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WESTERN RESEARCH INSTITUTE

QUARTERLY TECHNICAL PROGRESS REPORT

July - September 1992

OIL SHALE

TAR SAND

COAL RESEARCH

ADVANCED EXPLORATORY PROCESS TECHNOLOGY

JOINTLY SPONSORED RESEARCH

Under Cooperative Agreement DE-FC21-86MC11076

1.0 OIL SHALE

1.2 Oil Shale Process Studies

1.2.2 Process Studies (FY 1991 Mod.)

Objectives. The objective of this task is to investigate the use of a shale oil-derived, recycle oil to mediate the transfer of hydrogen to eastern oil shale. This task is composed of three subtasks: (1) the evaluation of a distillate from eastern shale oil as a recycle oil to mediate hydrogen transfer, (2) the determination of the catalytic hydrogenation conditions necessary to regenerate the recycle oil, and (3) the evaluation of the chemical and physical properties of the liquid products from the process to determine their appropriateness as feedstocks for the production of transportation fuels. The objective for this quarter was to become familiar with the operation of the hydrogenation equipment that was assembled last quarter.

Accomplishments. A series of hydrogenation experiments were conducted using a solution of model compounds.

Procedures. The hydrogenation equipment was operated at 600 and 625°F (316 and 329°C), 1900 psig, and hydrogen flow rates of 6000, 3000, and 2000 scf/bbl. The liquid-hourly-space velocity was one, and the catalyst was Shell 424, which is nickel/molybdenum supported on alumina. The feed to the reactor system was a solution of model compounds consisting of toluene, naphthalene, phenol, pyridine, thiophene, 1-octene, 1,3-pentadiene, and cylohexene. The current series of experiments are being conducted at 600, 575, and 550°F (316, 302, and 288°C), 1700 psig, and a hydrogen flow rate of 2000 scf/bbl. The feed to the reactor is the solution of model compounds.

Results. Plugging of the reactor due to coke buildup on the catalyst bed occurred at a hydrogen flow rate of 2000 scf/bbl and a temperature of 600°F (316°C). However, this may not be the result of the operating conditions established for the catalyst bed, but rather the mode of operation and the temperature of the gas-liquid separator. Increasing the temperature of the gas-liquid separator and not operating the system continuously (all night long) has resulted in no plugging problems. Preliminary evaluation of one of the products (600°F/316°C, 1900 psig, and 6000 scf/bbl) indicates that almost total conversion of the model compounds to saturate compounds occurred at the conditions used. In addition, very little gas was produced, indicating that hydrogenation rather than cracking of the compounds is the predominant reaction. The major gases produced are butane and hydrogen sulfide, probably resulting from thiophene.

1.2.4 Product Utilization Studies (FY 1992)

Objectives. The objective of this research is to determine unique applications of oil shale-derived products that have high market values. The research is concentrated toward development of highly specialized products for roadway pavement applications. The two areas being investigated are pavement joint and crack fillers and interactions of asphalt, including shale oil modified asphalt, with aggregate. The objective for the quarter was to complete testing and measurements on the sample materials.

Accomplishments. Extension testing according to ASTM Method D 3407 was completed in triplicate on all samples. Viscoelastic property measurements and bonding energy measurements were completed on all samples.

Procedures. Extension test samples were prepared in accordance with the procedure in ASTM D 3407. Briefly, one-half inch of the asphaltic material is poured between two concrete blocks that are each 1"x 2"x 3". After cooling, the edges are neatly trimmed and the specimen is placed into the extension testing machine and cooled to 0°F (-17.8°C) for two hours. The specimen is then pulled at a rate of 1/8" per hour until the specimen fails or a total extension of 1/2" is obtained. Three extension cycles comprise a complete test.

Viscoelastic property measurements are obtained by loading a 2 mm thickness of the softened asphaltic material between two parallel plates of a Rheometrics Mechanical Spectrometer, conditioning the sample for 20 minutes at the appropriate temperature, and then performing a dynamic frequency sweep over a range of 0.1 to 100 rad/sec. Data on samples at 140°F (60°C) are obtained on 25 mm plates at a strain of 50%, at 77°F (25°C) on 25 mm plates at a strain of 3%, and at 50°F (10°C) on 8 mm plates at a strain of 1%.

Viscoelastic property measurements on briquettes prepared with an asphaltic material sandwiched between two concrete wafers are obtained on a Brabender Rheotron using constant applied torque. The transmitted torque is recorded on a strip chart recorder. The sample is twisted until a constant slope is obtained on the strip chart recorder and then held fixed at that point until the curve decays to zero or a straight line. Relaxation time and the percent recovery are calculated from the curve.

Bonding energy measurements were obtained by first grinding and sieving the four aggregates (crushed concrete, two silicates, and a limestone) to a -35 to +48 Tyler mesh size. Two to three grams of the sized aggregate is placed into a small wire screen basket. Ten grams of the asphaltic material is placed into the microcalorimeter reaction cell and the wire screen basket containing the aggregate is placed directly above the asphaltic material. The assembly is conditioned in the microcalorimeter for 24 hours before contacting the aggregate and the asphalt. After contacting, a thermopile assembly detects the energy released as the asphalt bonds to the aggregate. The signal from the thermopile is amplified and recorded. Using a calibration curve, the area under the curve is expressed in terms of millicalories per gram of aggregate for a given time, typically two hours. All bonding energies were measured at 320°F (160°C).

Results. Results of the experiments are being formulated in the two milestone reports that are in preparation.

1.4 Miscellaneous Basic Concepts Studies and Technical Support

1.4.2 Unconventional Applications and Markets for Western Oil Shale (FY 1989)

Objective. The objective for the quarter was to complete the report on shale oil upgrading.

Accomplishments. The report, entitled "Upgrading of Western Shale Oil by Pyrolysis and Hydrotreating," was completed and submitted. This task is completed.

2.0 TAR SAND

2.2 Process Development

2.2.1 Recycle Oil Pyrolysis and Extraction (ROPE™) Process (FY 1991)

Objectives. The first objective of this task is to design and initiate fabrication of a modified 6-inch bench-scale unit that includes a twin-screw conveyor and a new feed system. This system will permit long runs required to evaluate the application of the ROPE™ process to tar sands. The second objective is to develop a process for the treatment of petroleum production wastes commonly termed tank bottom wastes. These wastes are a combination of oil, water, and solids with a water and solids content too high for refinery acceptance of the oil. The objective for the quarter was to prepare milestone reports 2.2.1B, results of two long-term tests of the modified 6-inch ROPE units, and 2.2.1C, results of tests on tank bottoms.

Accomplishments. Evaluation of data from the tests has been completed and preparation of the reports continued. The work on tank bottoms has resulted in funding from a private source, the state of Wyoming, and the JSR program for further development of the process.

3.0 COAL RESEARCH

3.1 Underground Coal Gasification

3.1.2 Rocky Mountain 1 Environmental Evaluation (FY 1992)

Objective. The objective for the quarter was to prepare the milestone report on the June 1992, limited suite sampling.

Accomplishments. The milestone report, "Sampling and Analyses Report for June 1992 Semiannual Postburn Sampling at the RM1 UCG Site, Hanna, Wyoming," was prepared and submitted. This task is completed.

3.2 Coal Combustion

3.2.2 Combustion of Low-Rank Coals and Industrial Wastes (FY 1991)

Objective. The objective for the quarter was to complete the report on preliminary tests and combustor design (milestone 3.2.2C).

Results. Evaluation of the study findings indicate little of technical significance to report. A request has been submitted to eliminate milestone 3.2.2C.

3.2.3 Gasification and Cogeneration (FY 1992)

Objectives. The objective of this research is to select and develop a combustor design and hot-gas cleanup system suitable for use with low-sulfur coal. The objectives for the quarter were to evaluate the experimental data and begin preparation of the milestone report.

Accomplishments. Experimental work, data reduction, and data analysis have been completed. The milestone report is being prepared.

Procedures. The WRI 6-inch fluidized bed reactor was used as an air-blown gasifier. Bed depths used were in the 8- to 13-inch range.

Results. Findings are consistent with those reported earlier that were based on the preliminary analysis of the data: that western sub-bituminous coals can be partially gasified at temperatures low enough that some of the contaminants, such as alkali compounds deleterious to downstream components in 2GPFBC systems, are not volatilized, remaining in the char. As a result, the hot-gas stream cleanup requirements for the overall system are reduced.

3.3 Integrated Coal Processing Concepts

3.3.4 Coal Coprocessing (FY 1992)

Objectives. The objectives of this research are to define more closely coprocessing conditions that improve the liquid yield through more efficient dispersion of iron-based catalysts and to characterize the acid sites on supported catalysts and their impact on the formation of coke. The objectives for the quarter were to complete the preparation of the experimental plan, to begin the experimental series involving pretreatment prior to coal/heavy oil coprocessing, to continue the assembly and evaluation of various catalysts for testing using solid-state nuclear magnetic resonance (NMR) spectroscopic analysis, and to continue the analysis of the products obtained from commercial organizations regarding hydrogen utilization.

Accomplishments. Preparation of the experimental plan was completed and submitted for review. A series of experiments were initiated to evaluate pretreatment conditions on the coprocessing yield of liquids from Illinois #6 and Eagle Butte (Powder River Basin, Wyoming) coal with Lloydminster crude oil residue. The Lloydminster crude oil was distilled to produce a 400°F+ (204°C+) residue. Four spent catalysts were received from the University of Wyoming, Chemical Engineering Department. Regarding the tracking of hydrogen during coal coprocessing and liquefaction, several samples from UOP and Consol were analyzed and the data were being evaluated.

Procedures. The pretreatment and coprocessing experiments are being conducted in tubing bombs. The pretreatment conditions include temperatures of 437, 527, and 617°F (225, 275, and 325°C) and cold pressures of 400 and 800 psig. The experiments are conducted in an atmosphere of helium or hydrogen, and the run time is 30 minutes. The coprocessing experiment is conducted at 752°F (400°C), 800 psig cold hydrogen, and has a run time of one hour. The catalyst is oil soluble, iron pentacarbonyl. To evaluate the effect of the various pretreatment conditions, coal conversion will be measured by determining the percentage of tetrahydrofuran solubles, and hydrogen consumption will be determined by gas chromatography.

The spent catalyst samples are being analyzed by carbon-13, solid-state NMR. It is planned that the aromaticities obtained for these samples will be correlated with liquefaction yield.

3.3.5 Agglomerating and Stabilizing Dried Coal (FY 1992)

Objectives. The objective of this task is to develop and test concepts for stabilizing dried Wyodak coal from the Powder River Basin. Objectives for this quarter were to complete tests and begin preparation of the milestone report.

Accomplishments. Other research activities precluded work being conducted on this task during this quarter.

3.3.6 High-Heating-Rate Process Studies (FY 1992)

Objectives. The objective of this research task is to determine oil yields from the rapid pyrolysis of coal in an entrained flow reactor. The objective for the quarter was to perform high-heating-rate studies in hydrogen-nitrogen and nitrogen atmospheres.

Accomplishments. Modifications were made to the system and a total of fourteen experiments were performed.

Procedures. In modification to the system, the pressure shell is now being filled with argon and the gas chromatograph has been reconfigured to detect argon. This modification allows the operators to quantify leakage from the pressure shell to the reactor. A fine filter has been added to the exit gas stream downstream from the char separator and liquid knockout traps. Anhydrous $CaSO_4$ is now being added to liquid products to extract water. This appears to provide for better water measurement than was previously attainable.

Results. Tests of up to two hours duration are now routine for western subbituminous coal. Experiments with eastern agglomerating coals are difficult and, because of intermittent plugging, provide no useful data.

3.4 Solid Waste Management

3.4.1 Use of Solid Waste for Chemical Stabilization (FY 1991 and FY 1992)

Objectives. The objective of this research is to determine a use for fly ash, such as that produced as waste during operations at the Dave Johnston Steam Electric Project, that would be economically and environmentally reasonable. Dave Johnston fly ash has been shown to have some affinity for selected organic compounds that have created problems in the environment. The objectives for the quarter were to continue evaluation of the data and to work on preparation of the experimental plan, 3.4.1A.

Accomplishments. Evaluation of the mass spectrometric data is continuing and the experimental plan is nearly completed.

3.4.2 Use of Solid Waste for Physical Stabilization (FY 1991 and FY 1992)

Objectives. The objectives of this research are: (1) to develop an understanding of the key properties of fly ash that are responsible for cementation and stabilization, (2) to study sodium and calcium wastes generated from clean coal technology in an effort to develop waste disposal technologies that result in stable land fills, (3) to provide detailed information on potentially toxic compounds from cemented fly ash and to evaluate the use of fly ash to enhance stabilization of hazardous materials planed in landfill sites, and (4) to develop methods to separate organic selenium species that may be found in coal fly ash materials. The objectives for this quarter were to complete research experiments and to complete the report on coal fly ash and soil stabilization mechanisms (FY 91 milestone 3.4.2C).

Accomplishments. Experiments described in the revised experimental plan have been completed. The FY 91 milestone report 3.4.2C has been written and is in final typing. Findings of the literature survey for FY 91 milestone 3.4.2A were not significant and a request has been submitted to eliminate this milestone. A request has also been submitted to incorporate the results of the experimental research in the report on the continuing work in the new cooperative agreement.

Procedures. Compressive strength characteristics for samples from the soil stabilization, the fly ash conditioning, and the physical stabilization of waste materials research were done using compression testers equipped to handle loads up to 10,000 psi.

4.0 ADVANCED EXPLORATORY PROCESS TECHNOLOGY

4.1 Advanced Process Concepts

4.1.7 In Situ Model of Pyrolysis (FY 1990)

Objectives. The objectives of this research effort are to predict solute transport and develop new control concepts that incorporate some of the more recent geochemical data obtained from research projects. The objective for the quarter was to make modifications to the 3-dimensional reservoir simulator.

Accomplishments. The horizontal well algorithm has been installed in the 3-dimensional reservoir simulator. It has been mechanistically checked for proper performance.

Procedures. Implementation of the horizontal well algorithm allows the user to orient the well in either the x- or y-direction and to "complete" the well in a single block or through several blocks. The single well completion may be useful for the simulation of slant injection or production wells.

4.1.8 APT Method Development (FY 1990)

Objectives. The objective of this task is to develop a technique for characterization of heavy distillates and residues. The objective for this quarter was to complete the fabrication of the system.

Accomplishments. A number of equipment and electronic problems over the course of this project have caused unexpected failures in getting the instrument operational. Allocated funds have nearly been depleted. A request has been submitted to terminate this task.

4.1.9 In Situ Process Modeling (FY 1991)

Objectives. The objectives of this research task are to conduct laboratory simulations and develop a numerical model for the simulation of the steamflood process in fractured reservoirs. The objectives for this quarter were to complete resaturation of the block samples to be used for laboratory simulation and conduct tests using blocking agents.

Accomplishments. Resaturation of the block samples was completed and simulation tests were initiated.

Procedures. The procedures are: (1) determine the appropriate blocking agent to use for steamflooding the Shannon formation, (2) conduct two three-dimensional physical simulations of the steamflood process with a blocking agent in samples containing either a vertical or horizontal fracture, and (3) transfer the data and results for numerical simulations.

Results. The Shannon sandstone block samples have been saturated. Core floods using the identified blocking agents are being conducted. The tests have not validated the projected performance as stated by the supplier of the commercially available blocking agent. Discussions have been held with the suppliers and other suppliers to identify the nonperformance problems and to identify better agents.

4.2 Advanced Mitigation Concepts

4.2.1 Treatment of Oil and Gas Product Waters (FY 1991)

Objective. The objective for the quarter was to complete the milestone report.

Accomplishments. The report was completed and submitted. This task is completed.

4.2.3 CROW™ Development (FY 1992)

Objectives. The objective of this research is to obtain baseline data that show the effectiveness and environmentally safe use of chemicals to enhance the CROW process. The objective for the quarter was to prepare milestone 4.2.3A, the experimental plan.

Accomplishments. Preparation of the experimental plan was nearly completed. Contaminated soil samples for the tests have been received from Midwest Gas and the initial analysis of the material has been started.

Procedures. Findings from a related study that is funded privately were evaluated in order to prepare a more meaningful experimental plan for this study.

4.2.4 Environmental Treatment of Process Gases (FY 1992)

Objectives. The objective of this research is to optimize vortex combustor design to obtain maximum thermal destruction efficiency at selected temperatures and retention times. The objective for the quarter was to prepare the milestone report on completed research.

Accomplishments. A draft of the milestone report was prepared and is undergoing internal review.

4.3 Oil and Gas Technology

4.3.1 Enhanced Oil Recovery (FY 1992)

Objectives. The objective of this research task is to determine the enhancement of oil recovery using steamflooding in conjunction with chemicals or gases and horizontal wells. The objective for this quarter was to continue preparation of the experimental plan, milestone 4.3.1A.

Accomplishments. A draft of the experimental plan is being prepared.

4.3.2 Natural Gas Cleanup (FY 1992)

Objectives. The objective of this work is to investigate a less complex and more cost effective method for gas cleanup The method is based on pressure swing adsorption. The objective for this quarter was to prepare the milestone report on the findings of the series of completed experiments to evaluate the pressure swing adsorption process and the regeneration of the adsorbent.

Accomplishments. Preparation of the milestone report is ongoing.

4.3.3 Thermal Reservoir Simulation (FY 1992)

Objectives. The objective of this research effort is to improve the capabilities of WRI's thermal reservoir simulation model. The objectives for the quarter were to continue modification of the compositional model to three-dimensional capabilities and improve execution speed of the model.

Accomplishments. Modifications were made to the model and alternative solution techniques were tested. Three-dimensional aspects of the thermal model were operational and undergoing testing.

Procedures. Enhancements made to the model include: incorporation of horizontal well terms, addition of linear source terms for the study of flow in fractures, ability to complete source/sink terms in single or multiple cell blocks and to orient the terms in either the x-, y-, or z-direction, addition of a hysteresis algorithm for the relative permeability terms, the ability to accommodate variable grid spacing, the capability of specifying either cell-centered or point-centered differencing schemes for the interblock flow terms, the incorporation of gravity-heads and capillary pressures to the interblock flow terms and the source/sink terms, and the ability to partition flow among layers in source/sink terms when constant rate conditions are specified.

Results. In its present state, the model is capable of simulating 1-, 2-, and 3-dimensional problems with thermal effects. The multi-compositional, reaction kinetics portion of the code has not been incorporated at this time. Running even modest size (7x7x7) problems has demonstrated the need for an iterative solver in the model.

5.0 JOINTLY SPONSORED RESEARCH

5.1 Occidental Oil Shale, Inc. Demonstration Program Support

This task was completed in previous quarters.

5.2 Investigation of ROPE Process Performed on Sunnyside Tar Sand

This task was completed in previous quarters.

5.3 Organic and Inorganic Hazardous Waste Stabilization

Objective. The objective for this quarter was to continue evaluation of data generated in simulated weathering experiments.

Accomplishments. Analysis and data reduction continued for samples obtained from weathering experiments. Discussions were held with the EPRI representative regarding redirection of the remaining work, and a proposal for redirection of the final work was submitted.

5.4 Optimization of Product Yields for the CHARFUEL Process

This task was completed in previous quarters.

5.5 Cold Flow Injector Mixer Project for the CHARFUEL Project

This task was completed in previous quarters.

5.6 CROW™ Field Demonstration with Bell Lumber and Pole

Objectives. The objective of this task is to design, construct, and operate a field demonstration of the CROW™ process technology to treat a site contaminated with organic wastes from the wood treatment process. The objective for the quarter was to prepare a technical progress report on the project.

Accomplishments. The technical progress report was completed and submitted.

Results. The two-well pilot test was successful. A proposal for additional work and funding was submitted and approved. The additional work is based on the increased magnitude determined for the project.

5.7 Development and Validation of a Standard Test Method for Sequential Batch Extraction Fluid

Objectives. The objectives for this quarter were to (1) keep informed of the progress of the last collaborative study participant still needing to submit data, (2) receive the last of the collaborative study data and tabulate and evaluate the data, (3) begin statistical evaluation of the collaborative study data, and (4) continue work on moving the draft method through the ASTM balloting process.

Accomplishments. The final set of collaborative study data were received, reviewed, and tabulated. Statistical evaluation of the collaborative study data to estimate the precision of the extraction procedure was started.

Procedures. Statistical evaluation of the collaborative study data is being performed as specified by ASTM Practice D-2777, Standard Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water. The collaborative data analysis includes (1) data tabulation, (2) evaluation of the data for rejection of outlier laboratories, (3) statistical calculations of the mean and standard deviation values, and (4) evaluation of the data for rejection of individual outliers. Data from both the analysis of the extracts and analysis of the analytical standards are being evaluated in this manner to determine total standard deviation and analytical standard deviation. Because the total standard deviation is due to a combination of both errors in performing the extraction procedure and analytical errors, the total standard deviation and the analytical standard deviation can be used to estimate the standard deviation of the extraction procedure. Statistical evaluations are also being performed to determine the effects of filter pore-size and digestion versus nondigestion on the analytical concentrations determined in the extracts.

After statistical evaluation of the data is completed, the ASTM research report and final reports for the project sponsors will be completed. Precision statements to be incorporated into the new method will be written and balloted within ASTM as a modification to the method.

Results. All collaborative study results have been received and tabulated. They are currently being statistically evaluated to estimate the precision of the sequential batch extraction method for the test materials and elements of interest in the collaborative study.

The draft method for sequential batch extraction of waste using acidic extraction fluid was approved as an ASTM standard test method by the society on August 15, 1992. The method will be available from ASTM in November 1992. It is designated as ASTM Method D-5284-92.

5.8 PGI Demonstration Project

Objectives. The objectives for the quarter were to complete the alkalinity study for the combustor, gas cleanup system, and turbine and to provide any additional information needed for the project environmental assessment.

Accomplishments. Work was completed on the corrosion (alkalinity) study of the PGI combustion system and the environmental assessment.

Procedures. As a preliminary step in the PGI Demonstration Project, a limited on-site test program was conducted to characterize the products of combustion in an atmospheric pressure wood-fired combustor. The objectives to the test program were to obtain preliminary information regarding the nature of particulate and vapor-phase alkali compounds produced and to assess any deleterious impact they might have on materials of construction. The proposed work was limited in scope and the data generated were used only as a guide in designing and in selecting equipment and material for a wood-fired gas turbine system.

Particulate and gas sampling were performed at a major sawmill complex where an atmospheric pressure, McConnell combustor was operated on dry saw dust and planar shavings. An air-cooled probe was also exposed to the combustor environment to collect deposit samples at temperatures expected in the gas path of the turbine of the PGI system. Particulate and deposits were analyzed for major ash constituents, and the particle size distribution was determined.

Results. Erosion of gas path components in the wood-fired PGI system should not be a concern, provided that the fuel does not contain large quantities of bark (overall low ash content). In a system fired with dry saw dust and planer shavings the uncontrolled dust loading in the gases entering the gas turbine might be in the 200 to 300 ppm (wt.) range. Conventional and high efficiency cyclones can reduce the level of particulate entering the turbine. Based on the available capture efficiency data, there does not appear to be a major advantage in using a high efficiency device. Both devices fall short of the level of particulate removal required to meet EPA emission levels. Major ash constituents are calcium and alkali. Calcium appears to concentrate in large ash particles, whereas alkali is concentrated in small ash particles. The fuel does not contain enough sulfur to convert all of the alkali and calcium to sulfates, and therefore deposits will contain alkali compounds such as chlorides and hydroxides. Deposits formed on the air-cooled probe were such that they could be easily removed. Therefore in the temperature range expected in the PGI system, periodic washing and/or nut shelling should be able to keep the turbine gas path free of major depositions.

5.9 Mild Gasification of Usibelli Coal

This task was completed in previous quarters.

5.10 Real-Time In-Situ Remote-Sensor Development

This task was completed in previous quarters.

5.11 Enhanced Gravity Drainage in the North Tisdale Reservoir Using Horizontal Wells

This task was completed in previous quarters.

5.12 Solid State NMR Analysis of Powder River Basin Shales

This task was completed in previous quarters.

5.13 Operation and Evaluation of the CO_2 HUFF-N-PUFF Process

Objectives. The objectives of this task are to (1) conduct in situ residual oil saturation determinations, (2) assist in the design, operation, and monitoring of well tests, (3) determine the characteristics of collected fluid samples, (4) assist in the development of phase equilibrium relationships with chemical and thermodynamic properties of selected crude oils, (5) assist in the development of a predictive numerical process model, and (6) assist in the analysis, reporting, and dissemination of collected data.

Accomplishments. All testing has been completed and all field samples have been collected. Analysis of collected field samples is 95% completed. The basic numerical model is operational and special functions that incorporate hysteresis, viscous fingering, and wettability and surface tension changes were used in evaluations. Analysis of samples collected for development of phase equilibrium relationships have been completed.

Procedures. Over 1,867 gas and 1,418 fluid samples have been taken from the field tests of the CO_2 Huff-n-Puff process. Routine gas analysis has been performed on approximately 1,675 of the gas samples. Oil-water separation has been completed on approximately 1,418 of the fluid samples with further analysis on approximately 275 of these samples.

Modifications to incorporate hysteresis, viscous fingering, and wettability and surface tension changes into the numerical model have been made and the model is operational.

The collected samples represent 21 fields in four of the major producing basins of Wyoming. Seven of the fields are part of the programs sponsored by the state of Wyoming; the remaining fields are being sampled for future analysis if funding permits. These additional fields will permit a more comprehensive analysis of the CO_2 Huff-n-Puff process.

Results. Preliminary well responses show mixed results as to the success of the CO_2 stimulations. The single well tracer tests have been shown to be invaluable in determining the potential of candidate wells for the CO_2 cyclic stimulation.

5.14 Fly Ash Binder for Unsurfaced Road Aggregates

Objectives. The objectives are to develop and demonstrate the use of Wyoming fly ash in two construction techniques: (1) fly ash stabilization of soils as applied to unpaved roads and (2) fly ash replacement of portland cement in conventional cement treated bases (CTB). Conventional fly ash stabilization techniques use cement and/or cement plus fly ash at levels of 20-25% to stabilize soils. The costs of these techniques when applied to unpaved roads are in the neighborhood of $30,000 to $40,000/mile. The development and demonstration of novel construction methods employing low fly ash dosage levels could result in lower construction costs, reduced maintenance costs, and a potentially large new market for Wyoming fly ash. Relative to the second fly ash application addressed in the project, fly ash use in standard CTB has been generally 20% of the portland cement content for the Wyoming Department of Transportation projects. Higher replacement percentages would result in lower costs of the CTB mixes through the reduction of portland cement costs and also provide an expanded market for Wyoming fly ashes. The objective for the quarter was to continue laboratory testing of various soils, fly ashes, and aggregates as related to both fly ash stabilization and CTB.

Accomplishments. Laboratory testing of soils, fly ash, and aggregate samples continued under subcontract to the University of Wyoming Department of Civil Engineering. Strength testing with selected soils and the Dave Johnston fly ash have been completed. Testing for freeze/thaw and wet/dry cycle durability are on-going. The testing for the CTB portion of the laboratory testing was completed.

Procedures. For the fly ash stabilization of unpaved roads portion of the laboratory testing, testing was conducted using three additional soils ranging from AASHTO soil types A-1b to A-6 (RS-1, RS-2, RS-5, and RS-7) with two additional fly ashes (Naughton and Laramie River).

The CTB portion of the laboratory testing was conducted using a scoria aggregate from Reno Junction, Type II portland cement from Mountain Cement and the three fly ashes (Dave Johnston, Naughton, and Laramie River). The fly ash replacement of the portland cement ranged from 20% to 75%. Approximately 8% portland cement or cement plus fly ash was used in the CTB mixes.

Results. The strength development at 7 and 28 days for the range of fly ash/soil mixtures ranging from 5% to 25% fly ash were in the range of 100 to 150 psi. This appears to be only marginally adequate for the application on unpaved roads. The results of the durability tests will provide the data on whether or not sufficient strength and durability can be realized at these low dosages under the climatic conditions of the Rocky Mountain region.

Relative to the CTB control mix (0% fly ash replacement), fly ash containing CTB mix strengths increase as the fly ash replacement percentage of portland cement increases to approximately 40 to 55% fly ash replacement and then decrease at higher fly ash replacement percentages. Strengths at 28 days were in excess of the control CTB mix for fly ash replacements of 40% for Dave Johnston, 40% for Naughton, and 65% for Laramie River. Wet/dry and freeze/thaw durability testing of the CTB mixes indicated that, even at the high replacement levels, the CTB mixes showed sufficient durability characteristics.

The interim report covering the fly ash treatment of unpaved roads and in particular the demonstration test section in Converse County that was submitted to DOE, PacifiCorp and STEA for final review and approval, is being converted into a final technical report on the Glenrock demonstration.

5.15 Evaluation of Products Recovered from Scrap Tires for Use as Asphalt Modifiers

Objective. The objective for the quarter was to complete the final report.

Accomplishments. The final report has been completed and submitted. This task is completed.

5.16 Solid State NMR Analysis of Mesaverde Group, Greater Green River Basin, Tight Gas Sands

Objectives. The objectives of this study are to apply solid-state ^{13}C NMR to measure changes in the organic structure of petroleum source rocks (kerogens) brought about by laboratory hydrous pyrolysis experiments and by maturation in the natural geologic environment as a result of depth of burial. These data, in conjunction with other analyses and kinetic measurements, will be used by the University of Wyoming Department of Geology and Geophysics to develop an innovative exploration and production strategy that will optimize the efficient exploitation of tight gas resources in the Mesa Verde Group, Greater Green River Basin, Wyoming. The objective for the quarter was to continue NMR measurements of changes in the organic structure of petroleum source rocks brought about by laboratory hydrous pyrolysis experiments and by maturation in the natural geologic environment as a result of depth of burial.

Accomplishments. Solid-state ^{13}C NMR measurements continued on coal samples from the Lance and Almond coal groups that were subjected to laboratory hydrous pyrolysis experiments in the temperature range of 554-680 °F (290-360 °C). Most of the NMR work has been completed.

Procedures. Solid-state NMR measurements were made on a Chemagnetics CMX 100/200 solids NMR spectrometer. ^{13}C and ^{1}H NMR spectra were obtained using cross polarization with magic-angle (CP/MAS) and combined rotation and multiple pulse spectroscopy (CRAMPS). The ^{13}C measurements were made at a frequency of 25 MHz, and the ^{1}H measurements were made at 200 MHz.

Results. The aliphatic portions of the NMR spectra of the hydrous pyrolysis were deconvoluted into three bands in order to discriminate between oil- and gas-prone carbon types. However, closure on the mass balances from the hydrous pyrolysis experiments was not good. Therefore, quantification of the NMR results will be difficult.

5.17 Flow-Loop Testing of Double-Wall Pipe for Thermal Applications

Objectives. The objectives of this research effort are to develop a numerical model that will predict down-hole steam quality, steam pressure, and temperature, to evaluate InterMountain Pipe Company's double-wall pipe for thermal application, and provide future industrial clients with a fully instrumented flow loop. The objectives for the quarter were to complete evaluation of the test data and prepare the final report.

Accomplishments. Evaluation of the data was completed and preparation of the final report was nearly completed.

5.18 Characterization of Petroleum Residua

Objectives. The objectives of this effort are to develop methods for and characterize petroleum residua from industry participants. The objective for the quarter was to continue characterization of residua samples received from the cosponsor.

Accomplishments. Methods were established and characterization was completed on residua samples provided by the cosponsor. There will be no more activity on this task until the cosponsor sends more residua samples in 1993.

Procedures. All experimental work with the received residua, designated A, B, and C, was completed. Each residuum was deasphaltened in heptane, and the heptane-soluble materials were separated into saturate, aromatic, and polar fractions on activated silica gel. The asphaltenes were separated into four fractions according to apparent molecular size by preparative size exclusion chromatography (SEC). The whole residua were evaluated for elemental composition, trace metals content, carbon residue, simulated distillation profile, specific gravity, pour point, and rheological profile. The asphaltenes and silica gel chromatographic fractions were evaluated for elemental composition, trace metals content, molecular weight, carbon residue, analytical SEC profiles, and aromaticity by nuclear magnetic resonance (NMR) spectroscopy. The preparative SEC fractions from the asphaltenes were evaluated for sulfur content, molecular weight, and trace metals content.

The toluene solutions for the preparative size exclusion fractions from residuum C asphaltenes for molecular weight determinations had to be made above 104°F (40°C) to maintain clear solutions. This had no detrimental effect on the vapor-phase osmometry measurements, which were made as usual at 140°F (60°C).

Results. Material balances showed that the data obtained on the fractions account for the data obtained on the original material. This indicates that the contributions of the properties of the fractions can be studied and related to properties of the whole material.

5.19 Shallow Oil Production Using Horizontal Wells with Enhanced Oil Recovery Techniques

Objectives. The objectives of this task are to demonstrate that enhanced oil recovery techniques can be successfully used with horizontal wells in shallow reservoirs to increase oil production significantly, to validate a numerical model with the use of physical simulations using an implemented enhanced oil recovery process with horizontal wells, and to provide the technical expertise and supervision for the implementation of a pilot test that will use the information generated in the study. The objective for the quarter was to prepare the facilities at the Chetopa Townsite oil field site for the field test.

Accomplishments. Problems were encountered in the well with the down-hole ignitor that had been designed and built to initiate combustion in the reservoir. Another ignitor had to be designed and fabricated to accommodate the well casing placed in the field.

Procedures. Attempts to position the originally designed and fabricated down-hole ignitor in the ground were unsuccessful because the drilling contractor down-sized the ignition well casing from specifications.

A new gas (propane-air) burner was fabricated for slim hole applications out of stainless steel, Type 304. The burner size was reduced from a 4.75-inch to a 3.5-inch diameter. Other design parameters that were changed included the installation of six mixing vanes and the placement of a thermocouple well six inches in front of the nozzle. The flame rod and ignition cable were potted with electrical insulating resin. To ensure the safety of operating personnel, a 1-inch check valve was installed upstream on the gas line.

Results. The new burner was inserted into a well simulator and ignition tests were conducted at pressures from 30 to 100 psig with heating rates ranging from 100,000 to 700,000 Btu per hour. This burner was fired for periods of eight hours. During these tests, air and propane were shut off for periods up to 8 minutes with re-ignition being easily accomplished.

5.20 "B" Series Pilot-Plant Tests

Objectives. The objective of this study is to conduct and evaluate tests using the K-FUEL series B pilot plant on selected western coals. The objectives for the quarter were to complete the project report and conduct tests using a different coal resource.

Accomplishments. The project report was completed, submitted, and approved. Additional tests were conducted.

Procedures. A series of tests was conducted at the K-Fuel®pilot plant to evaluate use of Caballo Rojo coal as feed for the process.

5.21 Surface Process Study for Oil Recovery Using a Thermal Extraction Process

Objectives. The objective for the quarter was to initiate research on the DOE portion of the task.

Accomplishments. Plans were formulated to initiate work on the DOE portion of the task.

5.22 NMR Analysis of Samples from the Ocean Drilling Program

Objectives. The objective of this study is to apply solid-state ^{13}C NMR to study samples collected from leg 139 of the Joint Oceanographic Institute (JOI) project on thermal maturation in areas of steep thermal gradient. The objective for the quarter was to begin making measurements on the samples.

Accomplishments. Solid-state ^{13}C NMR measurements were made on 10 kerogen concentrates and two whole rock samples collected from Leg 139 of the JOI cruise project by the Woods Hole Oceanographic Institution.

Procedures. Solid-state NMR measurements were made on a Chemagnetics CMX 100/200 solids NMR spectrometer. ^{13}C spectra were obtained at 25 MHz using cross polarization with magic-angle (CP/MAS) spinning. A large-volume spinner was used for analysis of whole rock samples.

Results. CP/MAS ^{13}C NMR spectra were acquired on samples received from the Woods Hole Oceanographic Institution. However, because of the low levels of organic matter in the sediments, kerogen concentrates had to be prepared. Even for these samples, 12 to 18 hours of signal averaging was required to obtain suitable spectra. However, these spectra were compromised by background signals from the probe. As a result, the probe background will have to be subtracted in order to determine the carbon aromaticities of the sedimentary material.

5.23 Menu Driven Access to the WDEQ Hydrologic Data Management System

Objectives. The objective of this study is to develop an enhancement to the Wyoming Department of Environmental Quality Data Management System that will provide menu-driven access. The objectives for this quarter were to complete the development and prepare the user documentation.

Accomplishments. The development was completed and a draft of the documentation was prepared and is in review.

Procedures. Since the original data base was developed using ORACLE, it was used for the development of menus. The ORACLE utility, SQL* Menu, was used to create the menus and the ORACLE utility, SQL* Forms, was used to alter the data entry forms.

Results. The menus that were developed work properly. The menus prevent the user from having to remember cryptic form names and make the data entry process more orderly and understandable.

Those forms that have been altered also appear to work properly and have made the data entry process easier and more efficient. The forms now test for missing information and will not allow the user to enter data if important information is missing, but will allow the user to both look-up what is known to the system and enter what is missing, without leaving the original data entry form.

5.24 Oil Field Waste Cleanup Using Tank Bottom Recovery Process

Objectives. The objective for the quarter was to initiate plans to proceed with the task.

Accomplishments. Plans have been formulated and work will begin in the next quarter.

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