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DIRECT LIQUEFACTION PROOF-OF-CONCEPT FACILITY

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We have no objection from a patent standpoint to the publication or dissemination of this material.
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PROOF OF CONCEPT FACILITY – DIRECT LIQUEFACTION

1. ABSTRACT

The main objective of the U.S. DOE, Office of Fossil Energy, is to ensure the United States a secure energy supply at an affordable price. An integral part of this program was the demonstration of fully developed coal liquefaction processes that could be implemented if market and supply considerations so required. Demonstration of the technology, even if not commercialized, provides a security factor for the country if it is known that the coal to liquid processes are proven and readily available.

Direct liquefaction breaks down and rearranges complex hydrocarbon molecules from coal, adds hydrogen, and cracks the large molecules to those in the fuel range, removes hetero-atoms and gives the liquids characteristics comparable to petroleum derived fuels.

The current processes being scaled and demonstrated are based on two reactor stages that increase conversion efficiency and improve quality by providing the flexibility to adjust process conditions to accommodate favorable reactions. The first stage conditions promote hydrogenation and some oxygen, sulfur and nitrogen removal. The second stage hydrocracks and speeds the conversion to liquids while removing the remaining sulfur and nitrogen. A third hydrotreatment stage can be used to upgrade the liquids to clean specification fuels.

The U.S. Department of Energy, Fossil Energy Program planned a contract with Hydrocarbon Research (HRI) to conduct a multi-year PDU (3 Ton/Day) demonstration program for two stage direct liquefaction entitled "Proof of Concept Facility". A four run PDU program was planned, this was later modified to an extended continuous Bench-Scale (20 KG/day) program at Hydrocarbon Technologies (HTI) with the option to scale up to PDU demonstration. The program on completion evolved chronologically to the following series of test runs.

Run Numbers	Year
POC Modifications	1992-3
POC-01, PDU RUN	1993-4
POC-02, PDU RUN	1994
PB-1 thru 9, BENCH-SCALE	1995-1998
POC-07, PDU RUN	1998
PB-10 BENCH-SCALE	1998

*POC-Proof of Concept PDU operations, 3 Tons/day
*PB-Bench-Scale Series of Runs, 50lbs./day

The program was completed in September, 1999 after a successful series of runs that included the scale-up of bituminous and sub-bituminous coal using a two-stage catalytic 750°F$^+$ extinction recycle process. Distillates from these operations were upgraded under

Bechtel's direction at Southwest Research Institute and by several refiners. The product fuels met or exceeded petroleum derived fuel specifications.

An extensive series of runs with coal plastics, heavy oil and other waste streams was successfully conducted to advance the U.S. DOE initiative to examine and develop this co-processing technology.

The developed process for both bituminous and sub-bituminous coals in combination with plastics and oil successfully achieved the conversion objectives and lowered the projected cost per barrel to the $20/bbl range. Further efforts have been shelved due to questionable collection infrastructure, cost and commercial incentive.

The process and catalysts developed for coal liquefaction based on dispersed catalyst in back mixed reactors with on-line fixed bed hydrotreating has attracted interest from the Peoples' Republic of China (PRC). They have signed an agreement with HTI to pursue a feasibility study to construct a 12,000 ton/day direct coal liquefaction facility in China. These Bench-Scale Runs PB-9 & 10 and PDU Run POC-07 evaluated several China coals.

The feasibility study program is continuing with private and some US DOE support.

2. BACKGROUND

The U.S. Department of Energy, Fossil Energy Program fostered the development of direct coal liquefaction technologies during the period 1965 to 1999. From 1965-1980, most processes under development were single stage and concentrated on the production of low sulfur fuel oil as the major product. With a change in demand and the need for lower sulfur and lighter products the emphasis shifted to two-stage processing.

Most of the large scale single stage Pilot Plant (6 Tons/Day) Testing was conducted at Wilsonville, Alabama under the auspices of the U.S. Department of Energy, EPRI (The Electric Power Research Institute) and Southern Services. In 1980, the facility was upgraded to two stages of reaction, both thermal and dispersed and supported catalyst modes were evaluated in various combinations of recycle and reactor arrangements. The Wilsonville facility became the major center for large scale, direct liquefaction demonstrations. In early 1990, the Wilsonville plant was closed due to limitations in funding and changes in the U.S. DOE fuels development strategy.

In 1992, a new program was approved by DOE called "Proof of Concept Facility". Major equipment was transferred from Wilsonville, Alabama to Hydrocarbon Research in Lawrenceville to modify their 3 Ton/day PDU. The equipment consisted of reactors, pumps, separators, valves and compressors. This strategy reduced operating costs since the HRI facility was self sufficient, thus DOE was able to reduce costs by operating intermittently.

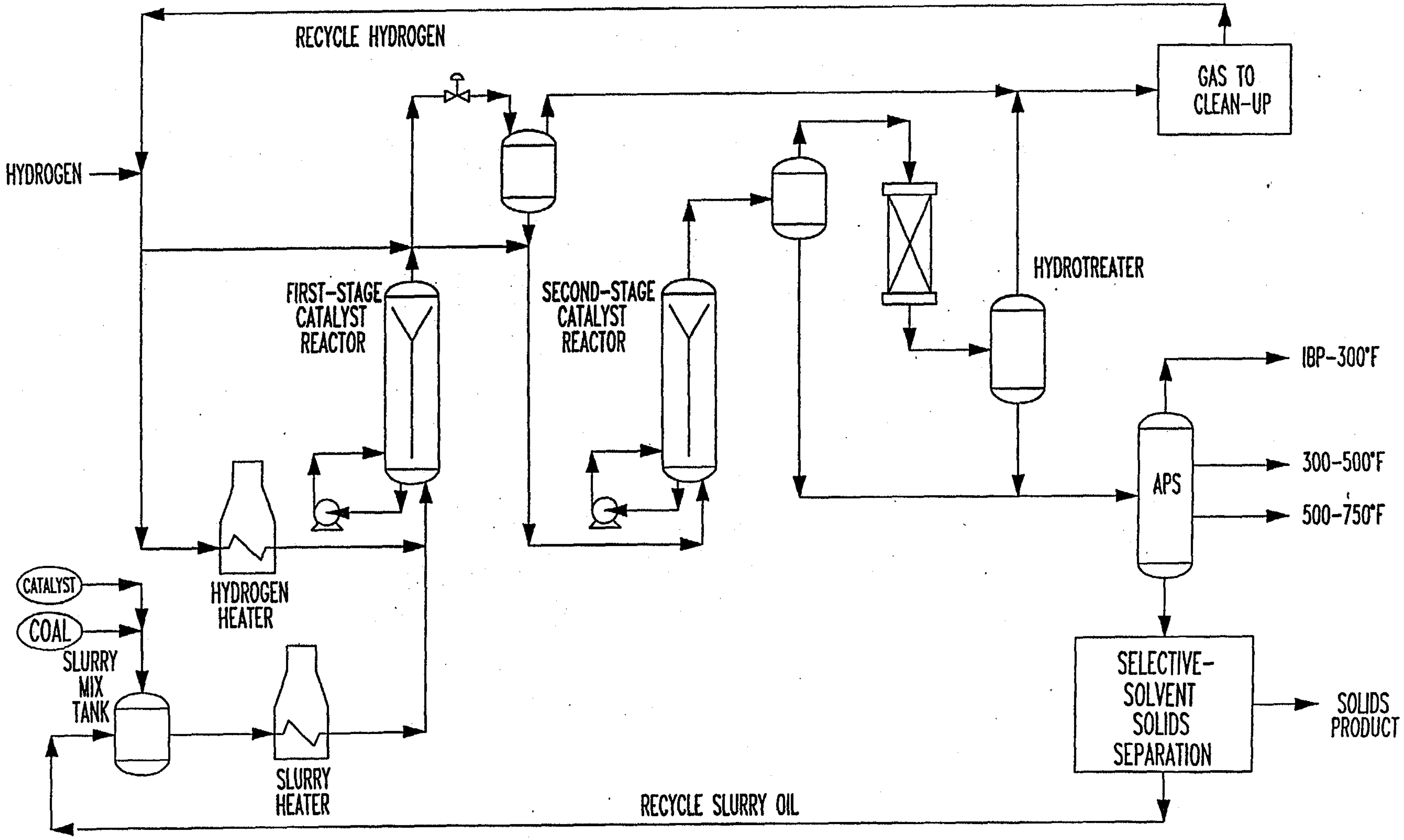
A five-year contract to evaluate the scale-up of sub-bituminous and bituminous coals was initiated in 1992. This culminated in an advanced two-reactor stage process incorporating on-line hydrotreating, solvent extraction or filtration of the bottoms.

POC runs were completed in 1993 and 1994 on bituminous Illinois #6 and Wyoming Black Thunder sub-bituminous coals. In 1995, the contract objective was modified into a series of Bench-Scale (50 lb./day) tests evaluating new catalysts and coal combined or co-processed with waste plastics, heavy oil and other waste organic materials.

The Hydrocarbon Technologies, Inc. (HTI) POC facility is a fully integrated unit consisting of two back-mixed reactors, an on-line fixed-bed hydrotreater, coal receiving and handling facilities, hydrogen compression, gas scrubbing and recycling, high pressure let-down, atmospheric and vacuum distillation and a choice of solvent extraction or continuous pressure filtration. Products for this process of coal liquefaction consist of over 60% of clean distillate fuels; with the balance being light gases for refining, plus elemental sulfur, ammonia and coal ash. *Figure 1* depicts the process flow for the Hydrocarbon Research (HRI) (Hydrocarbon Technologies) (HTI) POC facility (In 1995 HTI assumed the contractual DOE work from HRI).

FIGURE 1

POC FACILITY
AT HYDROCARBON TECHNOLOGIES, INC.
SIMPLIFIED FLOW PLAN



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As part of the National Energy Strategy an Advanced Research Strategic Thrust is identified as Advanced Research for Coal-Derived Liquid Fuels and has a primary objective "To evaluate novel concepts and establish the technology base for producing high quality hydrocarbon-based transportation fuels from coal to costs in the range of \$25-\$30/barrel of Crude Oil Equivalent". The advanced research thrusts focus on achieving objectives that support adoption of new technology into commercial practice in 5-10 years with some application in the near term (up to 5 years) as well. The Proof-of-Concept Program is the initial scale-up for direct coal liquefaction and establishes the basis of design for commercialization and proves the process economics. Under the Proof of Concept Program HRI (HTI) was chosen to operate a two-stage Process Development Unit for a period of 3 years followed by two optional years, later modified to include Bench-Scale Operations on variant liquefaction streams.

Research and development objectives included scale-up of advanced direct liquefaction technology involving two stage reactions, co-processing of crude oils with coal, studies of alternate processing modes, evaluation of materials and equipment, improving product quality and reducing product cost. By the use of strategic feedstocks, commercially available catalysts, prototype equipment and improved design techniques and materials of construction efforts have been and will be focused on improving process economics. The PDU produces hydrocarbon distillates and by-products in sufficient quantity to allow various research activities, such as, product fractionation, upgrading, engine testing, storage stability, small scale combustion testing, and refining into chemical feedstocks.

Modifications were made to the HRI PDU to improve reliability and to provide flexibility for operation in several alternate modes. Included were upgraded computer controls for automation and an alternate power supply to provide additional back-up in case of incoming power failure. The Kerr McGee ROSE-SR^{SM} Unit from Wilsonville was modified to be a single-stage unit using a pentane solvent and installed next to the U.S. Filter system to allow for a direct comparison of the two solid separation systems. A new reactor, hydrotreater, interstage sample system, a coal handling system to receive pulverized coal, a new ebullating pump, and improve instrumentation were installed over a period of about one year. A major part of this installation was a new reactor tower enclosing the high pressure, high temperature vessels and upgraded preheater.

The PDU is a totally integrated two reactor stage coal and oil hydrogenation process development unit. It includes coal and oil handling systems, slurry mixing, high pressure pumping, preheating, reaction, product separations, atmospheric and vacuum fractionation, naphtha stabilization, bottoms separation, product storage, data acquisition/storage/reporting and computer control. The PDU has been used to develop and scale-up the H-Oil® Process, H-Coal Process. Coal/Oil Co-Processing and CTSL processes. For this operation the PDU was equipped to remove solids via the ROSE-SR^{sm} critical solvent process, vertical leaf pressure filtration or via vacuum distillation.

2.1 Program Objectives

The following are the objectives of the Proof-of-Concept Direct Coal Liquefaction Program.

Develop direct coal liquefaction and associated transitional technologies which are capable of producing premium liquid fuels, which are economically competitive with petroleum and which can be produced in an environmentally acceptable manner.

Focus on further developing Two-Stage Liquefaction by utilizing geographically strategic feedstocks, commercially feasible catalysts, and prototype equipment. Include testing co-processing or alternate feedstocks and improved process configurations.

- Demonstrate the operation of a two-stage catalytic ebullated-bed reactor system with bituminous and sub-bituminous coals (or lignite) using commercially available supported catalysts having good physical strength and activity for comparison with a slurry reactor system using dispersed catalysts and for comparison to prior bench-scale and Wilsonville PDU results.

- Demonstrate variant liquefaction schemes, especially coal/oil co-processing, utilizing appropriate feedstocks with the scope of development depending on preliminary technical and economic evaluations. Co-Processing may enable early commercialization of coal liquefaction due to more favorable economics.

- Demonstrate satisfactory operation with alternate feedstocks (i.e., selection of another Illinois No. 6 coal and a lignite for pilot-scale tests is necessary as Burning Star #2 coal and Martin Lake lignite that were used in the past may not be readily available in the future).

- Focus on scale-up of PDU data to a commercial size unit by establishing operating parameters such as coal space velocity, bed exotherms, hydrogen gas rates/consumption, and reactor geometry/hydrodynamics.

  Prioritize process development for low-cost feedstocks based on distillate production rate and coal reactivity.

- Demonstrate suitable low-rank coal liquefaction conditions for obtaining low heteroatom and hydrocarbon gas yields and high coal conversions while eliminating potential solids deposition in the process units/lines.

- Obtain high distillate yields having good quality under low-severity conditions on a unit reactor volume basis.

- Demonstrate the economic viability of well dispersed, highly active catalyst (disposable as well as recoverable) for slurry reactor applications in two-stage liquefaction.

- Demonstrate optimum supported catalyst replacement rates with respect to coal throughput under steady-state catalyst activity conditions. Elucidate catalyst pore structure effects on reactant conversion and hydrogenation. Evaluate improved catalyst utilization concepts (e.g., regeneration, cascading).

- Produce premium products by in-line hydrotreating of distillate.

- Demonstrate improved hydrogen utilization in two-stage liquefaction by removing heteroatoms using pretreatment/preconversion methods (proven at bench-scale). Especially for low-rank coals ($CO+H_2O$) is a possible candidate).

- Define and demonstrate two-stage liquefaction product properties (e.g., end-point) for economic upgrading and refining to make specification-grade products.

- Perform process development with strategically important high and low-rank coals. When appropriate, select readily available low-ash coals that have good reactivity.

- Facilitate process development by studying the interaction between the first and second stages by developing appropriate sampling and analytical methods (e.g., evaluate conversions at preheater outlet, interstage, etc.).

- Demonstrate efficient and economic solids separation methods for different ranks of coal. Evaluate vacuum bottoms for determining the merits of schemes involving fluid or delayed coking.

- Study the merits of integrating advanced coal cleaning methods (e.g., agglomeration acid washing/coal beneficiation, etc.) with two-stage liquefaction.

- Improve overall process operability by selecting and monitoring advanced equipment and instrumentation that have improved tolerance of material degradation while handling slurries containing fine particulates, heavy resids, and corrosive streams under high severity conditions.

3. EXECUTIVE SUMMARY

The final report covers work performed under a multi-year Proof of Concept direct coal liquefaction program funded by the U.S. Department of Energy, FETC and Hydrocarbon Technologies, Inc. (HTI). The program was directed toward scaling up and demonstrating new liquefaction concepts that had the potential to lower the cost of synthetic liquid fuels to less than $30 per barrel. The work performed includes scale-ups to a 3 ton/day PDU unit and extensive work at 50 Kg/day on continuous bench-scale units investigating various feedstocks combined with coal.

This very successful program completed and met most of the objectives set forth in the original contract and are each individually summarized as follows:

- Develop direct coal liquefaction and associated transitional technologies which are capable of producing premium liquid fuels, which are economically competitive with petroleum and which can be produced in an environmentally acceptable manner.

  Fuels produced from PDU and Bench operations that included in-line hydrotreating were of exceptional quality, surpassing petroleum derived fuels specifications for purity and performance. C_4-750°F distillates exiting the process are refined to less than 10 ppm N&S with diesel fractions of 40+ Cetane Number Economic analyses of fuels produced from combined feeds of coal, plastics and oils show a cost of less than $20/bbl and for coal only under $30/bbl.

- Focus on further developing Two-Stage Liquefaction by utilizing geographically strategic feedstocks, commercially feasible catalysts, and prototype equipment. Include testing co-processing or alternate feedstocks and improved process configurations.

  During the early PDU runs a bituminous Illinois #6 and Black Thunder Wyoming sub-bituminous coal were evaluated, both strategically located in the U.S. Commercial type catalysts were used in all the supported catalyst studies and the dispersed systems is one that can easily be produced at commercial scale.

  During the program coal was co-processed with waste plastics, scrap rubber, automotive shredder residue, Hondo Oil and Pyrolysis Oils. Bench-Scale Studies examined preheaters, interstage separation, in-line hydrotreating, combined dispersed and supported catalysts and optional modes of solids separations and recycle.

- Demonstrate the operation of a two-stage catalytic ebullated-bed reactor system with bituminous and sub-bituminous coals (or lignite) using commercially available supported catalysts having good physical strength and activity for comparison with a slurry reactor system using dispersed catalysts and for comparison to prior bench-scale and Wilsonville PDU results.

POC Runs 1 & 2 were made with an experimental catalyst that was later commercialized by AKZO. The catalyst performed well with minimum attrition losses except for Black Thunder Coal runs. Data from these runs were compared with Wilsonville operations. HTI's dispersed catalyst was also compared directly with supported catalyst and found to perform as well when incorporating on-line hydrotreatment and donor recycle solvent.

- Demonstrate variant liquefaction schemes, especially coal/oil co-processing, utilizing appropriate feedstocks with the scope of development depending on preliminary technical and economic evaluations. Co-processing may enable early commercialization of coal liquefaction due to more favorable economics.

  This objective was the thrust for the Bench-Scale series of runs from PB-1 through PB-8 in which various combined feedstocks were co-processed with coal. A California "Hondo" heavy oil was used in several of the runs combined with coal and also with coal and plastics. Co-processing produced much more favorable economics.

- Demonstrate satisfactory operation with alternate feedstock (.e., selection of another Illinois No. 6 coal and a lignite for pilot-scale tests is necessary as Burning Star #2 coal and Martin Lake lignite that were used in the past may not be readily available in the future).

  A new source of Illinois #6 coal was selected and qualified for use in this program. "Crown II Mine" coal replaced the shut-in Burning Star Mine Coal. Black Thunder Mine sub-bituminous coal remained as low rank choice due to its availability and larger resources.

- Focus on scale-up for PDU data to a commercial size unit by establishing operating parameters such as coal space velocity, bed exotherms, hydrogen gas rates/consumption, and reactor geometry/hydrodynamics.

  Operating parameters were established in PDU Runs 01 & 02 and utilized by Bechtel and HRI/HTI to scale to commercial size and design. These data are also incorporated in the commercial design and feasibility study for the Shenhua China Project.

- Prioritize process development for low-cost feedstocks based on distillate production rate and coal reactivity.

  Distillate production and quality were established in POC-01 and 02 and further refined in the co-processing studies with waste plastics and heavy oils. The combined processing of waste-plastics, heavy oil and coal gave the maximum distillate yields and with on-line hydrotreating gave very high quality.

- Demonstrate suitable low-rank coal liquefaction conditions for obtaining low heteroatom and hydrocarbon gas yields and high coal conversions while eliminating potential solids deposition in the process units/lines.

  Utilizing Black Thunder coal in POC Run 1 with on-line hydrotreating led to the production of high quality distillate with less than 10 ppm S and less than 3 ppm N. There were no signs of solids deposition during this long 45 day operation demonstrating that low rank coal can be cleanly processed in back-mixed reactor systems.

- Obtain high distillate yields having good quality under low-severity condition on a unit reactor volume basis.

  At the POC level of scale-up, with sub-bituminous coal, C_4-524°C distillate yields of 62 W% of MAF and C_4-343°C yields of 54 W% were obtained at a space velocity of 460 Kg/hr/m^3 with heteroatom contents less than 30ppm in the C_4-343°C distillate. On a Bench-Scale distillate yields of 73 W% MAF were obtained on Illinois #6 coal at space velocities of 640 Kg/Hr/meter^3 with dispersed iron catalyst and at a projected cost of ($28/bbl equivalent crude oil price). On a Bench-Scale with Black Thunder Coal and using dispersed iron catalyst distillate yields of 67 W% MAF C_4-975°C$^+$ were obtained at space velocities of up to 720 Kg/h/m^3 with sulfur and nitrogen contents near 1ppm on the pressure filter liquid (PFL).

- Demonstrate the economic viability of well dispersed, highly active catalyst disposable as well as recoverable) for slurry reactor applications in two-stage liquefaction.

  During the Bench-Scale series of runs with coal, oil and plastics a dispersed catalyst system was developed based on an iron-moly phosphorus gel form catalyst. This dispersed catalyst system using the same configuration as for supported catalyst with back-mixing equaled, and at the same conditions surpassed the extrudate catalyst process in performance.

  When results from PB-03, dispersed catalyst run, are compared with PB-02 and POC-02 supported catalyst runs, a 4% higher conversion and yield are shown for the dispersed case.

- Demonstrate optimum supported catalyst replacement rates with respect to coal throughput under steady-state catalyst activity conditions. Elucidate catalyst pore structure effects on reactant conversion and hydrogenation. Evaluate improved catalyst utilization concepts (e.g. regeneration, cascading).

POC Run 02, a 45-day run on Wyoming Black Thunder coal, utilized deactivated catalyst from Run POC-01. This equilibrium operation was achieved in the first 10 days. The unit was operated with 0.5 and 1 Kg catalyst per ton coal for the first and second stages, respectively. The first stage spent catalyst was found to process 10-15% more activity than spent second-stage catalyst. Cascading and catalyst regeneration were not demonstrated nor were catalyst pore size effects studied due to a change in program goals to the use of dispersed catalysts.

- Produce premium products by in-line hydrotreating of distillate. The highest quality products ever achieved in direct liquefaction in the United States resulted from operations in POC-02 with on-line hydrotreating and extinction recycle of the 750°F$^+$ product. Distillate were further refined and blended through Bechtel and South West Research and produced gasoline diesel and jet fuel exceeding specifications with performance in some areas superior to petroleum derived distillate fuels.

- Demonstrate improved hydrogen utilization in two-stage liquefaction by removing heteroatoms using pretreatment/preconversion methods (proven at bench-scale), especially for low-rank coals (CO + H_2O) is a possible candidate).

During this program, no pretreatment or preconversion testing was included other than waste pyrolysis. However, heteroatom removal was accomplished via interstage separation and hydrogen utilization was also enhanced via the introduction of waste plastics and heavy oils with co-processing.

- Define and demonstrate two-stage liquefaction product properties (e.g., end-point) for economic upgrading and refining to make specification-grade products.

The distillate products made in POC-01 and POC-02 had end points at 96% below 343°C. In POC-01, 3,500 gallons of distillate were produced from Illinois #6 coal without hydrotreating and had a hydrogen content of 12.6 W%, sulfur 0.049% (490 ppm) and nitrogen .053% (530 ppm).

This distillate was hydrotreated and refined to specification grade products that showed a $2.35/bbl premium over petroleum prices. 3,200 gallons of premium hydrotreated product was collected from POC-02 on Wyoming Black Thunder Coal with nitrogen levels of 20 ppm and sulfur @ 5 ppm and 13 W% hydrogen. These products required much less severity for upgrading due to the on-line hydrotreatment. Resulting products were exceptional when compared to petroleum derived equivalents.

- Perform process development with strategically important high- and low-rank coals. When appropriate, select readily available low-ash coals that have good reactivity.

PDU runs at 3 tons/day and bench-scale tests at 50 kg/day were conducted on a new Illinois #6 seam from the Crown II Mine and with Wyoming Black Thunder sub-bituminous coal, a low ash seam (5.7%). These two coals were found to be good economic choices based on ash levels and reactivity.

- Facilitate process development by studying the interaction between the first and second stages by developing appropriate sampling and analytical methods (e.g., evaluate conversions at preheater outlet, interstage, etc. During the PDU operations, a limited number of interstage samples were taken as the result of a malfunctioning of the sample systems. However, kinetic studies were conducted and reported from POC-01 and interstage samples were analyzed by Consol, Inc. and results reported under Contracts DEAC22-94PC93054 and AC22-89PC89883.

- Demonstrate efficient and economic solids separation methods for different ranks of coal. Evaluate vacuum bottoms for determining the merits of schemes involving fluid or delayed coking.

  During POC (PDU) 01 and 02 operation tests were conducted on vertical leaf filter, vacuum still and critical solvent deashing solids separation. The ROSE-SR^{sm} system performed well in both POC-01 and POC-02. In Run 02, an energy rejection of only 13.6% was achieved at a bottoms solids of 60% when a mixed toluene – n-pentane solvent was used.

- Study the merits of integrating advanced coal cleaning methods (e.g., agglomeration acid washing/coal beneficiation, etc.) with two-stage liquefaction.

  These studies were performed in a Kentucky Center for Energy Research program. Agglomerated coal cleaning was performed by Consol and the Bench-Scale test conducted by HTI. Results were positive, the cleaned coal performed better than run-of-mine coal.

- Improve overall process operability by selecting and monitoring advanced equipment and instrumentation that have improved tolerance for material degradation while handling slurries containing fine particulates, heavy resids, and corrosive streams under high severity conditions.

  Under the POC program, material testing was performed for Oak Ridge National Labs and for NEDO of Japan. Additionally, improved nuclear detection equipment, solvent separation and feed system components were tested. The PDU unit now operates independently from a control room under computer monitoring and control.

POC PROGRAM (PDU & BENCH) RUN SUMMARY

RUN NO.	DATE FROM	TO	COAL FEED	CONDITIONS	RUN LENGTH	COMMENTS RESULTS
POC-01	10/93	2/94	Illinois #6 Crown II	Two Stage Catalytic Extinction Recycle of 370°C+. No on-line Hydrotreating with Critical Solvent Separation	58 Days	Achieved Extinction Recycle. Verified scale-up. Collected 3500 gallons of distillate for refining tests. Distillate yields of 5 bbls/ton MAF coal
POC-02	6/94	8/94	Wyoming Black Thunder	Two-Stage Catalytic with on-line Hydrotreating and extinction recycle and critical solvent separation. Also short operation with waste plastics, rubber and coal	45 Days	Successfully achieved extinction recycle and produced very clean upgraded distillate. Distillate yields of 4.3 bbls/ton Maf coal . 200 gallons of <10 ppm sulfur distillate were collected for upgrading. Successfully processed waste plastics, rubber and coal
POC-07	8/98	10/98	China Shangwan	Two-Stage Dispersed Catalyst @ on-line Hydrotreating and Critical Solvent Deashing	Intermittent 16 Days	Problems with feed coal being oversize. Equipment failure and deashing operating problems. Needs to be repeated.
PB-01	9/95	10/95	Black Thunder, MSW Plastics, Hondo	Sub-Bit. Coal Resid and Waste Plastics in various combination, low/high temperature operation. *On-line Hydro *Interstage Separation *Feed Preheater	41 Days	Beneficial Effect of Waste Plastics with Coal and Oil Stream, Lower Gas Make, Lower H_2 Consumption Higher Yield of light, clean distillate and performed well and lower distillate cost at $20/bbl. HTI Iron Catalyst performed well.
PB-02	12/95	1/96	Black Thunder, MSW Plastics	Hybrid Catalyst Operation Dispersed catalyst with supported ebullated catalyst in second stage, high/low temp operation. Process configured per PB-01.	43 Days	Higher gas make than low/high. Plastics had a positive effect. Lower gas make, H_2 consumption. High quality distillate produced 3 ppm sulfur 1 ppm N. 48-50° API slightly higher cost than dispersed system.

POC PROGRAM (PDU & BENCH) RUN SUMMARY

RUN NO.	DATE FROM	TO	COAL FEED	CONDITIONS	RUN LENGTH	COMMENTS RESULTS
PB-03	3/96	4/96	Black Thunder, MSW Plastics	Iron/Moly Dispersed Catalyst Evaluation with Process Configuration as in PB-01	32 Days	Modified Gel Cat™ with phosphorous improved overall yields and conversions by 4%. Higher catalyst loadings from 1000 to 5000 gave slightly higher distillate yields. Hydrotreated solvent improved yield and conversion.
POC-04	6/96	6/96	Black Thunder, Hondo Resid, ASR & MSW Plastics	Modified GelCat™, Dispersed Catalyst High Temperature and S.V., Same Configuration as PB-01	23 Days	Modified GelCat performance confirmed higher yields. ASR Performance is not as good as MSW Plastics, Performance is more like coal.
POC-05	8/96	8/96	Illinois #6, Hondo Resid MSW Plastics ASR	Modified GelCat Dispersed Catalyst Same Configuration as PB-01	24 Days	Great performance with Illinois #6 Coal exceptional distillate. Yields over 73% MAF at high S.V., addition of 50 ppm moly plus-no effect. 79% distillate yield and 90% resid conversion with coal/oil/plastics on performance of Illinois #6 coal
POC-06			Black Thunder, Plastics Pyrolysis Oil, Hondo Resid, MSW Plastics	Dispersed Catalyst Process per PB-01 Once through operation at pyrolysis oil	23 Days	Plastic derived pyrolysis oil did not perform as well as direct plastic feed with coal or oil. Coal derived recycle is needed for high conversion versus pyrolysis oil.
PB-07	3/97	3/97	Illinois #6	Study of Dispersed Catalyst Promoters preparation of Carbon Precursor Process per PB-01 (no preheater)	20 Days	Iron catalyst shown to promote cracking and hydrogenation as most critical promoter. Low levels 100 ppm of moly and phosphorus were not good for resid conversion. Carbon precursor for West Va. prepared at mild conditions.

POC PROGRAM (PDU & BENCH) RUN SUMMARY

RUN NO.	DATE FROM	TO	COAL FEED	CONDITIONS	RUN LENGTH	COMMENTS RESULTS
PB-08	8/97	8/87	Black Thunder, MSW Plastics Plastics Pyrolysis Oil, Tire Pyrolysis Oil	Study of coal and plastics pyrolysis oil and rubber tire oil conversion with dispersed catalyst system and process per PB-01	17 Days	Results with the pyrolysis oil were as good as direct plastic feed, low H_2 usage, low gas make, rich conversion and yields. Lower first stage temperature promotes hydrogenation.
PB-09	10/97	11/97	Shenhua Coal Seams #2 & #3	Process variable run on China Coal to optimize conversion and yield. Some configuration as PB-01 used varying amount of GelCat catalyst	29 Days	Shenhua Coal Seam #3 was superior to #2. Process performance with lower cost modified GelCat was equal or better than original. Yield and conversion for Coal Seam #3 were favorable
POC-10	11/98	11/98	Shangwan Coal Two Lots	Bench Scale Operation to confirm coal characteristics for conversion at the PDU Scale and to obtain data for a China Coal Liquefaction Plant Feasibility Study	20 Days	Design Basis Targets achieved 93.5 W% coal conversion. 85.9 W% MAF resid conversion. 67.2 W % C_4–975°F distillate. Recycle composition had a significant effect on performance.

Abstracts, Executive Summaries, Conclusions and Tables of Contents from each of the PDU and Bench-Scale Tests and other supporting economic and design activities are included in Appendix I and reference the formal reports.

4. POC PROGRAM REVIEW BY RUN NUMBER

4.1 POC-01 - PDU RUN 1

4.1.1 Scale-Up Of Illinois #6 Coal Two-Stage Liquefaction Process

The objective of this task was scale-up of the Catalytic Two-Stage Liquefaction (CTSL) process using Illinois #6 coal in the extinction recycle mode of operation. The total time of operation was 58 days. This was the first operation of the new POC facility which included an on-line hydrotreater, new reactors and ebullating pumps, a ROSE-SR^{SM} Solvent Deashing Unit, a new coal feeding system, a vertical leaf U.S. filter unit, an interstage sample system, new instrumentation, and a new reactor tower. Some start-up problems were encountered, including by-passing in the on-line hydrotreater, causing it to be placed off-line; however, overall the scale-up was achieved with yields of 70-74% C_4-750°F distillate, near extinction recycle of the 750°F$^+$ oils and periods of equilibrium operation of the ebullated catalyst beds with catalyst addition and removal. During this test, operation at oil to coal ratios down to 0.9 to 1.0 were achieved as was a level of 12.5% energy rejection from the ROSE-SR^{SM} Unit, scale-up from Bench data was achieved and 3,500 gallons of distillate were collected for upgrading tests.

The results of these tests performed by Amoco, MW Kellogg, Southwest Research Institute with Bechtel National as the major contractor and provider of the refining process were very positive. A refinery slate of ASTM specification fuels were produced and the coal derived tests fuels from Illinois #6 coal met advanced specifications and represent fuels as good as petroleum derived fuels with some better features such as freeze point and emissions.

4.2 POC-02 - PDU RUN 2

4.2.1 Scale-Up Of Sub-Bituminous Wyoming Coal Two-Stage Liquefaction Process

The objective of this run was to scale-up the CTSL process using Wyoming sub-bituminous coal in the extinction recycle mode of operation with on-line hydrotreating and critical solvent deashing. Other additional objectives were to study the effect of dispersed catalyst (soluble molybdenum) addition and the co-processing of coal with waste plastics and waste rubber. The run covered 45 days, with the final five days using waste rubber and then waste plastics with coal as feed.

This was the first successful PDU demonstration of CTSL technology for sub-bituminous coal resulting in many improvements over earlier tests of liquefaction processes in the U.S. and world-wide. Clean distillates with less than 20 ppm nitrogen and 5 ppm sulfur were produced at a rate of 4.3 barrels/ton and reduced the equivalent price of crude to $32/bbl versus previous $38/bbl.

More than 3,200 gallons of hydrotreated distillate was collected for upgrading studies under a DOE contract “Refining and End Use Study of Coal Liquids Test Fuel Production and Testing” to Bechtel National with Amoco Southwest Research Institute and Kellogg.

The results of this study showed the fuels from POC-02 were better than conventional petroleum derived fuels and had the lowest specific atmospheric reactivity of any of the gasoline test fuels and performed as well as petroleum test fuels formulated as diesel and jet fuels with particulates reduced for diesel in highway tests.

4.3 POC-02 – PDU RUN 2 EXTENSION

4.3.1 Plastics and Rubber Co-Processing with Coal

In the closing condition of Run POC-2, pulverized waste tires and mixed plastics were processed with coal at 3 tons/day to produce products, to study scale-up and to highlight process problems. Operations were sustained for several days with 25 percent tire rubber, 75 percent coal and 30 percent plastic and 70 percent coal. The component ratio of the plastics was 50 percent high density polyethylene, 35 percent polystyrene, and 15 percent polyethylene terephtatlate. A total of 15 tons of plastics, coal, and used tires and coal were converted to light (180-650°F) distillate of less than 10 ppm sulfur and 25 ppm nitrogen and cetane index over 40, thus demonstrating the feasibility of processing wastes with coal and defining areas requiring further R&D.

4.3.2 Bench Run PB-01

During this bench run, the direct liquefaction and the combined waste processing of Black Thunder mine sub-bituminous coal was studied, while some of the most successful process concepts coming out of the earlier CMSL Project were employed. This bench run established the technical success of the combined processing of waste plastics with coal and petroleum resid mixtures. The run was conducted in an "all dispersed" mode of catalytic operation. The presence of plastics, for both coal-only and coal/oil combined feeds, resulted in improving the process performance significantly, primarily by reducing the light gas make and chemical hydrogen consumption and by increasing the light distillate yields. The techno-economic assessment indicates that the waste plastics co-processing improves the overall process economics by reducing the crude oil equivalent price to about $20 per barrel.

4.3.3 Bench Run PB-02

The objectives of this bench operation were to study the direct liquefaction of Black Thunder mine coal and its co-processing with petroleum resid and small amounts of waste plastics (10 W%) in a "hybrid" mode of catalytic operation. This run also studied the effect of interstage internal recycle on the process performance. The main findings of this bench run were that waste plastics, even in small concentrations in feed with coal or petroleum resid, improve the process performance and hydrogen utilization significantly; the interstage internal recycle was not found to alter the overall process performance in any noticeable manner. The comparison, under identical operating conditions, between the first two bench runs, indicated that an "all dispersed" catalytic mode of operation was equally effective, if not better, than the "hybrid" mode of catalytic operation.

4.3.4 Bench Run PB-03

This bench run with Black Thunder Mine Coal studied effects of varying dispersed catalyst concentration on liquefaction performance. The effect of hydrotreatment of the recycle oil were also studied during this bench campaign. It was found that 5,000 ppm iron with 50 ppm molybdenum was very effective for achieving good performance in direct liquefaction. The addition of 100 ppm phosphorus to 5,000 ppm iron, in the form of HTI's gel catalyst, GelCAT^{TM}, resulted in the best performance levels. The hydrotreatment of recycle solvent was found to be beneficial in that it improved the distillate yields and resid conversion levels during the direct liquefaction operations.

4.3.5 Bench Run PB-04

The effect of HTI's new dispersed gel catalyst promoted with phosphorus, GelCAT^{TM}, upon direct liquefaction performance was studied. The combined processing of coal with automobile shredder residue (ASR), commonly called "auto-fluff", was also studied during PB-04. In all dispersed catalyst mode, with a phosphorus-modified iron catalyst, over 88 percent residuum conversion was obtained with as high as 68 percent distillate liquid yield, when the operation was carried out under near "extinction recycle" mode. Auto-fluff was convertible under liquefaction conditions, although the positive influence upon the overall process performance during the co-processing operations -- that was found with the mixed waste plastics -- was not observed with the auto-fluff. The dissolution technique and handling of the auto-fluff was successfully studied and mastered during PB-04 operations.

4.3.6 Bench Run PB-05

This was the first bench run that HTI ever conducted in an all dispersed slurry catalyst mode using a bituminous Illinois No. 6 coal. The results were very encouraging. Over 95 percent of coal conversions were obtained using dispersed catalysts only, with about 90 percent residuum conversions and about 75 percent distillate yields. The co-processing conditions were also successful in that the mixed waste plastics were found instrumental in improving the hydrogen utilization efficiency and distillate yields with Illinois No. 6 coal in the same manner as they had with the sub-bituminous Black Thunder mine coal. The economic analysis, based upon the process performance during PB-05, led to the crude oil equivalent prices of less than $30 per barrel for the "coal-only" condition, and between $20-25 per barrel for the co-processing conditions.

4.3.7 Bench Run PB-06

The primary objective of this bench operation was to integrate the mild pyrolysis of plastics (<425°C and 30 min. reaction time) with the direct liquefaction of Black Thunder mine coal. In such a scheme, the heavy oil product fraction ($343°C^+$) from the mild pyrolysis of waste mixed plastics was used to slurry the coal, and the combined stream was hydroconverted -- with and without and process-derived recycle. In general, it was found that a once-through type (no recycle) operation makes it possible to operate at very high throughput without a significant performance degradation. Also, the presence of some process-derived recycle oil was found essential for achieving good process performance. Accidentally, it was also established that the inadequate sulfidation of the dispersed slurry catalysts, can have a very detrimental effect on the activity of the catalysts.

4.3.8 Bench Run PB-07

Effect of Dispersed Catalyst Concentration

The primary goal of bench run PB-07 was to evaluate the effects of varying levels of iron, phosphorous, and molybdenum-dispersed slurry catalyst loadings on hydroliquefaction of Illinois No. 6 coal. Coal and resid conversions were very high: 96-97% MAF and 87-89% MAF, respectively; however, due to a large C_1-C_3 gas make, C_4-975°F distillate yields were lower than expected at 67-68% MAF. With iron loadings of 2,500 ppm as GelCAT™ and at prevailing reactor conditions, neither molybdenum or phosphorus had a significant impact on performance. Resid levels in the recycle solvent increased dramatically when iron catalyst was removed, and molybdenum and phosphorus were held at 100 ppm each.

During the last four days of operation, about 120 pounds of coal-derived bottoms were collected for carbon-based materials research at the University of West Virginia.

4.3.9 Bench Run PB-08

Performance of Plastics Derived Pyrolysis Oils and Sub-Bituminous Coal

Pyrolysis oils produced from tires, waste oils and plastics using a low temperature continuous thermal reactor system were combined with sub-bituminous Black Thunder coal and processed at several similar conditions as coal and coal plus curbside plastics. The combination of pyrolysis derived oils from tires and plastics gave the best overall yields and results with 69.2 W% MAF C_4-524°C distillate. Overall, the addition of pyrolysis oils derived via this continuous unit performed better than both derived oils and better than coal only. Light gas yields are less and hydrogen consumption is lowered leading to better economics at about $23/bbl equivalent crude oil price.

4.3.10 Bench Run PB-09

Evaluation of China Sub-bituminous Coals from the Shenhua Coal Company in Shaanxi and Inner Mongolia.

The run evaluated two coal seams designated as Shenhua #2 and Shenhua #3 at several space velocities and with two different GelCAT^{TM} versions. The two-stage liquefaction process with on-line hydrotreating and interstage separation with dispersed catalyst was very effective for the conversion of these coals. Distillate yields varied from 52 to 68% for Seam #3 and 54-63 W% MAF for Shenhua #2 Seam. Therefore, Shenhua #3 coal is superior to Seam #2 coal due to higher distillate production, although total coal conversion is slightly lower and C_1-C_3 gas yields slightly higher. The new lower cost version of GelCAT^{TM} proved as successful as the original version under similar conditions. Overall the yields obtained by this process far exceed those demonstrated by the China Coal Research Institute and NEDO in Japan.

4.5 POC-07 – PDU RUN NO. 7

Scale-Up of the Liquefaction of China Sub-bituminous Coal Using Two-Stage Technology.

The objective of the PDU Run was to scale-up the HTI Coal Process as used in PB-09 Run on the Shenhua coal from China and to collect design data as the basis for a feasibility study. The run, scheduled for 15 days on China coal, was fraught with problems and operated on and off from August 18 through October 17, 1998, with the longest continuous period being nine days during which a C_4-524°F MAF yield of 64.6% was attained in Period 8. However, since operations could not be sustained for over nine days, sufficient equilibrium data was not available for design purposes and PB-10, a continuous bench run, was scheduled.

In addition to mechanical problems, exasperated by a four year PDU shutdown, with preheater check valves, burner controls, and separator feed pumps and slurry mixing, the coal was found to be contaminated with plastic fibers and oversize particles.

After rescreening the coal and following the nine days of operation, mechanical issues with disastrous consequences resulting in an extended shutdown and repairs occurred. This was (1) failure of the slurry preheater flame controls that resulted in coking; and (2) failure of the pressure let-down system causing rapid depressurization and fouling of the unit.

Many corrective measures have been initiated for PDU operations as a result of experiences from this operation. Some very significant improvements have been made to the feed, preheaters, let down and separation systems that will insure continuous operation in the future.

4.5.1 Bench Run PB-10

An Evaluation and Demonstration of the Liquefaction Performance of China Shangwan Coal.

This was a 24-day operation that evaluated two China coal shipments; one that was used in the PDU-07 operation and a pre-shipment sample that had not undergone rescreening and exposure to oxidation.

PDU-07, PDU Run 7, was an attempt to scale-up China coal to the 3-4 ton/day level and to obtain data for a feasibility study. Due to coal and mechanical problems, the scale-up was unsuccessful; therefore, this bench-scale operation was made to test the coal but more importantly to provide the design basis for the feasibility study to be submitted under the 10th 5-year plan of the People's Republic of China for construction of a commercial plant.

The run was successful in providing design data for the feasibility study achieving 93.5 W% coal conversion, 85.9 W% MAF resid conversion and 67.2 W% C_4- 524°C distillate yield with hydrogen consumption of 8.8 W%. MAF. The hydrotreater had a large impact on product quality, lowering the heteroatom content sulfur 59 ppm, nitrogen < 1 ppm and raising the H/C atomic ratio from 1.48 to 1.85. Maximizing resid recycle was the key to high distillate yield. The preshipment sample of coal did give higher coal conversion indicating that the bulk sample had deteriorated due to excessive handling.

A complete feasibility study for a 12,000 ton/day plant has been completed and will be submitted to the Shenhua Group for submission in the 10th 5 year plan of the People's Republic of China, PRC, in April, 2000.

APPENDIX I

Abstracts, Executive Summaries, Conclusions and Table of Contents from PDU and Bench-Scale Tests

DIRECT LIQUEFACTION PROOF-OF-CONCEPT FACILITY

Hydrocarbon Technologies, Inc. , Lawrenceville, NJ

TOPICAL REPORT

POC-07, PDU Run 260-07

Work Performed Under Contract No. AC22-92PC92148

Prepared For

U.S. Department of Energy
National Energy Technology Laboratory

Prepared By

Hydrocarbon Technologies, Inc.

January, 2000

ABSTRACT

The China Shenhua group selected a new coal, "Shangwan", other than the two coal seams evaluated in Bench-Scale Run #9 (227-106). Tests on Shangwan coal were conducted at the China Coal Research Institute (CCRI) indicating that the new coal seam was akin to the Shenhua #2 and #3 seams previously tested.

A 15-day operation for the China Shenhua coal evaluation was planned followed by the collection of fuel for a jet fuel evaluation program. The objective was to scale-up China Coal using the latest coal liquefaction technology developed under DOE contract. This included two liquefaction reactors with back-mixing of dispersed catalyst, in-line hydrotreating, interstage reactor separation, and critical solvent solids separation as established in Bench-Scale Run PB-09. Design data for a feasibility study were to be collected during this operation.

The operations started on August 18, 1998 and ended on October 17, 1998. Probably due to an extended downtime of four years, various mechanical problems were encountered as well as problems with coal contamination and oversize particles. Further efforts to continue and complete the China Coal scale-up objective were placed on hold due to insufficient funding for PDU operations. Remaining funds were allocated for Bench Run PB-10 to obtain data for the feasibility study.

EXECUTIVE SUMMARY

The objective of POC-07 was to scale-up the HTI coal liquefaction process that comprised two back-mixed slurry reactors, with on-line hydrotreating, interstage separation and critical solvent solids separation using China "Shangwan" Coal and conditions from Bench-Scale Run PB-09. Data was to be collected for designs and for the preparation of a commercial plant feasibility study to be submitted under the 10th five year plan of the Peoples Republic of China (PRC).

A 15-day operation for the China Coal was scheduled to be followed by a period of collecting jet fuel for evaluation. The Shangwan coal was tested by CCRI and judged to be nearly the same in performance as the Shenhua #2 and #3 seams tested in PB-09. However, many problems were encountered in the processing of this coal in addition to numerous mechanical problems. Many of the mechanical problems were due to a long period of inactivity of the PDU equipment and others were aggravated by poor coal quality. The coal was found to contain oversize (>70 mesh) and pieces of plastic strands following the first two weeks of operation. The coal was re-screened; however, operating and mechanical problems persisted.

The longest sustained period of operation was about nine days during which a projected yield of 64.6%, C_4-524°C distillate was obtained with 94.2% coal conversion. Some of the operating problems encountered due to coal oversize and contamination were feed pump check failure, plugging of circulating pump lines and the vapor/liquid separators. Mechanical failure was compounded by the frequent loss of feed, pressure and flow control. Corrective actions led to system redesign and long lasting improvements to the operating systems.

A Bench-Run, PB-10, on Shangwan coal was completed following the PDU shutdown. The results obtained from PB-10 and POC-07 have been used to prepare a feasibility study for a commercial 12,000 ton/day plant.

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CHINA SHENHUA COAL DIRECT LIQUEFACTION PIONEER PLANT COMMERCIAL PROJECT

FEASIBILITY STUDY REPORT

VOLUME II – LIQUEFACTION SECTION

Submitted To:

SHENHUA GROUP CORPORATION, LTD.
PEOPLE'S REPUBLIC OF CHINA

Prepared By:

HYDROCARBON TECHNOLOGIES, INC.
LAWRENCEVILLE, NEW JERSEY, U.S.A.

December 24, 1999

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1. 1 PROJECT BACKGROUND AND SIGNIFICANCE*

China has vast resources of coal. China has 114.5 billion tons of recoverable coal reserves, accounting for 11.1% of world recoverable coal reserves and ranking third in the world. In 1995, China produced 1.29 billion tons of coal, accounting for 28.5% of world coal production and ranking first in the world.

Coal is the largest transportation commodity in China, taking up 45-50% of the total handling capacity of railways and sea ports. It is predicted that amount of coal to be shipped out from Shanxi, Shaanxi, and Inner Mongolia may reach 350 MMtons and 600 MMtons by 2000 and 2020, respectively. Transportation has become the restricting factor to the development of coal industry.

China's primary energy consumption mix was coal 75%, oil 17%, natural gas 2%, hydropower and nuclear power 6% in 1995, and has not changed much in recent years. Compared with developed countries, China's energy mix is heavily biased towards coal. This is a result of shortage in oil reserves and insufficient insufficient production capacity.

China's recoverable oil reserves are 3.3 billion tons, accounting for 2.4% of world reserves and ranking eleventh. China produces 149 MM tons of oil, accounting for 4.9% of world oil production, ranking fifth in the world.

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*Statistical data in this section are cited from Fan, Weitang: "Future Trends of Energy Development in China," Proceedings International Symposium on Clean Coal Technology, 1997, Xiamen, China, pp. 3-15.

China has recoverable natural gas reserves of 1.7 trillion cubic meters, accounting for 1.2% of world reserves. Natural gas production in China was 17.6 billion m^3, equivalent to 0.8% of world natural gas production. For a large and rapid-developing country like China, its oil and natural gas reserves and production are far from enough for the national economy. It is predicted that China will need to import up to 30-50 MM metric tons of oil by Year 2000, and 250 MM metric tons of oil and 120 billion m^3 of natural gas to meet its energy demand in 2050.

Coal combustion is obviously the major source of pollution in China. Since coal has been the major energy source in China, and coal combustion and utilization are not yet equipped with advanced clean coal technologies, China is facing severe environmental problems, especially in big cities like Beijing, Shanghai, Lanzhou, and Taiyuan.

To address the current and long term energy strategy, plans have been made at the national level. At present, focus is on energy conservation, development of technologies for clean and highly efficient utilization of fossil energy, such as clean coal technology. Coal direct liquefaction, which can convert coal into very clean liquid transportation fuels, will definitely play an important role. Air pollution and emission of greenhouse gases can be greatly reduced. Digesting large amount of coal at mine mouth will substantially mitigate transportation limitation. Producing tens of million of tons of coal-derived clean liquid transportation fuels is equivalent to developing several large oilfields, thus greatly reduce the necessity of importing huge amount of foreign oil, creating numerous job opportunities, stimulating national economy, and enhancing national security.

Chinese government leaders fully realize the importance of the strategic significance of the technical route of converting coal into oil. President Jiang Zeming, during his visit to China Coal Research Institute on January 19, 1996, inspected its coal liquefaction R&D program, gave clear instructions that the government should provide more leadership, care and support to scientific and technical development of coal liquefaction technology. On April 15, 1997, then Chairman of China State Planning Commission, Chen Jinhua indicated that if coal can be converted to oil to resolve the shortage of automobile fuels, it will contribute greatly to future development of the country.

Hydrocarbon Technologies, Inc. (HTI) is a R&D, technology and process developing and licensing company with world-known expertise in coal direct liquefaction, which has been developed in more than two decades under the auspices of US Department of Energy.

Based on above background, HTI, Shenhua Group Corporation, Ltd. (SHHG), and China Coal Research Institute (CCRI) signed an agreement on the **Feasibility Study of China Shenhua Coal Direct Liquefaction Pioneer Plant, Commercial Project** in September 1997, which was amended in December 1999. The objective of this study is to evaluate the technical feasibility and economical viability of using HTI COAL PROCESS™ and GelCat™ catalyst to construct a coal liquefaction plant in Shenhua coal field.

To date, three coal samples, from Ningtiaota seams Nos. 2 and 3, and then Shangwan mine were tested on HTI's 30-50 Kg/day continuous flow unit (CFU). Shangwan coal test results agree very well with those of Ningtiaota No. 3 coal, which are from the same coal seam. SHHG has decided that Shangwan coal will be the feed coal for the direct liquefaction plant, therefore, this report is prepared on the basis the test results of Shangwan coal CFU testing.

1.2 PROJECT SCOPE

1.2.1 PLANT CAPACITY

The study is based on charging 12,000 metric tons per day of moisture-free Shangwan coal to the liquefaction plant. The principal products from the Liquefaction Plant (Plant 2) are approximately: 1,820 mt/d gasoline or ethylene feedstock, 366 mt/d heavy naphtha (swing cut) which can be blended into gasoline or diesel fuel, or used as ethylene feedstock., and 2,633 mt/d diesel fuel (including FCC light cycle oil that is fed to in-line hydrotreater). The Liquefaction Plant also produces 1,740 mt/d atmospheric and vacuum gas oils, which serve as FCC (Plant 8) feedstock after hydrotreating. All gases are processed in Light End Recovery Plant (Plant 9) to recover liquefied petroleum gas (LPG) and light nathpha. Liquid fuel products from Plants 2, 8, and 9 all together are: 938 mt/d (LPG), 2,960 mt/d of naphtha, 366 mt/d heavy naphtha, and 3,580 mt/d diesel fuel. By-products are: C_1–C_2 fuel gas (1,007 mt/d), elemental sulfur (13.0 mt/d) and ammonia (12 mt/d). Phenol can be recovered from heavy naphtha and sour water.

Above numbers does not include LPG and gasoline produced in the FCC plant.

1.2.2 Overall Design Considerations

The Shangwan coal direct liquefaction plant will be a green-field complex to be located in a plant site close to a coal mine in Shenhua coal field along the border of Shaanxi and Inner Mongolia, as shown in Figure 1.1. It is a mine-mouth plant, therefore coal transportation load and cost are substantially reduced. With the exception of electricity, the plant will be a standalone and self-sustained complex, equipped with all necessary facilities.

The Coal Direct Liquefaction Plant of concern has a capacity of processing 12,000 tons/day of Shangwan coal. Shangwan coal is selected by SHHG in consideration of its good liquefaction performance, abundant reserves and established production capacity. Major products of the liquefaction complex are 7,844 tons/day of liquid transportation fuels, including LPG, gasoline (or ethylene feedstock naphtha), and diesel fuel, with by-products such as sulfur, phenols, etc. Liquid fuels are easy to transport, and are very much needed in the Shanxi-Shaanxi-Inner Mongolia-Ningxia area where there is a shortage in oil reserves and refining capacity.

The liquefaction plant uses HTI COAL PROCESS™ and GelCat™ for Shangwan coal liquefaction, because the combination of HTI's coal direct liquefaction technology and its proprietary catalyst gives the highest liquid product yield and ultra-clean transportation fuels ever made from coal.

1.2.3 OVERALL PLANT CONFIGURATION

The overall configuration of the entire Shangwan coal liquefaction complex is shown in Figure 1.2, which shows the interconnection of the primary process plants, specified as Inside Battery Limit (ISBL) plants. Besides these ISBL plants, there are a number of additional Outside Battery Limit (OSBL) plants which are not shown in this figure. Complete lists of these ISBL and OSBL plants are given in Tables 1.1 and 1.2.

Obviously, the liquefaction section, including solvent deashing and catalyst manufacture, is the core of the entire complex. Crushed, ground, dried, and screened feed coal is converted in the two-stage liquefaction plant into liquid transportation fuels, which flow to product blending or are further processed in downstream units such as fluid catalytic cracking. Hydrogen consumed in liquefaction is generated by coal/resid gasification, and partially by fuel gas steam reforming.

Per Meeting Minutes of Project Review Meeting held in December 1998, The Feasibility Study report will be written in two volumes. HTI is responsible for the preparation of Report Volume 2, which encompasses three core plants: Coal Liquefaction using HTI COAL PROCESS™, Solvent Deashing, and GelCat™ Manufacture. Shangwan coal CFU testing results obtained at HTI is used as the design basis. HTI's In-House Process Simulation and Economics Models, as well as the USDOE-Modified Bechtel Coal Direct Liquefaction model are used for liquefaction plant design.

In consideration of the limitation on reactor size due to transportation, the entire liquefaction plant consists of three identical trains with each train processing 4,000 mt/d of coal. Feed coal to the liquefaction plant contains 6% of moisture, supplied by Coal Preparation plant.

1.2.4 Work Objectives

The objectives of this part of the study so far as liquefaction plant is concerned are to:

- develop overall material balance, utility requirements, and flow distributions for the coal liquefaction (Plant 2) and solvent deashing (Plant 3).

- generate an equipment list for capital cost estimates for the liquefaction section, including Plants 2, 3, and 4 (Catalyst Manufacture).

- generate production cost estimates for plants 2, 3, and 4.
- carry out financial evaluation of the liquefaction section.

DIRECT LIQUEFACTION PROOF-OF-CONCEPT PROGRAM

Topical Report #12
Bench run PB-10 (HTI 227-109)

Work Performed under DOE Contract No. DE-AC22-92PC92148

Prepared for

US Department of Energy
Federal Energy Technology Center

Prepared by

Hydrocarbon Technologies, Inc.

December 1999

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EXECUTIVE SUMMARY

This report presents the results of the bench-scale test PB-10 (HTI Run No. 227-109), performed at HTI's facilities under DOE contract. The objective of this test was to demonstrate the feasibility of direct coal liquefaction on Shangwan coal utilizing various backend processing and recycle schemes. This bench test continues the work that was started in PDU testing 260-007. Additionally, this test collected all available data to allow for the best scale-up process design possible from this particular unit. Previous bench test (227-106, PB-09) was performed on different seams of Chinese coal (Shenhua Coal #2 & #3).

HTI's continuous Bench Scale Unit No. 227 was used for this run, spanning 24 days including start-up and shutdown. This unit employs two backmixed liquefaction reactors and a closely integrated fixed-bed hydrotreater. The coal/oil slurry is premixed offline and charged to a feed tank on a periodic basis. The reactors are close-coupled with the effluent from the first stage flowing directly to the second stage. The effluent from the second reactor was separated in a hot separator and the bottoms stream was sent to an atmospheric flash. The overhead from the 2nd stage hot separator was sent directly to the in-line hydrotreater. The hydrotreater outlet was sent to a cold separator and separated into a vent gas stream and a separator overhead stream (SOH). The vent gases were metered, sampled, and sent to flare. The overhead from the atmospheric flash was also sent to the hydrotreater as part of the feed charge. The bottoms stream from the atmospheric flash was separated offline by various processes depending on the particular recycle scheme being used for that condition. These streams were then analyzed. Part of the mid-distillate generated is used as a process oil in the buffer pumps for the first and second stage reactors. TNPS was used during startup to pre-sulfide the hydrotreater catalyst and TNPS and H2S were used during the run to activate the dispersed catalyst. During this test four different recycle schemes were used.

HTI's proprietary iron-based dispersed catalyst GelCat™ in different formulations were used in the entire run. The run includes 8 separate operating conditions with four different recycle schemes. Condition 1A (Periods 1-3A) used the base coal, Shangwan coal, which was used for the PDU testing (260-007). Part of the O-6 bottoms was recycled and the rest separated by pressure filtration. The pressure filter liquids were vacuum distilled and the bottoms recycled as well as a portion of the overheads. The pressure filter solids was solvent extracted and the toluene extracted oil was recycled while the toluene extracted solids was taken as a product. For Condition 1B this was changed to decreasing the total amount of O-6 bottoms recycled, recycling the pressure filter liquid directly and recycling the toluene extracted oil. For Condition 2A the same scheme was followed except the coal was changed from that used in the PDU program to L-1007 which was a smaller lot of the same coal that was ground by HTI. For Condition 2B the recycle of the pressure filter liquids was stopped and the vacuum still bottoms recycle was restarted. For Condition 3A a portion of the pressure filter solids was also recycled so as to resume solids recycle and the feed coal was changed back to that used in the PDU program. For Condition 3B the hydrotreater was bypassed to determine the quality and quantity of material flowing directly from the overhead of the hot separator to the hydrotreater. For Condition 4A the hydrotreater was placed back online and the O-6 bottoms was vacuum distilled twice recycling a

399°C+ fraction and a 399-538°C+ fraction. For Condition 4B the cut point of the first distillation was reduced and the overall recycle ratio was changed from 1.6 to 1.25.

The small lot of coal that was prepared by HTI does result in a slightly higher coal conversion of 1.8W% maf ff than the bulk coal sample used for the PDU testing. The reactor performance as measured by reactor (single-pass) resid conversion shows some variation based on the recycle scheme being used. This follows the pattern that the greater the recycle of resid material the lower the reactor performance. This is due to the recycle resid becoming more concentrated in refractory materials which are very difficult or impossible to convert. The process performance, as measured by the process (overall) resid conversion, shows a very strong impact from the recycle scheme. Even though the reactor resid conversion decreases with higher levels of resid recycle, the process resid conversion increases sharply as recycle ratio increases. The maximum process performance is achieved with the maximum recycle of resid. The performance achieved for the design basis 93.5 W% maf ff coal conversion, 85.9 W% maf ff resid conversion, and 67.2 W% C4-524°C distillate yield with a hydrogen consumption of 8.8 W% maf ff. The hydrotreater had a significant impact on final product quality; increasing the hydrogen content by 1.8 W%, increasing the H/C Atomic ratio from 1.48 to 1.85, increasing the API gravity from 21.3 to 36.0 and lowering the sulfur content from 1119 wppm to 59 wppm and the nitrogen content from 695 wppm to <1 wppm.

DIRECT LIQUEFACTION PROOF-OF-CONCEPT PROGRAM
Hydrocarbon Technologies, Inc., Lawrenceville, N.J.

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Topical Report
Bench Run 09 (227-106)

Work performed Under Contract No. DE-AC22-92PC92148

For

U. S. Department of Energy
Federal Energy Technology Center

By

Hydrocarbon Technologies Inc., Lawrenceville, N.J.

September 1998

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ABSTRACT

This report presents the results of the bench-scale work , Bench Run PB-09, HTI Run Number 227-106, conducted under the DOE Proof-of-Concept Option Program in direct coal liquefaction at Hydrocarbon Technologies, Inc. in Lawrenceville, New Jersey. Bench Run PB-09 was conducted using two types of Chinese coal, Shenhua #2 and Shenhua #3, and had several goals. One goal was to study the liquefaction performance of Shenhua #2 and Shenhua #3 with respect to coal conversion and distillate production. Another goal of Bench Run PB-09 was to study the effect of different GelCat™ formulations and loadings. At the same time, the space velocity and the temperature of the first reactor, K-1, were varied to optimize the liquefaction of the two Chinese coals.

The promoter-modified HTI GelCat™ catalyst was very effective in the direct liquefaction of coal with nearly 92 % maf coal conversion with Shenhua #3 and 93 % maf coal conversion with Shenhua #2. Distillate yields (C_4-524 °C) varied from 52-68 % maf for Shenhua #3 coal to 54-63 % maf for Shenhua #2 coal. The primary conclusion from Bench Run PB-09 is that Shenhua #3 coal is superior to Shenhua #2 coal in direct liquefaction due to its greater distillate production, although coal conversion is slightly lower and C_1-C_3 light gas production is higher for Shenhua #3. The new molybdenum-modified GelCat™ also proved successful in converting the two Chinese coals and, under some conditions, producing good distillate yields for a coal-only bench run.

EXECUTIVE SUMMARY

Bench Run PB-09 is part of the Proof-of-Concept Bench Option Contract between the United States Department of Energy and Hydrocarbon Technologies, Inc. (HTI). The primary goal of the run was to evaluate the direct liquefaction of two Chinese coals, Shenhua #2 and Shenhua #3, and to compare them with earlier data on the direct liquefaction of other coals. A further goal of the run was to evaluate a new promoter-modified GelCat™ at different loadings.

The entire bench run was conducted over thirty days and was divided into six operating conditions. PB-09 was initially scheduled to be a twenty six day long operation, but was increased to thirty days in an attempt to increase the distillate yields. Shenhua coal #3 was used in conditions one through four, while Shenhua #2 coal was used in the final two conditions. A modified GelCat™ was used throughout the run at varying catalyst flow rates. All six conditions used a GelCat™ with an Fe/Promoter atomic ratio of 100/4, except period two, at a ratio of 100/2.

The following points were the highlights of bench run PB-09.

-- The promoter-modified GelCat™ catalyst was effective in the direct liquefaction of both Chinese coals. Coal conversion, on a moisture and ash-free (maf) basis, was almost 92% with Shenhua #3 coal and 93 % with Shenhua #2 coal.

-- The C_4-524 °C distillate yield with Shenhua #3 coal varied from 52 to 68 % maf, and 53 to 64 % maf with Shenhua #2 coal. The 524 $°C^+$ residuum conversion varied from 70 to 84 % maf with Shenhua #3 coal, and 71 to 80 % maf with Shenhua #2 coal.

-- The C_1-C_3 light gas yield was slightly higher with Shenhua #3 coal than with Shenhua #2 coal (13% vs 12% maf, respectively).

-- The 524 $°C^+$ residuum yield was lower for Shenhua #3 coal, 7 % maf, than for Shenhua #2 coal, 13% maf.

-- Overall, both coals had superior direct liquefaction performance, and Shenhua #3 was better than Shenhua #2 coal under the process conditions in PB-09, as shown by the higher distillate yields, with only slightly higher C_1-C_3 light gas yields and slightly lower coal conversion.

-- The promoter-modified GelCat™ with an Fe/Promoter composition of 100/4 (L-942) was superior to the analogous catalyst with a ratio of 100/2 (L-943), as evidenced by product yields. Upon changing from L-942 to L-943 the C_4-524 °C distillate yield derived from Shenhua #3 coal decreased from 68 % maf to 66 % maf, the 524 $°C^+$ residuum conversion decreased from 84 % maf to 82 % maf, the C_1-C_3 light gas yields increased from 12 % maf to 13 % maf, and the 524 $°C^+$ residuum yield increased from 7% maf to 9 % maf, while the coal conversion stayed the same at 91 % maf.

CHINA COAL
227-109, PB-10

EXECUTIVE SUMMARY

This report presents the results of the Bench Scale test, PB-10, performed at HTI's facilities under DOE contract. The objective of this test was to demonstrate the feasibility of direct coal liquefaction on Shangwang coal utilizing various backend processing and recycle schemes. This bench test continues the work that was started in 260-007. Additionally, this test collected all available data to allow for the best scale-up process design possible from this particular unit. Previous bench test (227-106, PB-09) was performed on a different seams of Chinese coal (Shenhua Coal #2 & #3).

HTI's continuous Bench Scale Unit No. 227 was used for this run. This unit employs two main reactors which were operated as backmixed reactors. The coal/oil slurry is premixed offline and charged to a feed tank on a periodic basis. The reactors are close coupled with the effluent from the first stage flowing directly to the second stage. The effluent from the second reactor was separated in a hot separator and the bottoms were sent to an atmospheric flash. The overhead from the 2nd stage hot separator was sent directly to the hydrotreater. The hydrotreater outlet was sent to a cold separator and separated into a vent gas stream and a 2nd stage separator overhead stream (SOH). The vent gases were metered, sampled, and sent to flare. The overhead from the atmospheric flash was sent to the hydrotreater. The bottoms from the atmospheric flash were separated offline by various processes depending on the particular recycle scheme being used for that condition. These streams were then analyzed. Part of the mid-distillate generated is used as a process oil in the buffer pumps for the first and second stage reactors. TNPS was used during startup to pre-sulfide the hydrotreater catalyst and TNPS and H2S were used during the run to activate the dispersed catalyst. During this test four different recycle schemes were used.

The run includes 8 separate operating conditions. Condition 1A (Periods 1-3A) used the base coal, Shangwang coal, which was used for the PDU program (260-007. Part of the O-6 bottoms was recycled and the rest separated by pressure filtration. The pressure filter liquids were vacuum distilled and the bottoms recycled as well as a portion of the overheads. The pressure filter solids was solvent extracted and the toluene extracted oil was recycled while the toluene extracted solids was taken as a product. For Condition 1B this was changed to decreasing the total amount of O-6 bottoms recycled, recycling the pressure filter liquid directly and recycling the toluene extracted oil. For Condition 2A the same scheme was followed except the coal was changed from that used in the PDU program to L-1007 which was a smaller lot of the same coal that was ground by HTI. For Condition 2B the recycle of the pressure filter liquids was stopped and the vacuum still bottoms recycle was restarted. For Condition 3A a portion of the pressure filter solids was also recycled so as to resume solids recycle and the feed coal was changed back to that used in the PDU program. For Condition 3B the hydrotreater was bypassed to determine the quality and quantity of material flowing directly from the overhead of the hot separator to the hydrotreater. For Condition 4A the hydrotreater was placed back online and the O-6 bottoms was vacuum distilled twice recycling a 750F+ fraction and a 750-1000F+ fraction. For

Condition 4B the cut point of the first distillation was reduced and the overall recycle ratio was changed from 1.6 to 1.25.

The small lot of coal that was processed by HTI does result in a slightly higher coal conversion of 1.8W% maf ff than the coal used for the PDU program. The reactor performance as measured by reactor resid conversion shows some variation based on the recycle scheme being used. This follows the pattern that the greater the recycle of resid material the lower the reactor performance. This is due to the recycle resid becoming more concentrated in refractory materials which are very difficult or impossible to convert. The process performance, as measured by the process resid conversion, shows a very strong impact from the recycle scheme. Even though the reactor resid conversion decreases with high levels of resid recycle, the process resid conversion increases sharply as these materials are not taken as product. The maximum performance is achieved with the maximum recycle of resid. The performance achieved for the design basis 93.5 W% maf ff coal conversion, 85.9 W% maf ff resid conversion, and 67.2 W% C4-975F distillate yield with a hydrogen consumption of 8.8 W% maf ff. The hydrotreater had a significant impact on final product quality; increasing the hydrogen content by 1.8 W%, increasing the H/C Atomic ratio from 1.48 to 1.85, increasing the API gravity from 21.3 to 36.0 and lowering the sulfur content from 1119 wppm to 59 wppm and the nitrogen content from 695 wppm to <1 wppm.

DE-92148-TOP-10

DIRECT LIQUEFACTION PROOF OF CONCEPT
Hydrocarbon Technologies, Inc.

FINAL

TOPICAL REPORT
Bench Run 8 (227-105)

Work Performed Under Contract No AC22-92PC92148
For
U.S. Department of Energy
Pittsburgh Energy Technology Center

By

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DIRECT LIQUEFACTION PROOF-OF-CONCEPT PROGRAM
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FINAL

Topical Report
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For

U.S. Department of Energy
Pittsburgh Energy Technology Center

By

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The eighth bench scale test of POC program, Run PB-08, was successfully completed from August 8 to August 26, 1997. A total of five operating conditions were tested aiming at evaluating the reactivity of different pyrolysis oils in liquefaction of a Wyoming sub-bituminous coal (Black Thunder coal). For the first time, water soluble promoters were incorporated into the iron-based GelCat to improve the dispersion of the promoter metals in the feed blend. The concentration of the active metals, Mo and Fe, was 100 and 1000 ppm of moisture-free coal, respectively. Black Thunder coal used in this run was the same batch as tested in HTI's Run POC-02.

Similar to Runs PB-01 through 7, this run employed two back mixed slurry reactors, an interstage gas/slurry separator and a direct-coupled hydrotreater. In addition to the hot vapor from the second stage separator, the first stage separator overhead liquid was also fed to the hydrotreater, which was packed with Criterion C-411 hydrotreating catalyst. Pyrolysis oil was produced off-line from a pyrolysis unit acquired from University of Wyoming. Solids rejection was achieved by purging out pressure filter solid. The recycle solvents consisted of O-6 separator bottoms and pressure filter liquid (PFL).

The Run PB-08 proceeded very smoothly without any interruptions. Coal conversion consistently above 90W% was achieved. High resid conversion and distillate yield have been obtained from co-processing of coal and 343°C+ (650°F+) pyrolysis oil. Light gas (C_1-C_3) yield was minimized and hydrogen consumption was reduced due to the introduction of pyrolysis oil, compared with conventional coal-derived solvent. Catalytic activity was improved by incorporating a promoter metal into the iron-based GelCat. It seemed that lowering the first stage temperature to 435°C might increase the hydrogenation function of the promoter metal. In comparison with previous coal-waste coprocessing run (PB-06), significant improvements in the process performance were achieved due to catalyst modification and integration of pyrolysis technique into liquefaction.

DE-92148-TOP-09

DIRECT LIQUEFACTION PROOF-OF-CONCEPT PROGRAM
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Topical Report
Bench Run 7 (227-102)

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Pittsburgh Energy Technology Center

By

Hydrocarbon Technologies Inc., Lawrenceville, NJ,

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EXECUTIVE SUMMARY

The Bench Run PB-07 was the seventh of the nine runs planned in the POC Bench Option Contract between the U.S. DOE and Hydrocarbon Technologies, Inc. The primary goal of this bench run was to evaluate the effects of varying levels of iron and various promoters in a dispersed catalyst on hydroliquefaction of a high volatile bituminous Illinois No. 6 coal. The bench run PB-07 (HTI 227-102) was completed at the end of Period 20 (0400 HRS on 4/1/97). During the first 16 days of operation, a total of five run conditions were studied. Only four of these five conditions have been worked up for yields, because the original Condition 4, that employed the dispersed catalysts containing no iron, but only promoters, encountered plugging problems in the unit and resulted in a pre-mature unit shut-down. The last four days of this run were planned to produce the coal-derived heavy oil material, suitable for making carbon-based products, for West Virginia University, at the request of FETC. In general, the following observations were made during the run:

- Coal conversions were very high (96-97 % maf) and so were the resid conversions (87-89% maf); the C_4-524°C distillate yields were lower (67-68 % maf) than expected (72-75 % maf), from the high resid and coal conversion levels.
- With about 2500 ppm of iron, in the form of GelCat™, under the prevailing reaction conditions, neither promoter was found to have any significant impact on the overall process performance.
- Substantial hydrocracking was observed during the run, as exemplified by the abnormally high gas yields (15-16 % maf), high yields of light distillates, C_4-343°C (50-55 % maf), and low heavy VGO yields (2-3 % maf). The high gas yields were mainly due to high temperatures employed during the run. Lower reaction temperature or reduced fresh Fe catalyst loading may help minimize gas formation.
- In the absence of iron catalyst, with promoters only, the resid levels in the recycle solvent increased up to 50 w%, creating significant pumping problems and forcing a premature unit shut-down.
- During the last four days of operations, about 55 kg of the coal-derived O-6 bottoms material was produced for West Virginia University.

DE-92148-TOP-08

DIRECT LIQUEFACTION PROOF-OF-CONCEPT PROGRAM
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Topical Report
Bench Run 6 (227-98)

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For

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Pittsburgh Energy Technology Center

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DIRECT LIQUEFACTION PROOF-OF-CONCEPT PROGRAM
Hydrocarbon Technologies, Inc., Lawrenceville, N.J.

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Topical Report
Bench Run 06 (227-98)

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For

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Pittsburgh Energy Technology Center

By

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ABSTRACT

This report presents the results of bench-scale work, Bench Run Pb-06, conducted under the DOE Proof of Concept - Bench Option Program in direct coal liquefaction at Hydrocarbon Technologies, Inc. in Lawrenceville, New Jersey. The Bench Run Pb-06 was the sixth of the nine runs planned in the POC Bench Option Contract between the U.S. DOE and Hydrocarbon Technologies, Inc. The Bench Run Pb-06 had a primary objective of studying an alternative approach to conventional coal/plastics co-liquefaction. This alternative approach entailed mild pyrolysis of waste plastics in order to generate an oil fraction, to be used later for slurrying coal for direct liquefaction. Thus, PB-06 involved an integration of mild pyrolysis of waste plastics with direct liquefaction of Wyoming Black Thunder mine coal. The bench run Pb-06 employed a two-stage back-mixed slurry reactor system with an interstage V/L separator and an in-line fixed-bed hydrotreater.

The replacement of raw mixed plastics in the feed of Condition 2 (conventional coal/plastics co-liquefaction) by a 343°C+ oil (in Condition 3), obtained from the mild pyrolysis of raw mixed plastics, resulted in a slightly inferior process performance, probably because more of the refractory/unreactive plastics material was concentrated in the pyrolysis heavy oil feed. The once-through processing concept, tested during Condition 4, where coal was fed to the unit with Hondo resid VTB and pyrolysis oil (44 % resid material!), resulted in 86 % total feed conversion (to quinoline soluble products), 66 % residuum conversion, and 54 % distillate yield (all maf basis) at about twice as high a throughput (fresh feed basis) as in the other conditions of PB-06. This condition also resulted in the best hydrogen utilization efficiency in that the lowest light gas selectivity was obtained with the highest H_2 efficiency. It was evident from bench run PB-06 that complete elimination of recycle of the coal-derived oil results in performance deterioration; it is therefore necessary to recycle at least a part of process-derived oil even if other carrier solvents are available for pumping the coal slurry into the reaction system.

EXECUTIVE SUMMARY

The Bench Run PB-06 was the sixth of the nine runs planned in the POC Bench Option Contract between the U.S. DOE and Hydrocarbon Technologies, Inc. The primary goal of this bench run was to evaluate the integration of mild pyrolysis of mixed waste plastics with hydroliquefaction of Wyoming Black Thunder Mine coal. Bench Run PB-06 studied the effect of combined processing of coal and MSW plastics in a manner different from that practiced heretofore. During this run, MSW plastics (simulated mixture consisting of 40 % HDPE, 30 % polypropylene, 25 % polystyrene, and 5 % PVC) was subjected to mild pyrolysis (425-440°C , 30 min) reaction in order to obtain products that could, in principle, be utilized completely in the coal liquefaction process, i.e., light hydrocarbon gases for hydrogen production to meet the liquefaction hydrogen demand, the 343°C- light oil for supplementing the distillates from the liquefaction section, and the 343° C+ heavy oil (waxy material) to slurry the coal for feeding to liquefaction reactors, therefore, eliminating, either partially or completely, the recycle requirement for direct coal liquefaction. The run plan for PB-06 was designed to investigate all of these aspects.

The entire bench run was conducted during a 23-day long continuous operation, spanning over five operating conditions. The first operating condition, Condition 1, was run in a direct liquefaction or 'coal-only' feed mode and studied the effect of a phosphorous-modified iron catalyst, in the absence of added molybdenum catalyst, at high feed space velocity and in an all dispersed catalyst mode. Condition 2 studied the coprocessing of coal with mixed plastics in a conventional 'co-liquefaction' manner, practiced earlier at HTI. Condition 3 studied the coprocessing of pyrolysis oil with coal, at the same concentration of coal in the mixed feed, as in Condition 2. The Condition 4 looked at a special case of using 'no recycle oil' by practicing the 'once-through' mode of operation; the space velocity of the mixed feed (coal+pyrolysis oil+Hondo VTB resid) was increased during Condition 4 to correspond to an equivalent residence time, as in the other conditions of PB-06. The last condition, Condition 5, was similar to Condition 1, except that 100 ppm of molybdenum was added in addition to the iron catalyst, in the form of Molyvan-A. The interstage V/L separator was employed along with an in-line fixed-bed hydrotreater during PB-06. The recycle mode was "ashy" throughout the run, maintained by recyling the flash vessel bottoms material. The entire Bench Run PB-06 was initially scheduled to be a 25-day long operation although due to the operating problems encountered during the course of the run, the Run was pre-maturely shut-down.

Following were the highlights of bench-run PB-06:

- It is clear based upon the first and the fifth run conditions that, presence of adequate sulfur (or H_2S) is absolutely essential for dispersed slurry catalysts to be effective for coal and residuum conversions; it is not clear though, whether the significant improvement in process performance during Condition 5 over that during Condition 1 was entirely due to addition of 100 ppm of molybdenum to feed during Condition 5 or because of adequate amounts of H_2S in the reaction system.

- The addition of raw mixed plastics during Condition 2, helped to improve the distillate yields and hydrogen utilization efficiency of coal conversion.

- The replacement of raw mixed plastics in the feed of Condition 2 by 343°C+ oil (in Condition 3), obtained from the mild pyrolysis of raw mixed plastics, resulted in a slightly inferior process performance, probably because more of the refractory/unreactive plastics material was concentrated in the pyrolysis heavy oil feed.

- The once-through processing concept, tested during Condition 4, where coal was fed to the unit with Hondo resid VTB and pyrolysis oil (44 % resid material!), resulted in 86 % total feed conversion (to quinoline soluble products), 66 % residuum conversion, and 54 % distillate yield (all maf basis) at about twice as high a throughput (fresh feed basis) as in the other conditions of PB-06. This condition also resulted in the best hydrogen utilization efficiency in that the lowest light gas selectivity was obtained with the highest H_2 efficiency.

- It appears from PB-06 that complete elimination of recycle of the coal-derived oil results in performance deterioration; it is therefore necessary to recycle at least a part of process-derived oil even if other carrier solvents are available for pumping the coal slurry into the reaction system.

- In light of the results obtained during PB-06, and the fact that a steady-state equilibration could not be achieved during the mild pyrolysis of the plastics, more work should be conduced to study the integration of mixed plastics/used rubber tire pyrolysis with direct coal liquefaction, where a good control is obtained over the pyrolysis part of the integrated process so that an optimum disposition of the pyrolysis products and their usage in direct coal liquefaction/coal-oil coprocessing can be studied.

DE-92148-TOP-07

DIRECT LIQUEFACTION PROOF-OF-CONCEPT PROGRAM
Hydrocarbon Technologies, Inc., Lawrenceville, N.J.

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FINAL

Topical Report
Bench Run 05 (227-97)

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For

U.S. Department of Energy
Pittsburgh Energy Technology Center

By

Hydrocarbon Technologies Inc., Lawrenceville, NJ,

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ABSTRACT

This report presents the results Bench Run PB-05, conducted under the DOE Proof of Concept - Bench Option Program in direct coal liquefaction at Hydrocarbon Technologies, Inc. in Lawrenceville, New Jersey. Bench Run PB-05 was the fifth of the nine runs planned in the POC Bench Option Contract between the U.S. DOE and Hydrocarbon Technologies, Inc. Bench Run PB-05 had multiple goals. These included the evaluation of the effect of using dispersed slurry catalyst in direct liquefaction of a high volatile bituminous Illinois No. 6 coal and in combined coprocessing of coal with organic wastes, such as heavy petroleum resid, MSW plastics, and auto-shredder residue. PB-05 employed a two-stage, back-mixed, slurry reactor system with an interstage V/L separator and an in-line fixed-bed hydrotreater.

Coprocessing of waste plastics with Illinois No. 6 coal did not result in the improvement observed earlier with a subbituminous coal. In particular, decreases in light gas yield and hydrogen consmption were not observed with Illinois No. 6 coal as they were with Black Thunder Mine coal. The higher thermal severity during PB-05 is a possible reason for this discrepancy, plastics being more sensitive to temperatures (cracking) than either coal or heavy resid. The ASR material was poorer than MSW plastics in terms of increasing conversions and yields. HTI's new dispersed catalyst formulation, containing phosphorous-promoted iron gel, was highly effective for the direct liquefaction of Illinois No. 6 coal under the reaction conditions employed; over 95% coal conversion was obtained, along with over 85% residuum conversion and over 73% distillate yields.

EXECUTIVE SUMMARY

Bench Run PB-05 was the fifth of the nine runs planned in the POC Bench Option Contract between the U.S. DOE and Hydrocarbon Technologies, Inc. The primary goal of this bench run was to evaluate the direct liquefaction and coprocessing of a high volatile bituminous coal, (Illinois No.6), with organic wastes, such as MSW plastics (a mixture of HDPE, polypropylene, and polystyrene was used to simulate the MSW plastics), heavy resid, and auto-fluff. The unit was configured to have an interstage vapor-liquid separator and an in-line fixed-bed hydrotreating unit. The run consisted of 25 days of continuous operation, spanning six operating conditions. The effect of dispersed slurry catalyst activity and feed composition were evaluated at target operating conditions of reactor space velocity of 640 kg/h/m^3 reactor and reactor temperatures of 449 and 460°C.

The first two reaction conditions were carried out using 'coal-only' feed, with the objective of studying the effect of 50 ppm molybdenum, added as Molyvan-A, in improving performance over use of only iron and phosphorous in the form of HTI's gel catalyst (as in Condition 1 of PB-05). Conditions 3 through 6 focused on the coprocessing of organic wastes with coal; Condition 3 studied the coprocessing of coal with MSW plastics and Hondo VTB oil; Conditions 4 and 5 studied the coprocessing of coal with MSW plastics and auto-fluff material; and Condition 6 looked at coal/oil coprocessing at 50/50 w/w% feed concentration. The run was carried out in an "ashy-recycle" mode of operation, achieved by recycling part of the flash vessel, (O-6), bottoms back to the first stage reactor. The in-line hydrotreater operation was very successful (except for the last run condition); SOH product with a high H/C ratio and low heteroatom content was obtained.

Following were the highlights of Bench Run PB-05:

- HTI's new dispersed catalyst formulation, containing phosphorous-promoted iron gel, was highly effective for the direct liquefaction of Illinois No. 6 coal under the reaction conditions employed; over 95% total coal conversion was obtained, along with over 85% residuum conversion and over 73% distillate yields.

- The addition of 50 ppm molybdenum, in the form of Molyvan-A, to HTI's Fe/P gel catalyst did not bring about any significant improvement in process performance. It appears that the presence of phosphorous masks the effect of the molybdenum additive.

- The coprocessing of equal amounts of coal, MSW plastics, and Hondo VTB resid resulted in improved performance, e.g., about 90% conversion of resid was obtained, along with 79% distillate yield and 3.9% chemical hydrogen consumption.

- Coprocessing waste plastics with Illinois No. 6 coal did not result in the improvement observed earlier with a subbituminous coal. In particular, reduced light gas yields and hydrogen consumption were not observed with Illinois No. 6 coal as was the case with Black Thunder Mine coal. The higher thermal severity during PB-05 could be the reason for this discrepancy, plastics being more sensitive to temperatures (cracking) than either coal or heavy resid. The ASR material was poorer than MSW plastics in terms of contributing to conversion and yields.

- The last run condition, which studied conventional coal/oil coprocessing with minimal recycle, resulted in the best performance, although material recovery balance for that condition was poor.

DE-92148-TOP-06

DIRECT LIQUEFACTION PROOF-OF-CONCEPT PROGRAM
Hydrocarbon Technologies, Inc., Lawrenceville, N.J.

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FINAL

Topical Report
Bench Run 4 (227-95)

Work Performed Under Contract No. AC22-92PC92148

For

U.S. Department of Energy
Pittsburgh Energy Technology Center

By

Hydrocarbon Technologies Inc., Lawrenceville, NJ,

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DIRECT LIQUEFACTION PROOF-OF-CONCEPT PROGRAM

Hydrocarbon Technologies, Inc., Lawrenceville, N.J.

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FINAL

Topical Report
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Hydrocarbon Technologies Inc., Lawrenceville, NJ,

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ABSTRACT

This report presents the results of bench-scale work, Bench Run PB-04, conducted under the DOE Proof of Concept - Bench Option Program in direct coal liquefaction at Hydrocarbon Technologies, Inc. in Lawrenceville, New Jersey. The Bench Run PB-04 was the fifth of the nine runs planned in the POC Bench Option Contract between the U.S. DOE and Hydrocarbon Technologies, Inc. Bench Run PB-04 had multiple goals. These included the evaluation of the effects of dispersed slurry catalyst system on the performance of direct liquefaction of a subbituminous Wyoming Black Thunder mine coal under extinction recycle (454°C+ recycle) condition; another goal was to investigate the effects of the combined processing of automobile shredder residue (auto-fluff) with coal and other organic waste materials. PB-04 employed a two-stage, back-mixed, slurry reactor system with an interstage V/L separator and an in-line fixed-bed hydrotreater.

The HTI's newly modified P/Fe catalyst was very effective for direct liquefaction and coprocessing of Black Thunder mine subbituminous coal with Hondo resid and auto-fluff; during 'coal-only' liquefaction mode, over 93% maf coal conversion was obtained with about 90% residuum conversion and as high as 67% light distillate (C_4-975 F) yield, while during 'coprocessing' mode of operation, distillate yields varied between 58 and 69%; the residuum conversions varied between 74 and 89% maf. Overall, it is concluded, based upon the yield data available from PB-04, that auto-fluff, containing primarily polyurethanes and high impact polystyrene, is not as effective as MSW plastics in improving coal hydroconversion process performance. Auto-fluff did not increase light distillate yields nor decrease light gas make and chemical hydrogen consumption in coal liquefaction, as was observed to occur with MSW plastics.

EXECUTIVE SUMMARY

Bench Run PB-04 was the fourth of nine runs planned in the POC Bench Option Contract between the U.S. DOE and Hydrocarbon Technologies, Inc. The primary goal of this bench run was to evaluate the combined processing of automobile shredder residue (ASR) and Hondo VTB resid with Wyoming Black Thunder Mine coal. ASR is essentially the plastics and foam containing material that is recovered from automobiles when they are junked and shredded to remove most of the ferrous and non-ferrous metals. Typically about 600-700 pounds of ASR is recovered from an average-size U.S. automobile. The effects of using ASR, commonly called auto-fluff, in combined processing with coal were studied, along with the usage of MSW plastics, at 20, 25, and 30 w% of auto-fluff in the combined dry feed. The auto-fluff material was acquired from the Camden Metal & Recycling Company in New Jersey and was hand-picked to remove as much metal (and other dirt) as possible. The hand-cleaned fluff was found to contain mineral matter (ash) in the range of 14-20 w%. The auto-fluff was prepared for feeding to the hydroconversion reactors by predissolving it in either Hondo resid or coal-derived recycle solvent.

The bench run was conducted during a 23-day long continuous operation, spanning five operating conditions. The first operating condition, Condition 1, was run in a direct liquefaction or 'coal-only' feed mode and studied the effect of a phosphorous-modified iron catalyst (first used during one operating condition of the Bench Run PB-03) at high feed space velocity and in an all dispersed catalyst mode under extinction recycle (454°C+) conditions. Condition 2 studied the coprocessing of a heavy petroleum resid, Hondo VTB, with auto-fluff, while Condition 3 evaluated the combined processing of coal, resid, and auto-fluff under similar reaction severity. Condition 4 studied the coprocessing of coal with ASR, while the last condition, Condition 5, studied the coprocessing of coal with auto-fluff and MSW plastics. Bench Run PB-04 was initially scheduled to be a 25-day long operation, but due to feed line plugging problems encountered during Period 23, the run was prematurely shutdown.

Following were the highlights of Bench Run PB-04:

- HTI's newly modified P/Fe catalyst was very effective for direct liquefaction and coprocessing of Black Thunder Mine subbituminous coal with Hondo resid and auto-fluff; during the 'coal-only' liquefaction mode, over 93% maf coal conversion was obtained with about 90% residuum conversion and as high as 67% light distillate (C_4-975 F) yield. During the 'coprocessing' mode of operation, distillate yields varied between 58 and 69%; and residuum conversions varied between 74 and 89% maf.

- The combined processing of coal with Hondo resid and auto-fluff, carried out for the first time at HTI, resulted in about 84% residuum conversion and over 67% light distillate yield.

- When coprocessing a mixture of 75% coal and 25% auto-fluff, the total feed conversion, based upon quinoline solubility of the products, decreased; there was also a substantial drop in resid conversion and light distillate yield. When part of the auto-fluff was replaced by simulated MSW plastics, conversions and distillate yield increased markedly. Chemical hydrogen consumption decreased with MSW plastics in the feed.

- Based upon the yield data available from PB-04, it is concluded that auto-fluff, containing primarily polyurethanes and high impact polystyrene, is not as effective as MSW plastics in improving coal hydroconversion process performance. Auto-fluff did not increase light distillate yield nor decrease light gas make and chemical hydrogen consumption, as was osbserved to occur with MSW plastics.

DE-92148-TOP-06

DIRECT LIQUEFACTION PROOF OF CONCEPT FACILITY
Hydrocarbon Technologies, Inc., Lawrenceville, N.J.

Final PB-05

Topical Report
POC Bench Run ~~#~~5 (227-95)

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For
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Performed by
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DE-92148-TOP-05

DIRECT LIQUEFACTION PROOF-OF-CONCEPT PROGRAM
Hydrocarbon Technologies, Inc., Lawrenceville, N.J.

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FINAL

Topical Report
Bench Run 03 (227-93)

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For

U.S. Department of Energy
Pittsburgh Energy Technology Center

By

Hydrocarbon Technologies Inc., Lawrenceville, NJ,

DECEMBER 1996

DE-92148-TOP-05

DIRECT LIQUEFACTION PROOF-OF-CONCEPT PROGRAM
Hydrocarbon Technologies, Inc., Lawrenceville, N.J.

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FINAL

Topical Report
Bench Run 03 (227-93)

Work Performed Under Contract No. AC22-92PC92148

For

U.S. Department of Energy
Pittsburgh Energy Technology Center

By

Hydrocarbon Technologies Inc., Lawrenceville, NJ,

DECEMBER 1996

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ABSTRACT

This report presents the results of bench-scale work, Bench Run PB-03, conducted under the DOE Proof of Concept - Bench Option Program in direct coal liquefaction at Hydrocarbon Technologies, Inc. in Lawrenceville, New Jersey. The Bench Run PB-03 was the third of the nine runs planned in the POC Bench Option Contract between the U.S. DOE and Hydrocarbon Technologies, Inc. The Bench Run PB-03 had multiple goals. These included the evaluation of the effects of dispersed slurry catalyst loadings and types on the performance of two-stage direct coal liquefaction, the effect of HTI's new iron catalyst, modified with phosphorous, and the evaluation of the effect of recycle solvent hydrotreatment on the overall process performance. PB-03 employed a close-coupled (no interstage separator) configuration of hydroconversion reactors. Other features of PB-03 included the use of an in-line fixed bed hydrotreater for the net product.

No significant effects on process performance was found by changing the loadings of iron and molybdenum in the ranges of 1000-5000 ppm for iron and 50-100 ppm for molybdenum. However, the modification of HTI's iron-based gel catalyst with 100 ppm of phosphorous improved the process performance significantly. A newly tested Mo-Carbon dispersed catalyst was not found to be any better than Molyvan-A, which was used during all but one condition of PB-03. Hydrotreatment of part of the recycle solvent was found to have a positive influence on the overall performance.

EXECUTIVE SUMMARY

The Bench Run PB-03 was the third of the nine runs planned in the POC Bench Option Contract between the U.S. DOE and Hydrocarbon Technologies, Inc. The primary goal of this bench run was to evaluate the effects of type and amount of dispersed slurry catalyst used and also of the hydrotreatment of the recycle solvent on the overall process performance during direct liquefaction of a sub-bituminous coal. The entire bench run was conducted during a 32 day long continuous operation, spanning over nine operating conditions. The first four operating conditions studied the effect of iron and molybdenum dispersed catalyst loadings on process performance in a 2 x 2 test matrix; the concentration of iron catalyst was varied from 5000 to 1000 ppm at two molybdneum loadings, namely 50 and 100 ppm relative to feed coal. The variations in the dispersed catalyst loadings affected the coal and resid conversions only slightly while the light distillate yields were affected more significantly. During the next two conditions, 5 & 6, two new catalysts were investigated. Condition 5 employed HTI's iron-gel catalyst, modified with phosphorous, while condition 6 employed a molybdenum-carbon catalyst, made in a manner similar to what is known for Exxon's M-Coke catalyst. A significant positive impact on the overall process performance was obtained with the phosphorous-modified HTI's iron catalyst; the Mo-carbon catalyst, under the conditions of this test, was at best similar to the Molyvan-A precursor in terms of process performance.

The last three run conditions, 7 through 9, studied the impact of hydrotreating part of the recycle oil upon the overall process performance. It is believed that upon the catalytic hydrotreatment of highly aromatic recycle oil, the resulting product oil contains hydroaromatic compounds, known to be efficient H-transfer agents. In the interest of time and simplicity of continuous bench-scale operation, it was decided that an L-814 oil, which is a mixture of coal-derived material with mildly hydrotreated FCC decant oil, be used as a part of the recycle oil during these three conditions. This oil was first separated into a residuum-rich fraction (VSB) and a residuum-free fraction (VSOH) by vacuum distillation. The VSOH stream was hydrotreated in a fixed-bed catalytic reactor at 379°C at an LHSV of about 2.2 h^{-1}. During condition 7, the unhydrotreated VSOH was used in the recycle oil stream to establish a base-line for comparisons. During conditions 8 and 9, hydrotreated VSOH was used in the recycle oil stream; the operating severity was increased during condition 9. All three conditions also employed the residuum-rich VSB stream, derived from L-814, in order to maintain a total resid content of recycle oil around 30 w%. A definite improvement

in the overall process performance was obtained with the hydrotreated VSOH in the recycle stream. During the last three conditions, the catalyst loading was at 1000 ppm for iron and 100 ppm for molybdneum with fresh feed. A high coal space velocity of about 800-880 kg/h/m^3 reactor was employed throughout the entire run.

The following were the highlights of bench-run PB-03:

- The effect of changing iron and molybdenum catalyst loadings, between 1000-5000 ppm and 50-100 ppm respectively, was only significant in case of the C_4-524°C distillate yield and naphtha (lightest cut) formation; no noticeable effect was seen on either coal or residuum conversion.

- The modification of HTI's iron-based GelCat™ with 100 ppm of phosphorous improved process performance significantly; distillate yields and resid conversions increased by about 4 w% each, while coal conversion increased by one weight percent.

- Mo-carbon catalyst, made similar to M-Coke catalyst, was at best, as good as Molyvan-A.

- In general, net chemical hydrogen consumption was on the low side for PB-03, probably because no supported catalyst was used and space velocities were also very high. As a result, even though the in-line hydrotreated SOH product (IBP-400°C) had a high hydrogen content (1.8-1.9 H/C ratio), the unhydrotreated product which is the part of PFL that is not recycled had a very low hydrogen content (0.8-0.9 H/C ratio) and a high preasphaltene content (12-15 w% of whole PFL) which rendered the pressure filtrations extremely difficult.

- The hydrotreatment of part of the recycle oil had a positive influence; the resid conversion and distillate yields increased upon replacing part of the recycle solvent stream with a hydrotreated material.

RUN PB-03 (227-93)

EVALUATION OF DISPERSED CATALYST TYPE AND LOADING AND RECYCLE SOLVENT HYDROTREATMENT ON LIQUEFACTION OF SUB-BITUMINOUS COAL

EXECUTIVE SUMMARY

The Bench Run PB-03 was the third of the nine runs planned in the POC Bench Option Contract between the U.S. DOE and Hydrocarbon Technologies, Inc. The primary goal of this bench run was to evaluate the effects of type and amount of dispersed slurry catalyst used and also of the hydrotreatment of the recycle solvent on the overall process performance during direct liquefaction of a sub-bituminous coal. The entire bench run was conducted during a 32 day long continuous operation, spanning over nine operating conditions. The first four operating conditions studied the effect of iron and molybdenum dispersed catalyst loadings on process performance; the concentration of iron catalyst was varied from 5000 to 1000 ppm at two molybdneum loadings, namely 50 and 100 ppm relative to feed coal. The variations in the dispersed catalyst loadings affected the coal and resid conversions only slightly while the light distillate yields were affected more significantly. During the next two conditions, 5 & 6, two new catalysts were investigated. The condition 5 employed HTI's iron-gel catalyst, modified with phosphorous while condition 6 employed a molybdenum-carbon catalyst, made in a manner similar to what is known for Exxon's M-Coke catalyst. A significant positive impact on the overall process performance was obtained with the phosphorous-modified HTI's iron catalyst; the Mo-carbon catalyst, under the conditions of this test, was at best similar to the Molyvan-A precursor in terms of process performance.

The last three run conditions, 7 thru'9, studied the impact of hydrotreating part of the recycle oil upon the overall process performance. It is believed that upon the catalytic hydrotreatment of highly aromatic recycle oil, the resulting product oil contains hydroaromatic compounds, known to be efficient H-transfer agents. In the interest of time and simplicity of continuous bench-scale operation, it was decided that an L-814 oil, which is a mixture of coal-derived material with mildly hydrotreated FCC decant oil, be used as a part of the recycle oil during these three conditions. This oil was first separated into a residuum-rich fraction (VSB) and a residuum-free fraction (VSOH) by vacuum distillation. The VSOH stream was hydrotreated in a fixed-bed catalytic reactor at 379°C at an LHSV of about 2.2 h^{-1}. During condition 7, the unhydrotreated VSOH was used in the recycle oil stream to establish a base-line for comparisons. During conditions 8 and 9, hydrotreated VSOH was used in the recycle oil stream; the operating severity was increased during condition 9. All three conditions also employed the residuum-rich VSB stream, derived from L-814, in order to maintain a total resid content of recycle oil around 30 w%. A definite improvement in the overall process performance was obtained with the hydrotreated VSOH in the recycle stream. During the last three conditions, the catalyst loading was at 1000 ppm for iron and 100 ppm for molybdneum with fresh feed. A high coal space velocity of about 800-880 kg/h/m^3 reactor was employed throughout the entire run.

Following were the highlights of bench-run PB-03:

- The effect of changing iron and molybdenum catalyst loadings, between 1000-5000 ppm and 50-100 ppm respectively, was only significant in case of the C_4-524°C distillate yield and naphtha (lightest cut) formation; no noticeable effect was seen on either coal or residuum conversion.

- The modification of HTI's iron-based GelCat^{TM} with 100 ppm of phosphorous improved the process performance significantly; distillate yields and resid conversions increased by about 4 w% each while coal conversion increased by a percent.

- Mo-carbon catalyst, made similar to an M-Coke catalyst, was at best, as good as Molyvan-A precursor, in terms of its effect on process performance.

- In general, the net chemical hydrogen consumption was on the low side for PB-03, probably because no supported catalyst was used and the space velocities were also very high; as a result, even though the in-line hydrotreated SOH product (IBP-400°C) had a high hydrogen content (1.8-1.9 H/C ratio), the unhydrotreated product which is the part of PFL that is not recycled had a very low hydrogen content (0.8-0.9 H/C ratio) and typical high pre-asphaltene content (12-15 w% of whole PFL) which rendered the pressure filtrations extremely difficult.

- The hydrotreatment of part of the recycle oil material was found to have a positive influence on the overall process performance; the resid conversion and distillate yields increased upon replacing part of the recycle solvent stream with a hydrotreated material.

DE-92148-TOP-04

DIRECT LIQUEFACTION PROOF-OF-CONCEPT PROGRAM
Hydrocarbon Technologies, Inc., Lawrenceville, N.J.

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FINAL

Topical Report
Bench Run 02 (227-91)

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For

U.S. Department of Energy
Pittsburgh Energy Technology Center

By

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DIRECT LIQUEFACTION PROOF-OF-CONCEPT PROGRAM
Hydrocarbon Technologies, Inc., Lawrenceville, N.J.

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FINAL

Topical Report
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ABSTRACT

This report presents the results of Bench Run PB-02, conducted under the DOE Proof of Concept - Bench Option Program in direct coal liquefaction at Hydrocarbon Technologies, Inc. in Lawrenceville, New Jersey. Bench Run PB-02 was the second of the nine runs planned in the POC Bench Option Contract between the U.S. DOE and Hydrocarbon Technologies, Inc. The primary goal of this bench run was to evaluate the hybrid catalyst system, consisting of a dispersed slurry catalyst in one of the hydroconversion reactors and conventional supported extrudate catalyst in the other hydroconversion reactor, in a high-low two-stage temperature sequence, similar to the one operated at Wilsonville. This hybrid mode of operation with the high-low temperature sequence was studied during direct liquefaction of coal and in coprocessing of coal with Hondo resid and/or waste plastics under high space velocity operating conditions. Another important objective of Bench Run PB-02 was to investigate the novel "interstage internal recycle" of the second stage reactor slurry back to the first stage reactor. Other features of PB-02 included the use of an interstage separator and an in-line fixed bed hydrotreater.

In general, it was found during Bench Run PB-02 that the 'hybrid type' catalyst system was not effective for obtaining high levels of process performance as the 'all dispersed' catalyst system, tested earlier, especially at high coal space velocities. The interstage internal recycle of second stage reactor slurry to the first stage reactor feed line was not found to improve the liquiefaction kinetics or improve the process performance in any noticeable manner. The addition of small amounts of mixed plastics, representing a typical MSW waste plastic material, was found to improve the hydrogen utilization in both coal conversion and heavy oil hydrocracking reactions, i.e., plastics resulted in improving the overall distillate yield while at the same time reducing the light gas make and chemical hydrogen consumption.

EXECUTIVE SUMMARY

Bench Run PB-02 was the second of the nine runs planned in the POC Bench Option Contract between the U.S. DOE and Hydrocarbon Technologies, Inc. The primary goal of this run was to evaluate the hybrid catalyst system (dispersed slurry and supported extrudate catalysts) for direct coal liquefaction and for coprocessing of subbituminous Black Thunder mine coal with waste organics, such as waste plastics, and heavy resid. Bench Run PB-02 employed iron and molybdenum-based dispersed slurry catalysts in the first stage back-mixed reactor and supported NiMo/Alumina catalyst (Akzo AO-60) in an ebullated second stage reactor with an interstage high-pressure product separator and an in-line fixed bed hydrotreater. The overall run plan consisted of eleven operating conditions which included coal-only feed, resid-only feed, coal/resid combined feed, resid/plastics combined feed, and coal/resid/plastics combined feed. The flexibility of the unit to vary operating conditions, such as space velocities, reactor temperatures, and catalyst types and loadings, was demonstrated for five different feed mixtures over a span of 43 days. Among the significant objectives of this bench run were the investigation of "internal recycle" (interstage recycle) of reactor K-2 product to the first stage reactor K-1 without pressure let-down; to examine the beneficial effects of adding small amounts of waste plastics, and to study the effects of a hybrid catalyst system on the overall process performance. During the entire run, 50 ppm of molybdenum from Molyvan-A and 5000 ppm iron from HTI's iron catalyst were introduced with the feed to reactor K-1. Following are the highlights of bench-run PB-02:

- During the 'coal-only' feed conditions, coal conversions (based upon quinoline solubility) varied between 90 and 94 W% maf; 524°C+ resid conversions varied between 81 and 88 W% maf, while the C_4-524°C distillate yield changed from 57 to 64 W% maf. Hydrogen consumption was about 6 % (maf), and C_1-C_3 light gas yield varied between 8.5 and 12.5 W% (dry).

- The internal recycle of reactor K-2 product material to reactor K-1 during Condition 4 of the coal-only feed operation had a negative impact on the process performance; the residuum conversion and distillate yields dropped more sharply than can be explained by the batch deactivation of the second stage reactor supported catalyst. The impact of internal recycle on heavy oil hydrocracking was studied by comparing Periods 26 and 43; no significant change in the yield and conversions was found between these two periods.

- Condition 5 (Period 18) and Condition 8 (Period 34) were run in a coal/oil coprocessing mode, but Period 18 was with internal recycle of reactor K-2 product to reactor K-1. While Period 34 had no internal recycle, under comparable process severity, Period 34 showed better results than Period 18.

- Impact of hot-separator recycle appears to depend op the nature of the feedstock, ranging from negative to positive.

- Conditions 6, 7, and 11 were conducted with heavy oil (Hondo resid) alone at comparable process severities. Conversion, based on quinoline solubility, was over 99 W%, indicating that minimal coke was formed during the heavy oil conversion. The light gas yield was about 5 W%, while resid conversion was over 75 W% and distillate yield was as high as 72 W% (all maf). All this was observed at a low hydrogen consumption of 1.7 W% (dry).

- The presence of a small amount of coal (5 W%) with Hondo resid during Condition 7 (Period 30), marginally improved heavy oil hydrocracking, compared to Period 26 from Condition 6.

- The presence of small amounts of waste plastics (10 W%), with either coal or heavy resid, had a positive impact on process performance. The addition of waste plastics in small amounts to coal during Condition 9 (Period 38) reduced the light hydrocarbon gas yield from about 9-12 W% to 5.5 W% dry basis; chemical hydrogen consumption decreased significantly, while the distillate yield and residuum conversion decreased, as expected due to the deactivation of the second stage catalyst. The addition of waste plastics in small amounts had a similar effect on heavy oil hydrocracking.

- Hydrotreated second stage separator overheads (SOH) represent the net light distillate products from the process. The quality of these distillates was excellent, starting with the 'coal-only' feed conditions: high API gravities (35-42°), low heteroatom contents (less than 60 ppm nitrogen and sulfur), and high hydrogen contents (H/C ratios above 1.8). The quality of SOH oil improved very significantly in the remaining Conditions that fed various combinations of Hondo resid, coal, and waste plastics. During coprocessing conditions, API gravities increased to about 48-50° , while heteroatom contents decreased to below 30 ppm for sulfur and below 1 ppm for nitrogen. The H/C ratio increased to 1.9-2.0. The weight percent of the lightest naphtha fraction also increased to over 50 W% during coprocessing conditions.

- Economic assessment of PB-02 results shows a distinct advantage of using an all dispersed catalyst system with low/high staging, as used in PB-01, over the hybrid system with high/low temperature staging used in PB-02.

DE-92148-TOP-03

DIRECT LIQUEFACTION PROOF-OF-CONCEPT PROGRAM
Hydrocarbon Technologies, Inc., Lawrenceville, N.J.

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Topical Report
POC Bench Option Run 01 (227-90)

Work Performed Under Contract No. AC22-92PC92148

For

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Pittsburgh Energy Technology Center

By

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DIRECT LIQUEFACTION PROOF-OF-CONCEPT PROGRAM
Hydrocarbon Technologies, Inc., Lawrenceville, N.J.

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Topical Report
POC Bench Option Run 01 (227-90)

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For

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Pittsburgh Energy Technology Center

By

Hydrocarbon Technologies Inc., Lawrenceville, NJ,

April 1996

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ABSTRACT

This report presents the results of bench-scale work, Bench Run PB-01, conducted under the DOE Proof of Concept - Bench Option Program in direct coal liquefaction at Hydrocarbon Technologies, Inc. in Lawrenceville, New Jersey. The Bench Run PB-01 was the first of the nine runs planned in the POC Bench Option Contract between the U.S. DOE and Hydrocarbon Technologies, Inc. The primary goal of this bench run was to evaluate the most successful of the process improvements concepts, evolving out of the earlier CMSL Project, for direct liquefaction and coprocessing of a sub-bituminous Black Thunder mine coal with waste organics such as waste plastics and heavy resid. The interstage separation of light ends and gases was indeed found to reduce the overall light gas-make from the liquefaction process. The organic waste feeds such as mixed plastics and vacuum resid, employed during Bench Run PB-01, in combined processing with coal, resulted in making the overall process more hydrogen efficient by virtue of reducing the light gas make and also decreasing the hydrogen consumption from the process, while at the same time improving the yields and quality of the distillate products. A definite synergy was found during the combined processing of coal with mixtures of vacuum resid and mixed waste plastics. The application of an all dispersed catalyst conversion reactor resulted in higher feed throughput at equivalent process performance and also necessitated the use of an in-line hydrotreater for improving the quality of IBP-400°C distillate products. The combination of HTI's iron gel catalyst and Molyvan-A was found very effective in achieving high levels of process performance; although, in recycled form, these catalysts were not as effective as the freshly added precursors.

EXECUTIVE SUMMARY

The first Bench Run PB-01 in DOE's POC (Proof-of-Concept) Bench Option Program evaluated the long-duration continuous processing of organic wastes with sub-bituminous coal along with the demonstration of some of the most successful process concepts emerging out of the earlier CMSL Project. The Bench Run PB-01 employed an all dispersed slurry catalyst system of two-stage coal conversion reactors with an interstage high-pressure product separator and an in-line fixed bed hydrotreater. The overall Run Plan consisted of nine operating Conditions which included coal-only feed, resid only feed, coal/resid combination feed, resid/plastics combined feed, and coal/resid/plastics combined feed. The flexibility of the unit configuration and operating conditions such as feed velocities, reactor temperatures, and dispersed catalyst types and loadings was demonstrated for five different feed combinations over a span of 41 days. During the entire run, 50 ppm of molybdenum from Molyvan-A was introduced with feed to reactor K-1 and 5000 ppm iron from the HTI's iron catalyst was added only to reactor K-2 through the pump buffers. The mode of catalyst addition was switched during Condition 7 to see if it made any difference in process performance. Following were the highlights of bench-run PB-01:

- During the 'coal-only' feed conditions, coal conversion (based upon quinoline solubility) varied between 92.8 and 94.7 W% maf; 524°C+ resid conversions varied between 82.6 and 88.0 W% maf, while C_4-524°C distillate yield changed from 61.4 to 62 W% maf. Hydrogen consumption was about 6 % (maf), and C_1-C_3 light gas yield varied between 8.5 and 11.7 W% (dry).

- The recycle of catalyst from the unit pressure filter cake in the ashy recycle mode, condition 2, did not improve process performance. On the contrary, it resulted in a slight drop in total coal conversion as compared to Condition 1. Condition 3, with higher space velocity (876 kg/h/m^3) and higher (by 10°C) first stage reactor temperature, resulted in the lowest light gas formation and coal and resid conversions among the 'coal-only' feed conditions.

- Condition 4 was conducted with heavy oil (Hondo resid) alone at similar temperatures and space velocity (based upon the 524°C+ resid content of Hondo resid) as in Condition 3. The conversion, based on quinoline solubility, was 99.9 W%, indicating that no coke was formed during the heavy oil conversion. The light gas yield was about 5 W%, while the resid conversion was over 83 W%,

and distillate yield was as high as 76 W% (all maf); all this at a low hydrogen consumption of 1.72 W% (dry).

- When feed was changed from 100% Hondo resid to 50 w% Coal/50 w% Hondo (coal/oil coprocessing mode), the light gas make increased slightly to 7.2 W% (still lower than 'coal-only' feed conditions), while the combined feed conversion was 96.1 W% (coal conversion of 92.2 W% assuming complete conversion of Hondo resid to quinoline soluble materials). The distillate yield was lower (69.7 W% maf) than the 'oil-only' condition but much higher than the 'coal-only' conditions. The 524°C+ resid conversion levels were about the same for Conditions 3, 4, and 5. It is important to note that the recycle to feed ratio was reduced from 1.0 (during the 'coal-only' conditions) to 0.17 during the conditions employing Hondo resid. This was done because of the potential cost-reduction that can be brought about by lessening of recycle requirements. This adjustment in the recycle ratio seems to have had an adverse impact on the 524°C+ resid conversion levels, as the amount of resid material converted in a single-pass operation was less than desired (only in the lower 80s). It will be interesting to consider this unconverted 'resid stream' as an independent waste organic stream and coprocess it again, either with coal or plastics, so that valuable hydrogen in that stream can be mostly extracted before it goes to partial oxidation or steam reforming.

- Conditions 6 through 8 were conducted with a uniform feed comprised of equal parts of coal, Hondo resid and waste plastics. Reactor temperatures were raised by 10°C each during these conditions to achieve high cracking conversion of plastics, especially HPDE. To maintain overall process severity about the same as the earlier process conditions, feed space velocity was increased by 25 %. The overall performance during this 'semi-long-term' testing (12 days) of combined feed operation was very good and held fairly uniform. Total feed conversions of over 96 W% were obtained with 524°C+ resid conversion of about 84% and C_4-524°C distillate yield of about 73.5 W% (all maf). The light gas yields were low (5-7.5 W%), and hydrogen consumption was also low (3.1 to 3.34 W% dry). The switching of dispersed catalyst addition mode during Condition 7, during which HTI's iron catalyst was added to reactor K-1 and Molyvan-A to reactor K-2, resulted in a slight increase in hydrogen consumption, light gas yield, and 524°C+ resid conversion. This could be an effect of iron catalyst, which, in the new mode of addition, was residing in the system for a longer time and bringing about more hydrocracking than is done by the molybdenum catalyst. The ashy recycle mode, practiced again during Condition 8, did not improve process performance, confirming earlier results with the 'coal-only' Condition 2. The best part of the product distribution during these three combined feed conditions was that much higher (than at any other conditions) yields of naphtha and middle distillates were obtained.

- The last test Condition 9, was operated without any coal in the feed (50 w% of waste plastic and 50 w% Hondo resid). Interestingly, the distillate yield increased (to 76.2 W% maf), while the light gas make (4.27 W% dry) and chemical hydrogen consumption (1.34 W%) decreased. Overall performance during Condition 9 was very similar to that obtained during earlier Condition 4 which employed Hondo resid alone in the feed at comparable process severity.

- The hydrotreated second stage separator overheads (SOH) represent the net light distillate product from the process. The quality of these distillates was excellent starting with the 'coal-only' feed conditions: high API gravities (38-42°), low heteroatom contents (less than 60 ppm nitrogen and sulfur), and high hydrogen contents (H/C ratios of above 1.8). The quality of SOH oil improved very significantly in the remaining conditions that employed various combinations of Hondo resid, coal, and waste plastics. During coprocessing conditions, API gravities increased to about 48-50°, while the heteroatom contents were reduced to below 30 ppm for nitrogen and sulfur. The H/C ratio increased to 1.9-2.0. The weight percent of the lightest naphtha fraction also increased to over 50 W% during coprocessing conditions.

- The technical assessment of the performance of bench run PB-01 indicates that using HTI's iron and molybdenum dispersed catalysts, the crude oil equivalent price from 'coal-only' feed condition is about $32.50 per barrel, a tad lower than that obtained from a simulated base-case employing the conventional supported extrudate catalyst in both liquefaction reactor stages.

- Partial replacement of coal in the feed to liquefaction with either heavy petroleum oil, waste plastics, or mixtures thereof, results in a substantial cost savings, primarily because the distillate production is markedly improved and hydrogen consumption in substantially reduced. For examples, the crude oil Equivalent price for coal/oil coprocessing type operation was $26.86 per barrel; that for a combined coal/oil/plastics operation was only $21.92 per barrel while for plastics/oil operation without any coal, this price was only $20.48 per barrel.

DE-92148-TOP-02

DIRECT LIQUEFACTION PROOF-OF-CONCEPT PROGRAM
Hydrocarbon Technologies, Inc., Lawrenceville, N.J.

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Topical Report
POC Run 02 (260-05)

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For
U.S. Department of Energy
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By

Hydrocarbon Technologies Inc., Lawrenceville, NJ,

and

Kerr-McGee Corporation, Oklahoma City, Oklahoma

FEBRUARY 1996

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ABSTRACT

This report presents the results of work conducted under the DOE Proof of Concept Program in direct coal liquefaction at Hydrocarbon Technologies, Inc[1]. in Lawrenceville, New Jersey, from February 1994 through April 1995. The work included modifications to HRI's existing 3 ton per day Process Development Unit (PDU) and completion of the second PDU run (POC Run 2) under the Program. The 45-day POC Run 2 demonstrated scale up of the Catalytic Two-Stage Liquefaction (CTSL Process) on a sub-bituminous Wyoming Black Thunder mine coal to produce distillate liquid products at a rate of up to 4 barrels per ton of moisture-ash-free coal. The combined processing of organic hydrocarbon wastes such as waste plastics and used tire rubber with coal was also successfully demonstrated during the last nine days of operations of Run POC-02.

Prior to the first PDU Run POC-01 in this Program, a major effort was to modify the PDU to improve reliability and to provide the flexibility to operate in several alternate modes. The Kerr McGee Rose-SR^{SM} unit from Wilsonville, Alabama, was redesigned and installed next to the U.S. Filter installation to allow a comparison of the two solids removal systems. The facility upgrade also included was a new enclosed reactor tower, upgraded computer controls and a data acquisition system, an alternate power supply, a newly refurbished reactor, an in-line hydrotreater, interstage sampling system, coal handling unit, a new ebullating pump, load cells and improved controls and remodeled preheaters.

The 45-day CTSL Wyoming Black Thunder mine coal demonstration run achieved several milestones in the effort to further reduce the cost of liquid fuels from coal. The primary objective of the PDU Run POC-02 was to scale-up the CTSL extinction recycle process on sub-bituminous coal to produce a total distillate product using an in-line fixed-bed hydrotreater. Of major concern was whether or not calcium-carbon deposits would occur in the system as has been evident in other low rank coal conversion processes. An additional objective of major importance was to study the co-liquefaction of plastics with coal and waste tire rubber with coal. This was a direct scale-up from microautoclaves and one liter reactors to a 3 ton per day unit. In the first 36 days of the coal liquefaction operations, typical coal conversions of 92-94 W%

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[1] Hydrocarbon Technologies, Inc. is the successor to Hydrocarbon Research, Inc.

were obtained with 84-86 % resid conversions and as high as 66 % light distillate yields (all maf basis). The distillate products from the in-line fixed bed hydrotreater were very clean, containing as low as 20 ppm nitrogen and 5 ppm sulfur, with high H/C atomic ratio (1.78). The effects of feed space velocity, reaction severity, addition of a dispersed catalyst (molybdenum), and recycle stream composition on the overall process performance were studied. In the final nine days of the Run POC-02, pulverized waste tires and mixed plastics were processed with coal at 25 % tire rubber with coal and 30 % mixed plastics with coal. A total of about 15 tons of coal, tire rubber, and plastics were converted to light distillates containing less than 10 ppm sulfur and 25 ppm nitrogen with a cetane index over 40.

This was the first successful demonstration of Catalytic Two Stage Liquefaction technology at the 3 ton per day scale for a sub-bituminous coal and featured many improvements over the earlier testing conducted at the Wilsonville, Alabama Pilot Plant. Distillate liquid yields of 4.3 barrels per ton of moisture ash free coal (about 66 wt% on MAF coal) were achieved. Solvent Recycle rates were reduced from the 2-2.5 to 1 ratio demonstrated at Wilsonville to as low as 1.2 to 1 during the recent test. This greatly improves the process efficiency, process performance and economics. Coal feed rates were increased during the test by 50 - 100 % while maintaining process performance at a marginally higher reactor severity. This offers the potential for further reduction of commercial plant investment per unit of coal feed. More than 3200 gallons of hydrotreated distillate fuels were collected for end use evaluation and upgrading studies by DOE and their contractors. The ROSE-SR^{SM} Process was operated successfully using a pentane solvent in a steady-state mode. The energy rejection of the ash concentrate was consistently below prior data, being as low as 13 %, allowing improved liquid yields and recovery.

EXECUTIVE SUMMARY

This report is prepared under a multi-year Proof-of-Concept direct coal liquefaction program funded by the U.S. Department of Energy's Pittsburgh Energy Technology Center, Kerr-McGee Corporation, and Hydrocarbon Technologies, Inc. (HTI). The program is directed toward scaling up and demonstrating new liquefaction concepts that can potentially lower the cost of synthetic liquid fuels to less then $30 per barrel. The work reported herein includes modifications to the Proof-of-Concept facility at HTI's Lawrenceville, New Jersey, R&D Center and completion of a 45-day demonstration run on Wyoming Black Thunder mine sub-bituminous coal in a Catalytic Two-Stage Liquefaction mode. Operations at the 3 ton of coal per day facility produced yields of over four barrels of clean distillate liquid products per ton of coal. The high quality liquid products can be readily refined into gasoline and diesel fuel.

The 45 day demonstration run processed a sub-bituminous coal alone as feed for the first 36 days of operation and the same coal with either 25 % used tire or with 30 % mixed plastics during the last nine days of operation using Catalytic Two-Stage Liquefaction (CTSL) Technology. In the CTSL Process (*See Figure 3.1*), the first stage reactor operates at lower temperature (385-415°C) to hydrogenate the coal and recycle oil, while the second stage operates at a higher temperature (425-440°C) to convert the coal and heavy oils to clean distillate liquid products. The products can be utilized for gasoline, jet fuel, or diesel transportation fuels, or as home heating utility or combustion turbine fuels. Unconverted coal and ash are separated from recycle oils and valuable products using solids separation techniques such as filtration or solvent extraction. Kerr-McGee's ROSE-SR^{SM} solids separation technology was also demonstrated during this Black Thunder Mine coal demonstration run.

The scale-up of the CTSL process in POC Run 02 on Wyoming Black Thunder mine coal was the culmination of a ten year effort devoted to the development of this two stage ebullated-bed reactor system using a low to high temperature sequence. POC-02, the second PDU Run of this program, was completed on July 28,1994, after 45 days of on-stream coal liquefaction and coal/waste co-liquefaction operations. The effects of feed space velocity, reaction severity, addition of a dispersed catalyst (molybdenum), recycle stream composition, and the combined processing of plastics and rubber with coal on the overall process performance were studied.

The General Objectives of the PDU Run POC-02 were:

- To demonstrate the scale-up of the CTSL Process with a Wyoming sub-bituminous coal
- To demonstrate in-line hydrotreating to provide clean distillate liquid products which need minimal refining
- To demonstrate the CTSL Process with integrated solids separation
- To study the combined processing of mixed plastics and used tire rubber with coal in the CTSL Process mode.

The major accomplishments from POC Run No. 2 were:

- Successfully demonstrated the catalytic two-stage liquefaction of Wyoming sub-bituminous coal in a recycle extinction mode yielding a total distillate product
- Processed 350 tons of Black Thunder Coal over 36 days of self sustained operation, with no evidence of calcium-carbon deposition in the reaction and separation train
- Demonstrated the reliability of low/high temperature staging, operating at a low solvent ratio of 1-1.2 without the use of external (or make-up) solvent
- Attained high coal conversion of 91-93% and distillate yield of up to 4 barrels/ton of coal at a space velocity of 320 $kg/m^3/h$. Increasing the coal throughput to 600 $kg/m^3/h$ only reduced the distillate yield to about 3.5 barrels/ton.
- Operated the ROSE-SR^{SM} unit with mixed solvent and achieved organic rejections as low as 13 W% MAF coal.
- Demonstrated the concept of combined processing of coal and waste hydrocarbons; processed about 9 tons of waste plastics (a mixture of polystyrene, and polyethylene terephthalate) and waste tire rubber.

- Successfully operated a direct-coupled hydrotreated producing premium distillate (IBP-343°C) containing 25-50ppm nitrogen and 1-10ppm sulfur. 3200 gallons of net distillate (Naphtha Stabilizer Bottoms) was collected for "End-Use" studies.

Conclusions

The overall conclusions from the run based on observations and analytical results are:

- Wyoming Black Thunder mine coal demonstration at the POC scale was a successful scale-up from the earlier Bench-Scale operations at HTI facility and more successful in terms of operations and technical achievements than the Wilsonville operations 262 E and 263 J.

- A clean, IBP-360°C (IBP-680°F) distillate (sulfur content of 1-10 ppm and nitrogen content of 20-40 ppm) can be produced with in-line hydrotreating.

- The CTSL Process with sub-bituminous coal is operable at slurry oil/coal ratios as low as 1.2 to 1.

- The ROSE-SR^{SM} Process separation efficiency is highly dependent on the asphaltene content of the feed and the solvent utilized. An energy rejection of 13.6 % was achieved at a bottoms solids content of 60% when a mixed solvent consisting of 10 w% toluene in n-pentane was used.

- Within the limitations of the ROSE-SR^{SM} unit to recover resid, extinction recycle can be achieved.

- Wyoming Black Thunder mine coal resulted in lower total conversion levels and distillate yields than Illinois No. 6 coal used in the POC-01 PDU operations; in general, coal conversions during POC-02 varied between 91-93 % MAF and distillate yields between 56-66 % MAF during the 'coal-only feed' operations.

- Equilibrated Akzo AO-60 catalyst, used during POC-02 operations, was found to undergo some attrition probably as a result of increased water vapor concentration in the reactor with high oxygen-containing subbituminous coal; the extent of catalyst attrition even increased during the last nine days of coal/waste coprocessing operations.

- The ROSE-SR^{SM} unit efficiency is unaffected by whether the liquefaction recycle system is operated with or without ashy recycle.

- Total combined conversion to quinoline soluble products, as measured in atmospheric bottoms product, and the ash concentrate indicate that during the coal/waste coprocessing operations, some retrograde reactions were occurring in the ROSE-SR^{SM} unit as observed previously with higher boiling ROSE-SR^{SM} solvents.

- Addition of 150 ppm of a soluble molybdenum dispersed slurry catalyst improved the total coal conversion by over a percent; it was found that the molybdenum from soluble precursor, added to reactor, was depositing at low levels onto the supported extrudate catalyst in the reactor.

- Although due to short periods of operations during coal/plastics or coal/rubber feed conditions, the process equilibration was never achieved resulting in the usage of significant proportions of an extreneous make-up oil (negative solvent-balance), the coprocessing Periods resulted in higher light distillate yields, lower gas make and reduced chemical hydrogen consumptions.

Recommendations

- CTSL type processing of low rank coals using either a combination of dispersed slurry and supported extrudate catalysts or dispersed slurry catalyst only reaction systems would be interesting to study in the future for further improving the overall liquefaction economics.

- The combined processing of the organic hydrocarbon wastes with coal should be studied under the conditions of a net positive recycle solvent balance, i.e., under process equilibrated or steady-state conditions.

- The reliability of the catalyst addition system needs to be improved.

- Other unit operations that require redesign for improved operability are:

  Oil/Water Separation, External Separation, Let-down Valves, Slurry Heat Exchange, the U.S. Filter, the ROSE-SR^{SM} Bottoms Removal and Heat Exchange, Coal Feed System and the Interstage Sampling System.

- A further operation on sub-bituminous coal with in-line hydrotreating and interstage products separation using synthesis gas as a reducing gas in the first stage dissolution reactor is also recommended.

DE-92148-TOP-01

DIRECT LIQUEFACTION PROOF-OF-CONCEPT FACILITY
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Technical Progress Report
POC Run 01 (260-04)

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and

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SECTION I

ABSTRACT

This report presents the results of work conducted under the DOE Proof of Concept direct coal liquefaction at Hydrocarbon Research, Inc. in Lawrenceville, New Jersey from October 1992 through April 1994. The work included extensive modifications to HRI's existing 3 ton per day Process Development Unit (PDU) and completion of the first PDU run (POC Run 1) under the Program. The 58-day POC Run 1 demonstrated scaleup of the Catalytic Two-Stage Liquefaction (CTSL Process) on Illinois No. 6 coal to produce distillate liquid products at a rate of up to 5 barrels per ton of moisture-ash-free coal.

During the first fiscal year, the major effort was to modify the PDU to improve reliability and to provide the flexibility to operate in several alternate modes. The Kerr McGee Rose-SR^{SM} unit from Wilsonville, Alabama was redesigned and installed next to the U.S. Filter installation to allow a comparison of the two systems. Also included was a new enclosed reactor tower, upgraded computer controls and a data acquisition system, an alternate power supply, a newly refurbished Wilsonville reactor, an in-line hydrotreater, interstage sampling system, coal handling unit, a new ebullating pump, load cells and improved controls and remodelled preheaters.

The 58-day CTSL Illinois coal demonstration run achieved several milestones in the effort to further reduce the cost of liquid fuels from coal. This was the first demonstration of HRI's Catalytic Two Stage Liquefaction technology at the 3 ton per day scale and featured many improvements over the earlier testing conducted at the Wilsonville, Alabama Pilot Plant. Distillate liquid yields of 5 barrels per ton of moisture ash free coal (about 75 w% on MAF coal) were achieved. Coal slurry recycle rates were reduced from the 2-2.5 to 1 ratio demonstrated at Wilsonville to as low as 0.9 to 1 during the recent test. This greatly improves the process efficiency, process performance and economics. Coal feed rates were increased during the test by 50% while maintaining process performance at a marginally higher reactor severity. This offers the potential for further reduction of commercial plant investment per unit of coal feed. Sulfur in the coal was reduced from 4 w% to about 0.02 w% sulfur in the clean distillate fuel product. More than 3500 gallons of distillate fuels were collected for evaluation and upgrading studies by DOE and their contractors. The ROSE-SR^{SM} Process was operated for the first time with a pentane solvent in a steady-state mode. The energy rejection of the ash concentrate was consistently below prior data, being as low as 12%, allowing improved liquid yields and recovery.

SECTION III

EXECUTIVE SUMMARY

This report is prepared under a multi-year Proof-of-Concept direct coal liquefaction program funded by the U.S. Department of Energy's Pittsburgh Energy Technology Center, Kerr-McGee Corporation, and Hydrocarbon Research, Inc. (HRI). The program is directed toward scaling up and demonstration new liquefaction concepts that can potentially lower the cost of synthetic liquid fuels to less then $30 per barrel. The work reported herein includes modifications to the Proof-of-Concept facility at HRI's Lawrenceville, New Jersey R&D Center and completion of a 58-day demonstration run on Illinois No.6 bituminous coal in a Catalytic Two-Stage Liquefaction mode. Operations at the 3 ton of coal per day facility produced yields of five barrels of clean distillate liquid products per ton of coal. The high quality liquid products can be readily refined into gasoline and diesel fuel.

The 58 day demonstration run processed a high sulfur (4 w%) Illinois bituminous coal using HRI's Catalytic Two-Stage Liquefaction (CTSL) Technology. The process is similar to that utilized in HRI's commercially demonstrated H-Oil® Process for heavy oil conversion. In the CTSL Process, (*See Figure 3.1*) the first stage reactor operates at lower temperature (385-415°C) to hydrogenate the coal and recycle oil while the second stage operates at a higher temperature (425-440°C) to convert the coal and heavy oils to clean distillate liquid products. The products can be utilized for gasoline, jet fuel, or diesel transportation fuels, or as home heating utility or combustion turbine fuels. Unconverted coal and ash are separated from recycle oils and valuable products using solids separation techniques such as filtration or solvent extraction. Kerr-McGee's ROSE-SR^{SM} solids separation technology was demonstrated during the Illinois coal demonstration run.

The scale-up of the CTSL process in POC Run 01 on Illinois #6 Coal was the culmination of a ten year effort devoted to the development of this two stage ebullated-bed reactor system using a low to high temperature profile.

POC-01, the first PDU Run of this program, was completed on February 19,1994 after 58 days of on-stream coal operations.

Some of the major accomplishments from the run were:

- Successfully commissioned and operated the newly installed equipment and the completely integrated two-stage coal liquefaction unit, including the ROSE-SR^{SM} solids-separation unit.

- Achieved operation with a more concentrated coal feed slurry at a 0.9 to 1.0 oil/coal ratio (53% Coal). This greatly improves the process efficiency and economics as compared to the 2-2.5 to 1.0 ratios demonstrated at Wilsonville.

- Successfully operated the ROSE-SR^{SM} unit using a pentane solvent in a steady-state mode. Demonstrated energy rejection of the ash concentrate consistently below prior data achieving 12% energy rejection for a sustained period.

- Collected 3500 Gallons of Distillate product (IBP to 350°C) for upgrading studies and engine testing.

- Demonstrated distillate production at C_4-524°C MAF levels of 70-74% and Coal Conversions of 95-96% with Illinois #6 Crown II Mine bituminous coal. *(See Table 3.1 following this section)*

- Produced an IBP-350°C Product with an API of 33, Nitrogen Content of 0.06 wt% and a Sulfur Level of 0.03 wt%.

- Identified several design improvements for the ROSE-SR unit, Hot Separator and Coal Feeding System.

- Met and exceeded total distillate product yields achieved earlier at Wilsonville with Illinois No.6 coal in a Catalytic Two-Stage Liquefaction Mode.

- Collected samples from various process streams for other DOE Contractors.

- Tested several materials of construction supplied by Oak Ridge Labs in the reactors and at elevated temperature locations downstream.

Several objectives were not achieved during this run and are being rescheduled for POC-2, they are:

- Operation of the in-line hydrotreater; After several days of operation bypassing around the fixed catalyst bed was indicated and it was taken off-line.

- Operation of the U.S. Filter; By-Passing around the filter leaves was observed and confirmed later.

- Operation of the Interstage Sample System; Plugs occurred on the high pressure side of the sample tap. Only two interstage samples were obtained.

- With increasing asphaltene content of the bottoms stream in the latter stages of the run, true extinction recycle of the 360°C+ oils could not be sustained due to a decrease in the ROSE-SR separation efficiency. Mixed solvents are planned to be used in future PDU operations.

Conclusions

The overall conclusions from the run based on observations and analytical results are:

- Within the limitations of the ROSE-SR unit to recover resid, extinction recycle can be achieved.

- A clean, IBP -360°C (IBP-680°F) distillate (sulfur=450ppm & nitrogen=550ppm) can be produced without hydrotreating.

- The CTSL Process is operable at slurry oil/coal ratios as low as 0.9-1.0.

- The Rose-SR Process separation efficiency is highly dependent on the asphaltene content of the feed and the solvent utilized. Using pentane and with a Quinoline Insolubles level of 33% in the feed, an energy rejection of 12.5% was achieved at a bottoms solids content of 65%.

- Crown II Mine, Illinois #6 Coal is a good candidate coal for liquefaction with demonstrated coal conversions up to 96% and residual oil (524°C+) conversions of over 85%.

- Akzo, AO-60 catalyst is a strong attrition resistant catalyst with high activity for coal liquefaction.

- The ROSE-SR unit efficiency is unaffected by whether the liquefaction recycle system is operated with or without ashy recycle.

- Coal conversion as measured in atmospheric bottoms product and the ash concentrate indicate that retrograde reactions are not occurring in the ROSE-SR unit as observed previously with higher boiling solvents.

Recommendations

- Operation of the ROSE-SR unit must be improved to recover more of the asphaltenes for recycle and extinction. Use of a mixed solvent is recommended.

- The Hydrotreater internals must be modified to prevent by-passing of the fixed catalyst bed.

- Further studies at higher coal feed rates (space velocities) are warranted to improve process economics.

- The reliability of the catalyst addition system needs improvement.

- Other areas that require redesign for improved operability are:

  Oil/Water Separation, External Separation, Let-down Valves, Slurry Heat Exchange, the U.S. Filter, the ROSE-SR Bottoms Removal and Heat Exchange, Coal Feed System and the Interstage Sampling System.

- A further operation on bituminous coal with in-line hydrotreating and improved solid separation and heavy oil recovery is recommended.

TABLE 3.1
POC-01 PROCESS PERFORMANCE

Coal: Illinois No. 6 Crown II Mine (10.4 w% Dry Ash)
Catalyst Akzo AO-60 1/16" NiMo Extrudates in both Reactors

CONDITION	2
Process	CTSL
Period/s	24-26
Solids-Separation	ROSE-SR
Recycle Type	Ash-free
Space Velocity, Kg/hr/m^3 (Stage)	310
K-1: Temperature, °C	407
Cat Replace. Rate, Kg/Kg Ton MF Coal	0.7
K-2: Temperature, °C	432
Cat Replace. Rate, Kg/Kg Ton MF Coal	1.4
Flow Rates	
Coal Feed, Kg/hr	70
Solvent/Coal Ratio, Kg/Kg	1.26
Material Balances	
Liquefaction Section Recovery, W%	99.1
Overall Material Recovery, W%	98.1
YIELDS, W% MAF COAL (Based on Liquefaction Section)	
H2S	2.45
NH3	1.45
H2O	9.91
COx	0.05
C1-C3	5.66
C4-177 C	19.03
177-288 C	29.04
288-343 C	17.52
343-524 C	8.61
524 C+	8.45
Unconverted Coal	4.97
Hydrogen Consumption	7.14

TABLE 3.1 (cont'd)
POC-01 PROCESS PERFORMANCE

Coal: Illinois No. 6 Crown II Mine (10.4 w% Dry Ash)
Catalyst Akzo AO-60 1/16" NiMo Extrudates in both Reactors

PROCESS PERFORMANCE, W% MAF COAL

Coal Conversion	95
524 C+ Conversion	86.6
Desulfurization (Organic), W%	97.7
Denitrogenation, W%	82.5
C_4-343°C Net Distillates	65.6
C_4-524°C Distillates	74.2
, Barrels/MAF Ton	5.0
C_1-C_3 Selectivity, Kg/Kg of C_4-524°C (X 100)	7.6
H_2 Efficiency,Kg C4-524°C/Kg H_2	10.4

DEASHER PERFORMANCE

Organic Rejection, W% MAF	15.2
Energy Rejection, %	16.5
Deasher Coal Conversion, W% MAF	95.1

TABLE 3.1

PROOF-OF-CONCEPT DIRECT LIQUEFACTION UNIT AT HYDROCARBON RESEARCH, INC.

SIMPLIFIED FLOW PLAN