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FINAL REPORT

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For
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Office of Fossil Energy
National Energy Technology Laboratory
Morgantown, West Virginia

By
Western Research Institute
Laramie, Wyoming

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EXECUTIVE SUMMARY

Cooperative Agreements, DE-FC26-08NT43293, DOE-WRI Cooperative Research and Development Program for Fossil Energy-Related Resources began in June 2009. The goal of the Program was to develop, commercialize, and deploy technologies of value to the nation's fossil and renewable energy industries. To ensure relevancy and early commercialization, the involvement of an industrial partner was encouraged. In that regard, the Program stipulated that a minimum of 20% cost share be achieved in a fiscal year. This allowed WRI to carry a diverse portfolio of technologies and projects at various development technology readiness levels. Depending upon the maturity of the research concept and technology, cost share for a given task ranged from none to as high as 67% (two-thirds).

Over the course of the Program, a total of twenty six tasks were proposed for DOE approval. Over the period of performance of the Cooperative agreement, WRI has put in place projects utilizing a total of $7,089,581 in USDOE funds. Against this funding, cosponsors have committed $7,398,476 in private funds to produce a program valued at $14,488,057. Tables 1 and 2 presented at the end of this section is a compilation of the funding for all the tasks conducted under the program.

Goals of WRI's Cooperative Research & Development Program

Increase the production of United States energy resources energy resources

Enhance the competitiveness of United States technologies

Reduce the dependence on foreign energy supplies and strengthen National and regional economies

Minimize the environmental impact of energy production and utilization

The goal of the Cooperative Research and Development Program for Fossil Energy-Related Resources was to through collaborative research with the industry, develop or assist in the development of innovative technology solutions that will:

- Increase the production of United States energy resources – coal, natural gas, oil, and renewable energy resources;
- Enhance the competitiveness of United States energy technologies in international markets and assist in technology transfer;
- Reduce the nation's dependence on foreign energy supplies and strengthen both the United States and regional economies; and
- Minimize environmental impacts of energy production and utilization.

Success of the Program can be measured by several criteria. Using the deployment of the federal funding with industrial participation as a performance criterion, over the course of the program, the copsonsors contributed more dollars than the federal funds. As stated earlier, a little more than half of the funding for the Program was derived from industrial partners. The industrial partners also enthusiastically supported the research and development activities with cash contribution of $4,710,372.67, nearly 65% of the required cost share.

Work on all of the tasks proposed under the Cooperative Agreement has been completed. This report summarizes and highlights the results from the Program.

Under the Cooperative Agreement Program, energy-related tasks emphasized petroleum processing, upgrading and characterization, coal and biomass beneficiation and upgrading, coal combustion systems development including oxy-combustion, emissions monitoring and abatement, coal gasification technologies including gas clean-up and conditioning, hydrogen and liquid fuels production, and the development of technologies for the utilization of renewable energy resources. Environmental-related activities emphasized cleaning contaminated soils using microbial fuel cells, development of processes and sorbents for emissions reduction and recovery of water from power plant flue gas, and biological carbon capture and reuse. Technology enhancement activities included resource characterization studies, development of improved methods, monitors and sensors. In general the goals of the tasks proposed were to enhance competitiveness of U.S. technology, increase production of domestic resources, and reduce environmental impacts associated with energy production and utilization.

Technologies being brought to commercialization as a result of the funds provided by the Cooperative Agreement contribute to the overall goals of the USDOE and the nation. Each has broad applicability both within the United States and abroad, thereby helping to enhance the competitiveness of U.S. energy technologies in international markets and assisting in technology transfer.

Under the Cooperative Agreement Program, WRI has furthered the development of two different coal upgrading technologies. River Basin Energy technology was scaled-up and demonstrated at a nominal 40 tpd size. Similarly, WRI’s patented mercury removal technology further developed into WRITE Coal technology which was then integrated into oxy-combustion and gasification systems for IGCC and fuels production. Integrated systems with WRITE Coal technology applied at the front end represent substantial environmental and efficiency gains. A variation of the RBE coal upgrading technology is being commercialized as a torrefaction technology for woody biomass. WRI worked with EPRI and NIST to develop and improve mercury calibration standards for emissions monitoring. Working with Chart Energy and Chemicals, WRI scaled-up compact reactor technology for the synthesis of fuels and chemicals from syngas. Compact reactor technology represents a five-fold increase in productivity over conventional reactors making smaller-scale distributed synthesis plants an economical viability. Similarly, WRI's patented mixed alcohol synthesis catalyst production is being scaled-up in collaboration with a commercial catalyst manufacturer.

Table 1. A List of Approved Tasks and Associated DOE Budgets under the Cooperative Agreement

Task No.	Title	BP1	BP2	BP3	Total	Start Date
00-N1	Program Management	$76,755	$75,000	$75,000	$234,337	May-08
01-S1	Production of Ethanol-Based Fuels from Natural Gas	$361,166			$360,349	January-09
02-S1	Petroleum Processing Efficiency Improvement	$100,000	$175,000	$100,000	$356,180	January-09
03-S1	Integrated Freezer System	$50,000	$50,000		$98,042	May-09
04-S1	Pilot-Scale Demonstration of Cowboy Coal Upgrading Process	$250,000	$200,000	$250,000	$700,000	March-09
05-S2	WRI's Pre-Gasification Treatment of PRB Coals for Improved Advanced Clean Coal Gasifier DEsigns	$185,000	$269,951		$448,841	March-09
06-S2	Alternate Environmental Processes/Sorbents to Reduce Emissions and Recover Water for Power Plant Use	$225,000	$140,780	$189,801	$474,646	May-09
07-N3	Screening Used Oil for Chlorinated Solvent Contamination	$75,000			$72,186	March-09
08-S2	Unconventional Energy: Energy Production and Contamination Using Microbial Fuel Cell Systems	$135,000			$128,668	March-09
09-S2	Techniques for Mitigation of the Environmental Footprint of Fossil Fuel Production	$150,000		-$122,492	$26,069	May-09
10-S1	THAI Process for Heavy Oil	$125,000			$137,966	May-09
11-S1	Development and Testing of CHER for Synthesis of Liquid Fuels	$160,000	$160,000	$200,000	$550,583	March-09
12-S1	Development and Testing of Carbons from Oxy-Combustion	$50,000			$50,000	May-09
13-S1	Evaluation of Oil Shale Multipollutant Emissiosn Control	$100,000			$100,000	May-09
14-S1	Novel Gasifier for Wyoming Coals	$170,000		$188,000	$326,656	May-09
15-S1	Gasification Kinetics with a Drop Tube Reactor		$100,000		$87,795	August-09
16-S3	Mercury Emission Calibration Standards		$75,000		$73,018	August-09
17-S2	Performance and Cost Evaluation of a Membrane-Based Treatment Process for Desalination of Produced		$54,900		$54,141	August-09
18-S1	Comparative Performance of MoS2-and Mo2C-Based Mixed Alcohol Synthesis Catalyst		$200,000		$199,897	August-09
19-S2	A Novel Integrated Oxy-combustion Flue Gas Purification Technology: A Near-Zero Emissions Pathway		$340,817	$714,484	$1,163,127	January-10
20-S1	Novel Sorbents for Emission Control From Coal Combustion		$50,000	$130,000	$180,000	January-10
21-S1	Hydrogen Separation		$250,000	$149,989	$399,989	January-10
22-N1	Conversion of Low-Rank Wyoming Coals into Gasoline by Direct Liquefaction		$200,000	$200,000	$400,000	June-10
23-S1	Mercury Continuous Emission Monitor Calibrator Source Stability			$135,000	$132,977	##########
24-N1	Reduction of Heavy Oil Viscosity Using Solid Sorbents			$125,000	$119,201	##########
25-S1	Soy Derived Additives for Producing Utility Fuels from Coal/Biomass			$30,000	$29,979	April-11
26-S2	Chemoautotrophic (CAT) Biological Carbon Capture and Re-use Process			$297,492	$311,995	January-12
	Total	**$2,212,921**	**$2,341,448**	**$2,662,274**	**$7,216,642**	

Table 2. Task-by-task Breakdown of Cost Share Provided by Cosponsors

Task	DOE	Cost Share	Percent Match
00-N1	$234,337		
01-S1	$360,349	0	0%
02-S1	$356,180	169,998	32%
03-S1	$98,042	114,170	54%
04-S1	$700,000	1,891,506	75%
05-S2	$448,841	398,203	47%
06-S2	$474,646	189,250	29%
07-N3	$72,186		
08-S2	$128,668	98,594	43%
09-S2	$26,069	0	0%
10-S1	$137,966	268,197	66%
11-S1	$550,583	761,400	58%
12-S1	$50,000	29,424	37%
13-S1	$100,000	102,407	53%
14-S1	$326,656	393,977	55%
15-S1	$87,795	13,158	13%
16-S3	$73,019	75,000	51%
17-S2	$54,141	40,000	42%
18-S1	$199,897	302,448	60%
19-S2	$1,163,127	1,280,584	52%
20-S1	$180,000	122,198	43%
21-S1	$399,989	470,000	54%
22-N1*	$400,000	566,789	60%
23-S1	$132,977	40,000	23%
24-N3	$119,201		
25-S1	$29,979	71,172	71%
26-N2	$311,995		
Total	**$7,216,642**	**$7,398,476**	**51%**

*Task was revised and converted to a cost-shared task after initial DOE approval

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BACKGROUND

Cooperative Agreement DE-FC26-08NT43293, DOE-WRI Cooperative Research and Development Program for Fossil Energy-Related Resources began in June 2009. The objective of the Cooperative R&D Program was to conduct both fundamental and applied research to assist industry in developing, deploying, and commercializing efficient, nonpolluting fossil energy technologies that can compete effectively in meeting requirements for clean fuels, chemical feedstocks, electricity, and water resources in the 21st century. The goal of the Program was to develop, commercialize, and deploy technologies of value to the Nation's fossil and renewable energy industries. To ensure relevancy and early commercialization, the involvement of an industrial partner was encouraged, requiring at least 20% non-Federal cost-share.

To realize the overall objectives of the Cooperative R&D Program, WRI's research and development efforts focused in four major areas:

1. Energy Program emphasized energy independence through increased production and use of domestic energy resources coal, natural gas and biomass. Projects conducted support coal and biomass upgrading, heavy oil upgrading; coal and biomass utilization and conversion, development of gas-to-liquids and coal-to-liquids technologies; and development of technologies for the production of hydrogen.

2. Environmental Program had the goal of minimizing the impact of energy production. Efforts under the Program focused on technologies and technical services for mitigation of emissions and effluents from utilization and conversion of fossil resources.

3. Technology Enhancement Program activities included improvements to current technologies to minimize the environmental impacts and/or improve the efficiency of energy production processes.

4. Technology Transfer/Training Program activities encompassed education, training, and collaborative research between the State of Wyoming, UW, and WRI.

Over the course of the Cooperative R&D Program DOE approved twenty-six technical tasks authorizing $7,216,642 in federal funds. Non-federal sponsors for these tasks provided $4,710,373 in cash and $2,730,456 in-kind contribution resulting in a $14.5 million energy and related environmental research program.

This report highlights the up-to-date results of the Cooperative Agreement R&D Program. In order to portray a cohesive picture of the work performed under this Program, in this report we have combined the discussion of topically similar tasks. This approach also preserves the confidentiality of our cosponsors yet allowing us to disseminate as much information as possible.

RESEARCH HIGHLIGHTS

Coal and Biomass Upgrading Technology Developments

Task 04 – Pilot-Scale Demonstration of Cowboy Coal Upgrading Process

Task 25 – Soy Derived Additives for Producing Utility Fuels from Coal/Biomass

There are four primary types of coal. Anthracite, bituminous, subbituminous, and lignite, all four types of these coals principally contain carbon, hydrogen, nitrogen, oxygen, and sulfur, as well as moisture. However, actual concentrations of these elements and moisture vary widely from rank-to-rank. For example, anthracite, the highest ranking coals contain about 98 % carbon, while lignite, the lowest ranking coals may only contain about 30 % carbon. The amount of moisture in anthracite and bituminous coals can be less than 1%, but for subbituminous and lignite coals the moisture content can be in the 25 – 40%, range. The high-moisture subbituminous and lignite coals have lower heating values and their high moisture content adversely affects coal-fired power plant performance and emissions. High moisture content results in significantly lower boiler efficiencies and higher unit heat rates. The high moisture content of the coal can also raise fuel handling, transportation and fuel preparation issues.

Figure 1. RBE's 40 tpd coal/biomass upgrading test facility at WRI Advanced Technology Center

Under a previous cooperative agreement, WRI supported the bench- and pilot-scale development and successful testing of a novel coal upgrading technology. River Basin Energy's (RBE) coal upgrading process, involves heating the coal in a bubbling fluidized bed-based reactor operating at near ambient pressures. The process heat required for drying is derived from the coal itself. Upgrading process being a fluidized bed-based technology is a continuous process that allows high throughputs thereby reducing the processing costs. Maintenance costs are also low since the only moving parts are in the air blower(s). The RBE Coal Upgrading Process is the only technology that uses an oxidizing environment for processing the coal. The oxidative environment removes the more active oxygen components of the coal, thereby contributing to the stability of the product. The product is rehydrated to the equilibrium moisture content, further

enhancing the product stability and pyrophobicity. Since the processing is carried out in air at conditions mild enough that compared to other coal upgrading technologies, the produced water is not as difficult to treat.

RBE Coal upgrading technology offers combined energy, environmental and economic solutions, producing clean, efficient and affordable energy. Cowboy coal product can meet the specific needs of vital industrial, international and public utility market customers. The proprietary process transforms low BTU coals into a more energy efficient, and lower emission fuel. A co-benefit of the process is the removal of significant amounts of mercury and reductions in the emissions of carbon dioxide, sulfur dioxide and nitrogen oxides.

As a part of this Program, a nominal 40-tons per day test facility was constructed and operated at the WRI's Advanced Technology Center. Coals received from several Western US mines in the Powder River Basin and from Alaska and Indonesia have been used to demonstrate universal applicability of the process. A comparison of the feed coal and product is displayed in Table 3 below.

Table 3. Typical Feed and Product Analyses

Representative Feed and Product Sample Analysis		
Proximate Analysis Method: Astm D-5142	**Feed Coal As received Wt%**	**Product Coal As received Wt%**
Moisture	**24.29**	**6.61**
Ash	3.62	4.22
Volatile Matter	29.42	38.08
Fixed Carbon	42.67	51.09
Total	100	100
Ultimate Analysis Method: Astm D-5142/5373	**Feed Coal As received Wt%**	**Product Coal As received Wt%**
Moisture	**24.29**	**6.61**
Hydrogen	2.88	3.12
Carbon	56.48	68.5
Nitrogen	0.87	0.99
Sulfur	0.34	0.35
Oxygen	11.52	16.21
Ash	3.62	4.22
Total	100	100
Heating Value - Btu/lb Method: ASTM D-5865	**9470**	**11274**

The RBE Process can also be used as a torrefaction technology for biomass. The technology can also be used to manufacture high heating value, coal/biomass mixtures as a "green" fuel for the utilities with a prescribed amount of biomass bend. Work concluded under the Cooperative R&D Program, showed that a similar process configuration is indeed possible to process biomass

and biomass/coal mixtures. Co-processing of coal and biomass in a single reactor to produce a homogeneous fungible product is cheaper both from capital investment and from operations and maintenance costs. For the combustion systems, the product produced can be used by utilities in existing installations with no equipment modifications. Co-feeding of coal and biomass in the gasification process for power generation as well as the production of alternative liquid transportation fuels, hydrogen, and industrial chemicals strengthens our Nation's energy security while reducing the overall process greenhouse gas emissions (GHG).

As a part of the Cooperaive R&D Program white wood chips were torrified in the demonstration facility to produce a product with excellent "grindability" and hydrophobic characteristics suitable for outdoor storage in the utility coal stockpile, pulverizing and co-firing with coal. Heating value of the wood chips was increased to about 9,400 Btu/lb. The product can be directly co-fired in a utility boiler with little impact on the plant fuel preparation equipment. Using soy-derived lubricants and binder or other similar additives the torrefied biomass can be pelletized by itself, or combined with coal to produce a coal/biomass pellet (green coal).

Figure 2. Raw (left) and torrefied (center) white wood, and coal/biomass pellets (right)

<u>Fuels and Chemicals Synthesis</u>

Task 01 – Production of Ethanol-Based Fuels from Natural Gas
Task 11 – Development and Testing of CHER for Synthesis of Liquid Fuels
Task 18 – Comparative Performance of MoS_2- and Mo_2C-Based Mixed Alcohol Catalyst

Realizing that as a nation US has a very large appetite for transportation fuels, WRI began the development of synthesis technologies in early 2000. Under a previous cooperative agreement, WRI developed a molybdenum carbide-based mixed alcohol synthesis catalyst with the reasoning that a fungible product, oxygenated gasoline additive, can be synthesized from syngas. Depending upon the feedstock such as landfill gas, digester gas, coal-bed methane, natural gas the technology was viewed as a GTL process. For biomass, solid waste, agriculture waste, and other similar solid feedstock, in conjunction with an appropriate gasification technology, the technology serves as a CTL and CBTL process. Based on successful bench-scale testing in a single tube fixed-bed reactor, a nominal 2 bbl/d synthesis facility (Figure 3) was completed under the previous cooperative agreement with USDOE and cosponsor support.

Figure 3. A photograph of 2 bbl/d synthesis plant

Further development of the molybdenum carbide catalyst was continued under this Cooperative R&D Program. In addition, based on shakedown tests in the 2 bbl/d synthesis plant whereby neither the slurry reactor nor the fixed-bed reactor could provide sufficient heat and mass transfer, the need for advanced reactors was identified. A task dealing with the development and testing of a compact heat exchange reactor was included in the Cooperative R&D Program. The mixed alcohol synthesis process based on molybdenum-carbide offers several advantages over conventional FT synthesis. Sulfur poisoning of the catalyst is a major problem in a number of other processes and usually requires a reduction in the sulfur levels in the synthesis gas before it can be admitted to the reactor. The catalyst formulation for this process is sulfur tolerant and hence such a conditioning step is not critical. The product from this catalyst requires very little treatment to be used as a motor fuel, dewatering. FT processes require the equivalent of a mini refinery to convert the product to a usable motor fuel.

Compact reactor technology developed in collaboration with Chart Energy and Chemicals and with partial support from University of Wyoming School of Energy Resources, was demonstrated to offer up to five-fold process intensification over conventional fixed-bed reactor technology. A bench-scale compact reactor (Figure 4 a) with a 10x3 array of channels (Figure 4b) and a catalyst volume of 66 ml was assembled in a test skid (Figure 4c). The entire assembly was self contained with provisions for heating and cooling the reactor with an electrically heated hot-oil system. The syngas composition could be varied over a wide range of carbon monoxide and hydrogen ratio including inert components. Temperature and pressure monitoring, product collection and sampling were an integral part of the computer-controlled data logging. The assembly was used to optimize a number of issues about adapting the Compact Heat Exchanger design for synthesis applications. These included: (a) appropriate form of the catalyst, (b) catalyst loading and unloading, (c) catalyst activation and regeneration, (d) reaction start-up, (e) proper reactant distribution over the entire volume of the reactor, and (f) product removal.

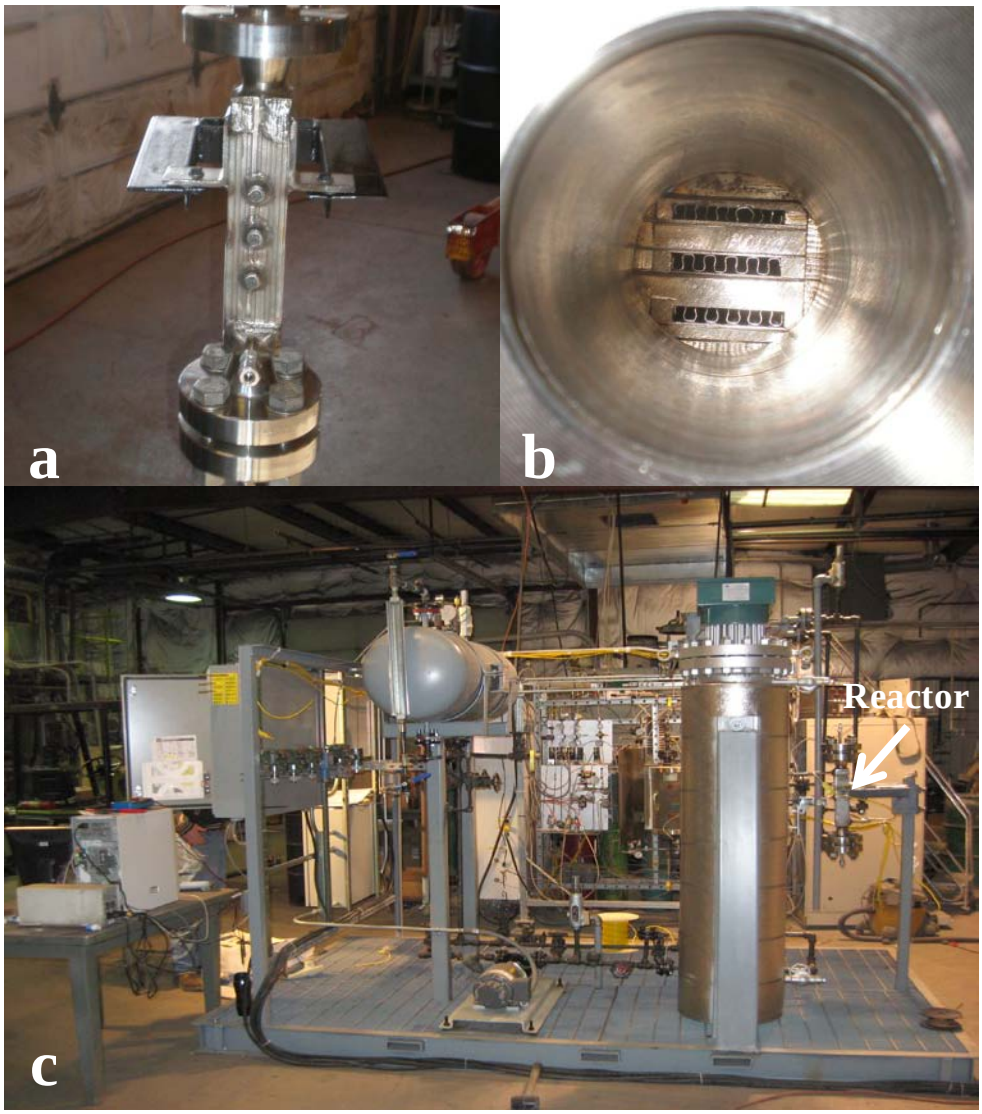

Figure 4. Bench-scale CHER skid with a 10x3 channel reactor

Under the Cooperative R&D Program, methanol, DME, mixed alcohols and conventional FT catalysts were successfully tested in the bench-scale reactor. As an example of the superior reactor performance, Figure 5 shows observed temperature increase of the catalyst vs. catalyst activity for an advanced FT catalyst. A one-month long run of a highly productive Fischer-Tropsch catalyst was carried out. The run was continuous and in the most part autonomous under pc-based controls. From the data in Figure 5, more than an order of magnitude increase in the catalyst activity i.e., greater than ten-fold increased heat released by the reaction was easily managed by the reactor with only a six degree increase in the catalyst temperature. In conventional fixed bed reactors such high activity catalysts, if at all, can only be managed by diluting the catalyst bed.

The bench-scale CHER skid was also used to perform comparative testing of molybdenum carbide and molybdenum sulfide catalysts. Performance of the two were found to be identical

with carbide formulation producing more hydrocarbons than the sulfide whereas sulfided catalyst led to sulfur contamination in the product.

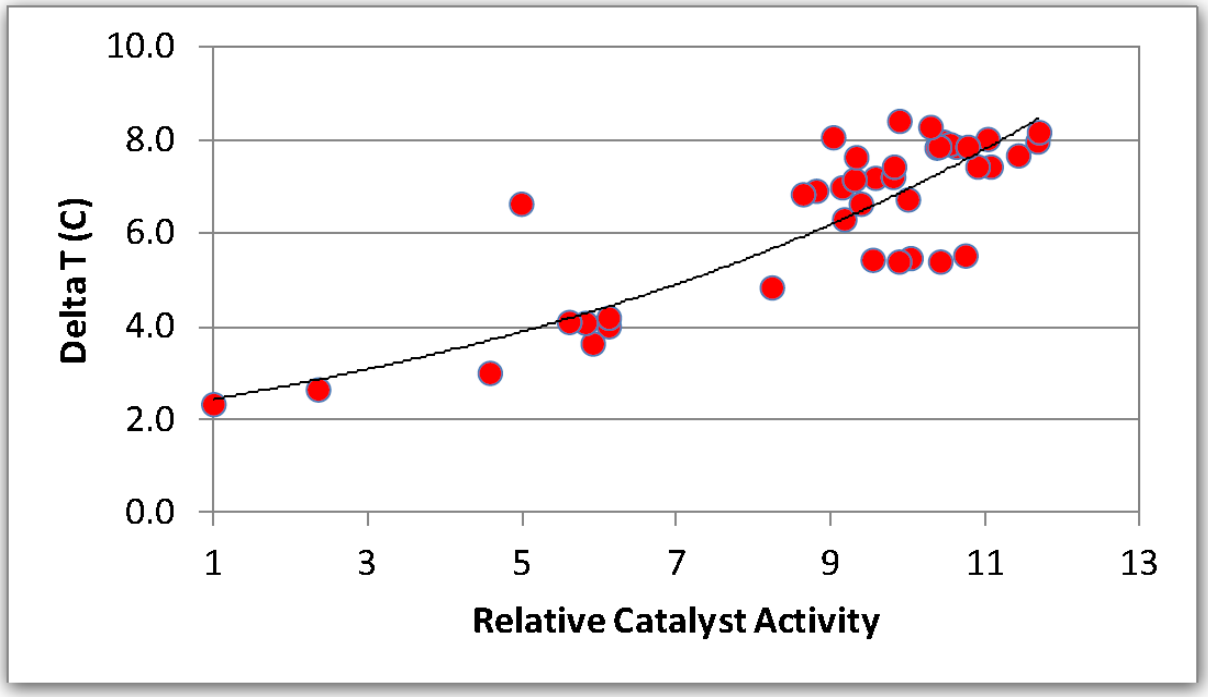

Figure 5. Observed Catalyst Temperature vs. Catalyst Activity for an FT catalyst in the Bench-Scale CHER

Further development of CHER under the Cooperative R&D Program was a x30 scale-up to a nominal two-liter catalyst capacity. A side-by-side comparison of the bench- and pilot-scale reactor sizes and channel pattern is displayed in Figure 6.

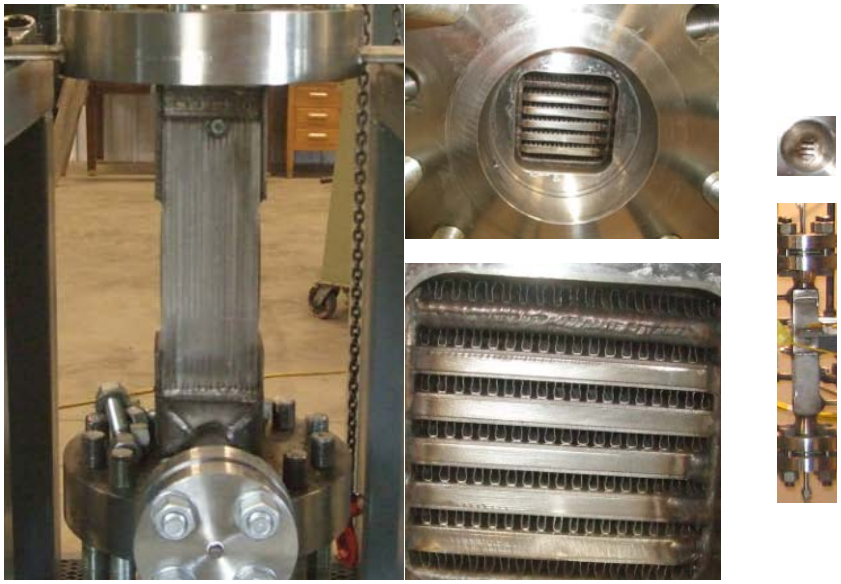

Figure 6 - Comparison of the Pilot-(left) and Bench-scale (right) reactors. Pilot-scale reactor is twice as long, has ten-times more and slightly larger channels than the bench-scale reactor.

Pilot-scale reactor was assembled onto a skid and integrated into the balance of the 2 bbl/d plant and operated with commercially available methanol synthesis catalyst. Operational parameters such as temperature, pressure, space velocity, H_2/CO ratio, recycle ratio are being optimized. Data from several test runs covering nearly three hundred hours of operations are summarized in the Figure 7 below.

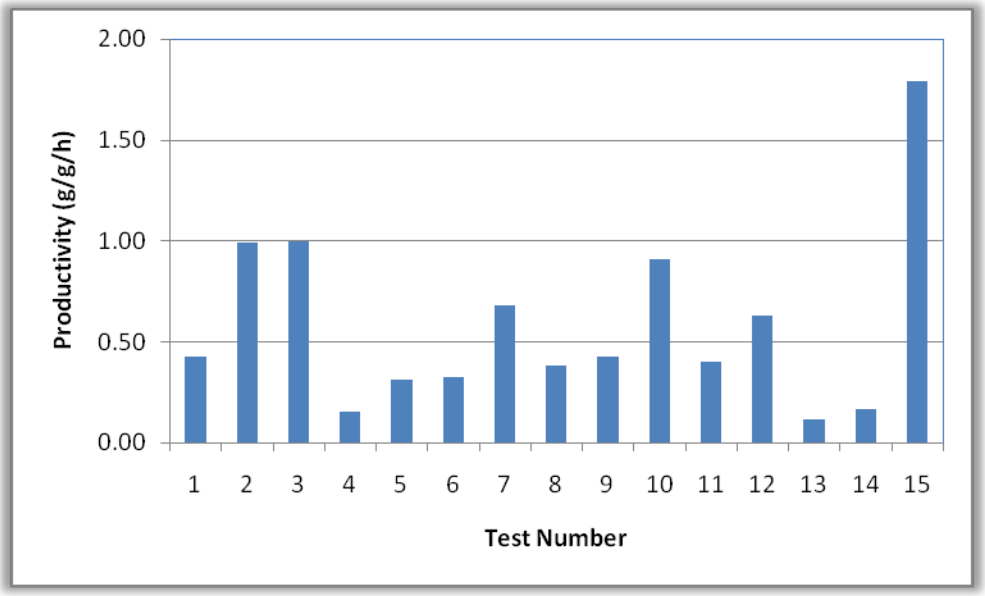

Figure 7. Pilot-scale CHER productivity data with a commercial methanol synthesis catalyst

The data presented in Figure 7 confirms the performance gains observed in the bench-scale reactor. Nearly x4 gain in productivity (Test 1 vs. Test 15) over conventional reactors affirms the superior heat dissipation performance of the reactor. During these high space velocity tests with recycle, the pressure drop across the reactor is was observed to be quite low and easily manageable.

Technology developed under the auspices of the Cooperative R&D Program in this area is ready for commercialization. WRI is working with a major European catalyst manufacturer to scale-up the production of Molybdenum carbide-based catalyst formulation. Similarly, two separate entities CompRex LLC and BgtL LLC have been established to commercialize the CHER technology and build commercial small-scale, modular gas-to-liquid plants for distributed production of fuels and chemicals.

Emissions Abatement and Monitoring

Task 12 – Development and Testing of Carbons from Oxy-Combustion

Task 13 – Evaluation of Oil Shale Multi-pollutant Emission Control

Task 16 - Mercury Emissions Calibration Standards

Task 20 – Novel Sorbents for Emission Control From Coal Combustion

Task 23 - Mercury Continuous Emission Monitor Calibrator Source Stability

Coal combustion technologies that make coal combustion cleaner and more environmentally efficient are receiving a great deal of attention in the industry. Under a previous Cooperative Agreement WRI acquired a 250000 Btu/h Combustion Test Facility. A pilot-scale coal combustion facility that simulates a pulverized coal-fired utility boiler is set up to simulate a tangential-fired boiler. The facility can easily be adapted to wall-fired or other configurations. The facility is equipped with appropriately sized heat-recovery surfaces (water-cooled waterwall section, and air-cooled superheater, reheater, and economizer simulators). There are provisions for preheating the combustion air to mimic a utility air preheater. Several over-fire air injection ports are incorporated in the design to allow for combustion staging. Base particulate clean-up device is a two-bag two compartment bag filter that allows isolation and collection of flyash samples from different plant operations. Stack gas analysis system includes on-line analyzers for the monitoring of O_2, NOx, SO_2, CO, CO_2, as well as elemental and oxidized vapor-phase mercury.

As a apart of the Cooperative R&D Program, the facility was upgraded with partial support from various cosponsors to include a dry flue gas scrubber, in-furnace injection equipment, and an ESP. On-line analytical equipment was also upgraded for faster turnaround of the data.

The Combustion Test facility was used to test sorbents and other emissions abatement techniques for various clients. List of recent clients included Nalco-Mobotec/Ecolabs, ReCommunity Energy LLC, Yara International, Novinda, Asia Minor Mining, ADA-ES Inc., Idaho National Laboratories, Linde/Tata Chemicals, Headwaters, Chem-Mod, FuelTech, University of Wyoming, Jupiter Oxygen, BHP Billiton, Hydrogen Technology Applications, and Safe Fire.
Several proprietary multipollutant control technologies and sorbents were evaluated. For one of the cosponsors, potential of in-furnace injection of oil shale was investigated. Finely ground western US oil shale was injected in various parts of the furnace. It was postulated that calcium in the shale will act as a sulfur sorbent, carbonaceous material will act as a reburn fuel thereby lowering NOx formation and emissions, and increase particulate loading will enhance mercury capture. Based on a series of tests cosponsor concluded that the approach though feasible was not economical.

Several proprietary non-carbon mercury capture sorbents were tested in the Combustion Test Facility and some of those are now commercially available. For one of the cosponsors, NETL's patented Thief Carbon technique was tested whereby the Combustion Test Facility was operated in oxy-combustion mode to collect thief carbon. The collected carbons were then characterized and evaluated for use as mercury sorbents with very encouraging results.

Under a previous Cooperative Agreement WRI collaborated with NIST and EPRI to evaluate the performance of commercially available mercury monitors. Working very closely with NIST, calibration methodologies based on gas cylinders, and on elemental and oxidized mercury vapor generators were developed and evaluated. The use of mercury vapor generator as calibrators

requires the use of oxidized mercury generators followed by an efficient conversion of the oxidized mercury to elemental mercury. Evaporative mercuric chloride generators using standard solutions traceable to NIST SRM 3133 have been noted to produce 7-9% less mercury (as mercuric chloride) than elemental mercury generators when both units are set to provide the same concentration. As a part of this Cooperative R&D Program, WRI identified two causes for the discrepancy: (1) lower threshold limit of acid preservative below which the mercuric chloride solutions are unstable, and (2) insufficient equilibration time over mercury vapor generator. Once the causes were identified, the fixes were relatively simple to adopt in the testing and calibration protocols. Similarly, mercury vapor generators were found to passivate with time. Work concluded under the Cooperative R&D Program identified the root cause of the passivation to be air-borne silica. Again, once the cause was identified, the fix was relatively simple and inexpensive to implement in the commercial equipment.

Carbon Capture and Reuse

Task 06 – Alternate Environmental Processes/Sorbents to Reduce Emissions and Recover Water for Power Plant Use

Task 26 – Chemoautotrophic (CAT) Biological Carbon Capture and Re-use Process

The increased concern about emissions of greenhouse gases leading to climate changes has been a driver for research regarding the capture and sequestration of carbon dioxide emitted to the atmosphere from coal-based power generation. However, capture and sequestration require large parasitic loads and capital costs which significantly increase the cost of electricity.

Net carbon dioxide emission reduction can be achieved by increasing energy conversion efficiency, by switching to less carbon-intensive fuels, and by using alternative fuels. However, fossil fuels are likely to remain a major part of power generation worldwide. Capture and storage of carbon dioxide will thus be a method used for reducing CO2 emissions. Membrane separation, absorption with solvents, and cryogenics techniques have been used to separate CO2 from power plant flue gases and other waste gas streams. However, these methods are energy-intensive. As an alternative, as a part of the Cooperative R&D Program, WRI collaborated with University of Wyoming researchers to develop regenerable solid sorbents constituted from inexpensive alkali metals and alkali earth metals. Such sorbents can be regenerated with the heat recovered from the waste gas streams including flue gas and thus can provide cost-effective removal of carbon dioxide from flue gas.

An inexpensive K-Fe-based sorbent was developed using K_2CO_3 and nanoporous FeOOH. The carbon dioxide separation performance of the sorbent was investigated in a fixed bed tube reactor under various operating conditions. The regenerable sorbent has a capture capacity nearly seventy times larger than that of pure K_2CO_3 powder. Early testing has shown that the energetics and kinetics of sorption and desorption are very favorable. However, future work needs to be done before the technology can be commercialized.

Biological carbon dioxide capture technologies, while still under development, require much smaller parasitic loads and have the added benefit of potentially producing beneficial products from the carbon that is captured. Algae-based capture technologies require sunlight and therefore require extensive land area to be effective. As a part of the Cooperative R&D Program, WRI's patent-pending CAT process was tested. The CAT process promises to be an alternative form of biological carbon capture that can address many of the short comings of Algae-based systems. The process is based on a synthetic symbiosis of bacteria, in which a chemical energy shuttle is created through the recycling of inexpensive and abundant materials. Bacteria from bioreactors can be harvested and refined into bioproducts, such as biofuels, bioasphalt binder, green plastics and other petroleum replacement products. The non-lipid residue from the biorefining process can be recycled as nutrients for the bioreactors.

Based on data collected under the Cooperative R&D Program, the CAT process is expected to have significant advantages over biofuel production in algae. While volumetric productivities of bacteria in the CAT process are similar to those observed with algae strains being tested for large-scale use, the light-independent nature of the CAT process makes this technology a viable and likely more economical route to biodiesel production.

The CAT process provides the fossil energy sector with a carbon capture and re-use technology that produces saleable products, thereby turning an environmental hazard and expense into a valued resource with potential to significantly reduce foreign oil imports and domestic consumption. Sale of CAT-based bioproducts enable carbon capture and re-use with the potential for less than 10% increase in cost of electricity, an economic benefit to the industry as well as the ratepayers.

Direct Conversion of Coal

Task 22 – Conversion of Low-Rank Wyoming Coal into Gasoline

Among the strategies for converting coal into liquid fuels, direct liquefaction (DCL) is considered as one of the most environmentally friendly, resource-conserving, and technically efficient approaches. DCL breaks the coal species – a three-dimensional network of alkylated polycyclic aromatics, Figure 7 – into small hydrocarbons and increases their H:C mol. ratio from ≤ 0.7 to ≥ 1.7. In DCL, a yield of hydrocarbon product liquid in excess of 70% wt. has been demonstrated on a pilot scale. Overall, thermal efficiency (% calorific value of the input fuel converted to finished products), for DCL averages at 67%, while the value for indirect liquefaction typically does not exceed 50%. Importantly for the targeted application, DCL preserves the cyclic structures inherent in coal, converting the coal matrix into a liquid hydrocarbon mixture rich in naphthenes – valuable components of transformer and engine oils and jet fuels.

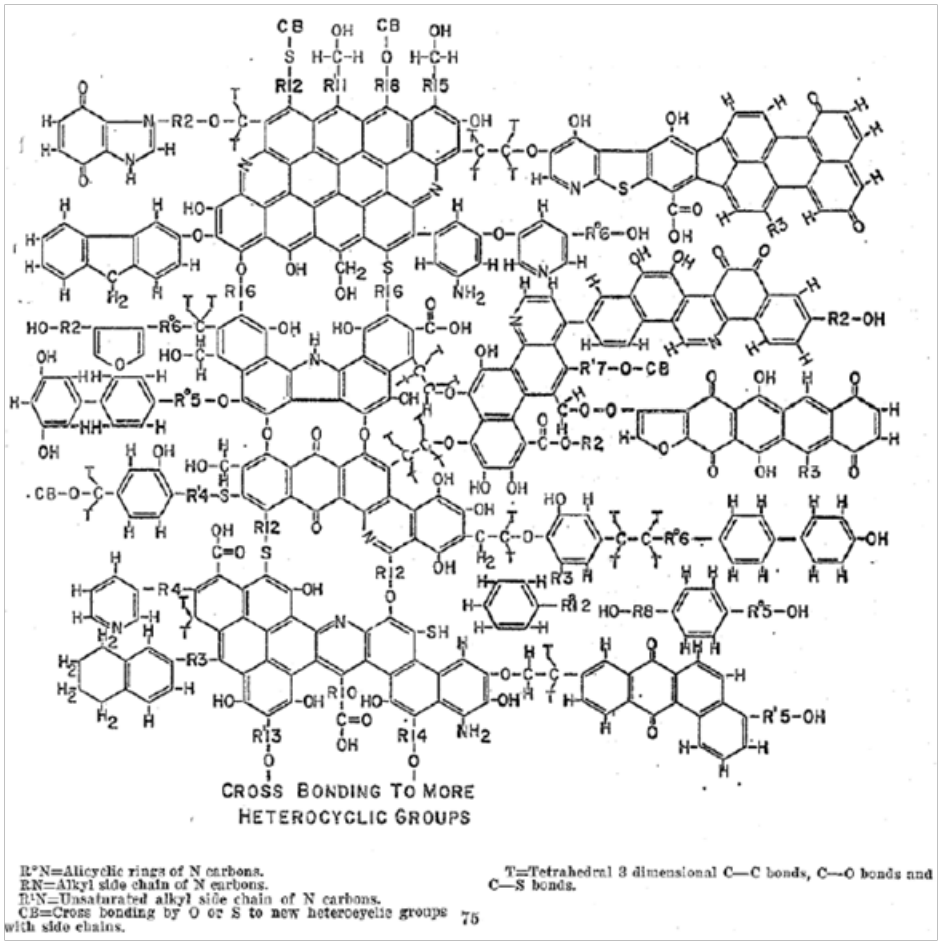

Figure 8. Supposed structure of mid-rank coal

Under the auspices of the Cooperative R&D Program, early work involved solvothermal depolymerization (STD) of coals and lignin. A series of experimental runs performed primarily in a batch reactor as well as in a newly developed continuous-flow and fixed-bed reactors. The effect of the reaction conditions (the nature of solvent, solvent/lignin ratio, temperature, pressure, heating rate, and residence time) on the conversion of carbonaceous feedstocks was investigated with not so encouraging results. Pure water, water-methanol, and water-phenol mixtures were used as solvents. Although a significant progress has been achieved in controlling the lignin conversion into small-molecular-weight components, the side reactions – formation of considerable amounts of char and gaseous products – appeared to be unavoidable. Furthermore, the conversion of coals was found to be substantially smaller than in conventional direct liquefaction

Focus of the work then shifted to studying better-performing Bergius-type process – direct liquefaction of carbonaceous feedstocks involving organic solvents and high pressures of hydrogen (DCL). The effect of a number of additives (including lignin, model lignin compounds, lignin-derivable chemicals, and inorganic radical initiators), solvents, and catalysts on DCL was systematically studied. Most additives did not appreciably affect the process at all

or had a negative effect on the conversion. Ammonium persulfate $(NH_4)_2S_2O_8$ has a pronounced positive effect, increasing the total conversion by ~10% and, in particular, increasing the yield of hexane-soluble oil fraction. While possibly not practical, use of persulfate demonstrates a promising concept and identifies a novel way towards DCL intensification – utilizing radical initiators. In certain conditions, Raney Ni was found to increase the conversion of DCL by as much as 20% and to increase the yield of oil fraction by as much as 35%. Contrary to other catalysts, nanoparticles of metallic Ni can be regenerated after liquefaction using well-developed Mond process.

Overall, the research completed showed that a judicious choice of catalysts, solvents, and additives might enable practical and economically efficient direct conversion of Wyoming coals into liquid fuels.

Integration of Advanced Conversion and Utilization Technologies with WRITECoal™

Task 05 – WRI's Pre-Gasification Treatment of PRB Coals for Improved Advanced Clean Coal Gasifier Designs

Task 19 – A Novel Integrated Oxy-combustion Flue Gas Purification Technology: A Near-Zero Emissions Pathway

Under previous cooperative agreements WRI developed a patented coal upgrading process, WRITECoal™, that is uniquely applicable to high moisture fuels such as subbituminous and lignite coals. Under the Cooperative R&D Program, the technology was integrated with IGCC and oxy-fired pc power plants.

Novel IGCC configuration with WRITECoal™ (Figure 9) offers key benefits such as increase in conversion efficiency, reduction in emissions, including volatile species like mercury, arsneic and selenium that are evolved during the thermal treatment of the coal prior to gasification. Water liberated during upgrading can be used to offset raw water consumption. The concept also uses recycled CO_2 as an oxidant. The net result of these features is a reduction in the size of the gasifier, reduction in parasitic load from the Air Separation Unit (ASU), and an overall increased power output from the integrated system per unit of coal feed. Overall plant capital costs are also reduced.

As a part of the work conducted under the Cooperative R&D program, WRI teamed with GTI in the testing and assessing the performance of WRI upgraded coals in their gasification systems. WRI also teamed with EEI and URS E&C in performing an economic study of the commercial-scale application of the integrated WRI WRITECoal™ gasification/IGCC process.

The WRITECoal™ gasification/IGCC process shows improved gasifier cold gas efficiency and IGCC efficiency, unique syngas compositions and the ability to use recovered water/steam for IGCC use and CO2 recycle as an oxidant source in the IGCC system.

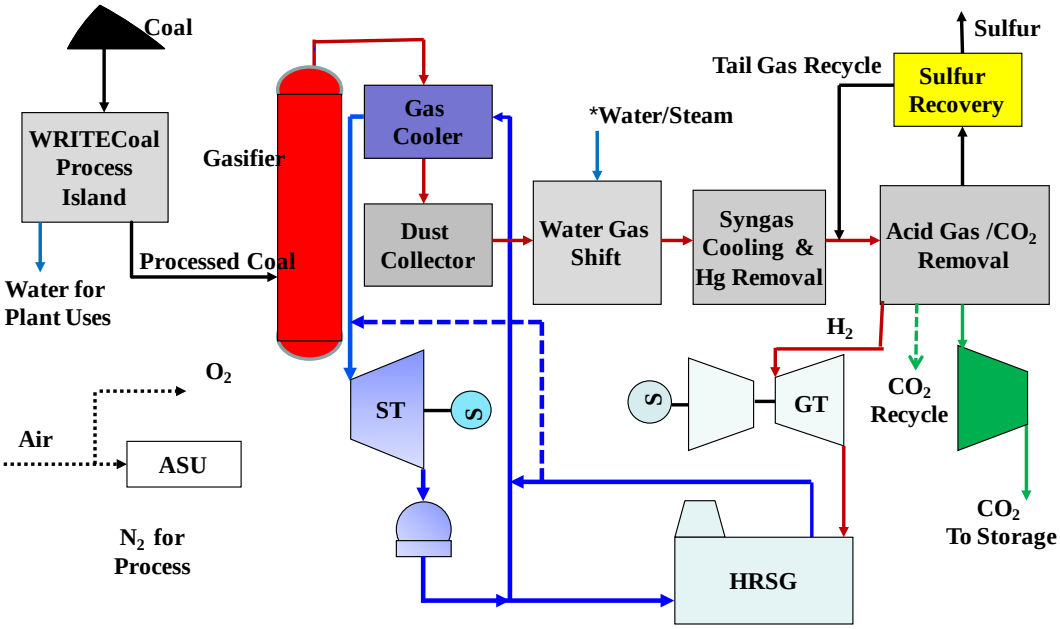

Figure 9. Schematic of a Typical WRITECoal™ Gasification/IGCC Integration

Study of the WRITECoal™ process integrated with an existing oxy-combustion pulverized coal (pc) power plant (Figure 10) showed that the process is feasible with attendant emission control and increased plant output and lowered cost of electricity (COE). In addition, the potential for generating a high CO_2-rich flue gas that is amenable for separation and sequestration was established.

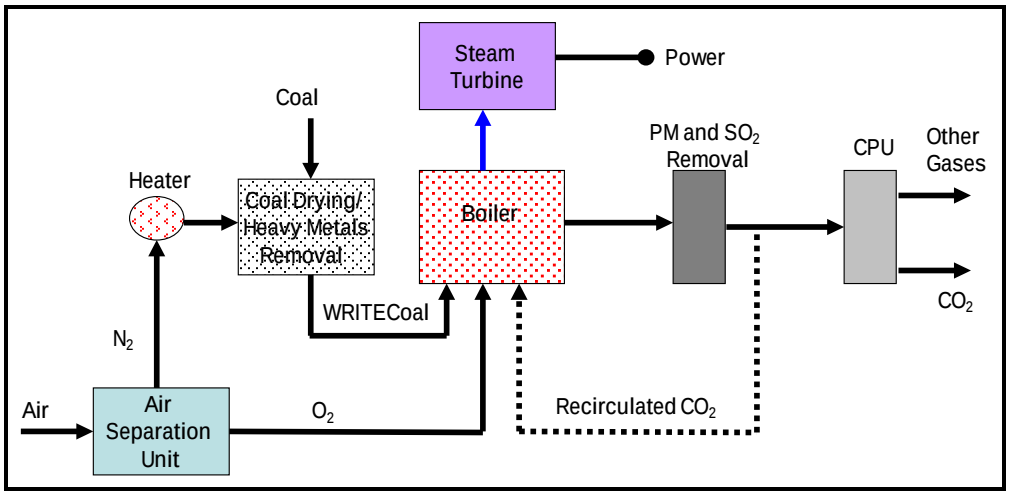

Figure 10. Schematic of the WRITECoal™-Based Oxy-Combustion Plant

Work completed showed that the deployment of the WRITECoal™ process can improve both oxy-fired and air-fired systems heat rate and COE. The WRITECoal™ oxy-combustion process

has higher efficiency, lower net heat rates and lower cost of electricity compared to oxy-combustion without WRITECoal™ and compared with air-fired units with Econamine CO_2 capture.

Further development of the WRITECoal™ technology requires a scale-up of the process to a larger scale (e.g., 5-10MWth) demonstration to resolve possible scale-up and integration issues.

Hydrogen Production

Task 21 – Hydrogen Separation
Task 14 - Novel Gasifier for Wyoming Coals
Task 15 - Gasification Kinetics with a Drop Tube Reactor

The driver for these tasks was the production of hydrogen from fossil and renewable solid carbonaceous feedstocks. Task 15 was proposed as a collaboration with a UW faculty to develop a laboratory-scale set-up to investigate the gasification kinetics. Task 14 involved the installation and operation of an Emery Energy gasifier (Figure 11) at the WRI Advanced Technology Center and to operate it with various coals, biomass and coal-biomass mixtures. Task 21 dealt with development of an integrated water-gas shift catalyst and hydrogen separation membrane module to produce hydrogen from syngas.

Figure 11. Flex-Fuel Gasifier installed at the WRI's Advanced Technology Center

Under the Cooperative R&D Program, the Flex-Fuel gasifier ran for a total of 1,376 hours producing a syngas suitable for synthesis to fuels and chemicals, meeting all the stated objectives.

A hydrogen test facility was assembled under the Cooperative R&D Program to test two different approaches to hydrogen separation from synga, (a) sorbent-based separation and (b) membranes.

Testing of a thermal cycle process based on a barium cerate-based sorbent showed that in the temperature regime where such a sorbent could be operated suffered from water and carburization issues from reverse water gas shift and Boudouard Reactions. The process as proposed indeed offers advantages however, hydrogen absorbent needs to be developed which is either tolerant of the presence of water in the gas stream or works in a temperature range where reverse water gas shift and Boudouard reactions are favored.

Testing of amorphous alloy-based membranes showed them to be stable in the 200˚ - 300˚ C range. These new membranes on porous stainless steel tubes can be easily incorporated into commercial devices. Similarly, polymer membranes based on polyimides and polyamides have been successfully tested on porous stainless steel substrates in coal derived syngas for over 1000 hours and as hollow fiber bundles for up to 400 hours.

Oil Refining/Upgrading

Task 02 – Petroleum Processing Efficiency Improvement
Task 10 - THAI Process for Heavy Oil
Task 24 - Reduction of Heavy Oil Viscosity Using Solid Sorbents

Under our previous cooperative agreements, a series of tasks led to the development of a predictive model for petroleum residua coke formation with the expressed intent that rapid laboratory diagnostic analyses or on-line analytical concepts will lead to refining efficiency improvements. Those concepts were further developed under the Cooperative Research and Development Program. WRI's Asphaltene Determinator developed unfer the Program is a solubility based separation technique that can be used to optimize distillation efficiency, optimize hydrotreater efficiency, replaces the use of gravimetric asphaltenes, and allows the selection of selection of optimal oils for refinery processing

As a part of the Cooperative Research and Development Program, methods and techniques were developed to reduce the viscosity of heavy oils such as Canadian bitumen. One of the technologies developed and tested involves the use of solid sorbents to preferentially adsorb highly pericondensed polar aromatic molecules from oil, resulting in lowered viscosity. The technology has been licensed to a major oil company.

Commercial Products Development

Task 03 – Integrated Freezer System

As a part of the Cooperative Research and Development Program, work was conducted to develop an integrated freezer system that uses a frozen phase change liquid (PCL) formulation in specifically modified coolers to maintain freezer temperatures for shipping environmental samples from the field to the laboratory. Ice packs and commercial freezer packs are currently used to keep environmental samples for volatile organic compound (VOC) analysis at

temperatures near 4 ºC as a means of preservation during shipment to the laboratory for analysis. Using freezing as a preservation technique, sample holding time can be extended from 48 hours to 14 days.

Figure 12. Completed Freezer System

The integrated freezer system design developed under the Program includes foam-foil insulation along the walls, top, and bottom of a commercial polyethylene cooler and a less expensive polystyrene cooler. Thin sheets of frozen PCL line all six walls of the cooler. The cooler design meets the ASTM / EPA criteria for frozen preservation during storage/shipping.

Commercial Products Development

Task 07 - X-wand

Under the Cooperative Research and Development Program, WRI developed a new methodology and a test kit to screen soil or water samples for halogenated volatile organic compounds (HVOCs) in the field. The technology has been designated the X-Wand® screening tool. The new device uses a heated diode sensor that is commonly used to detect leaks of refrigerants from air conditioners, freezers, and refrigerators. This sensor is selective to halogens. It does not respond to volatile aromatic hydrocarbons, such as those in gasoline, and it is not affected by high humidity. The use of X-Wand is described in ASTM D 7203-06, (TCE)-Contaminated Media Using a Heated Diode Sensor.

Figure 13. X-Wand Screening Tool

Produced Water Treatment

Task 17 - Evaluation of Membrane-based Treatment Process for Desalination of Produced Water from Oil Production

Produced water is subsurface formation water co-produced during oil and gas production. Produced water from oil production contains salts and hydrocarbons that are damaging to the environment. Therefore, treatment processes which remove hydrocarbons, mainly oil & grease, and reduce total suspended solids (TSS) and total dissolved solids (TDS), are required before discharging produced water into the environment.

As a part of the Cooperative Research and Development Program, work was completed to evaluate treatment options for produced water that can meet the proposed discharge limits. The project involved operating a membrane-based water treatment system at an oil production site

located in Fremont County, WY, where large amounts of produced water were discharged. A membrane based treatment train was implemented at the site and was composed of pre-treatment unit operations to remove hydrocarbons and other organic matter before desalination by membrane technology. Based on extensive testing, the final overall system design (Figure 14), was developed and the test results demonstrated that concentrations of most key constituents in the water, including oil & grease, TSS, TDS, chloride, toluene, ethylbenzene, and xylene, could be removed to meet state DEQ requirements.

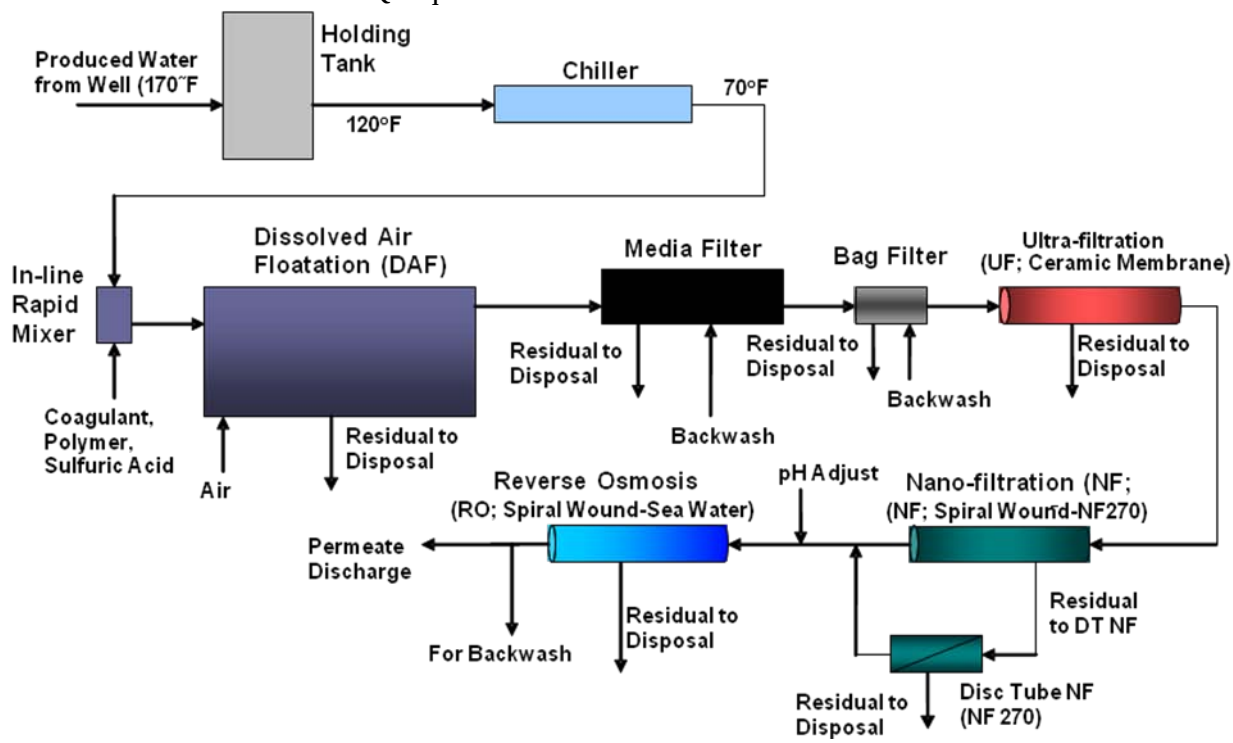

Figure 14. Process Flow Diagram of Final System Design for Produced Water Treatment

IN CONCLUSION

Over the course of the Program, a total of 26 tasks were proposed for DOE approval. The Program was conceived as a five-year Cooperative Research and Development Program, but funds were provided only for three of the five years. Therefore, some of the work originally conceived and proposed could not be brought to a logically conclusion. Nevertheless, the Program was quite successful in leveraging commercial, industrial, University of Wyoming and state of Wyoming participation.

Over the five-year period of performance of the Cooperative Research and Development Program, WRI put in place projects utilizing a total of $7,216,642 in USDOE funds. Against this funding, cosponsors have committed $4,710,373 in cash and $2,730,456 in-kind contribution to produce an R&D program valued at $14,488,057. Using the deployment of the federal funding with non-federal participation, over the period of performance, the cosponsors contributed more

dollars than the federal funds. Nearly 51% of the funding for the Program was derived from non-federal sources. A measure of the enthusiasm of the support for the research and development activities undertaken is cash contribution by cosponsors. Non-federal cash contribution for projects conducted under the Cooperative Research and Development Program averaged in excess of the 63% of the cost share.

Under the Program, energy- and environment-related tasks emphasized fossil and renewable resource development. Fossil energy projects in the most part dealt with economically reducing and or eliminating environmental consequences of fossil energy systems with renewable energy projects addressing economic issues to make renewable systems more competitive.

Technologies being brought to commercialization as a result of the funds provided by the Cooperative Research and Development Program contribute to the overall goals of the USDOE and the nation. Each has broad applicability both within the United States and abroad, thereby helping to enhance the competitiveness of U.S. energy technologies in international markets and assisting in technology transfer.

As envisioned during the establishment of the Program, the Cooperative Research and Development Program funded high-risk research in areas based on several factors:

- Our Nation's need for cheap electricity underscored the need to research, develop and demonstrate technologies for cleaning the stacks of existing coal-burning power plants.
- Our Nation's need for cheap electricity in the carbon constrained future, underscored the need for research, development and demonstration of enabling technologies toward zero emissions power plants of the future.
- Our Nation's appetite for transportation fuels and our desire to maintain our way and quality of life underscored the need for research, development and demonstration of technologies for the production of clean-burning liquid fuels.
- Our Nation's desire for energy independence underscored the need for technologies to upgrade and convert North American resources, unconventional resources such as oil shale.
- Our Nation's desire to curtail and reduce carbon emissions means cost-effective, sustainable renewable resources need to be integrated in our future energy mix. Technologies that co-develop renewable options within the fossil systems are likely to be more cost effective and efficient than stand-alone.
- Wyoming is the Btu capital of the Nation. There is a need for research activities dedicated to developing value-added energy products and associated economic benefits for the state and the region.

Under the Cooperative Research and Development Program and earlier Cooperative Agreements, WRI has responded to the energy research needs of our Nation and the region. The program has contributed significant benefits over the years for industry.

- WRI has built a modular, well-instrumented coal combustion test facility that mimics a coal-fired utility boiler in residence time and furnace temperature profile. This facility is being used for technology development and technology verification projects for national and international utilities, for coal technology companies, and for combustion and emissions control equipment manufacturers.

    - working with our clients, we are testing new and cheaper methods for reducing NOx emissions such as injection of coal and biomass-based slurries, injection of hydrogen and syngas, injection of ozone;
    - working with our clients, we are testing cheaper sorbents and methods for capturing mercury. One such scheme reinjects the unburnt carbon recovered from the fireball of the boiler to capture mercury. This technology, thief carbon, can reduce the cost of mercury capture to a fraction of that for conventional activated carbon. Thanks to our cooperative agreement with the USDOE, the thief carbon WRI made in the CTF was recently injected by a utility in a 600MW unit to show that indeed thief carbon is nearly as effective as activated carbon;
    - working with our clients we are testing advanced combustion concepts such as oxy-fuel combustion as a multi-pollutant control strategy for not only the sequestration-ready, power plants of the future but developing a technology that can benefit our existing fleet of power plants; and
    - working with our clients, we are looking to the future and testing cheaper ways of making oxygen. Novel concepts for separating oxygen from air for use in the coal combustion processes are being tested at the combustion test facility.

- WRI has developed synthesis technologies to produce transportation fuels. Catalyst and reactor development projects have enabled technologies that can convert any carbonaceous feedstock into a mixture of alcohols, and the mixture is ready for use as a gasoline blend.

- Compact reactor technology developed under the Program is making small-scale, modular GTL plants economically possible thereby making stranded natural gas and flare gas a resource for conversion into transportation fuels and chemicals. In conjunction with the appropriate gasification scheme synthesis technologies developed will eventually make coal-to-liquids technology economically and environmentally competitive. For biogas-based system, this technology is a means of capturing and converting green house gasses into a useful product.

- Under the auspices of the Cooperative Agreement, WRI has developed and patented a process for upgrading PRB coal (WRITECoal™ process) by thermally removing mercury prior to combustion at the power plant, thus eliminating the need for costly carbon injection to meet new mercury regulations. A recent economic study for the Electric Power Research Institute has shown this process to be one of the lowest-cost technologies

for removing mercury from PRB coal-fired power plants. The deployment of the WRITECoal™ process can improve the efficiency of both oxy-fired combustion systems and the gasification technologies.

- Coal and biomass upgrading technologies developed under the Cooperative Research and Development Program enable the utilities to cofire coal and biomass in their boilers without any major equipment modifications.

- As a part of the Cooperative R&D Program, WRI developed a patent-pending bacteria-based CO_2 reuse technology, Chemoautotrophic Biological Carbon Capture Process (CAT process). The CAT process promises to be an alternative form of biological carbon capture that can address many of the short comings of Algae-based systems. The process is based on a synthetic symbiosis of bacteria, in which a chemical energy shuttle is created through the recycling of inexpensive and abundant materials. Bacteria from bioreactors can be harvested and refined into bioproducts, such as biofuels, bioasphalt binder, green plastics and other petroleum replacement products. The non-lipid residue from the biorefining process can be recycled as nutrients for the bioreactors.

- As a part of the Cooperative Research and Development Program, methods and techniques were developed to reduce the viscosity of heavy oils such as Canadian bitumen. One of the technologies developed and tested involves the use of solid sorbents to preferentially adsorb highly pericondensed polar aromatic molecules from oil, resulting in lowered viscosity. The technology has been licensed to a major oil company.

- WRI has developed several environmental testing and sampling instruments currently (or soon to be) commercially available. Examples include Soil Test Kit for in-the-field quantitative analysis of hydrocarbon contaminants in soil, integrated storing field soil samples for volatile analysis, and the X-Wand, an instrument for measuring halogenated volatile organic compounds, a common but difficult to measure class of contaminants. For shipping and storing environmental samples, WRI also developed an advanced Phase Change Liquids-based cooler system. All of these products are commercially available.

Cooperative Research and Development Program was a successful program resulting in several publications and technical presentations by WRI staff. Technological developments also led to several patents. A list of publications and patents applications and filed under the Program is presented in a following section.

Conference Papers, Proceedings, and Journal Articles

WRI promotes technology transfer by encouraging WRI scientists and engineers to publish all non-confidential research they undertake. Following is a list of publications and presentations based on the work completed under the Cooperative R&D Program.

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Jin, S., P.H. Fallgren, J.M. Morris, and R.B. Gossard. 2008. Biological source treatment of acid mine drainage using microbial and substrate amendments: microcosm studies. *Mine Water and the Environment* 27:20-30.

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Morris J.M. and Jin. S. 2009. Influence of NO_3 and SO_4 on Power Generation from Microbial Fuel Cells. Chemical Engineering Journal, 153: 127-130.

Morris, J.M., Fallgren, P.H. and Jin, S. 2009. Enhanced denitrification through microbial and steel fuel-cell generated electron transport. Chemical Engineering Journal, 153: 37-42.

Morris, J., S. Jin, B. Crimi, and A. Pruden. 2008. Enhanced anaerobic biodegradation of diesel in microbial fuel cell. Chemical Engineering Journal, 145: 160-163.

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Jin, S., Fallgren, P., Morris, J., and Edgar, E. 2008. TCE degradation in groundwater by supplemented electrons. Chemical Engineering Journal, 140: 642-645.

Jin, S., Fallgren, P.H., Morris, J. M., and Cooper, J.S., 2008. Assessment of diesel contamination in groundwater using electromagnetic induction geophysical techniques. Journal of Environmental Science and Health-Part A, 43: 584-588.

Jin, S., Fallgren, P.H., Morris, J. M., and Cooper, J.S., 2008. Source treatment of acid mine drainage at a backfilled coal mine using remote sensing and biogeochemistry. Water, Air and Soil Pollution, 188: 205-212.

Morris, J. M. and Jin, S. 2008. Feasibility of using microbial fuel cell technology in bioremediation of hydrocarbons in groundwater. Journal of Environ. Sci. Health, Part A., 43: 18-23.

Fallgren, P.H. and Jin. S. 2008. Biodegradation of Petroleum Compounds in Soil by a Solid-phase Circulating Bioreactor with Poultry Manure Amendments. Journal of Environ. Sci. Health, Part A., 43: 1-7.

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Khalid Omar, Philip Martin, Vijay Sethi, Robert Carrington, Brian Higgins, Guisu Liu and Richard Boardman, "Multi-pollutant Emissions Control from Coal Combustion with Oil Shale", Proceedings of the 34th International Technical Conference on Coal Utilization and Fuel Systems, Clearwater, FL, 2009.

John F. Schabron and Joseph F. Rovani, "Asphaltene Subfractions: New Insight into Heavy Oil Chemistry" presentation at national ACS symposium on Heavy Oil, Production, and Fouling, San Francisco, March 2010.

John F. Schabron, Eric W. Kalberer, and Joseph F. Rovani, "Investigation of Liquid vs. Headspace Calibration Standards", invited presentation at the EPRI CEM User Group Conference, Cleveland, OH, May 2010.

John F. Schabron and Joseph F. Rovani, "What's in Your Asphaltenes? Automated Solubility Based Separations Provide More Information than Gravimetric Techniques), invited presentation at Petrophase 2010, Jersey City, NJ, June 2010.

John F. Schabron and Joseph F. Rovani, "Total Pericondensed Aromatic (TPA) Determination and an Alternative to Gravimetric Asphaltenes, National American Chemical Society Meeting, Anaheim, CA March 30, 2011.

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