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**Continuous Bench-Scale Slurry Catalyst Testing
Direct Coal Liquefaction of Rawhide Sub-bituminous Coal**

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Introduction

In 1992, the Department of Energy (DOE) sponsored research to demonstrate a dispersed catalyst system using a combination of molybdenum and iron precursors for direct coal liquefaction. This dispersed catalyst system was successfully demonstrated using Black Thunder sub-bituminous coal at Wilsonville, Alabama by Southern Electric International, Inc. The DOE sponsored research continues at Exxon Research and Development Laboratories (ERDL).

A six month continuous bench-scale program using ERDL's Recycle Coal Liquefaction Unit (RCLU) is planned, three months in 1994 and three months in 1995. The initial conditions in RCLU reflect experience gained from the Wilsonville facility in their Test Run 263. Rawhide sub-bituminous coal which is similar to the Black Thunder coal tested at Wilsonville was used as the feed coal. A slate of five dispersed catalysts for direct coal liquefaction of Rawhide sub-bituminous coal has been tested. Throughout the experiments, the molybdenum addition rate was held constant at 100 wppm while the iron oxide addition rate was varied from 0.25 to 1.0 weight percent (dry coal basis). This report covers the 1994 operations and accomplishments.

Objective

The objective of this project taken from the Statement of Work (DE-AC22-94PC94051) is to test advanced and novel slurry phase catalysts for direct coal liquefaction. These novel slurry phase catalysts were developed in other DOE sponsored research programs. The properties of the catalysts are presented in Table 1. A number of such catalysts have shown initial promise in laboratory-scale research, typically by experimentation in small batch autoclaves. The efficacy and application of these catalysts is expected to be strongly dependent upon the process steps and overall configuration envisioned for a particular liquefaction process. The most favorable catalysts and relevant approaches must be evaluated in a continuous flow bench-scale facility in order to define and verify the steady-state product yield structures in response to operating parameters and process changes.

In order to help guide the research effort a set of goals was targeted. A summary of the major project goals as listed in DOE's Statement of Work is presented below:

- Demonstrate mechanical operability of continuous bench unit.
- Verify suitability of system design, including use of plug flow reactors.
- Define suitable catalyst screening conditions.
- Test three iron catalysts.
- Test two molybdenum catalysts.
- Conduct limited optimization studies.
- Obtain mass and elemental balances for chosen data periods.
- Define product yield structures for chosen data periods.

Table 1
Properties of Slurry Catalysts

Catalyst	Particle Size, Microns	Surface Area, m ² /g	Bulk Density, g/cm ³	Physical Form	Composition wt %
NANOCAT [®] Superfine Iron Oxide (SFIO)	0.003	250	0.05	Reddish-brown powder	100 % Fe ₂ O ₃
Bayferrox PK 5210 Technical Iron Oxide	0.020	123	n/a	Reddish-brown powder	100 % Fe ₂ O ₃
Bailey Iron Oxide	96 wt%<44	n/a	n/a	Reddish-brown powder	100 % Fe ₂ O ₃
MOLYVAN L, Molybdenum containing lubricant	n/a	n/a	1.08	Dark green liquid	8.1 % Mo
MOLYVAN A, Molybdenum containing powder	5 to 10	n/a	1.58	Yellow-orange powder	30.0 % Mo
Ammonium heptamolybdate	n/a	n/a	2.50	White powder	54.3 % Mo

Process Overview and Simplified Process Flow Plan

The Recycle Coal Liquefaction Unit (RCLU) is located at the Exxon Research and Development Labs in Baton Rouge, Louisiana. RCLU is a highly automated, highly instrumented pilot plant designed to process 34 kg (75 lbs.) of coal per day. It has redundant computer control and data acquisition systems allowing for efficient trouble shooting, data analysis and material balance calculations. Over the years, RCLU has been re-configured many times to meet specific data requirements for coal and heavy hydrocarbon conversion. Hence, RCLU is versatile and easy to re-configure. RCLU has been a very reliable tool in the past, with many runs over 1000 continuous hours. An overview of the process is described below and a simplified process flow plan is presented in Figure 1.

Slurry Mixing

In this process, coal, make-up catalysts, recycle solvent and recycle bottoms are prepared in 6 to 8 hour batches in the mix tank to form a homogeneous feed slurry. The

equipment in the slurry mix area are the mix tank, spared recirculation pumps, the coal/bottoms bin and the solvent tank. The mix tank is totally enclosed to prevent dust and vapors from entering the process streams. The slurry temperature is typically held around 135- 143 °C (275-290 °F) to ensure an easily pumpable slurry. The pressure is held at atmospheric or slightly above during non-charging periods. However, a vacuum can be drawn on the solvent tank to aid during feed charging. The tank is equipped with a mixer to mix the coal, bottoms, solvent and catalyst. The feed slurry is further mixed by the recirculation pump.

Slurry Feed

The slurry feed section is used to provide continuous slurry flow to the liquefaction reactors. The major equipment in the area include the feed tank, spared recirculation pumps, and high pressure feed pumps. Periodically, the feed tank is charged with a fresh batch of slurry from the mix tank. The slurry is continuously mixed and recirculated to ensure a homogeneous slurry in the feed tank. The high pressure pumps are used to pump a slip-stream of slurry from the recirculation loop to the liquefaction reactors. Typical holding tank operating conditions are 135- 143 °C (275-290 °F) and atmospheric pressure.

Liquefaction Reactors

The liquefaction reactor system consists of a pretreater and two reactors in series and their associated sandbaths. The pretreater consists of two or three 25 mm (1") ϕ 316 stainless steel pipes and each reactor consists of four or six 25 mm (1") ϕ 316 stainless steel pipes. The reactor pipes are 1.22 m (4 ft) in length and are connected by 9.5 mm (3/8") ϕ 316 stainless steel tubing. The reactors operate in an upflow mode and are capable of having interstage hydrogen addition. The sandbaths are electrically heated and are used to control the reactor temperatures.

The slurry is pumped from the feed tank to the pretreater at a rate of 3.6 to 5.5 kg/hr (8 to 12 lbs/hr). The purpose of the pretreater is to activate the catalyst by sulfiding the iron oxide. The catalyst is activated by treat gas containing 10 volume percent H₂S in H₂. The activated slurry leaving the pretreater is blended with pure H₂ treat gas before it is fed to the first stage reactor. Most of the coal is converted to liquid hydrocarbons and gas via a combination of thermal and catalytic processes in the two liquefaction reactors.

The residence time within the pretreater and each reactor can be varied by varying slurry feed rate or by varying the number of reactor pipes in each sandbath. The nominal residence time of the pretreater ranges from 20 to 30 minutes while the nominal residence time of each reactor ranges from 40 to 55 minutes. The pretreater and liquefaction reactors operate at 17.2 Mpa (2500 psig). The pretreater operates between 296 - 302 °C (565 - 575 °F) while the liquefaction reactors operate between 427 - 454 °C (800 - 850 °F). A slight exotherm exists in the first two tubes of the first stage reactor. Otherwise, the reactors operate close to isothermal operation and have minimal pressure drop.

High Pressure Separations

RCLU uses high pressure separation vessels to separate the heaviest fraction of the reactor product from the lighter fraction. The high pressure separations consist of both hot and cold separators operating at slightly below reactor pressure. The hot separator is used to split the reactor effluent into two streams; an overhead stream consisting of gases, water and light oil and an underflow stream consisting of heavy oil and mineral matter. The overhead stream from the hot separator passes through two heat exchangers before entering the cold separator. The exchangers cool the stream, thus condensing some of the light oils which are captured in the cold separator. The hot separator underflow stream proceeds to the bottoms stripper where it is stripped with the offgas from the cold separator. The cold separator underflow stream proceeds to fractionation.

Bottoms Stripping

The bottoms stripper separates nominally 1000 °F- hydrocarbons from heavier hydrocarbons and mineral matter (bottoms). Bottoms are periodically withdrawn into a bucket and allowed to cool and solidify. The bottoms is then crushed and a fraction is recycled to the mix tank. The overhead gas and the stripped hydrocarbons are cooled before going to fractionation.

Fractionation

The cold separator underflow stream and the bottoms stripper overhead stream are combined in the fractionator feed surge tank. The product gas passes through several flowmeters before the stream is released to the flare vent. A slipstream of the gas is sent to an online process gas chromatograph (GC) system after the flowmeters. The GC system samples the product gas continuously and analyzes the stream for H₂, H₂O, CO, CO₂, N₂, H₂S, O₂, C₁, C₂, C₃, C₄ and C₅+. The information from the product gas flowmeters and GC system are used to develop daily online material balance closures and later for the complete data workup.

The liquid is pumped from the fractionator feed surge tank to a preheater before it is fed to the fractionator. The fractionator is designed to split the nominally 1000 °F-stream into two components, solvent (also called VGO) and light oil (naphtha/distillate). The heavier component has an initial boiling point (IBP) between 550 °F and 650 °F depending upon tower temperatures. The lighter component has a C₅ IBP. The tower underflow stream is periodically removed and partially recycled to the mix tank. The overhead stream is condensed, refluxed and periodically removed.

Operations Synopsis

Operations were initiated in August, 1994 following a period of about 2 months of equipment modifications, pressure testing and instrument calibrations. During the period

of August 7, 1994 to October 29, 1994, twenty-four yield periods were successfully completed. Below is a synopsis of the pilot plant operations.

Typically, the ash content of the recycle bottoms stream provides a good indication of coal conversion level. As the coal conversion levels off the unit approaches steady state operations. The analytical tests for bottoms ash content showed that the first set of yields periods were not at steady state. Since the analytical ash tests cannot be conducted daily, screening ash tests were used to determine if the operations were near steady state. However, the initial screening tests were inaccurate and needed to be revised because of incomplete ashing. The revised screening ash tests gave similar results to the analytical ash tests.

During the third balance of condition 1 (YP411) the feed tank scale malfunctioned. The coal slurry feed rates were calculated from the mix tank weights because of the problems with the feed tank scale. The measured material balance was poor for this period. However, the other data was more than adequate for reliable data reconciliation.

Molyvan A was used for conditions 2A, 2B and 3 because Molyvan L was not available. The operations for condition 2A were smooth.

Several computer boards went bad during condition 2B after completing the second yield period (YP416). The control programs were not operating for several hours, but the boards were changed in time to avoid shutting down the unit. The conditions were allowed to stabilize for 30 hours before collecting data for the third yield period of condition 2B (YP418).

A slight tuning problem with the first stage reactor temperature was experienced during condition 3. The temperature profile was sinusoidal with swings of 2.8 °C (5 °F). The controls were re-tuned before condition 4 to reduce the temperature swings.

The first stage reactor heaters were shutdown temporarily during the third yield period of condition 4 (YP424) due to a low pressure alarm. The low pressure alarm was set off by plugged lines. Once the lines were unplugged the heater operations returned to normal. However, the average reactor temperature was 2.8 °C (5 °F) low for YP424. Otherwise operations were smooth for condition 4.

During condition 5, the first stage reactor thermocouple relays went bad. The thermocouples were reading 2.8 °C (5 °F) low during the first two yield periods of condition 5 (YP425 & YP426). The average sand bath temperatures were substituted for the average reactor tube temperatures of YP425 & YP426. After the thermocouple relays were replaced, the difference between the average sand bath and the average reactor tube temperatures was within 0.3 °C (0.5 °F) for the remaining yield periods (YP427-YP433).

One of the two dry test meters that measures the product off gas rate gave inaccurate readings for condition 6 and subsequently was taken out of service before condition 7. Therefore, the product off gas rate was based only on one dry test meter

rather than the average of two. The yield periods for condition 6 were collected before approaching steady state because of the limited supply of Mach 1 catalyst.

The second dry test meter became unreliable during condition 7. A restriction in the second dry test meter caused a high pressure drop across the flow meter. Consequently, the upstream roots meter was adversely affected by this high pressure drop. The roots meter gave an erroneously low reading for the product off gas rate because it did not correct the flow rate for the higher pressure condition. Since the feed gas and product gas rates were nearly constant for the previous two conditions the product off gas rate for condition 7 was approximated based on the product off gas rates for conditions 5 & 6. The approximations were fairly good since the reconciliation program made only slight adjustments to the product off gas rates.

Material Balancing and Analyses Procedures

Material balances are based on a 24 hour operating period at constant conditions. Ideally, the conditions are at or near steady state before a yield period (material balance period) is initiated. There is a compromise between the number of conditions and the approach to steady state for a given amount of operating time. For these experiments, some approach to steady state was sacrificed for maximizing the number of operating conditions. The yield periods were initiated when the bottoms conversion started to level off.

From past experience at Exxon, the ash content of recycle bottoms provides a good indication of coal conversion level with known feed coal ash content. In typical bottoms recycle pilot plant operations, the ash content of the recycle bottoms are monitored daily in a screening test. The final ash content in the recycle bottoms is conducted by the analytical labs several weeks later. The procedure for both tests are essentially the same. The main differences are that the analytical tests are automated and use a different purge gas. The ash content of bottoms are measured in duplicate by combustion of small samples of bottoms at 950°C for at least three hours. The average ash content of bottoms and known feed coal ash content are input to a computer model with an equation built in assuming 100% ash balance. The model calculates DAF coal conversions and data are plotted daily to monitor the trend of new conditions vs. the previous conditions. In a typical case, a significant change in the coal conversion is observed in the first few days after starting a new condition. The coal conversion gradually levels off in about 3-5 days after the change to the new condition. The yield periods are initiated when the bottoms ash content begins to level off. The screening tests compare well with the analytical lab tests.

Material balances are conducted after a yield period is complete. RCLU utilizes two levels of material balancing. The first level is on-line material balancing and the second level is material balancing that utilizes data reconciliation techniques. The on-line material balances are often completed within 24 hours after the end of the yield period. They are

used to guide unit operations, identify data acquisition problems, and provide preliminary product yields leading to the determination of subsequent run conditions.

The raw data and process variables of each yield period are stored in the RCLU computer system. The on-line material balancing program retrieves these raw data from the RCLU computer system along with input data from unit engineers to calculate the overall material balance, DAF coal conversion, hydrogen consumption, and gaseous and distillate yields for each yield period. The input data from unit engineers include moisture and ash contents of feed coal, and percents of 1000°F⁺ material in the recycle solvent and 1000°F⁻ material in the recycle bottoms. In order to cross-check the data, balances and yields are calculated using three different slurry feed bases. If balances are poor or yields deviate substantially from the expected then the weights and analyses are re-checked for errors. If no errors are found, an investigation is initiated to determine possible unit material losses and/or errors in data acquisition.

The second level of material balancing utilizes the results of the on-line material balances as well as elemental analyses of each feed and product stream, and simulated distillation by gas chromatography (GCD) analyses of hydrocarbon streams. The reconciled balances are usually not finalized until at least three weeks after the end of a given yield period. Reconciled balances are considered the finalized results and are the results most often reported. Once finalized, reconciled results are used to compare the effects of process variables and/or catalysts on product yields and product distribution.

In order to reconcile the data, a mainframe computer program which utilizes geometric programming techniques is used to adjust the data to comply with a set of constraint equations. The objective of data reconciliation is to legitimately adjust data values to balance elemental weights of feed and product streams. Data is therefore adjusted by taking into account the reliability of each data measurement. Those variables which have poor reliability are preferentially changed in order to achieve data consistency. Neither the constraint equations nor variable reliabilities are changed from yield period to yield period.

Data reconciliation is an iterative procedure that is designed to be used only when "as-measured" balances are good. Typically, data reconciliation requires that the total material balances are between 98 and 102%. However, material balances between 95 and 102% are tolerable. If the balances do not meet the above criterion, the data is re-analyzed for obvious errors and suspect samples are resubmitted for analyses.

Data from any single reconciled yield period should not be used in data comparisons due to operational variations. Rather, the results from several yield periods (≥ 3) at one condition should be used for comparison purposes.

Results and Discussion

Eight conditions were tested during the 1994 operations, covering the impact of solvent to coal ratio, time-temperature trade off, and type and make-up rate of iron oxide catalyst as shown in Table 2. The molybdenum make-up rate remained constant throughout the experiments. However, the source of molybdenum was varied. A summary of the operating conditions are presented in Table 3. Three 24 hour balances (yield periods) were performed at each condition. A summary of the reconciled yields and overall conversion are presented in Table 4. The values shown in Tables 3 & 4 are the average values at each condition.

Table 2
Summary of Experimental Design

Condition	Comment	Yield Periods of Interest
1	Initial conditions.	409-411
2A	Reduced solvent to coal ratio compared with initial conditions.	412-414
2B	Reduced H ₂ S treat rate compared with conditions 1 and 2A.	415, 416, 418
3	Increased first stage reactor temperature and increased mass flow rate compared with previous conditions.	419-421
4	Switched from Bailey iron oxide to Bayferrox PK5210 iron oxide catalyst.	422-424
5	Reduced iron oxide addition rate from 1.0 to 0.25 wt% on dry coal.	425-427
6	Switched from Bayferrox PK5210 to Mach 1-Nanocat SFIO catalyst.	428-430
7	Switched from organic to inorganic source for molybdenum catalyst and switched back to Bayferrox PK5210 iron oxide.	431-433

Table 3
Summary of Test Conditions

Condition	Fe ₂ O ₃ Type	Fe ₂ O ₃ wt %	Mo Type	S/C: B/C	H ₂ S as S wt %	NRT, min.	Reactor 1 st °C (°F)	Temperatur 2 nd °C (°F)
1	Bailey	1.03	Org.	1.07:0.85	5.8	49	430.6 (807.0)	450.6 (843.0)
2A	Bailey	0.99	Org.	0.94:0.71	6.0	53	431.1 (808.0)	451.1 (844.0)
2B	Bailey	1.00	Org.	0.90:0.75	2.7	50	431.3 (808.3)	449.3 (840.7)
3	Bailey	1.02	Org.	0.95:0.79	3.4	41	441.3 (826.3)	450.0 (842.0)
4	Bayferrox	1.00	Org.	0.94:0.76	3.3	41	439.3 (822.7)	449.6 (841.3)
5	Bayferrox	0.25	Org.	0.91:0.80	3.0	41	441.5 (826.7)	450.6 (843.0)
6	Mach 1	0.26	Org.	0.91:0.83	3.1	42	440.9 (825.7)	450.4 (842.7)
7	Bayferrox	0.26	Inor.	0.98:0.85	3.1	41	440.9 (825.7)	450.0 (842.0)

Table 4
Summary of Reconciled Yields and Conversion,
(wt% Based on Dry Ash-Free Coal)

Condition	Yield Period	H ₂	C ₁ -C ₄	C ₅ -350	350-650	650-1000	Conversion
1	409-411	-6.12	15.34	14.48	33.93	9.06	88.56
2A	412-414	-6.11	14.51	13.54	32.55	13.57	89.26
2B	415-418	-5.77	13.69	12.86	31.35	14.87	88.60
3	419-421	-5.76	13.31	12.30	29.61	14.59	86.88
4	422-424	-5.43	12.48	12.71	31.33	13.70	85.62
5	425-427	-5.76	14.08	12.24	31.22	13.54	87.01
6	428-430	-5.46	12.82	11.66	30.69	14.67	85.19
7	431-433	-5.65	12.61	12.27	32.14	12.57	85.74

General Observations

In general, catalyst changes had very small impact on performance. Of all of the changes tested, one process change, reducing the recycle ratio had the most striking impact. Apparently, recycle ratio has more impact on performance than catalyst over the range of the tests. It may be that the constant addition of 100 wppm molybdenum is masking other changes, such as type and amount of iron catalyst addition rate. Discussions with PETC have indicated to us that the constant molybdenum addition rate was specified based on results at Wilsonville.

Reduced Recycle

The impact of reduced recycle is shown by comparing condition 1 with 2A. The total recycle was reduced from 1.92 to 1.65 on dry ash free (DAF) coal. The result was a significant shift towards a heavier product slate, and higher conversion.

Reduced Sulfur Addition Rate

The impact of reduced sulfur addition rate is shown by comparing condition 2A and 2B. The result was a small reduction in gas yields and hydrogen consumption. No other statistically significant changes were observed. While statistically significant, a small systematic error in the feed gas or product gas sulfur content may have clouded the data. Thus our interpretation of the test result is that the reduction in sulfur had no significant impact on yields or conversion.

Increased Stage 1 Temperature and Mass Velocity

The impact of increasing the first stage reactor temperature and the mass velocity can be seen by comparing condition 3 with 2B. Conversion and liquid yields dropped. Conversion went from 88.60 to 86.88 wt % on DAF coal. C_5 -1000°F dropped from 59.1 to 56.5 wt% DAF coal. The temperature and mass velocity were increased to make the impact of a better catalyst easier to detect.

Changed Iron Oxide Catalyst

The impact of iron catalyst type, Bailey vs. Bayferrox is shown by comparing conditions 3 and 4. There was an unintended drop in the first stage reactor temperature of about 2 °C during condition 4, otherwise, conditions were held nominally constant. Conversion, gas yield, and hydrogen consumption all dropped significantly. As with all of these tests, the molybdenum addition rate was held steady at 100 wppm on dry coal. Liquid yields held their own and gas selectivity ($100 \times C_1$ to C_4 yield/total conversion) decreased. Directionally this seems to indicate that an improved iron catalyst could lead to a more selective liquefaction process.

Reduced Iron Oxide Addition Rate

The impact of reducing the iron oxide addition rate from 1.0 to 0.25 wt% DAF coal is shown by comparing condition 4 and 5. The temperature control was improved during condition 5, resulting in an apparent increase of 2 °C in the first reactor stage temperature. The most notable changes were a significant increase in conversion, gas yield, and hydrogen consumption. Conversion increased from 85.62 to 87.01 wt%, C_1 to C_4 increased from 12.48 to 14.08, and hydrogen consumption increased from 5.43 to 5.76 wt % on DAF coal, all statistically significant. Liquid yields remained steady. Notionally, the small increase in temperature may have contributed to the small but significant increase in conversion, while the reduction in catalyst may have lead to the deterioration in gas/liquid selectivity ($100 \times C_1$ to C_4/C_1 to 1000 °F).

Changed Iron Oxide Catalyst

The impact of iron catalyst type, Bayferrox vs. Mach 1 are shown by comparing conditions 5 vs. 6. The results were small, but significant drops in conversion, C_1 to C_4 , and hydrogen consumption. Conversion dropped from 87.0 to 85.2 wt% DAF coal, while C_5 to 537.7°C (1000°F) liquid yields held steady at 57.0 wt % on DAF coal.

Changed Molybdenum Source

The impact of changing the Molybdenum source from Organic, Molybdenum Van L, to inorganic, ammonium heptamolybdate is shown by comparing conditions 5 and 7. The change resulted in a significant drop in conversion, from 87.0 to 85.7, and lower C_1 to C_4 from 14.1 to 12.6. Even though conversion and gas yields dropped in going from the organic to the inorganic molybdenum source, selectivity to liquids improved.

Figure 1
Schematic Flow Plan of RCLU Pilot Plant

