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ADVANCED LIQUEFACTION USING COAL SWELLING
AND CATALYST DISPERSION TECHNIQUES

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By

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EXECUTIVE SUMMARY

The overall objective of this project is to develop a new approach for the direct liquefaction of coal to produce an all-distillate product slate at a sizable cost reduction over current technology. The approach integrates coal selection, pretreatment, coal swelling with catalyst impregnation, liquefaction, product recovery with characterization, alternate bottoms processing, and carrying out a technical assessment including an economic evaluation. The project is being carried out under contract to the United States Department of Energy. The primary contractor is Amoco Oil Company, and the subcontractors are Foster Wheeler Development Company, Auburn University, Pennsylvania State University, and Hazen Research, Inc.

The solvent and coal feedstocks have been obtained. The beneficiation of samples of Martin Lake lignite and Black Thunder subbituminous coal has been carried out. Black Thunder coal containing about 4 wt% ash has been prepared using aqueous sulfurous acid. Further reduction to about 2 wt% was achieved using agglomeration and froth flotation. Coal swelling ratios were determined using samples of Black Thunder subbituminous, Illinois No. 6 bituminous, and Martin Lake lignite. Only marginal levels of coal swelling were observed for the hydrocarbon solvents, but swelling greatly increased with the use of solvents having polar functionality. A sizeable level of solvent synergism was observed.

The evaluation of various catalyst precursors for pyrene hydrogenation and coal conversion continued. Higher coal conversions were observed for the SO₂-treated coal than the raw coal, regardless of catalyst type. Coal conversions were highest for Molyvan-L, molybdenum naphthenate, and nickel octoate. A technique to measure the effect of coal swelling and catalyst impregnation upon coal liquefaction has been developed, and experimentation is under way. Reactivity tests have been performed using SO₂-treated and untreated swelled Black Thunder Coal. Thermal reactions with swelled coals yielded much less coal conversion and pyrene conversion than did the swelled coal reactions with Molyvan-L.

The study of bottoms processing consists of coupling solvent deasphalting with delayed coking to maximize the production of coal-derived liquids while rejecting solids within the coke drum. The batch deasphalting screening tests have been completed. While n-butane/pentane solvent blends initially appeared best, pentane alone at 380°F provided an oil yield (63.6 wt%) that was desired for subsequent tests. The production of asphalt for the transport tests is underway. The target deasphalted oil yields are 40, 50 and 60 wt% of feed. This would produce asphalt with ash levels ranging from 20 to 30 wt% with which to run the transport tests.

PROGRAM OBJECTIVES

The objective of this project is to develop a new approach to the direct liquefaction of coal to generate an all-distillate product slate at a sizable cost reduction over current technology. The approach will integrate all aspects of the coal liquefaction process, including coal selection, pretreatment, coal swelling with catalyst impregnation (and parallel runs with dispersed catalyst); coal liquefaction experimentation including solvent evaluation, product recovery with characterization, alternate bottoms processing, and a technical assessment including an economic evaluation. The three tasks of this program are:

1. Task 1: Laboratory-Scale Experimentation--The goals are to obtain samples of coals and Wilsonville-derived solvents and vacuum tower bottoms and to establish experimental procedures.
2. Task 2: Laboratory-Scale Operation--The goals are to:
 - (1) Reduce the concentration of mineral matter and alkali metals in low rank coals, (2) swell and impregnate coals with dispersed catalysts, (3) characterize the resulting catalyst solids, (4) evaluate the effectiveness of the procedures using liquefaction runs, and (5) study solids separation and alternative bottoms handling, which includes observing pumping characteristics, deasphalting, and coking.
3. Task 3: Technical Assessment--The goals are to analyze the data, develop descriptive models, and carry out an economic evaluation.

The research is being carried out in cooperation with the following subcontractors: Foster Wheeler Development Corporation (FWDC), Auburn University (AU), Pennsylvania State University (PSU), and Hazen Research Inc. Appropriate meetings and correspondence are being maintained to ensure effective completion of the project.

PROGRAM MILESTONES

The keystones are based upon the date of approval to initiate experimentation, namely obtaining the authorization of the NEPA form. This authorization was obtained on May 28, 1992. (A request has been made to DOE/PETC to modify the milestone schedule, as shown in Figure 1.) The first key milestone was to obtain the appropriate feed stocks for the experiments. The second milestone was preparing the beneficiated bulk samples of coal for subsequent experiments. The feedstocks have been obtained, and the beneficiation of samples of Martin Lake lignite and Black Thunder subbituminous coal has been done by Hazen Research Inc. The laboratory-scale coal swelling and catalyst screening program has started. Sufficient data has been obtained to establish conditions for initial bench-scale liquefaction experiments that will start in January, 1993. The batch deasphalting and coking experiments will be completed by the end of the fifth quarter after the start of experimentation by FWDC. Experimentation should be essentially complete by the end of the seventh quarter in order to complete the project within a two-year period. The

request for program modification currently calls for program completion on May 31, 1994.

SUMMARY OF RESULTS AND ACTIVITY

The objective of this project is to develop a new approach for the direct liquefaction of coal to produce an all-distillate product slate at a sizable cost reduction over current technology. All aspects of the process are included with emphasis upon coal pretreatment, coal swelling with catalyst impregnation, and alternate bottoms processing. Research is under way at Amoco Oil Company, Foster Wheeler Development Company, Auburn University, Pennsylvania State University, and Hazen Research, Inc.

The beneficiation of bulk samples of Martin Lake lignite and Black Thunder subbituminous coal has been completed. The Black Thunder coal sample contained about 4 wt% ash. A technique to further reduce this to 2 wt% ash has been developed with a combination of agglomeration and froth flotation. The study of coal swelling is complete with the exception of planned runs in which catalyst impregnation tests will be combined with coal swelling.

The evaluation of various soluble catalyst precursors for coal conversion continued. Higher coal conversions were observed for the SO₂-treated coal than the raw coal. Coal conversions were highest for Molyvan-L followed by molybdenum naphthenate and nickel octoate. A technique to measure the effect of coal swelling and catalyst impregnation upon coal liquefaction has been developed, and experimentation is under way. Reactivity tests have been performed using SO₂-treated and untreated swelled Black Thunder Coal. Thermal reactions with swelled coals yielded much less coal conversion and pyrene conversion than did the swelled coal reactions with Molyvan-L.

Activity is now centering upon (1) further beneficiating Black Thunder coal using froth flotation, (2) undertaking swelling experiments in combination with catalyst impregnation using raw and SO₂-treated Black Thunder coal, (3) studying the liquefaction behavior of swollen coals that have been impregnated with catalyst precursors, and (4) carrying out flow experiments with asphalts prior to undertaking coking experiments.

SUMMARY OF RESULTS AND ACTIVITY

Project Documentation

A request for a modification of the Milestone Schedule and budget was submitted to DOE/PETC in the period following this quarter; the revised Milestone Schedule is attached as Figure 1 for reference.

Task 1.0: Laboratory-Scale Experimentation

Subtask 1.1: Laboratory Support

The feedstocks are on hand, and analyses are complete as reported below and in previous quarterlies. An additional 10-drum sample of Black Thunder Mine (Thunder Basin Coal Co./ARCO Coal Co.) is being ordered to provide a fresh sample for sulfurous acid treatment followed by froth flotation tests planned for Hazen Research, Inc.

Task 2.0: Laboratory-Scale Operation

Subtask 2.1: Coal Pretreatment

Initial Coal Preparation:

Bulk samples of both Martin Lake lignite and Black Thunder subbituminous coal were pretreated to provide beneficiated coal for subsequent experiments. The treatment included crushing, sizing, contacting the coarse fraction with aqueous SO_2 to remove alkali and alkaline metals, and subsequent gravity separation to recover a fraction having particularly low ash content. Two 55-gallon drums of Martin Lake (Texas) lignite and three drums of Black Thunder subbituminous coal were processed at Hazen Research, Inc.

The SO_2 -treated subbituminous coal was subjected to heavy media (finely dispersed magnetite) cyclone tests, but it was not possible to isolate an overhead (float) fraction having a coal recovery of about 80 wt%. When the gravity was increased from 1.25 to 1.30, the recovery of the float fraction increased from 23% to essentially 100% with no rejection of a high-ash heavy fraction. This sort of distribution occurred even though five or more check runs were carried out. Therefore, the bulk samples of raw and SO_2 -treated coals were returned to Amoco for characterization and use. The results are described in the second quarterly report.

As a further test of the above results, subsequent laboratory-scale experiments with the SO_2 -treated coal centered upon "washability" tests using heavy chlorinated solvents for gravity (density) separation. This work was done both at Hazen Research and at Standard Laboratories, Inc., Gould Energy Division, Cresson, PA. The distribution of coal yields and ash contents of the Gould experiments are summarized in Table I. A number of observations are noted. The lightest sample (1.20 density float) was recovered in low yield (0.2%), and it contained an exceptionally high level of ash (18.4%). This cut could have been composed of resinous material with trapped minerals containing gas pockets, or it could have

been dispersed minerals that were not completely wetted by the solvent and therefore floated on the surface. The 1.30 to 1.35 gravity fraction made up about 50% of the total feed, and it contained only 1.55% ash. The 1.35 to 1.40 fraction made up 36% with an ash content of 2.7%. The heaviest gravity cut (1.40+) was only 7.5% of the feed coal, and it had an ash content of 16.6%. Based on washability alone, the obvious approach would be to run a gravity separation unit at about 1.40, thereby reducing the coal ash content from 3.2% to 2.1% with a recovery in excess of 92%. However, a problem was pointed out by Hazen Research, Inc. The treated coal swelled in the presence of the chlorinated solvents used for the washability separation. The degree of separation was enhanced by the extent of swelling and by the swelling time. While this was an interesting observation, it was not likely to lead to a commercial beneficiation process. Therefore, this research aspect was dropped.

Flotation/Agglomeration Experiments:

The program undertaken at Pennsylvania State University was directed toward beneficiating coal by a combination of chemical treatment and physical separation methods. Untreated and SO₂-treated Black Thunder coal samples were taken from the above Hazen Research, Inc. product.

Grinding: When grinding was done in a laboratory ball mill with steel media, an increase in ash content of the product was observed. Such contamination was coming from the grinding mill and the media as can be seen in Table II. The ash content of the material increase with grinding time. To decrease the contamination, an agate planetary mill with agate balls was used in subsequent work. This latter grinding mill was relatively inefficient, and long grinding times were needed. Only 35% of the material was -400 mesh in this mill, whereas it was 59% in the steel mill after only 5 minutes of grinding. To establish the grinding time for flotation experiments, size distribution of the ground material was measured as a function of grinding time for both wet and dry grinding conditions. The results are given in Figures 2 and 3, respectively. The size distribution is given in Table III.

Flotation: Flotation of the treated sample with dodecane as the collector and methyl iso-butyl carbinol (MIBC) as the frother, was effective in cleaning coal. A coal product of about 2.2% ash was obtained. The recovery in flotation separation was a function of the dodecane concentration as shown in Tables IV and V. The flotation recovery was very poor when the sample was wet ground as can be seen from the results in Table VI. To improve coal recovery, a spherical agglomeration step was introduced prior to flotation as discussed below.

Spherical Agglomeration: The recovery of coal increased substantially when it was agglomerated with oil prior to flotation. The results of spherical agglomeration are given in Table VII. A clean coal product containing 2.0% ash was obtained after the first 30 seconds of flotation. The combustible matter recovery (CMR) was 46%. After flotation for two minutes, the CMR was 85% and the ash content was 2.23%.

Effect of Surfactant: To improve the flotation efficiency, spherical agglomeration-flotation tests were performed in the presence of a surfactant. The results are given in Table VIII. The effectiveness of flotation increased considerably. A clean coal product of 2.11% ash at 96% CMR recovery was obtained. Further studies are being performed to determine the effect of surfactant type and concentration.

Subtask 2.2: Catalyst and Swelling Studies

Literature: The literature concerning coal swelling, both alone and in combination with coal liquefaction, was reported in Quarterly Number Q-03 (April-June, 1992).

Summary of Swelling Results: The results of subsequent coal swelling experiments were reported in Quarterly Number Q-04 (July-September, 1992).

The results are summarized below:

1. The reproducibility of the swelling experiments was good. At low swelling ratios, such as those of the methanol runs (average Q of 1.28), the standard deviation averaged about ± 0.06 . At high swelling ratios (tetrabutyl ammonium hydroxide, Q averaging about 2.5), the standard deviation averaged about ± 0.14 .
2. Solvent type affected coal swelling. Only marginal levels of coal swelling were observed for hydrocarbon solvents including hexane, cyclohexane, single-ring aromatics, and tetralin, which is a hydroaromatic hydrogen-donor solvent often used in coal liquefaction experiments. Swelling greatly increased with the introduction of hetero-functionality. Equilibrium swelling ratios of Black Thunder subbituminous, Burning Star bituminous and Martin Lake lignitic coals with alcohols, ketones, and methyl acetate were in the range of 1.15 to 1.4. There appeared to be no consistent effect of the molecular weight of the alcohol or ketone, but the Black Thunder coal swelled to a greater extent than the other coals. Cresol was a more effective swelling agent than the above oxygenates only in the case of Burning Star, Illinois No. 6 coal. Tetrahydrofuran (THF) was significantly more effective than the other oxygenates (Q ratios ranged from 1.38 to 1.63). The nitrogen-containing compounds varied greatly in their swelling effectiveness. Tetrabutylammonium hydroxide (TBAH), was very effective (Q ratios of 2.18 to 2.66). Aniline was effective for Burning Star and Black Thunder coals (1.94 and 1.64, respectively), but it was ineffective (1.19) for Martin Lake lignite. Nitrobenzene was poor (1.11 to 1.19). Dimethylsulfoxide was particularly effective for the Black Thunder and Burning Star coals and moderately effective for Martin Lake lignite (2.39, 2.15, and 1.63, respectively).
3. There was little or no effect of coal particle size upon the swelling ratio.

4. The SO₂-treated coal swelled to a greater extent than that of the raw coal. The removal of alkali and alkaline earth ions from the subbituminous coal reduced the interaction of coal species with each other (particularly in the case of divalent metal ions).
5. There was no effective correlation of coal swelling with solvent dipole moment (polarity). While coal swelling generally increased with increasing solvent dipole moment, the correlation was poor.
6. Solvent blends were more effective than individual solvents. Swelling ratios were much greater with blends than that derived from a linear correlation between the pure solvents. There is an advantage of using solvent blends, because relatively low levels of swelling agent would be needed to be effective in treating coal feed slurries for the liquefaction plant.
7. The rate of coal swelling was effected by the size distribution of the coal. The rate of swelling is greatest with the fine coal typically used for liquefaction feed.

UV-visible Spectroscopy for the Analysis of Molybdenum in the Penetration Experiments: It was first necessary to establish an effective technique to quantify the level of organo-molybdenum compounds present in the solvents being used for the coal swelling/penetration experiments.

The first proposed technique was to use UV-visible spectroscopy. The calibration runs were carried with Molyvan-L, which is an additive containing sulfur and phosphorus (sulfurized oxymolybdenum organophosphorodithioate) that is soluble in petroleum bases. UV-visible spectra were obtained on an HP-8452A diode array spectrometer using integration times ranging from 10-25.5 seconds. Quartz UV cells were used for solution measurements, with pathlengths of 0.1-2.5 cm, as appropriate.

In summary, Molyvan-L proved to be an elusive species with regard to detection by means of UV-visible spectroscopy. A series of solutions were prepared in tetralin/isopropyl alcohol (IPA) (tetralin:IPA $\approx$ 2:1), and spectra were obtained using a 1 cm cell. Figure 4 shows the spectrum (solvent reference spectrum subtracted) of a solution containing 190 ppm of Mo in tetralin/IPA. An intense feature, centered near 318 nm, would appear to be useful for quantitative detection. However, in the process of adsorbing Molyvan-L onto the surface of the coal, coal liquids will be extracted by the solvent. The extracted coal liquids showed intense absorbances in the 300-350 nm region, making quantitative detection impossible due to detector saturation and lack of appropriate "reference" spectra for the extracted coal liquids. A weaker feature was observed in the region 500-780 nm, presumably due to d-d transitions on the Mo centers (Figure 5). The Beer-Lambert law appears to roughly hold for this envelope (Figure 6) when the 193 ppm and 1000 ppm Mo samples are compared. However, a spectrum of a sample containing 5100 ppm of Mo could not be obtained until a 515 nm cutoff filter was placed in the spectrometer before the sample. We assume that luminescence of the strong feature near 318 nm interfered with obtaining the absorption spectrum in the region 500-780 nm. Once the cutoff filter was incorporated, the spectrum

obtained of the 5100 ppm Mo sample exhibited significantly different spectral features than the samples containing lower levels of Mo (Figure 7).

Because of the behavior exhibited by Molyvan-L at higher concentrations in tetralin/IPA, other solvents were investigated for use. Molyvan-L was dissolved in toluene, DMSO, and IPA in the concentration range of approximately 0.02-0.20% by weight. The greatest sensitivity for detecting Molyvan-L was found in toluene. The characteristic band could not be detected above the noise level for the lowest concentration in IPA. In addition, at the highest concentration in DMSO, a notable phase separation was observed. Figure 8 shows the spectrum of the sample containing 0.22% Molyvan L in toluene, along with the baseline used to determine the net absorbance at 714 nm.

A solvent system of toluene/IPA was to be used in adsorbing Molyvan-L onto coal. A set of calibration samples were provided containing 16 ppm, 48 ppm, and 99 ppm, respectively, of Mo in a 70:30 solution of toluene/IPA (by weight). Only the most concentrated sample exhibited the d-d transition bands at a level that was differentiable from the noise level. A solution containing 99 ppm of Mo was used to impregnate the coal; in the course of impregnation, a considerable quantity of coal liquids were extracted, leading to a high baseline absorbance in the region of detection for Molyvan-L (Figure 9). As a result, residual Mo could not be detected by UV-visible spectroscopy using this spectral region.

In summary, while UV-visible spectroscopy originally held promise for detection, the sensitivity of the features due to Molyvan-L are insufficient to overcome the signals arising from extracted coal liquids.

Inductively Coupled Plasma Spectroscopy for the Analysis of Molybdenum in the Penetration Experiments: ICP is capable of simultaneously determining up to 30 elements including Mo, Ni, Fe and Cr. However, it is necessary to prepare a calibration curve with each solvent system. A series of laboratory experiments was carried using the current solvent systems including alcohols, THF, and V-1074 Wilsonville coal-derived liquids. The reproducibility was within 1% for samples within the calibration limits. Therefore, this technique was used for subsequent liquefaction and coal swelling experiments.

Subtask 2.3: Reactivity of Swelled Coals with Dispersed Catalysts

Coal Swelling Reactivity Test:

A coal swelling reactivity test was developed to evaluate the reactivity of low rank coal with and without swelling in various solvents. The reaction conditions are given in Table IX. Three different solvents were chosen for the coal swelling reactivity test: 9,10-dihydroanthracene (DHA), 1-methylnaphthalene (1-MN) and V1074, a 650-1000°F coal-derived solvent from Wilsonville. The reactivity of the coal and pyrene in the coal swelling test system was measured by determining the amount of coal

conversion to tetrahydrofuran (THF) solubles and the amount of pyrene conversion to hydrogenated products.

The reactions with 1-MN were performed with both untreated and SO₂-treated Black Thunder coal. Three catalysts were used: Molyvan-L, nickel octoate, and chromium (III) naphthenate. The amount of pyrene conversion and coal conversion that occurred under catalytic conditions is given in Tables X and XI. Several experiments with DHA and chromium naphthenate were also performed and are reported in the tables. The results from the previous quarter's work are included for completeness.

As shown in Table X, average solvent effectiveness for coal conversion in the presence of the catalyst precursors fell in the order DHA, V-1074, 1-MN. SO₂-treated Black Thunder coal had higher levels of conversion than raw, untreated coal. On the average, catalyst precursor effectiveness occurred in the following order: Molyvan-L, nickel octoate, cobalt naphthenate, and chromium naphthenate.

Chromium naphthenate in 1-MN yielded a particularly low coal conversion of 53% with untreated Black Thunder coal. Likewise, with SO₂-treated coal, chromium naphthenate in 1-MN resulted in a low coal conversion of 52%. By contrast, chromium naphthenate in DHA with both untreated and SO₂-treated Black Thunder coals yielded coal conversions that averaged 77% and 79%, respectively. Evidently, the solvent was quite influential in interacting with the chromium naphthenate catalyst in the conversion of coal. The hydrogen donation from the solvent DHA was instrumental in achieving coal conversion with a catalyst which was not active when a solvent was not a hydrogen donor.

Pyrene conversion did not follow trends for coal conversion. In particular, pyrene conversion with Molyvan-L was highest in 1-MN when compared to that in both DHA and V1074 in the case of both untreated and SO₂-treated Black Thunder coal. The primary product from pyrene in 1-MN with Molyvan-L was dihydropyrene (DHP), and the secondary product was tetrahydropyrene (THP) (Tables XII and XIII).

Pyrene was not hydrogenated when in the system of 1-MN and chromium naphthenate. A small amount of pyrene reacted in the presence of DHA and chromium naphthenate. The primary product recovered was DHP with lesser amounts of THP and hexahydropyrene (HHP).

Coal Swelling/Liquefaction Methodology Development:

A procedure was developed for swelling coal with the primary requirement being that the swelled coal must be transferred quantitatively shortly after swelling into a reactor for a reactivity experiment. Experimentation included collecting the solvents needed for the experiments, fabricating an apparatus in which to swell coal, developing a test procedure for swelling the coal and performing reactivity studies with the swelled coals. Emphasis is being directed toward the following solvents: tetrahydrofuran (THF), isopropanol, methanol, and dimethylsulfoxide. Phenol or cresol may also be used. Current work centered on utilizing THF. The swelling time was 24 hr and the time

allowed for the coal to dry after removal of the swelling solvent was 7 hr. For the initial experiment, the mass ratio of solvent to coal was 5:1.

An apparatus was fabricated in which to swell the coal and remove the solvent. A diagram of the apparatus is given in Figure 11. The requirements for this glass apparatus were that the tube be narrow so that the height of the coal could be readily measured to determine the volume change but large enough so that the needed amount of solvent could be introduced. The tube was designed to have two parts: the bottom is 90 mm (3.5") long and 13 mm in diameter, and it contains the solvent and coal. This tube is attached to a detachable top that has a glass frit that is flush with the bottom of the glass. Both the tube and detachable part of the swelling apparatus have ends that flare to allow clamping together. A Viton O-ring is used for sealing the two parts together. The detachable portion has a hose fitting which allows removal of the solvent from the coal after the swelling experiment is completed.

The swelling experiments were performed by introducing ~3 g of coal to the narrow tube. Solvent was then added, and the coal was allowed to swell for 24 hr. Typically, the coal had swelled to its maximum height after only 2 hr. Therefore, the procedure was modified to calculate the swelling ratio, Q , using the heights of coal feed and that after 2 hr. The sample was then allowed to sit for 24 hr before the solvent was removed. Measurement of the coal height after 24 hr was difficult, because the THF solvent tended to be cloudy.

The next step in the procedure was to remove the solvent from the coal, by using the apparatus previously described. A vacuum trap was attached to the hose fitting. Then the tube was inverted. A slight vacuum was applied and the liquid was removed from the tube and trapped in liquid nitrogen cooled trap. The swelled coal after solvent was then allowed to stand at room temperature exposed to air. The coal was dried to a semi-dry state. The time for drying with the THF solvent was determined by making hourly measurements of the coal height in the tube. When the coal height began to drop, then the time was selected 1 hr less than the time of shrinkage. Seven hours were determined to be the drying time for THF.

The swollen coal remained in the tube during solvent removal, and it was then placed directly in the tubular reactor. The reaction was started immediately. Because it was difficult to remove all of the coal from the tube, the following equation was used to calculate the amount of coal placed in the reactor.

$$W_{TB} = (T_c - T_0) - \frac{(T_f - T_0)(T_c - T_0)}{(T_{cs} - T_0)}$$

where, W_{TB} - mass of coal transferred to the tubular reactor in terms of its mass in the unswelled state
 T_0 - mass of the swelling tube without coal
 T_c - mass of the swelling tube with coal
 T_{cs} - mass of the swelling tube plus swelled coal after solvent removal
 T_f - mass of the swelling tube after removal of the swelled coal

This equation assumes that all coal remaining in the tube is in a swelled state and that the proportional change in the weight of this coal from an unswelled state to a swelled state is constant for all the coal used in the experiment.

The percent change in volume of the coal from an unswelled state to a swelled state is given by

$$\% \Delta V = \frac{\pi r^2 h_1}{\pi r^2 h_0} \times 100\% = \frac{h_1}{h_0} \times 100\%$$

where, ΔV - the volume change of the coal
 r - the inside radius of the tube
 h_0 - the initial height of the coal in the tube in an unswelled state
 h_1 - the height of the coal in the tube in a swelled state

Coal Swelling Reactivity Test:

Both untreated and SO_2 -treated Black Thunder coals were swelled and reacted in the coal swelling reactivity test. The conditions for the swelling and the subsequent reactivity test are given in Table XIV. The solvent used for swelling was THF, and the coal liquefaction solvent was 1-MN. Molyvan-L was used as catalyst precursor in selected runs.

Table XV presents both the coal conversion and pyrene conversions obtained from the above mentioned reactions. Results from the catalytic reactions are compared to previously performed reactions containing Molyvan-L and corresponding unswelled coal. No thermal reactions were performed with the unswelled, raw coal and 1-MN. For reference, reactions with SO_2 -treated, unswelled coal and no catalyst resulted in less coal conversion than the corresponding SO_2 -treated swelled coal.

The levels of coal conversion achieved with swelled, raw and swelled, SO_2 -treated Black Thunder coals were dependent upon the presence of catalyst precursor but not upon pretreatment with SO_2 . Both the untreated and SO_2 -treated, swelled coals yielded thermal conversions between 51 and 66%.

Both showed a fairly large variability in coal conversion. By contrast, both untreated and SO₂-swelled coals in the presence of Molyvan-L yielded conversions above 86%. In addition, the results had much less variability. The conversion of untreated, swelled Black Thunder coal averaged 87.3%, while that of SO₂-treated, swelled coal averaged 91.2%.

A similar difference in conversion in the presence of Molyvan-L was observed with the unswelled coals. The conversion of SO₂-treated coal was 88.5%, while that of the untreated coal was 82.4%. Therefore, the pretreatment by SO₂ appeared to cause a small increase in coal conversion with Molyvan-L when coal was in both the swelled and unswelled states.

The presence of swelled coal affected the level of pyrene hydrogenation. The average pyrene conversion in the swelled coal system was 18.6%, and that in the unswelled system was 30.0%. The difference observed between swelled and unswelled SO₂-treated coal was not as large. Pyrene conversion was 25.3% when swelled coal was present and 27.8% with unswelled coal. There was no conversion of pyrene in the thermal reactions.

The product distributions of hydrogenated pyrene from the runs made with swelled coals are given in Table XVI. The primary product from the runs made in the presence of Molyvan-L was DHP. The reactions with higher pyrene conversions also produced a small amount of THP.

Subtask 2.4: Bench-Scale Studies

The continuous feed two-stage reactor system, AU-51L, has been modified and flushed with coal-derived solvent. Preliminary experiments have been carried out using SO₂-treated Black Thunder subbituminous coal. The results will be reported in the next quarterly.

Subtask 2.5: Solids Separation/Alternative Bottoms Processing

The objective of this subtask is to evaluate and develop a solids separation and alternative bottoms processing route that includes direct delayed coking and the ASCOT process. The ASCOT process couples solvent deasphalting with delayed coking to maximize the production of coal-derived liquids while rejecting troublesome solids within the coke drum. A preliminary economics assessment of the battery limits of solvent deasphalting units, delayed coking units, or both, as incorporated in an integrated processing scheme, will be then be undertaken.

The batch deasphalting screening tests have been completed. Theses results and those of the analysis of the feedstock (Wilsonville atmospheric residue) are summarized in Tables XVII and XVIII. Figures 12 through 14 show the effect of temperature and solvent composition on the deasphalted oil (DAO) yield for three solvent categories.

Figure 12 indicates the effect of temperature on the DAO yield for the solvents that were deemed "too effective"--pentane, hexane, heptane, and xylene. Here, it is evident that the controlling variable was the type of

solvent (i.e., paraffin or aromatic). The DAO yield was essentially independent of temperature and solvent/feed ratio. The yield averaged 61.3 wt% for the paraffin solvents and was 80.6 wt% for the single test with xylene. These numbers are consistent with the feedstock characterization of 65.9 wt% oil (paraffin-soluble material) and 76.8 wt% soluble in toluene. None of these solvents provided the means for readily achieving lower yields and placing us in the desired 40 to 60 wt% DAO yield range.

Figure 13 shows the effect of temperature on the DAO yield when using n-butane as the solvent. This was the first solvent that readily permitted the use of temperature as a controlling variable. Butane's solvent power, however, limited the maximum yield to about 50 wt% DAO. It must also be used at an undesirable temperature range, as is evident by its yield versus temperature curve. As the temperature was lowered from near the critical temperature (306°F), the DAO yield increased, peaked, and then fell off precipitously. This occurs in solvent deasphalting when the extraction temperature is reduced to the degree that the asphalt phase becomes too viscous for effective extraction. Potentially extractable material is then trapped in the asphalt.

Figure 14 shows the relationship between oil yield and temperature for butane/pentane blends. With increasing pentane level above about 50 vol%, the yield peaked and then decreased. This was the same phenomenon noted with 100 percent n-butane when the extraction temperature was lowered. It appears that as more oil was extracted with successively higher concentrations of pentane in the blend, the asphalt phase became too viscous for effective extraction at the test temperature (290°F). The oil yield at 290°F for n-butane/pentane will not likely exceed 55 wt%. However, pentane alone at 380°F provided an oil yield (63.6 wt%) that should satisfy our needs. A dashed line is drawn on Figure 14 to show that a 60+ wt% oil yield is achievable if low temperature is eliminated as the controlling variable. The appropriate temperature(s) needed when using between 50 vol% pentane and 100 vol% pentane is not discernible from our data; it is not needed at this time.

Table XIX tabulates the ASTM D-1160 distillation data from eight selected batch tests. The distillation data shows that the solvent deasphalting step always extracted a deashed resid fraction. This data will be used to approximate the amount by defining deashed resid as "the volume percent of deasphalted oil (DAO) corresponding to the 900°F+ fraction from its ASTM D-1160 distillation". Figure 15 plots the relationship of DAO yield to deashed resid yield showing the linear regression line and equation. The correlation coefficient, r was 0.77.

The production of asphalt for the transport tests is underway. The target deasphalted oil yields are 40, 50 and 60 wt% of feed. This would produce asphalt with ash levels ranging from 20 to 30 wt% with which to run the transport tests.

Asphalt production, approximating a 50 wt% DAO yield, was completed. The desired target was achieved using straight pentane as the solvent. The results for asphalt production are:

<u>Solvent</u>	<u>S/F Ratio</u> <u>V/V @ 60°F</u>	<u>Temp.</u> <u>°F</u>	<u>Yields, wt%</u>			<u>Ash-wt%</u>	
			<u>Oil</u>	<u>Asphalt</u>	<u>Recov.</u>	<u>Oil</u>	
<u>Asphalt</u>							
90%C ₄ , 10%C ₆	4	290	41.0	58.0	99.0	0.001	21.03
Pentane	4	340	54.1	48.9	103.0	0.008	24.14

The next set of extraction parameters, designed to produce approximately a 60 wt% yield will use hexane as the solvent, because pentane produced a somewhat lower yield than indicated from the screening tests and moving up to a better solvent should achieve the desired yield.

CONCLUSIONS AND FUTURE WORK

Experimentation is confirming the validity of the process concept. Black Thunder subbituminous coal can be effectively beneficiated to about 4 wt% ash using aqueous sulfurous acid pretreatment. This treated coal can be further beneficiated to about 2 wt% ash using commercially available procedures. All three coals (Black Thunder subbituminous, Burning Star bituminous, and Martin Lake lignite) are effectively swelled by a number of solvents. The most effective solvents are those having hetero-functionality. In addition, a synergistic effect has been demonstrated, in which solvent blends are more effective than the pure solvents alone. Therefore, it will be necessary to use only low levels of swelling agents and yet promote the impregnation of catalyst precursors. Experimentation with the impregnation of catalyst precursors into swollen coal is underway. The continuous flow unit (AU-51) has been tested and prepared for operation. The solvent system for the deasphalting process has been established, and the bottoms stream transport tests are under way.

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12/15/92

Table I

BLACK THUNDER COAL DENSITY DISTRIBUTION

Goal: To reject the heavy fraction sthat contain high levels of mineral matter and inertinites

Technique: "Washability" test using high density liquids

<u>Gravity</u>	<u>Raw Coal</u>		<u>SQ,-Treated</u>	
	<u>%Wt</u>	<u>%Ash</u>	<u>%Wt</u>	<u>%Ash</u>
1.20	0.4	31.4	0.2	18.4
1.25	0.4	9.3	0.8	4.8
1.30	2.0	5.1	4.8	3.3
1.35	38.6	4.1	50.7	1.6
1.40	49.2	5.3	36.0	2.7
1.40S	9.6	16.6	7.5	16.6

Table II

Size & ash distribution of the SO₂ treated material for grinding in a ball mill
Feed ash: 3.15%

SIZE (mesh)	Weight(g)	Weight(%)	Cumulative Weight(%)	Ash (%)	Cumulative Ash(%)
Grinding time: 2.5 min.					
+70	4.84	8.76	8.76	3.64	3.64
70x100	5.24	9.49	18.25	3.63	3.63
100x140	7.29	13.20	31.45	3.85	3.73
140x200	8.64	15.64	47.09	3.85	3.77
200x270	6.35	11.50	58.59	4.15	3.84
270x400	4.92	8.91	67.50	4.30	3.90
-400	17.95	32.50	100.00	7.22	4.60
Total	55.23	100.00		4.60	

SIZE (mesh)	Weight(g)	Weight(%)	Cumulative Weight(%)	Ash(%)	Cumulative Ash(%)
Grinding time: 5.0 min.					
+70	0.34	0.65	0.65	2.70	2.70
70x100	0.70	1.34	1.99	3.19	3.03
100x140	2.34	4.48	6.47	3.43	3.31
140x200	5.49	10.52	16.99	3.59	3.48
200x270	6.32	12.10	29.09	3.87	3.64
270x400	6.34	12.14	41.24	3.99	3.75
-400	30.68	58.76	100.00	6.12	4.66
Total	52.21	100.00		4.66	

SIZE (mesh)	Weight(g)	Weight(%)	Cumulative Weight(%)	Ash(%)	Cumulative Ash(%)
Grinding time: 10.0 min.					
+100	0.15	0.28	0.28	4.00	4.00
100x140	0.33	0.63	0.91	4.03	4.02
140x200	1.71	3.25	4.16	3.78	3.83
200x270	3.46	6.57	10.73	3.96	3.91
270x400	5.12	9.72	20.45	4.15	4.02
-400	41.89	79.55	100.00	5.96	5.56
Total	52.66	100.00		5.56	

Table III

Size & ash distribution of SO₂ treated material for dry grinding in a planetary mill

SIZE (mesh)	Weight(g)	Weight(%)	Cumulative Weight(%)	Ash (%)	Cumulative Ash(%)
Grinding time: 1.0 min.					
+70	21.70	54.22	54.22	2.92	2.92
70x100	5.28	13.19	67.42	2.85	2.91
100x140	4.14	10.34	77.76	2.88	2.90
140x200	3.00	7.50	85.26	2.98	2.91
200x270	1.92	4.80	90.05	3.28	2.93
270x400	1.16	2.90	92.95	3.56	2.95
-400	2.82	7.05	100.00	6.46	3.09
Total	40.02	100.00		3.09	

SIZE (mesh)	Weight(g)	Weight(%)	Cumulative Weight(%)	Ash(%)	Cumulative Ash(%)
Grinding time: 2.5 min.					
+70	9.39	24.75	24.75	2.88	2.88
70x100	5.90	15.55	40.30	2.78	2.84
100x140	5.82	15.34	55.64	2.74	2.81
140x200	4.76	12.55	68.19	2.73	2.80
200x270	3.31	8.72	76.91	2.88	2.81
270x400	2.35	6.19	83.10	3.15	2.83
-400	6.41	16.90	100.00	5.36	3.06
Total	37.94	100.00		3.06	

SIZE (mesh)	Weight(g)	Weight(%)	Cumulative Weight(%)	Ash(%)	Cumulative Ash(%)
Grinding time: 5.0 min.					
+70	0.96	2.29	2.29	3.88	3.88
70x100	3.15	7.50	9.79	3.24	3.39
100x140	6.30	15.00	24.79	3.04	3.18
140x200	7.08	16.86	41.65	2.83	3.04
200x270	5.26	12.53	54.18	3.00	3.03
270x400	4.52	10.76	64.94	3.10	3.04
-400	14.72	35.06	100.00	4.73	3.63
Total	41.99	100.00		3.63	

Table IV

Experiment type: Flotation Kinetics
Material Type: SO₂ treated sample from AMOCO

Collector: Dodecane 200 ul
Frother: MIBC 50 ul

Conditions: *Grinding:*
 Dry grinding of a 50 g. sample for 5.0 min. in a planetary mill.
Flotation:
 5 min. conditioning – oil addition – 3 min. conditioning – frother addition –
 2 min. conditioning – 1000 rpm – Natural pH (2.90).

Feed ash : 3.20%

Product	Yield(%)	Cumulative Yield(%)	Ash(%)	Cum. Ash (%)	CMR (%)	Cumulative CMR (%)
20 sec.	69.59	69.59	2.20	2.20	70.24	70.24
40 sec.	14.74	84.33	2.49	2.25	14.83	85.07
1 min.	2.44	86.77	2.80	2.27	2.44	87.52
2 min.	0.91	87.68	3.56	2.28	0.90	88.42
4 min.	0.10	87.78	4.05	2.28	0.10	88.52
8 min.	0.00	87.78	0.00	2.28	0.00	88.52
16 min.	0.00	87.78	0.00	2.28	0.00	88.52
Refuse	12.22	100.00	9.00	3.10	11.48	100.00
Total	100.00				100.00	

Table V

Experiment type: Flotation Kinetics
Material Type: SO₂ treated sample from AMOCO

Collector: Dodecane 3000 ul
Frother: MIBC 50 ul

Conditions: *Grinding:*

Dry grinding of a 50 g. sample for 5.0 min. in a planetary mill.

Flotation:

5 min. conditioning – oil addition – 3 min. conditioning – frother addition –
 2 min. conditioning – 1000 rpm – Natural pH (2.90).

Feed ash : 3.20%

Product	Yield(%)	Cumulative Yield(%)	Ash(%)	Cum. Ash (%)	CMR (%)	Cumulative CMR (%)
20 sec.	73.62	73.62	2.16	2.16	74.26	74.26
40 sec.	15.16	88.78	2.42	2.20	15.25	89.52
1 min.	4.47	93.25	2.73	2.23	4.49	94.00
2 min.	2.79	96.04	3.29	2.26	2.78	96.78
4 min.	0.00	96.04	0.00	2.26	0.00	96.78
8 min.	0.00	96.04	0.00	2.26	0.00	96.78
16 min.	0.00	96.04	0.00	2.26	0.00	96.78
Refuse	3.96	100.00	21.19	3.01	3.22	100.00
Total	100.00				100.00	

Table VI

Experiment type: Flotation Kinetics
Material Type: SO₂ treated sample from AMOCO

Collector: Dodecane 3000 ul
Frother: MIBC 50 ul

Conditions: *Grinding:*
 Wet grinding of a 50 g. sample in 100 ml of water for 6.5 min. in a planetary mi
Flotation:
 5 min. conditioning – oil addition – 3 min. conditioning – frother addition –
 2 min. conditioning – 1000 rpm – Natural pH (2.90).

Feed ash : 3.20%

Product	Yield(%)	Cumulative Yield(%)	Ash(%)	Cum. Ash (%)	CMR (%)	Cumulative CMR (%)
20 sec.	3.12	3.12	3.00	3.00	3.13	3.13
40 sec.	2.66	5.78	2.93	2.97	2.67	5.79
1 min.	1.95	7.73	3.20	3.03	1.95	7.74
2 min.	6.94	14.67	2.66	2.85	6.97	14.71
4 min.	9.60	24.27	2.65	2.77	9.64	24.35
8 min.	13.01	37.28	2.52	2.68	13.09	37.45
16 min.	14.59	51.87	2.55	2.65	14.67	52.12
Refuse	48.13	100.00	3.64	3.12	47.88	100.00
Total	100.00				100.00	

Table VII

Experiment type: Spherical Agglomeration/Flotation
Material Type: SO₂ treated sample from AMOCO

Collector: Dodecane 4500 ul
Frother: MIBC 50 ul

Conditions: *Grinding:*

Wet grinding of a 50 g. sample in 100 ml of water for 40 min. in a planetary mill.

Spherical Agglomeration:

The slurry from the mill was completed to 500 ml. 50 ml slurry was taken and completed to 500 ml and was put in ultrasonic bath for 10 min. It was mixed in a blender for 1 min. at a setting of 2. Oil was added and the slurry was blended for 3 more min. at a setting of 4. A final blending of 2 min. at a setting of 2 was applied before flotation.

Flotation:

1 min. conditioning; 50 ul MIBC; 1 min. conditioning; flotation

Feed Ash 3.2%

Product	Yield(%)	Cumulative Yield(%)	Ash(%)	Cum. Ash (%)	CMR (%)	Cumulative CMR (%)
30 sec.	45.31	45.31	2.00	2.00	45.86	45.86
1 min.	20.31	65.63	2.52	2.16	20.45	66.31
2 min.	15.63	81.25	2.54	2.23	15.73	82.04
Refuse	18.75	100.00	(7.26)	3.18	17.96	100.00
Total	100.00				100.00	

Table VIII

Experiment type: Spherical Agglomeration
Material Type: SO₂ treated sample from AMOCO

Surfactant: BC1 250 ul
Collector: Dodecane 2250 ul
Frother: MIBC 50 ul

Conditions: *Grinding:*

Wet grinding of a 50 g. sample in 100 ml of water for 40 min. in a planetary mill.

Spherical Agglomeration:

The slurry from the mill was completed to 500 ml. 50 ml slurry was taken and completed to 500 ml and was put in ultrasonic bath for 10 min. It was mixed in a blender for 1 min. at a setting of 2. Oil was added and the slurry was blended for 3 more min. at a setting of 4. A final blending of 2 min. at a setting of 2 was applied before flotation.

Flotation:

1 min. conditioning; 50 ul MIBC; 1 min. conditioning; flotation

Feed Ash 3.2%

Product	Yield(%)	Cumulative Yield(%)	Ash(%)	Cum. Ash (%)	CMR (%)	Cumulative CMR (%)
1 min.	95.41	95.41	2.11	2.11	96.51	96.51
Refuse	4.59	100.00	26.40	3.22	3.49	100.00
Total	100.00				100.00	

Table IX

**Reaction Conditions for Coal Swelling Reactivity Test
Using Unswelled Coals**

Parameters	Coal Swelling Test System
Temperature	410°C
Pressure	1250 psig H ₂ at ambient temperature
Time	30 minutes
Coal	1.33 g maf SO ₂ or untreated Black Thunder Coal
Pyrene	0.67 g
Solvent	2.00 g of either 9,10-dihydroanthracene, V1074 from Wilsonville or 1-methylnaphthalene
Catalyst Loading	600-700 ppm (based on feed)
Catalysts	Molyvan I nickel octoate cobalt naphthenate chromium naphthenate

Table X

Pyrene and Coal Conversions for Untreated Black Thunder Coal

Catalyst Type	Catalyst Loading (ppm)*	Added Coal (wt%)	Pyrene Conversion (mole %)	Coal Conversion (wt%)
Solvent: 9,10-dihydroanthracene*				
Molyvan L	693	30.5	18.4	89.8
	660	30.5	12.0	89.5
Nickel Octoate	576	30.7	5.1	85.8
	554	30.6	3.6	88.2
Cobalt Naphthenate	654	30.4	2.0	83.1
	648	30.5	2.3	83.3
Chromium Naphthenate	697	29.9	4.0	79.7
	623	29.8	4.0	73.8
Solvent: V1074				
Molyvan L	664	30.3	12.9	85.4
	639	30.2	16.8	84.0
Nickel Octoate	647	30.6	1.9	82.3
	730	30.5	10.1	80.6
	650	30.6	8.5	81.7
Solvent: 1-Methylnaphthalene				
Molyvan L	681	30.5	26.2	80.3
	736	30.5	33.8	84.5
Nickel Octoate	599	30.7	7.0	67.8
	608	30.5	6.6	73.6
Chromium Naphthenate	625	29.8	0.0	54.0
	628	29.8	0.0	51.5

* Based on feed.

Table XI

Pyrene and Coal Conversions for SO₂ Treated Black Thunder Coal

Catalyst Type	Catalyst Loading (ppm)*	Added Coal (wt%)	Pyrene Conversion (mole %)	Coal Conversion (wt%)
Solvent: 9,10 dihydroanthracene				
Molyvan L	674	31.3	23.9	92.9
	634	31.3	17.7	91.9
Nickel Octoate	675	31.4	2.7	95.9
	652	31.4	4.7	88.8
Cobalt Naphthenate	602	31.3	2.4	86.4
	613	31.2	3.0	85.3
Chromium Naphthenate	650	30.6	2.0	74.6
	651	30.6	3.8	82.6
Solvent: V1074				
Molyvan L	598	31.4	18.9	88.5
	638	31.4	23.2	92.2
	618	31.0	20.3	90.9
Nickel Octoate	864	31.0	3.9	84.2
	667	31.4	0.0	79.9
Solvent: 1-methylnaphthalene				
Molyvan L	614	31.4	29.9	89.0
	631	31.3	25.7	88.0
Nickel Octoate	595	31.4	10.0	73.3
	797	31.4	15.0	79.2
Chromium Naphthenate	644	30.5	0.0	50.9
	644	30.5	0.0	52.5

* Based on feed.

Table XII

**Product Distributions from Pyrene Hydrogenation in Presence
of Untreated Black Thunder Coal**

Catalyst	ppm	% HYD (% Coal)	Product Distribution (mole %)					
			PYR	DHP	THP	HHP1	HHP2	HHP3
Solvent: 9,10-Dihydroanthracene								
Molyvan L	693	6.6 (30.5)	81.6	17.4	0.5	0	0	0.5
	660	4.1 (30.5)	88.0	11.6	0.4	0	0	0
Nickel Octoate	576	2.3 (30.7)	94.9	4.3	0	0	0	0.8
	554	1.8 (30.6)	96.4	2.7	0	0	0	0.9
Cobalt Naphthenate	654	1.2 (30.4)	98.0	1.0	0.5	0	0	0.5
	648	1.3 (30.5)	97.7	1.3	0.5	0	0	0.5
Chromium Naphthenate	697	2.6(29.9)	96.0	1.1	1.9	0	0	1.0
	623	2.6(29.8)	96.0	1.0	2.2	0	0	0.0
Solvent: V1074								
Molyvan L	664	4.9 (30.3)	87.1	11.7	0.6	0	0	0.6
	639	6.4 (30.2)	83.2	15.2	0.8	0	0	0.8
Nickel Octoate	647	0.6 (30.6)	98.1	1.9	0	0	0	0
	730	3.6 (30.5)	89.9	9.3	0.8	0	0	0
	650	3.0 (30.6)	91.5	8.0	0.5	0	0	0
Solvent: 1-Methylnaphthalene								
Molyvan L	681	9.5 (30.5)	73.8	23.9	2.3	0	0	0
	736	12.9 (30.5)	66.2	30.1	2.5	0	0	1.2
Nickel Octoate	599	2.3 (30.7)	93.0	7.0	0	0	0	0
	608	2.2 (30.5)	93.4	6.6	0	0	0	0
Chromium Naphthenate	625	0.0 (29.8)	100.	0	0	0	0	0
	628	0.0 (29.8)	100.	0	0	0	0	0

PYR = pyrene
 DHP = dihydropyrene
 THP = tetrahydropyrene

HHP1, HHP2, HHP3 = isomers of hexahydropyrene
 % HYD = hydrogenation

Table XIII

**Product Distributions from Pyrene Hydrogenation
in the Presence of SO₂ Treated Black Thunder Coal**

Catalyst	ppm	% HYD (% Coal)	Product Distribution (mole %)					
			PYR	DHP	THP	HHP1	HHP2	HHP3
Solvent: 9,10-Dihydroanthracene								
Molyvan L	674	8.5 (31.3)	76.1	22.5	1.4	0	0	0
	634	6.3 (31.3)	82.3	16.6	1.1	0	0	0
Nickel Octoate	675	1.4 (31.4)	97.3	1.9	0	0	0	0.8
	652	2.1 (31.4)	95.3	3.9	0	0	0	0.8
Cobalt Naphthenate	602	1.4 (31.3)	97.6	1.2	0.6	0	0	0.6
	613	1.8 (31.2)	97.0	1.5	0.7	0	0	0.8
Chromium Naphthenate	650	1.3 (30.6)	98.0	0.5	1.0	0	0	0.5
	651	2.6 (30.6)	96.2	0.8	2.1	0	0	0.9
Solvent: V1074								
Molyvan L	598	6.8 (31.4)	81.1	18.1	0	0	0.8	0
	638	8.3 (31.4)	76.8	21.5	1.7	0	0	0
	618	7.8 (31.0)	79.7	18.0	1.5	0	0	0.8
Nickel Octoate	864	1.3 (31.0)	96.1	3.9	0	0	0	0
	667	0.0 (31.4)	100.0	0	0	0	0	0
Solvent: 1-Methylnaphthalene								
Molyvan L	614	10.8 (31.4)	70.1	27.4	2.5	0	0	0
	631	9.3 (31.3)	74.3	23.4	2.3	0	0	0
Nickel Octoate	595	3.3 (31.4)	90.0	10.0	0	0	0	0
	797	5.0 (31.4)	85.0	15.0	0	0	0	0
Chromium Naphthenate	644	0.0 (30.5)	100	0	0	0	0	0
	644	0.0 (30.5)	100	0	0	0	0	0

PYR = pyrene
DHP = dihydropyrene
THP = tetrahydropyrene

HHP1, HHP2, HHP3 = isomers of hexahydropyrene
% HYD = hydrogenation

Table XIV

**Reaction Conditions for Coal Swelling Reactivity Test
Using Swelled Coals**

Coal	Black Thunder (untreated and SO ₂ treated)
Temperature	410°C
Agitation	500 cpm
H ₂ Pressure	1250 psig for SO ₂ treated coal 1200 psig* for untreated coal
Pyrene	0.67 g
Coal	1.33 g
Solvent	2.0 g
Solvent for Reaction	1-methylnaphthalene
Solvent for Coal Swelling	THF
Swelling Time	24 hr
Analysis	(1) Coal products removed from reactors with THF
	(2) GC analysis performed for pyrene products
	(3) Coal conversion to THF solubles determined

* We had difficulty in obtaining high pressure H₂ during part of December; hence, the slightly lower pressure was used for the untreated coal.

Table XV

**Coal and Pyrene Conversions Obtained from Coal Swelling
Reactivity Test Using 1-Methylnaphthalene as Solvent**

Catalyst Type	Catalyst Loading (ppm)	Change in Volume (%)	Added Coal (wt%)	Pyrene Conversion (mole %)	Coal Conversion (wt%)
Black Thunder Untreated - Not Swelled					
Molyvan L	681	NA ^a	30.5	26.2	80.3
	736	NA	30.5	33.8	84.5
Black Thunder Untreated - Swelled					
None	NA	29.2	30.8	0.0	66.0
	NA	39.1	30.8	0.0	53.4
Molyvan L	684	36.4	30.6	17.7	86.2
	638	39.1	30.7	19.5	88.4
Black Thunder SO₂ Treated - Not Swelled					
None	0	NA	31.6	0.7	48.1
	0	NA	31.6	2.3	46.5
Molyvan L	614	NA	31.4	29.9	89.0
	631	NA	31.3	25.7	88.0
Black Thunder SO₂ Treated - Swelled					
None	0	85.7	31.5	0.0	64.7
	0	89.5	31.6	0.0	51.2
Molyvan L	720	80.0	31.3	25.3	90.1
	645	78.9	31.2	25.4	92.2

^a NA: not applicable.

Table XVI

**Table 8. Product Distribution for Pyrene from Coal Swelling
Reactivity Test Using Swelled and Unswelled Coals**

Catalyst Type	Catalyst Loading (ppm)	% HYD (% Coal)	Product Distribution (mole %)					
			PYR	DHP	THP	HHP1	HHP2	HHP3
Black Thunder Untreated - Not Swelled								
Molyvan L	681	9.5(30.5)	73.8	23.9	2.3	0.0	0.0	0.0
	736	12.9(30.5)	66.2	30.1	2.5	0.0	0.0	1.2
Black Thunder SO ₂ Treated - Swelled								
None	NA	0.0(30.8)	100.0	0.0	0.0	0.0	0.0	0.0
	NA	0.0(30.8)	100.0	0.0	0.0	0.0	0.0	0.0
Molyvan L	684	5.9(30.6)	82.3	17.7	0.0	0.0	0.0	0.0
	638	6.5(30.7)	80.5	19.5	0.0	0.0	0.0	0.0
Black Thunder SO ₂ Treated - Not Swelled								
None	0	0.2(31.6)	99.3	0.7	0.0	0.0	0.0	0.0
	0	1.2(31.6)	97.7	1.6	0.0	0.0	0.0	0.0
Molyvan L	614	10.8(31.4)	70.1	27.4	2.5	0.0	0.0	0.0
	631	9.3(31.3)	74.3	23.4	2.3	0.0	0.0	0.0
Black Thunder SO ₂ Treated - Swelled								
None	0	0.0(31.5)	100.0	0.0	0.0	0.0	0.0	0.0
	0	0.0(31.6)	100.0	0.0	0.0	0.0	0.0	0.0
Molyvan L	720	9.2(31.3)	74.7	23.1	2.2	0.0	0.0	0.0
	645	9.0(31.2)	74.6	23.8	1.6	0.0	0.0	0.0

PYR = pyrene; DHP = dihydropyrene; THP = tetrahydropyrene; HHP1, HHP2, HHP3 = hexahydropyrene isomers.

Nomenclature

% HYD = percent hydrogenation

1-MN = 1-methylnaphthalene

DHA = dihydroanthracene

DHP = dihydropyrene

HHP = hexahydropyrene

PYR = pyrene

THF = tetrahydrofuran

Table XVII

FEEDSTOCK INSPECTIONS:
WILSONVILLE ATMOSPHERIC RESIDUE⁽¹⁾

FW Identification No.	22777
Specific Gravity @ 60/60°F	1.187
Asphaltenes, ⁽²⁾ wt%	10.9
Toluene Insolubles, wt%	23.2
Quinoline Insolubles, wt%	22.2
Ash, wt%	11.49
Softening Point (R&B), °F	124
Conradson Carbon Residue, wt%	38.1
Sulfur, wt%	1.40
Carbon, wt%	77.6
Hydrogen, wt%	7.4
Metals, ppm:	
Fe	16200
Ni	36
V	43
Cu	46
Na	426
ASTM Distillation (D-1160), °F ⁽³⁾	
IBP	634
2 vol%	704
5	765
10	810
20	858
30	900
40	975
41	⁽⁴⁾

(1) Source: Liquefaction of Wyoming Black Thunder subbituminous coal.

(2) Asphaltenes Precipitation with Normal Heptane, Method IP143.

(3) Corrected to atmospheric pressure.

(4) Cracking at still temperature of 650°F.

DCC/ml/92839

12/15/92

Table XVIII

Summary of Batch Deasphalting Test Results

Run No.	Solvent	S/F Ratio V/V @ 60°F	Temp. °F	Yields - wt %		Ash - wt %	
				Oil	Asphalt	Oil	Asphalt
3015	Heptane	8	475	60.4	32.0	0.010	27.75
3016	Heptane	8	500	58.5	30.5	0.006	27.23
3017	Xylene	8	565	80.6	25.3	2.27	33.06
3018	Heptane	4	500	60.6	35.8	0.030	27.85
3019	Heptane	8	520	60.9	28.8	0.060	28.44
3020	Heptane	8	550	65.3	40.3	0.024	28.00
3021	Hexane	4	430	59.8	33.7	0.017	30.70
3022	Pentane	4	380	63.6	35.7	0.020	26.00
3023	Butane	4	290	32.5	69.8	0.017	15.88
3024	Butane	4	240	30.4	68.4	0.006	17.04
3025	Butane	4	265	49.5	52.5	0.0044	20.33
3026	80%C ₄ , 20%C ₅	4	290	47.9	49.4	0.0037	21.51
3027	70%C ₄ , 30%C ₅	4	290	50.0	47.0	0.0053	23.77
3028	50%C ₄ , 50%C ₅	4	290	54.0	46.3	0.0055	25.63
3029	70%C ₄ , 30%C ₅	8	290	57.9	38.4	0.0071	25.98
3030	20%C ₄ , 80%C ₅	4	290	50.5	44.8	0.014	25.48

S/F Ratio = Solvent/Feed Ratio

Table XIX

Table 4
Distillations of Deasphalted Oil

Run No.	3015	3017	3018	3023	3024	3026	3027	3028
DAO Yield, wt%	60.4	80.6	60.6	32.5	30.4	47.9	50.0	54.0
*API @ 60°F	4.6	4.4	4.7	14.2	11.6	10.9	10.0	8.9
ASTM D-1160, °F ⁽¹⁾								
IBP	612	574	-	490	524	539	561	540
2 Vol%	700	717	653	652	601	618	615	619
5	743	753	752	722	671	691	681	676
10	775	783	783	768	719	743	732	721
20	802	819	817	805	759	778	766	758
30	828	855	843	827	784	807	789	772
40	854	914	875	851	811	831	819	810
50	886	928	916	879	828	857	843	838
60	930		977	912	857	890	878	873
70	1010		1014 ⁽³⁾	972	895	932	924	907
80	1044 ⁽²⁾			1048 ⁽⁴⁾	952	1009	992	961
90					997 ⁽⁵⁾	1024 ⁽⁶⁾	1026 ⁽⁷⁾	1008 ⁽⁵⁾
95								
EP								

(1) Temperature reported at 760 mm Hg. Distillation terminated at 750°F flask temperature.

(2) 75 vol%

(3) 68 vol%

(4) 77 vol%

(5) 86 vol%

(6) 81 vol%

(7) 84 vol%

Figure 1b
U.S. DEPARTMENT OF ENERGY
MILESTONE SCHEDULE ☒ PLAN ☐ STATUS REPORT

FORM APPROVED
OMB NO. 1901 1400

1. TITLE		2. REPORTING PERIOD		3. IDENTIFICATION NUMBER		4. PARTICIPANT NAME AND ADDRESS		5. START DATE		6. COMPLETION DATE		7. REPORTING ELEMENT		8. DURATION		9. PERCENT COMPLETE	
				DE-AC22-91PC91051		Amoco Oil Company P. O. Box 3011 Naperville, IL 60566		October 1991 *		May 31, 1994				O N D J F M A M		a. Plan b. Actual	
Task 1.1	Lab Support																
Task 1.2	Lab Support - FWDC																
Task 2.1	Pretreat																
Task 2.2	Cat and Swelling																
Task 2.3	Reactivity																
Task 2.4	Bench-Scale																
Task 2.5	Solids Separation																
Task 2.6	Feedstock																
Task 3.1	Tech Assessment																
<p style="text-align: center;">NEPA APPROVAL</p>																	
<p>* The start of laboratory research was delayed to June 1992; a contract extension has been requested for project completion on May 31, 1994.</p>																	
<p>11. SIGNATURE OF PARTICIPANT'S PROJECT MANAGER AND DATE</p>																	

Figure 2

SIZE DISTRIBUTION OF AMOCO SAMPLE AS A FUNCTION OF GRINDING TIME
USING WET PLANETARY MILLING

Figure 3

SIZE DISTRIBUTION OF AMOCO SAMPLE AS A FUNCTION OF GRINDING TIME
USING DRY PLANETARY MILLING

Figure 4

UV-visible spectrum of Molyvan L in tetralin/IPA, with a Mo content of 193 ppm, along with that of the reference solvent system.

Figure 5

UV-visible spectrum of Molvan L in tetralin/IPA, Mo content = 193 ppm. Bands in this region presumably arise from metal d-d transitions.

Figure 6

UV-visible spectra of 193 ppm Mo and 1000 ppm Mo samples of Molyvan L in tetralin/IPA.

Figure 7

UV-visible spectra of 1000 ppm Mo and 5100 ppm Mo samples of Molyvan L in tetralin/IPA. Spectra are not drawn to scale, but have been autoscaled to highlight the change in shape.

Figure 8

Spectrum of 0.22% Molyvan L in toluene, showing baseline drawn to determine net absorbance at 714 nm.

Figure 9

upper: UV-visible spectrum of Molybdenum L in toluene/IPA (Mo level = 99 ppm); lower: comparison with coal extract liquids in toluene/IPA.

Figure 10

upper: spectrum of 99 ppm Mo (as Molyvan L) in toluene/IPA;
lower: comparison with coal extract liquid after 5 minutes.

Figure 11: Swelling Apparatus

Figure 12: Effect of Temperature on DAO Yield

Appendix B

Total Recovery Determination

The total recovery of all the contents in the tubular microreactors is performed by first knowing the mass of all the contents placed into the bombs. Solvent, H₂ gas, pyrene, coal, and catalyst are charged into the bombs at measured quantities (usually 4.1 to 4.4 grams total).

Upon completion of the reaction, the gas is removed and measured volumetrically by placing into a gas bag. Then it is measured by area in the GC against a standard of H₂ gas of an equal volume. This area will determine how much of the H₂ gas was recovered. The other contents of the bomb are removed with THF. All insoluble THF products can be isolated and their mass determined by removing the THF soluble products. This insoluble portion determines how much coal conversion occurred during the reaction.

Pyrene is measured in area by using the GC using biphenyl as the standard. The other contents are completely recovered in the THF and accounted for.

By adding all of the recovered contents; coal + solvent + pyrene + gas, then this total is divided into the original mass of contents placed into the bomb and multiplied by 100 which gives the percent recovery. The sum of course is the total recovery.

Pyrene presented a special problem by collecting in the GC, failing to be read out in the GC output at the correct concentration. For example, when 90% of pyrene might be expected to be recovered, the GC says only 25% of pyrene is recovered. A known amount of pyrene was measured by the GC and only 21% of that value was read out in the output so an adjustment was made to account for the error in the GC area pyrene readings. Graphically, it was displayed with each usage of the GC with pyrene, less and less pyrene was being read out in the output.

(This problem is currently being solved by raising the temperature of the column and washing with methylene chloride to remove any residual pyrene on the column.) So, taking a line produced from a graph of number of GC uses with a pyrene sample versus percent pyrene recovery, this line was employed in calculating a new percent pyrene recovery estimating that this line represented a 90% pyrene recovery. The equation for the line became

$$y = -.58x + 40.35$$

where x is the number of uses of the GC with a pyrene sample and y is the 90% pyrene recovery point. The new percent pyrene recovery (Y) was then calculated from

$$Y = 100 * P / y$$

where P is the percent pyrene recovered before correction. The amount pyrene recovered (P1) then is

$$P1 = 0.01 * Y * p$$

where p is the original amount of pyrene placed into the bomb.

Now this value of P1 can be added with the other contents recovered from the bomb to give the total recovery.

Appendix C

Table C.1. Total Recovery of Untreated Black Thunder Coal Reaction System

Catalyst Type	Catalyst Loading (ppm)	Coal Introduced (Wt %)	Coal Conversion (%)	Recovery (%)
Unswelled Coal 9,10-Dihydroanthracene				
Molyvan L	693	30.5	89.8	111.5
	660	30.5	89.5	103.4
Ni Octoate	576	30.7	85.8	100.8
	554	30.6	88.2	100.3
Co Naphthenate	654	30.4	83.1	99.6
	648	30.5	83.3	100.2
Cr Naphthenate	697	29.7	79.7	96.8
	623	29.8	73.8	96.7
Unswelled Coal V1074				
Molyvan L	664	30.3	85.4	95.4
	639	30.2	84.0	102.1
Ni Octoate	647	30.6	82.3	89.6
	730	30.5	80.6	104.9
	650	30.6	81.7	99.5
Unswelled Coal 1-Methylnaphthalene				
Molyvan L	681	30.5	80.3	95.2
	736	30.5	84.3	98.6
Ni Octoate	599	30.7	67.8	95.9
	608	30.5	73.6	97.6
Cr Naphthenate	625	29.8	54.0	96.8
	628	29.8	51.5	96.7
Swelled Coal 1-Methylnaphthalene				
None	0	30.8	66.0	91.8
	0	30.8	53.4	96.0
Molyvan L	684	30.6	86.2	96.6
	638	30.7	88.4	91.9

Table C.2. Total Recovery of SO₂ Treated Black Thunder Coal Reaction System

Catalyst Type	Catalyst Loading (ppm)	Coal Introduced (Wt %)	Coal Conversion (%)	Recovery (%)
Unswelled Coal 9,10-Dihydroanthracene				
Molyvan L	674	31.3	92.9	107
	634	31.3	91.9	104.2
Ni Octoate	675	31.4	95.9	102.1
	652	31.4	88.8	101.1
Co Naphthenate	602	31.3	86.4	100.0
	613	31.2	85.3	96.3
Cr Naphthenate	650	30.6	74.6	100.8
	651	30.6	82.6	100.1
Unswelled Coal V1074				
Molyvan L	598	31.4	88.5	98.8
	638	31.4	92.2	104.9
	618	31.0	90.9	101.6
Ni Octoate	864	31.0	84.2	102.7
	667	31.4	79.9	89.1
Unswelled Coal 1-Methylnaphthalene				
None	0	31.6	48.1	101.7
	0	31.6	46.5	117.3
Molyvan L	614	31.4	89.0	97.7
	631	31.3	88.0	95.4
Ni Octoate	595	31.4	73.3	96.8
	797	31.4	79.2	95.7
Cr Naphthenate	644	30.5	50.9	90.4
	644	30.5	52.5	91.6
Swelled Coal 1-Methylnaphthalene				
None	0	31.5	64.7	89.9
	0	31.6	51.2	96.0
Molyvan L	720	31.3	90.1	101.1
	645	31.2	92.2	103.3

END

**DATE
FILMED**

9/2/93