morphological changes during synthesis, the fate of certain species, like sulfur, and the properties of the carbon products.

One of the most significant results is that surface areas in the range of commercial interest are developed at heat treatment temperature (HTT) around 450°C. At higher temperatures the surface areas tended to decline. It was also found that coal cleaning can have a profound effect on increasing the carbon surface area and pore volume.

Conversion of Illinois Coals to Activated Carbons

September 1, 1991 - August 31, 1992

A second contract was funded beginning in September of 1991. The primary goals of this research are to investigate the utility of selected Illinois coals as precursors for the synthesis of activated carbons by chemical activation, using a combination of carbon cleaning by column flotation, followed by reaction with phosphoric acid or potassium hydroxide.

Specific objectives are:
- to examine the cleaning of selected Illinois coals by column flotation.
- to conduct research with phosphoric acid and cleaned coals that will involve: a study of the influence of low temperature reactions on activated carbon properties; establishing reliable mass balances and compositional information on the reaction products; studying the composition, yield and potential utility of the liquid products; determining the importance of sulfur forms to H,S formation; relating processing behavior to coal characteristics.
- to investigate KOH as an alternative reagent to H,PO, and to address: its applicability to bituminous coals; the potential advantages in ease of reagent recovery for recycle; the ability to exert further control in tailoring the adsorptive properties and capacities of the carbons; the effect of KOH on sulfur redistribution.

Carbon-Carbon Composites for Fusion Energy Devices

December 1, 1990 - November 30, 1991

Carbon-Carbon Composites are candidates for first wall applica-
tions in nuclear fusion reactors. It is important to understand structural changes to carbon-carbon composites that may occur in use.

This project attempts to characterize, qualitatively and quantitatively, structural features of these materials. The distribution of pores and cracks is particularly important. Quantitative image analysis methods are being applied to the study.

Oil Shale Resids as Carbon Fiber Precursors
July 1, 1991 - June 30, 1992
Oil shale is predominantly considered as a resource for conversion to liquid fuels. This alternative research, will look at shale oil as a potential raw material for the synthesis of high value carbon products. Potential applications include: carbon fibers, microbeads, binders and graphitic carbons. The initial study will be a survey of the carbonization of the solid products.

Management and Operations (Library)

Data Conversion
July 1, 1991 - June 30, 1992
This project will incorporate the CAER's extensive holdings of coal and fuel science manuscripts, books and reports on the UK NOTIS on-line public access catalog and the national OCLC bibliographic data base. This will permit access to CAER Library holdings by UK and other institutions in Kentucky, and in the nation, through the Interlibrary Loan Network.

The project began last fiscal year and continues through July 1992. During this second year, catalogue records for all CAER library books will be converted to MARC format. The records will then be added to the University's on-line catalog. This project is partially funded by the Kentucky Department for Libraries and Archives.