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Advanced Direct Liquefaction Concepts for PETC Generic Units - Phase II

**Quarterly Report
October 1 - December 31, 1996**

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ABSTRACT

Reported here are the results of Laboratory and Bench-Scale experiments and supporting technical and economic assessments conducted under DOE Contract No. DE-AC22-91PC91040 during the period October 1, 1996 to December 31, 1996. This contract is with the University of Kentucky Research Foundation which supports work with the University of Kentucky Center for Applied Energy Research, CONSOL, Inc., LDP Associates, and Hydrocarbon Technologies, Inc. This work involves the introduction into the basic two stage liquefaction process several novel concepts which include dispersed lower-cost catalysts, coal cleaning by oil agglomeration, and distillate hydrotreating and dewaxing.

This report includes a description of run ALC-2, the second continuous run in which Wyodak Black Thunder coal was fed to a 2 kg/h bench-scale unit. The objective was to expand upon results obtained in ALC-1 in which high yields of distillate product were produced while operating in a mode in which essentially all of the residual material was recycled to extinction. In this run the liquefaction of lower-cost Mo precursors impregnated onto Wyodak coal are compared with results from ALC-1 Condition #1 in which a combination of Molyvan A (100 mg Mo/kg dry coal) and HTT's FeOOH/SO₄ (1% Fe/dry coal) was used as catalyst. The precursors included ammonium heptamolybdate (100 mg Mo/kg dry coal), which was used alone as well as in combination with ferrous sulfate (1% Fe/dry coal) or nickel sulfate (50 mg Ni/kg dry coal). The fourth precursor was phosphomolybdic acid which was used at a level of 100 mg Mo/kg dry coal. The feed coals were prepared prior to the run using a ribbon mixer by spraying salt solutions of the precursors onto Wyodak coal containing 9% moisture. A modified downstream product separation system was installed and operated during this run. That included a on-line continuous vacuum still, a distillate reduced-pressure still and a unit for extracting vacuum still bottoms with toluene for solids separation. The run lasted for 30 days which included 21 days of actual run time. The overall run plan, operation and status are discussed.

Exploratory work on development of dispersed catalysts is discussed. The effect of moisture on a series of Fe-Mo impregnated coals was examined in microautoclave liquefaction runs. The results indicate that increasing the moisture content on coal had only a small negative effect on resid conversion and essentially no effect on conversion into THF soluble product. It was also found that pretreating impregnated coals containing different moisture levels in H₂S/H₂ at 200 °C over a range of pressures had no effect on THF solubilization and gave a slightly lower resid conversion for high moisture containing coal. An extensive evaluation of coals impregnated with phosphomolybdic acid (PMA) is reported. PMA acts as an excellent precursor for liquefaction and is at least equal to both Molyvan L and Molyvan A. The thermal behavior of PMA in both H₂ and H₂S/H₂ streams is reported.

TABLE OF CONTENTS

ABSTRACT	iii
TABLE OF CONTENTS	iv
SUMMARY	1
SECTION ONE - UK/CAER	1-1
WORK PERFORMED	1-2
TASK 2.1 LABORATORY SUPPORT	1-2
Activity of Fe-Mo Impregnated Coal	1-2
Effect of moisture on coal liquefaction	1-2
Effect of H ₂ S/H ₂ Pretreatment on Liquefaction	1-3
Phosphomolybdic Acid Precursor	1-4
Experimental	1-4
Reaction Procedure	1-6
Sulfidation of PMA	1-7
TG/MS Analysis	1-7
Results and Discussion	1-7
Liquefaction Activity of PMA	1-8
Effect of sulfur on PMA	1-11
TASK 3.1 CONTINUOUS OPERATIONS/PARAMETRIC STUDIES	
ALC-2 Run Description and Status	1-11
Objectives	1-10
Catalysts	1-12
Preparation of Feed Coals	1-12
Unit Configuration	1-13
Operation	1-13
Run Conditions	1-14
Selection of Conditions	1-14
Deferred Conditions	1-15
Run Status	1-16
Simulated Distillation	
Aromaticity of the BP vs Retention Time Calibrant	1-17
What Distillation is Simulated	1-18
Conclusions and Future Work	1-18
References	1-19
Tables	1-22
Figures	1-27
SECTION TWO - CONSOL	
Summary of Technical Progress	2-2
TASK 2-2 LABORATORY SUPPORT	2-3
Characterization of Run ALC-1 samples	2-3
Elemental Balances for Run ALC-1 Agglomeration Runs	2-3
Laboratory Support for Run ALC-2	2-3

Characterization of Sandia Hydrotreating Samples	2-3
TASK 3-2 CONTINUOUS OPERATIONS	
Run ALC-2 Sample Request	2-4
Support for Run ALC-2	2-4
Formulation of Plans for Run ALC-3	2-4
 TASK 4-2 TECHNICAL ASSESSMENT	 2-4
 SECTION THREE - LDP Associates	 3-1
TASK 4-4 TECHNICAL ASSESSMENT	3-2
ALC-1 Analysis	3-2
ALC-2 Run	3-2
ALC-2 Operations	3-2
ALC-2 Analysis	3-3
Economic Assessment	3-3
Tables	3-4
 Abbreviations and Acronyms	

SUMMARY

TASK 2.1 LABORATORY SUPPORT (UK/CAER)

Activity of Fe-Mo Impregnated Precursors The effect of both moisture concentration and H_2S pretreatment on liquefaction of BT coal impregnated with Fe and Mo salts was studied. Moisture present in the coal will impact not only plant investment costs associated with drying equipment but the operating pressure of the system because of the necessity to maintain hydrogen partial pressure in the system. It also may have an impact on catalyst activity due to its involvement in the conversion of metal precursors into active catalysts since water is an oxidant to metals in reduced and sulfided forms. Therefore, the presence of moisture during reaction may impact on formation of catalytically active sites, particularly during the initial reaction stage. If resid conversion decreases in the presence of water, it may indicate that water influences the chemical form of the active catalysts. A series of Fe-Mo impregnated coals containing from 9 to 59 wt% water (based on dry coal) were run at 440 °C for 30 minutes using solvents comprising Wilsonville produced heavy distillate and deashed resid from Run 258 and 262. The impregnated coals contained Mo equivalent to 100 mg/kg dry coal and Fe equivalent to 1.0 wt% Fe_2O_3 on dry coal. The experimental results indicate that increasing the moisture content on coal had only a small negative effect on resid conversion and essentially no effect on conversion into THF soluble product. Overall, it appears that the active catalytic phase generated under these reaction conditions does not affect coal conversion in this test.

In order to determine whether moisture can affect catalyst presulfidation, a series of tests were made on the same coals described above by pretreating them in a gas flow reactor for 30 minutes at 200 °C and a pressure ranging from 0.1-7.0 MPa (0-1000 psig) with either pure H_2 or H_2 containing 8 vol% H_2S . Subsequent liquefaction of these pretreated coals in both H_2 and H_2S/H_2 gave basically the same coal conversion as observed without pretreatment. However, resid conversion improved after pretreating in H_2 , especially at the higher H_2 pressures. Likewise, resid conversion also improved for coals having higher moisture contents. The biggest change in resid conversion was observed for a coal having 59% moisture which gave a resid conversion of 83.3% on maf coal versus 75.4% when the coal was not pretreated. A similar observation was made for impregnated coal that was pretreated with H_2S . Resid conversion decreased for coal containing 9% moisture after pretreating in both H_2 and H_2S/H_2 at atmospheric pressure, but significantly recovered after pretreatment at 500 psig. In a H_2S/H_2 environment, the resid conversion was relatively independent of the pretreating pressure and gave slightly lower resid conversion for high moisture containing coal.

Pretreating apparently involves not only the removal of moisture from the coal, but also a change in the chemistry of the catalyst precursor that affects the formation of the active catalyst phase. Under the pretreating conditions, high moisture and high H_2 pressure favors higher resid conversion. By contrast, there was no obvious advantage to pretreating coal slurry in the presence of H_2S , especially in the presence of high moisture concentration. Of course, in these pretreating experiments, the 1 wt% Fe_2O_3 in the metal impregnated coal may be overwhelming the contribution by Mo. Although the H_2S appeared to have no effect on conversion, there are undoubtedly conditions that would show

a direct effect of sulfiding agent. We are continuing to investigate the effect of catalyst presulfiding on the liquefaction results using Mo catalyst at elevated temperatures.

Phosphomolybdic Acid Precursor The thermal properties of PMA in flowing streams of H_2 and mixtures of H_2S/H_2 was investigated using a TGA-MS. Although PMA loses water when heated at temperatures up to 350 °C, the Keggin ion is apparently stable. At higher temperatures it begins to decompose being completely destroyed at 450 °C. In H_2 , the thermal behavior is very similar except that MoO_2 is formed rather than MoO_3 . In a mixture of H_2S/H_2 , as water is lost at temperatures up to 150 °C, the H_2S not only is being incorporated into the PMA but it is being changed, presumably oxidized, and swept out of the system in the flowing gas. The resulting material is stable upon further heating up to 275 °C while H_2S in the effluent stream returns to its original baseline concentration. Further heating up to 350 °C results in a weight loss via an exothermic process (maxima at 325 °C) which is accompanied by a corresponding increase in water concentration in the effluent gas. As before, the concentration of H_2S in the carrier gas stream simultaneously decreases. Over the entire temperature range that was investigated, SO_2 was not detected in the effluent gas, probably because of the very limited amount of oxygen in the PMA sample.

A series of H_2S/H_2 treated PMA samples were prepared in a flow reactor at five different temperatures up to 450 °C for periods from 1-4 hours. The H_2S used in the treatments, expressed as the ratio of gram atoms sulfur per gram atom Mo, ranged from 0.3 to 123. Elemental analysis indicate that the amount of sulfur incorporated into the sample was greatest at 450 °C and increased as the amount of H_2S passed over the sample increased. The highest concentration of sulfur incorporated into the samples (19.1%) was obtained at 450 °C with a H_2S treat rate of 12.3 g atoms S/g atom Mo. The amount of sulfur trapped by the sample was equivalent to 7% of that H_2S fed to the reactor. At this level of sulfur incorporation, the atomic ratio of S/Mo in the treated sample was 0.81. At temperatures below 450 °C the PMA behaved much differently. The amount of incorporated sulfur was much less. At the same H_2S treat rate of 12.3 g atoms S/g atom Mo, the treated samples contained from 3.1 to 4.2 w% sulfur. Materials prepared by H_2S treatment were examined by FTIR. All of the samples, except for the sample treated at 450 °C, contained bands consistent with the continued presence of the Keggin ion. For the sample prepared at 450 °C, the IR spectra indicates complete destruction of the Keggin ion. However, the resulting solid was identified as MoO_2 by XRD.

Liquefaction Activity of PMA Crystalline PMA is an active catalyst for liquefaction of Wyodak coal. When added directly to the reaction mixture, 80.7% THF conversion was obtained versus 66.3% in its absence. The corresponding resid conversion increased to 42.7 w% maf coal in the presence of PMA versus 28.1 w% in its absence. Although Exxon had reported that PMA is oil-soluble, our observations are that PMA is insoluble in common hydrocarbon solvents. We found that the activity of PMA is comparable to MoO_3 , a crystalline solid which is not soluble in organic media, but not as active as Molyvan L or Molyvan A, both of which are either soluble or easily dispersed in the heavy hydrocarbon oils. Coals impregnated with PMA gave considerably higher activity than crystalline PMA with THF conversions ranging from 91 to 95 w% and resid conversions ranging from 61 to 70 w% with large standard deviations indicating overlap for all the values. The activities observed for impregnated coals were at least equal to both Molyvan L and

Molyvan A. Impregnated coals were prepared using four different recipes which included widely different amount of water. The performance of these coals in the liquefaction tests indicated that they were either statistically the same or the differences were very small. The conclusion is that impregnated PMA is an excellent catalyst precursor that is not significantly affected by the method used to impregnate the coal.

A series of spiked coals were prepared using this same sequence of preparative methods. These impregnated samples were prepared by depositing precursor equivalent to 3000 mg/kg dry coal onto coal which was subsequently mixed with raw coal in a ratio of 1/9 (dry basis) to give spiked coals containing a final precursor concentration equivalent to 300 mg Mo/kg dry coal. THF conversions for the four differently prepared spiked coals ranged from 89 to 93% with standard deviations indicating overlap for all the samples. The average THF conversion ignoring the difference in preparation was $91.6 \pm 2.7\%$ ($n=11$). Resid conversions were narrowly grouped with an average conversion from combining the 4 groups of $61.2 \pm 4.4\%$. Therefore, the data indicate that impregnating the PMA precursor onto only a small portion of the feed coal produces an excellent catalyst precursor that is unaffected by the method used to impregnate the coal. Results from impregnating the precursor onto all of the coal versus only 10% of the coal indicates that both THF and resid conversions are statistically the same for both groups. The conclusion is that the same level of activity of the final catalyst can be achieved by putting the precursor unevenly onto the coal. To what extent this maldistribution can be carried isn't known except that in the extreme where the PMA is not impregnated onto the coal a very sharp drop in activity occurs.

Coals were also prepared in which the PMA was impregnated onto activated carbon and then mixed with the coal to give Mo concentrations equivalent to 300 mg Mo/kg dry coal. Results indicate that THF conversions are significantly lower than observed for the impregnated coal samples. Resid conversions, however, are comparable to those observed for the impregnated coals. Although the decrease in THF conversion suggests a lower activity for the resulting Mo catalyst, and possibly poorer distribution through the reaction media, the high resid conversion suggests that either the Mo becomes dispersed or the deposited catalyst on the carbon is highly active. In order to understand these results, further work will be necessary.

A sample of column-floated cleaned BT coal was impregnated with PMA equivalent to 300 mg Mo/kg dry coal. This sample gave THF solubility and resid conversion equivalent to the impregnated BT coal indicating that the column flotation technique did not alter the reactivity of the resulting clean coal. Liquefaction of a sample of corresponding spiked cleaned coal was essentially the same.

The effect of sulfur on the activity of the PMA precursor was tested with crystalline PMA. The result showed that the presence of H_2S had a strong promoting effect on both THF solubilization and resid conversion. In the absence of H_2S , the THF and resid conversions were 66.9% and 29.3%, respectively, while in the presence of H_2S the corresponding values were 80.7% and 42.7%, respectively. We also observed that both Molyvan L and Molyvan A, both of which already have sulfur in their structures, had higher activity when H_2S was added. Therefore, the activity of the

PMA is directly affected by the presence of sulfur, even though the form of the resulting Mo catalyst may be different than generated when molybdate is used as precursor.

TASK 3.1 CONTINUOUS OPERATIONS/ PARAMETRIC STUDIES - UK/CAER

ALC-2 Run Description and Status

Continuous processing for the second run, ALC-2, began on 24 November at HTI. The objective was to expand upon results obtained in ALC-1 Condition #1 in which high yields of distillate product were produced while operating in a mode in which essentially all of the residual material was recycled to extinction. Since considerable savings can be realized by using a lower-cost Mo precursor relative to commercially available organically soluble organo-molybdenum compounds, another objective was to identify lower-cost Mo precursors that can impart activity equivalent to the Molyvan A used in ALC-1. In addition, changes in the process equipment were made to further improve process selectivity by shifting the 426 °C+ (800 °F+) distillate product into lower boiling fractions.

The primary objective of the run was to test various impregnated Mo catalyst precursors in combination with Fe and/or Ni precursors and to determine the necessity for uniform dispersion of impregnated metal precursors onto the feed coal. Prior to the run the downstream flow configuration was changed to include an on-line continuous vacuum still (CVS) and an on-line continuous reduced-pressure still (RPS). Solids separation was handled by a batch extraction unit for preparing toluene insolubles with filtration as an alternative. All of the CVS solids-free bottoms were to be recycled to extinction. During the run the effect of accumulated catalyst concentration on process performance was to be determined.

The activity of precursors containing molybdenum in combination with iron or nickel were to be compared to the activity of the Molyvan A and HTI's FeOOH/SO₄ combination used in ALC-1 Condition #1. The test of each precursor was to be made at the same unit configuration and conditions (temperature, coal space rate, H₂/coal feed rate, pressure, Mo make-up rate of 100 mg Mo/kg dry coal) as used in ALC-1 Condition #1. The plan was to maintain a 0.30 solids to dry feed coal ratio, which was slightly higher than the 0.20 ratio used in ALC-1. As a check on the sensitivity of conversion and selectivity to accumulated catalyst in the recycle stream, one of the precursors was also to be run at a solids/dry coal feed ratio of 0.10. It was predicted that total Mo concentration, including recycle, at a 0.30 solids to dry feed coal ratio would be approximately 400 mg/kg dry coal, while at the lower 0.10 recycle ratio the Mo concentration would be approximately 200 mg/kg dry coal. The plan was to do this evaluation at the end of the run.

The feed coals were prepared at HTI during October and early November using a ribbon mixer that could handle approximately 136 kg (~300 lb) of wet coal per batch. Aqueous solutions of the precursor salts were sprayed onto the coal using a reservoir/sprayer apparatus that was set up to deliver solution to the mixer at a rate of ca 1500 g/hr. After the specified amount of impregnating solution had been sprayed onto the coal, the coal was agitated for an hour to insure uniform mixing.

After the impregnation was complete, samples of the prepared coal were taken from the mixer and three submitted for Ni, Mo, Fe, moisture and ash analyses. The finished impregnated coals were stored in plastic bags and sealed in barrels, each of which held about 68 kg (150 lb).

The equipment configuration for ALC-2 up to the O-3 flash vessel remained essentially the same as in ALC-1 except that the volume of the slurry mix tank was increased in order to have at least a 4 hr capacity and have the capability of heating the slurry to approximately 200 °C (400 °F) to facilitate mixing, if necessary. Also, addition of sulfiding agents to the two reactors was changed such that H₂S was fed to the pretreater at a rate of 2 w% S on dry coal and DTNPS was fed to the 2nd stage reactor at a rate of 0.5 w% S on dry coal. The material from the high pressure separator underflow accumulator vessel, O-6, was transferred to the continuous vacuum still to produce an overhead distillate fraction and a solids-containing bottoms product. The overhead was passed to the reduced pressure still to provide an overhead product having a final cut point that was initially set at 398 °C (750 °F). Early in the run RPSOH was passed to the on-line hydrotreater K-3. However, later in the run, this was discontinued and the fraction was drummed as product. A fraction of the continuous vacuum still bottoms containing the amount of solids to be removed from the system was separated and sent to the toluene extraction unit. The remaining bottoms was returned to the slurry mix tank. The toluene extracted solids (TES) were drummed and the toluene extract distilled to recover toluene as distillate and toluene extracted oil was recycled to the slurry mix tank. The on-line hydrotreater was operated throughout ALC-2 under conditions that were essentially the same as in ALC-1. Early in the run the total overhead product from the RPS was combined with the 2nd-stage hot separator overhead and fed to the on-line hydrotreater to produce a low nitrogen and sulfur product. Because it was difficult to maintain a steady flow of feed to this unit due to demands further back in the product handling system, this was discontinued later in the run. Thereafter, RPSOH was drummed as product without further treatment.

The run lasted for 30 days in which 4 conditions were tested. The unit initially started up on about 20 November and went on coal on the 23rd. However, several problems occurred that delayed start up until 29 November. The unit operated satisfactorily for three periods but a plug developed in the cold separator overhead line from the on-line hydrotreater on 2 December and the unit had to be shutdown for repair. The unit was restarted and brought on coal on 5 December continuing with Condition #1, Period 4. Thereafter the unit operated continuously until completion of Condition #4 Period 21 at 0400 on 23 December.

Because of equipment problems, there were only 21 days of actual run time during this run.

Originally, six different conditions were to be tested over a 30 day period, each condition scheduled to last for 5 days. Because of a number of factors including the shortened on-stream time, only four conditions were actually run. Before the start of the run it was predicted that the solids turnaround time would be no more than 14 hours. This was important since the accumulated solids contained catalysts from previous conditions. Therefore, in order to get a representative solids during the balance period, the turnaround could not be too long. It appears now that the turnaround time was about 12 hours, however the composition of the solids in the system clearly did not follow the

expected pattern due to the inability to effectively remove solids during the run.

The sequence of impregnated coals that were tested in the run were:

- Condition #1- ammonium molybdate (100 ppm Mo) and ferrous sulfate (2500 ppm Fe_2O_3)
- Condition #2 - ammonium molybdate (100 ppm Mo)
- Condition #3 - ammonium molybdate (100 ppm Mo) and nickel sulfate (50 ppm Ni)
- Condition #4 - phosphomolybdic acid (100 ppm Mo)

In all these conditions the target solids level in the feed slurry was 0.30 w% dry coal. During the Condition #1 balance period 7, the recycle solids/dry coal ratio in the feed slurry reached only approximately 0.21. During this time 65-70% of the CVSB was being. As the run proceeded it was decided to drop the recycle solids/dry coal feed ratio target to the 0.2 level and keep the CVSB recycle/solids separation split at a 2/1 ratio. However, solids continued to accumulate with the recycle solids/dry coal ratio reaching approximately 0.25 during Period 12, the balance period for Condition #2. It was apparent that solids were accumulating and the amount being removed from the unit was less than expected. Throughout this time the quinoline insolubles in the TES remained inordinately low indicating a large amount of quinoline soluble material was being rejected with the solids rather than being recycled. It became apparent later that solids were contained in the TEO which was being recycled to the coal slurry tank. During Condition #3, Period 15, solids separation by filtration was started when toluene extraction was abandoned. Filtration seemed to operate satisfactorily for 20 hrs after which the efficiency for removing solids dropped dramatically. After being unable to make filtration effective, it was abandoned after completion of the material balance period for Condition #3. Starting in Period 18, CVSB was vacuum distilled to an end point of approximately 535 °C (1000 °F) to initiate a more effective solids removal method. Presently work is continuing in the laboratory to understand the unusual behavior of these solids-containing streams and why solids removal did not function as expected.

Presently, HTI is continuing analysis of the samples taken from the unit. Following completion of the analysis of the data a draft report will be prepared and circulated for comment. Simultaneously, work is continuing on trying to understand the unusual behavior of the solids contained in the products from all of the conditions. Before further runs are made a method of removing this solids must be identified and verified to insure that these materials can be handled. It will also be desirable that an alternative method be developed in case the prime separation fails to operate.

Simulated Distillation Work has been done at UK/CAER to develop simulated distillation (SIMDIS) to support the continuous runs. The method being used at CAER is a High Temperature Extended ASTM Method D2887 (also known as HT 750) using proprietary software developed by AC Analytical Controls and Hewlett Packard. A GC method is used in which samples boiling point to a final boiling point of 750 °C+ (1380 °F+) is eluted. Samples from the four balance periods of ALC-2 have been analyzed. Patterns for a *n*-paraffin calibrant is compared with the actual samples. Also, comparisons have been made to an aromatic calibrant. The corresponding D1160 distillation data from HTI are also available.

Highly paraffinic and low boiling range liquids compare well with the paraffinic calibrant. However, the high boiling resids, which contain varying amounts of aromatics, depart significantly from the paraffinic standard. Aromatics, including multiple-ring aromatics, have a propensity to elute faster than paraffins of the same boiling point from silicone rubber columns. To address this problem CAER developed an aromatic calibrant plus a correction procedure for heavier materials.

Data are provided in this report that show for heavy distillates and resids that the aromatic correction to the SIMDIS data correlate well with the observed distillation curve. However, this correction method has not worked for the lighter fractions. We are presently obtaining coal derived liquids from ALC-1 whose TBP data have already been determined, along with similar materials from other sources for use in the revised correlation.

TASK 4 CONCEPTUAL PROCESS DESIGN

TASK 4.4 PRELIMINARY TECHNICAL ASSESSMENT (LDP ASSOCIATES)

A molybdenum balance calculated for each condition of ALC-1 indicated that the moly leaving the unit was much greater than the reported moly input. The comparative costs of catalysts to be used in ALC-2 were presented at the Quarterly Review Meeting. The feed flowrates to the toluene extraction unit were compared for the proposed ALC-2 run conditions of 0.1 and 0.3 recycle solids to coal feed ratio. ALC-2 operation was interrupted twice during the first week due to a leak in a sulfiding line and a plugged vapor overhead line. Comments on the restarts of ALC-2 were discussed with CAER, CONSOL and HTL. ALC-2 operation was resumed on December 5 and was completed on the morning of December 23 after 18 consecutive operating days. All facets of the run were monitored onsite. Activities included run planning, data analysis, suggestion of back end distillation system operating conditions, solid-liquid separation system performance evaluation and troubleshooting and co-ordination with CONSOL and CAER.

SECTION ONE.

**UNIVERSITY OF KENTUCKY
CENTER FOR APPLIED ENERGY RESEARCH**

WORK PERFORMED

TASK 2.1 LABORATORY SUPPORT (UK/CAER)

Activity of Fe-Mo Impregnated Coal (X. Zhan)

In the previous report, DOE/PC/91040-72, the effect of the relative concentrations of Fe and Mo on the liquefaction of impregnated BT coal was reported. This study has now been extended to determine the influence of moisture concentration and coal pretreatment in the presence of H_2S on liquefaction of BT coal impregnated with Fe and Mo salts.

Effect of moisture on coal on liquefaction. In the catalyst screening tests reported previously with Fe and Mo catalyst, these metal impregnated coals were all vacuum dried at 100 °C to remove water before reaction. Moisture present in the coal will impact not only plant investment costs associated with drying equipment but the operating pressure of the system in order to maintain a set hydrogen partial pressure in the system. It may also have a deleterious effect on conversion of low-rank coals either because of the high temperatures that may occur upon drying or the modification of the structure of the coals that occurs when water is removed. A deleterious effect on liquefaction of subbituminous coal due to drying has been reported in the literature, though was never confirmed in tests run at Wilsonville.

It has also been suggested that the presence of moisture in the reaction system may have an impact on catalyst activity due to its involvement in the conversion of metal precursors into active catalysts. Since activity is influenced by the nature and number of active sites available to the reactants, the catalyst will undoubtedly be influenced by the conditions under which this transformation occurs. Since water is an oxidant to metals in reduced and sulfided forms, the presence of moisture during reaction may have an impact on the formation of catalytically active sites, particularly during the initial reaction stage. If resid conversion decreases in the presence of water, it may indicate that water influences the chemical form of the active catalysts. In addition, owing to the high activity of an iron surface toward oxygenated compounds, the presence of moisture in the reaction system may induce particle agglomeration due to repeated oxidation-reduction at the surface.

In this study, a Fe-Mo impregnated coal containing 9 to 59 wt% water (based on dry coal) were run at 440 °C for 30 minutes using solvents comprising Wilsonville Run 262e V-1074 heavy distillate and V-130 deashed resid or Wilsonville Run 258b V-1074 heavy distillate and Run 258a V-130 deashed resid. Coals were impregnated with aqueous solutions of ammonium molybdate, at a loading of 100 mg Mo/kg dry coal, and ferrous sulfate, at a loading of Fe equivalent to 1.0 wt% Fe_2O_3 on dry coal. The experimental results, summarized in Table 1 and Figure 1, indicate that increasing the moisture content on coal had only a small negative effect on resid conversion in both Run 262 and Run 258 solvents, but essentially no effect on conversion of coal into THF soluble product. Overall, it appears that the active catalytic phase generated under these reaction conditions does not affect coal conversion in this test. In these cases, a possible upper conversion limit due to inherent coal reactivity or limits due to thermodynamics and/or kinetics cannot be ruled out completely. In other words, the activity of catalysts generated under these different conditions may

not be distinguishable because of these limitations. We are continuing to investigate these matters, together with the catalyst activation methods, so that the catalyst can be optimally designed.

In these tests, although the impregnated coals were all vacuum dried to remove moisture, it is very probable that there is still small amount of moisture present on coal. Also, water can be produced in the reaction system as a result of deoxygenation reactions. This water may be sufficient to affect the formation of the active catalytic phase. It is possible that the excess moisture introduced to the reactor with coal has only a small effect on the chemical phase of active catalysts. As a result, resid conversion decreased only slightly while THF solubilization was basically unchanged.

Effect of H_2S/H_2 Pretreatment on Liquefaction

In order to determine whether moisture removal in a controlled gas environment could affect catalyst presulfidation, and presumably catalyst activation which would affect liquefaction, a unique reactor was designed and built in our lab. In this reactor, coal slurry can be pretreated continuously with flowing hydrogen or H_2S and then reacted at liquefaction conditions without exposing the treated material to air. A series of tests were made on coal containing a Mo loading of 100 mg/kg dry coal and an Fe_2O_3 loading of 1.0 wt% on dry coal in Wilsonville Run 262e solvent. The moisture on coal varied from 9 to 59 wt% on dry coal. Prior to reaction at 440 °C, the coal slurry was pretreated for 30 minutes at 200 °C and a pressure ranging from 0.1-7.0 MPa (0-1000 psig) with either pure H_2 or H_2 containing 8 vol% H_2S . The gas flowrate was 200 cc/m in all of the tests. At the conclusion of pretreatment, the reactor was cooled to room temperature and then pressurized to 7.0 MPa (1000 psig) with H_2 containing 3 vol% H_2S . The reaction procedure afterwards was the same as those without pretreatment.

The effect of coal slurry pretreating conditions on liquefaction is shown in Table 2 and Figures 2-3. At different moisture levels, coal conversions after pretreatment in both H_2 and H_2S/H_2 was basically the same as observed without pretreatment, as described above. Generally, resid conversion improved after pretreating in H_2 , especially at the higher H_2 pressures. Likewise, resid conversion also generally improved for coals having higher moisture content. The biggest change in resid conversion was observed for a coal having 59% moisture which gave a resid conversion of 83.3% maf coal versus 75.4% when the coal was not pretreated. The only exception is the coal which contained 9% moisture that was pretreated at atmospheric pressure.

A similar observation was made for impregnated coal that was pretreated with H_2S . Resid conversion decreased for coal containing 9% moisture after pretreating in both H_2 and H_2S/H_2 at atmospheric pressure, but significantly recovered after pretreatment at 500 psig (see Figure 3). In a H_2S/H_2 environment, the resid conversion was relatively independent of the pretreating pressure and gave slightly lower resid conversion for high moisture containing coal.

Apparently the pretreating process does not simply involve the removal of the moisture from the coal. There appears to be a chemical change to the catalyst precursor that participates in the formation of an active catalyst phase. Under the pretreating conditions that were used in this study, high moisture and high H_2 pressure favors higher resid conversion. By contrast, there was no

obvious advantage to pretreating coal slurry in the presence of H_2S , especially in the presence of high moisture concentration. Of course, in these pretreating experiments, the 1 wt% Fe_2O_3 in the metal impregnated coal may be overwhelming the contribution by Mo. In addition, the pretreating temperature of only 200 °C may not be sufficiently high to convert the precursors to a fully active phase. Even though under these conditions H_2S appeared to have no effect on conversion, there are undoubtedly other conditions that would show a direct effect of sulfiding agent. We are continuing to investigate the effect of catalyst presulfiding on the liquefaction results using Mo catalyst at elevated temperatures so that more conclusive information can be obtained.

Phosphomolybdic Acid Precursor (B. Demirel)

In this program, a number of different coal impregnated Mo precursors have been tested for their activity. This approach has provided highly active catalysts that are presumably related to their dispersion in the reaction phase. These highly active reaction systems eliminate the cost associated with preparing organically soluble precursors. Through judicious selection of the impregnating metal salts, catalyst cost can be reduced to a level that is only marginally greater than for the first stage product from the processed ore. PMA is such a water soluble form of Mo that can be prepared by a very simple procedure starting with MoO_3 , the first stage product from processing Mo-containing ores.¹

There have been a number of patents issued regarding the use of dispersed catalysts prepared from PMA for conversion of heavy hydrocarbons and carbonaceous containing materials. Most of the work relates to conversions of heavy hydrocarbons. There are, however, a few examples that describe the use of PMA in conversion of coal. In one of the earliest patents, Gleim and Gatsis² claimed a process for hydrotreating a petroleum oil at 400 °C and 100 atm to which PMA dissolved in isoamyl alcohol had been added. They claimed that a colloidal dispersion of PMA was obtained when the isoamyl alcohol was removed by distilling at 130 °C.³ In the hydroconversion of Wyodak coal, higher oil yield and lower coke make was reported for PMA relative to molybdenum naphthenate, both of which were claimed to be soluble in the heavy distillate solvent.⁴ In another case, addition of phenolic solutions of PMA to coal slurries has been reported to give higher liquid yields.⁵ Several cases claim preparation of catalyst concentrates from either aqueous or isopropyl alcohol solutions of PMA that were mixed with oil and heated at 385 °C (725 °F) for 30 min with a gaseous mixture containing 5% H_2S in H_2 .^{6,7,8,9} Adding phosphoric acid or hydrogen halides to PMA have been reported to improve catalyst activity.^{10,11} Combinations of MoO_3 and PMA have also been reported to give better resid conversion than either PMA or MoO_3 alone.^{12,13,14}

Experimental Various metal-containing BT coals were prepared by mixing aqueous solutions containing dissolved PMA with BT coal containing 8.9 w% moisture. In several cases, these impregnated coals were then further mixed with coal thereby reducing the concentration of Mo based on the total amount of coal in the mix. In every case the concentration of PMA in the final coal mix was equivalent to approximately 300 mg Mo/g dry coal. The methods used to prepare these individual metal-impregnated coals is described here. Unless otherwise noted, coal refers to the starting BT coal containing 8.9 w% moisture.

PM-1: A slurry was prepared by mixing coal with 3 times its weight of water that contained

PMA equivalent to 300 mg Mo/kg dry coal. The slurry was mixed with a magnetic stirrer at ambient temperature for 2 h after which excess water was removed by evaporation at 50-60°C. The resulting cake was dried at 96 °C and 33 kPa (250 torr) overnight to remove essentially all of the moisture.

PM-1-10C: A coal was prepared in which the Mo was selectively impregnated onto only 10% of the coal present in the mix. The portion of coal that was impregnated with the Mo was prepared by the procedure described for PM-1 except that the PMA in the slurry was equivalent to 3000 mg Mo/kg dry coal. The resulting dried impregnated coal was then mixed with 9 times its weight of BT coal (dry basis) giving a final moisture content of 8.0 w% on dry coal.

PM-2: A slurry having the same composition as in PM-1 was prepared and placed in a round bottom flask at room temperature for 2 h after which excess water was removed in a rotary evaporator at 17 kPa to give a final moisture content of 1.77 w%.

PM-2-10C: The Mo in this sample was selectively impregnated onto only 10% of the coal present in the mix. The portion of coal that was impregnated with the Mo was prepared by the procedure described for PM-2 except that the slurry contained PMA equivalent to 3000 mg Mo/kg dry coal. Unlike PM-2, this coal was dried to a final moisture content of 12.79 w%. After combining impregnated coal (dry basis) with 9 times its weight of BT coal (dry basis) the final moisture content was 9.3 w%.

PM-3: To coal was slowly added in a dropwise manner a solution (0.45 g solution/g dry coal) containing PMA equivalent to 300 mg Mo/g dry coal. The powdered coal was continually stirred while adding the solution to assure even distribution. The impregnated coal was then dried at 96°C and 30 kPa (0.3 atm) overnight to a moisture level of 3.93 w%.

PM-3-10C: The Mo in this sample was selectively impregnated onto only 10% of the coal present in the mix. The portion of coal that was impregnated with the Mo was prepared by the procedure described for PM-3 except that the impregnating solution contained PMA equivalent to 3000 mg Mo/g dry coal. The impregnated coal (dry basis) was then mixed with 9 times its weight of BT coal (dry basis) to give a final moisture content of 9 w%.

PM-4: A technique similar to that used in PM-3 was used except that the required PMA was dissolved into a smaller amount of water, i.e. 0.03 g/g dry coal. The impregnated coal was not further dried before use and contained 11.3 w% moisture.

PM-4-10C: The Mo in this sample was selectively impregnated onto only 10% of the coal present in the mix. The portion of coal that was impregnated with the Mo was prepared by the procedure described for PM-4 except that the impregnating solution contained PMA equivalent to a Mo loading of 3000 mg Mo/g dry coal. The impregnated coal (dry basis) was then mixed with 9 times its weight of BT coal (dry basis) giving a final moisture content of 11.3 w%.

PM-10AC: A slurry was prepared by mixing activated carbon with 3 times its weight of water that contained PMA equivalent to 3000 mg Mo/kg activated carbon. The slurry was mixed with a magnetic stirrer at ambient temperature for 2 h after which excess water was removed by evaporation at 50-60°C. The resulting cake was dried at 96 °C and 33 kPa and then mixed with 10 times its weight of BT coal (dry basis) to give a impregnated coal containing 8.9 w% moisture.

PM-5AC: Dried impregnated activated carbon containing PMA equivalent to 9000 mg Mo/kg dry activated carbon, prepared by the method described in PM-10AC, was mixed with 20 times its weight of BT coal to give an impregnated coal containing 8.9 w% moisture.

PM-CC: PMA was impregnated by the method described in PM-1 onto a cleaned BT coal

containing 5.91 w% ash (ASTM) and 4.18 w% moisture prepared by column flotation as described previously (DOE/PC/91040-69, page 1-12). The resulting impregnated cleaned coal was completely dried.

PM-CC-10CC: A coal prepared by the method described for PM-CC was impregnated with PMA equivalent to 3000 mg Mo/kg dry coal. The impregnated coal was mixed with 9 times its weight of BT cleaned coal to give a final Mo concentration of 300 mg/kg dry coal containing 4 w% moisture.

Reaction Procedure Reactions were conducted at 440 °C for 30 minutes in 50 cc microautoclaves that were equipped with a thermocouple and connected to a pressure transducer for monitoring temperature and pressure, respectively, during the reaction. In a typical experiment, 1.75 g of heavy distillate, 2.8 g of ash-free resid, and 2.45 g of metal impregnated dry coal were added to the reactor. In these experiments, the precursors were either particulate materials (MoO₃, Molyvan A, PMA) or organic solutions of the Mo precursor (Molyvan L). The particulate materials are all insoluble in the organic media, however Molyvan A is easily dispersed in heavy hydrocarbon solvents. In each case the specified amount of the precursor was loaded directly into the reactor. The reactor was submerged in a fluidized sand bath and continuously agitated at a rate of 400 cycles per minute while maintaining the specified temperature. At the end of the reaction period, the reactor was removed from the sand bath, quenched to ambient temperature and the gaseous products collected and analyzed by gas chromatography. The solid and liquid products were removed from the reactor using THF and the mixture was extracted in a Soxhlet extraction apparatus for 18 hours. The THF insoluble material was dried (80 °C at 17 kPa) and weighed. Vacuum distillations were performed using a modified ASTM D-1160 procedure starting with the residue from THF extraction of the total reactor effluent.¹⁵ Cut points were adjusted in several cases based upon a GC simulated distillation procedure that had been developed at the CAER. The yield of THF insoluble product was determined as follows:

$$\text{Yield IOM} = ([\text{IOM}]_{\text{Products}} - [\text{IOM}]_{\text{Feed}}) / \text{Coal (maf)} * 100$$

Material balances are based upon a forced ash balance with any loss and error being accounted for in the distillate product. Product distributions using the distillation method are calculated by subtracting the weights of gases, residue, ash and IOM in the product from the weight of each in the feed. Resid conversion was calculated as follows:

$$\text{Resid Conv} = 100 \left[1 - \frac{[\text{IOM} + 565^{\circ}\text{C} * \text{Resid (maf)}]_{\text{Products}}}{[\text{Coal (maf)}]_{\text{Feed}}} \right]$$

Standard deviations calculated for the procedure were: THF insolubles, 1.3; hydrocarbon gases, 0.2; CO+CO₂, 0.1; PA+A, 0.6; oils, 1.4; 565 °C distillate, 5.5; resid conversion, 2.2. Coal conversion equals 100 minus the yield of IOM.

Sulfidation of PMA An approximately 2-4 mm thick layer of PMA in a porcelain boat was placed in a 4 cm quartz tube within a tubular furnace. Air was purged from the system using nitrogen after which a stream comprising 8 vol% H_2S in H_2 at 0.10 MPA was passed over the sample. Heat was applied to bring the reactor to the specified temperature and held at temperature for the specified time period. Afterwards, the reactor was purged with N_2 as the reactor was cooled to ambient temperature. The sample was removed and analyzed.

TG/MS Analysis Thermogravimetric analysis was carried out in a Seiko SSC/5200 Thermal Analyzer connected to mass spectrometer. A weighed amount of sample was heated at $20^\circ\text{C}/\text{min}$ from ambient up to 650°C in He, H_2 and a mixture of 7.93 vol.% H_2S in H_2 .

Results and Discussion

PMA is an especially unique form of Mo that has already found extensive use as catalyst in a number of other processes.^{16,17} Catalysis has been attributed to the uniquely combined electron transfer and acidic properties of the Keggin anion, i.e. $(\text{PMo}_{12}\text{O}_{40})^{3-}$. However, application of PMA to coal liquefaction differs from previous applications, which were largely oxidation applications. In liquefaction, not only does the reaction take place in a reducing atmosphere but the reaction temperature is higher and sulfur is present, which may affect the actual form of the resulting catalyst.¹⁸ PMA, when heated in an inert atmosphere (He), loses approximately 15% weight that corresponds to the loss of crystalline water, or water of hydration, which occurs via an endothermic process at temperatures up to about 175°C (Figure 4). Further heating to $\sim 450^\circ\text{C}$ results in a further loss corresponding to ~ 1.5 molecules of constitutional water. Above 350°C , the Keggin ion begins to decompose being completely destroyed at 450°C . In H_2 , the thermal behavior, as shown in Figure 5, is very nearly the same as in He except for the different form of the decomposed structure. Tsigdinos observed in N_2 that only MoO_3 is formed, whereas in H_2 , Yong et al observed both MoO_2 as well as free metal are formed.

The reaction of PMA with H_2S in the presence of H_2 was studied by treating a sample of PMA in a flowing stream of 8 vol% H_2S in H_2 at a range of temperatures. At temperatures up to 150°C , the sample loses water and the H_2S concentration in the carrier gas stream decreases (see Figure 6). Apparently as water removal proceeds, H_2S is either being incorporated into the PMA or oxidized and swept out of the system in the flowing gas. The resulting material is stable upon further heating up to 275°C while H_2S in the effluent stream returns to its original baseline concentration. Further heating up to 350°C results in a weight loss via an exothermic process (maxima at 325°C) which is accompanied by a corresponding increase in water concentration in the effluent gas. As before, the concentration of H_2S in the carrier gas stream simultaneously decreases. Over the entire temperature range that was investigated, SO_2 was not detected in the effluent gas, probably because of the very limited amount of oxygen in the PMA sample. Because of the very large excess of H_2S in the carrier gas relative to the size of the sample, any increase in sulfur concentration in the sample would not account for the magnitude of the decrease in H_2S concentration in the gas stream.

PMA was treated with $\text{H}_2\text{S}/\text{H}_2$ at five different temperatures up to 450°C for periods from 1-4 hours. The amount of sulfur passed over the samples, expressed as the ratio of gram atoms sulfur per gram

atom Mo, ranged from 0.3 to 123. Elemental analysis of these treated materials indicate that the amount of sulfur in the sample was greatest at 450 °C and increased as the amount of H₂S passed over the sample increased (see Table 3). Treatment at 450 °C with a H₂S treat rate of 12.3 g atoms S/g atom Mo gave a sample containing 19.1% sulfur, which corresponds to the consumption of 7% of the H₂S fed to the reactor during the treatment period. At this level of sulfur incorporation, the ratio of S/Mo in the treated sample was 0.81. At temperatures below 450 °C the PMA behaved much differently. The amount of incorporated sulfur was much less. At the same H₂S treat rate of 12.3 g atoms S/g atom Mo, the treated samples contained from 3.1 to 4.2 w% sulfur, which corresponds to incorporation of only 1-2% of the H₂S in the gas stream.

Larger samples, i.e., 10 g, were prepared in order to make sufficient sample for characterization. A sample treated for 1 hr at 450 °C with H₂S at a treat rate of 0.3 g atom S/g atom Mo reacted rapidly with H₂S consuming 60% of the H₂S in the gas phase to give a sample containing 4.2 w% sulfur with a S/Mo ratio of 0.18. A sample produced at the same H₂S flow rate over a 4 hr period contained about twice as much sulfur (8.9 w%).

Infrared analysis of the materials prepared at the lowest H₂S treat rate of 0.3 g atoms S/g atom Mo indicate that all, except for the sample treated at 450 °C, contained strong absorptions in the 600-1100 cm⁻¹ region (see Figure 7). These bands are consistent with the continued presence of the Keggin ion.^{18,19} In the Keggin ion, terminal Mo=O vibrations are observed at 960 cm⁻¹, asymmetric Mo-O-Mo stretching vibrations at 860 and 780 cm⁻¹, and asymmetric stretching vibrations of the PO₄ tetrahedra at 1060 and 590 cm⁻¹. Both S-S and Mo-S vibrations are normally found only below 600 cm⁻¹, they do not overlap with the Mo-O bands in the 600-1000 cm⁻¹ region.²⁰ Unfortunately bands that appear in the spectra in the 500 to 600 cm⁻¹ region for the 125 to 200 °C sulfided samples that could suggest the presence of sulfur overlap with bands already present in the original sulfur-free material.

For the sample prepared at 450 °C, bands in the 600-1100 cm⁻¹ region are absent indicating complete destruction of the Keggin ion as well as the absence of any Mo-O bonds due to the presence of the MoO₂ structure. Agreement between the XRD shown in Figure 8 with the pattern for MoO₂ shown in the JSPDS-ICDD Powder Diffraction-2 Database confirmed the presence of MoO₂ in this sample. Since the sample contained a relatively small amount of sulfur, most of the molybdenum in the sample had to be present either as an oxide, i.e. MoO₂, or as an oxysulfide.

Liquefaction Activity of PMA A test used at UK/CAER was developed to measure the activity of various metal containing precursors for liquefaction of Wyodak coal. It simulates, as closely as possible, actual process conditions that would exist in a plant recycle operation. The test is run in microautoclave reactors at conditions that produced coal conversions and distillate yields comparable to that observed in the large scale plant.²¹ The solvent composition comprises 565 °C- (1050 °F-) distillate material and a 565 °C+ (1050 °F+) solids-free resid that was produced at Wilsonville in Run 258. The resid component was a solids-free 565 °C+ (1050 °F+) material produced by the ROSE-SR unit, which made up only about 7% of the total plant recycle solvent. The other major component in the Wilsonville recycle solvent was an ashy resid recycled from the vacuum distillation tower.

In the screening test, the distillate and deashed resid components are blended with feed coal in a way to give a resid/maf coal ratio of approximately 1.2, which was similar to that used at Wilsonville. The composition of the reaction mixture in the catalyst screening test, as determined from distillations on the feed solvent in our laboratory, was 35 w% dry coal, 25 w% 524 °C- heavy distillate and 40 w% 524 °C+ solids-free resid. The reaction temperature of 440 °C was chosen which is the same as used at Wilsonville. Sulfiding agent was added by introducing 3 vol% H₂S in H₂ (4 w% S on dry coal) with an initial starting pressure of 1350 psig to provide a hydrogen to feed coal ratio of 18 wt % on dry coal at a total pressure at operating temperature of approximately 2500 psig. A reaction time of 30 min was selected which provided a range of resid conversions for the various precursors that were added at a level of approximately 300 mg Mo/kg dry coal.

Direct addition of crystalline PMA to the reaction mixture resulted in a level of reactivity that was considerably greater than for the non-catalyzed case (see Table 4). THF conversion increased to 80.7% in the presence of PMA versus 66.3% in its absence. The corresponding resid conversion increased to 42.7 w% maf coal in the presence of PMA versus 28.1 w% in its absence. Aldridge and Bearden had seen similar results in their work with Wyodak coal claiming that PMA was oil-soluble which apparently increased its dispersion in the reaction solvent.⁴ Our observations on the solubility of PMA agree with Tsigdinos who reported that PMA is insoluble in common hydrocarbon solvents.¹ The activity of PMA is comparable to MoO₃, a crystalline solid which is not soluble in organic media, which suggests that PMA is not well dispersed in the system. On the other hand, Molyvan L, which is soluble in heavy hydrocarbon oils, gives much higher THF and resid conversions than either the crystalline PMA or MoO₃. Molyvan A, which, according to the manufacturer, is easily dispersed in these systems, performs even better than Molyvan L.

One method to improve the dispersion of the Mo in the system is to impregnate the PMA onto coal. This method has been shown to result in highly active catalysts when starting with ammonium heptamolybdate. Coals impregnated with PMA gave considerably higher activity than crystalline PMA (see Table 5). Averaged THF conversions for each impregnated coal which were prepared by four different methods ranged from 91 to 95 w%. Standard deviations indicated considerable overlap with PM-2 being slightly higher than the others. PM-2 was prepared by rotovaping off excess water to produce a coal containing 1.8 w% moisture. Ignoring this slight bias, the average THF conversion for the four different preparations was 92.3±2.4 (n=11). Clearly, THF conversion for the impregnated coals is significantly higher than when PMA is added directly to the reaction mixture as a crystalline solid.

Averaged resid conversions for this series of four coals ranged from 61 to 70 w% with large standard deviations indicating overlap for all the values. Therefore, the conversion values for these differently impregnated coals suggest that the method of impregnation does not affect performance. Assuming no difference between the differently prepared coals, the average resid conversions were 64.5±2.4 (n=11). The impregnated coals produce significantly higher conversions than adding crystalline PMA directly to the reaction system. The activities observed for impregnated coals were at least equal both Molyvan L and Molyvan A, which gave the best activity of any precursors shown in Table 4. The conclusion is that impregnated PMA is an excellent catalyst precursor that is not significantly

affected by the method used to impregnate the coal.

If the high activity resulting from the conversion of PMA into a catalytically active form is related to the dispersion of the active form in the reaction media, the distribution of Mo on the surface of the coal may influence formation of this active form. If an even distribution is necessary to achieve an active catalyst, this undoubtedly will influence processing costs. To test the limits of achieving an even distribution, each of the methods used in this study to impregnate coal was applied to samples onto which precursor was impregnated onto only 10% of the total feed coal. These impregnated samples were prepared by depositing precursor equivalent to 3000 mg/kg dry coal onto coal which was subsequently mixed with raw coal in a ratio of 1/9 (dry basis) to give spiked coals containing a final precursor concentration equivalent to 300 mg Mo/kg dry coal. The results from testing those coals are shown in Table 6. THF conversions for the four differently prepared spiked coals ranged from 89 to 93% with standard deviations indicating overlap for all the samples. The average THF conversion ignoring the difference in preparation was $91.6 \pm 2.7\%$ ($n=11$). Resid conversions were narrowly grouped with an average conversion from combining the 4 groups of $61.2 \pm 4.4\%$. The value for PM-1-10C was significantly higher than for the other coals but little importance can be ascribed to this single determination. Therefore, the data indicate that impregnating the PMA precursor onto only a small portion of the feed coal produces an excellent catalyst precursor that is unaffected by the method used to impregnate the coal. Further, results from impregnating the precursor onto all of the coal and only 10% of the coal indicates that both THF and resid conversions are statistically the same. The conclusion is that the same level of activity of the final catalyst can be achieved by putting the precursor unevenly onto the coal. To what extent this maldistribution can be carried isn't known except that in the extreme where the PMA is not impregnated onto the coal a very sharp drop in activity occurs.

Another approach toward introducing a non-miscible precursor into the reaction system is to disperse it onto carbon or other low-cost support. Two PMA-impregnated activated carbon samples that were mixed with BT coal to each give Mo concentrations equivalent to 300 mg Mo/kg dry coal were prepared and tested for their liquefaction activity. Results shown in Table 7 indicate THF conversions are significantly lower than observed for the impregnated coal samples. Resid conversions, however, are comparable to those observed for the impregnated coals. Although the decrease in THF conversion suggests a lower activity for the resulting Mo catalyst, and possibly poorer distribution through the reaction media, the high resid conversion suggests that either the Mo becomes dispersed or the deposited catalyst on the carbon is highly active. In order to understand these results, further work will be necessary.

A sample of column-floated cleaned BT coal that was prepared earlier (DOE/PC/91040-69, page 1-12) was impregnated with PMA equivalent to 300 mg Mo/kg dry coal (PM-CC). This sample gave THF solubility and resid conversion equivalent to the impregnated BT coal. This suggests that the column flotation technique did not alter the reactivity of the resulting clean coal (see Table 7). Liquefaction of a sample of spiked cleaned coal was essentially the same, assuming comparable standard deviations to the earlier run, as the cleaned coal onto which the Mo was impregnated onto all of the sample.

Effect of sulfur on PMA At the outset of this study the necessity for having sulfur present during the reaction wasn't clearly known. The unique catalytic activity of PMA in a number of other reactions suggested that this material may have activity completely unrelated to the formation of Mo-S structures. Therefore, it was necessary to determine the effect of sulfur on the activity of PMA. The test was done on crystalline PMA that was added directly to the reaction mixture. The result showed that the presence of H_2S had a strong promoting effect on the reaction, as shown in Table 8. In the absence of H_2S , the THF and resid conversions to 66.9% and 29.3%, respectively, while in the presence of H_2S the corresponding values were 80.7% and 42.7%, respectively. With both Molyvan L and Molyvan A, both of which already have sulfur in their structures, the presence of H_2S promotes the activity of their resulting catalysts for both THF and resid conversion. Therefore, these results suggest that the activity of the PMA is directly affected by the presence of sulfur, even though the form of the resulting Mo catalyst may be different than generated when the molybdate is used as precursor.

TASK 3.1 CONTINUOUS OPERATIONS/ PARAMETRIC STUDIES - UK/CAER

ALC-2 Run Description and Status

Objectives

Continuous processing for the second run, ALC-2, began on 24 November at HTL. The run plan was developed to expand upon results obtained in ALC-1 Condition #1 in which high yields of distillate product were produced while operating in a mode in which essentially all of the residual material was recycled to extinction. Since considerable savings can be realized by using a lower-cost Mo precursor relative to commercially available organically soluble organo-molybdenum compounds, an objective of this run was to identify lower-cost Mo precursors that can impart activity equivalent to the Molyvan A used in ALC-1. In addition, changes in the process equipment were made to further improve process selectivity by shifting the 426 °C+ (800 °F+) distillate product into lower boiling fractions. Such a shift could provide a cost advantage through production of a higher value product. The specific objectives and the selection of the various catalyst precursors and run conditions are presented below.

Objectives of the run were:

- To test various impregnated Mo catalyst precursors in combination with Fe and/or Ni precursors;
- To determine the necessity for uniform dispersion of impregnated metal precursors onto the feed coal;
- To operate in an all-slurry process configuration to produce a distillate product having only a minimum amount of heavy distillate;
- To operate with a modified downstream flow configuration having;
 - On-line continuous vacuum still (CVS);
 - On-line continuous reduced-pressure still (RPS);

Batch extraction unit for preparing toluene insolubles for solids rejection;
Alternative filtration system for solids separation.

- To recycle all CVS solids-free bottoms to extinction;
- To determine the effect of accumulated catalyst concentration on process performance.

Catalysts

A series of catalyst precursors containing molybdenum in combination with iron or nickel were available for testing. The objective was to compare the activity of these precursors to a reference Molyvan A and HTI's FeOOH/SO_4 combination used in ALC-1 Condition #1. The plan was to test each precursor at the same unit configuration and conditions (temperature, coal space rate, H_2 /coal feed rate, pressure, Mo make-up rate of 100 mg Mo/kg dry coal) used in ALC-1 Condition #1. The plan called for maintaining a 0.30 solids to dry feed coal ratio, which was slightly higher than the 0.20 ratio used in ALC-1. As a check on the sensitivity of conversion and selectivity to accumulated catalyst in the recycle stream, one of the precursors was also to be run at a solids/dry coal feed ratio of 0.10. It was predicted that total Mo concentration, including recycle, at a 0.30 solids to dry feed coal ratio would be approximately 400 mg/kg dry coal, while at the lower 0.10 recycle ratio the Mo concentration would be approximately 200 mg/kg dry coal. The plan was to do this evaluation at the end of the run.

The key advantage of using these precursors is their low cost and, presumably, simplicity of impregnating them onto the coal. Since all of these precursors are water soluble, the approach was to spray aqueous solutions containing these materials onto the coal with an amount of water that would increase the moisture content of the coal by only approximately 3%. By minimizing the amount of water used to impregnate the coal, costs associated with subsequently removing the water would be minimized. Another factor that could affect the performance of these metal-impregnated coals is the uniformity of dispersion onto the feed coal. Laboratory data had shown that coals in which the metal precursor was dispersed onto only 10% of the feed coal performed just as well as coals onto which the metal precursor was evenly distributed over 100% of the coal. Obviously, the lower the sensitivity of conversion to the metal distribution on the starting coal, the less likely additional equipment would be necessary for impregnating the metal precursors in a commercial plant.

Preparation of Feed Coals

In order to test this method of adding the precursor into the reaction system, it was necessary to prepare the feed coals prior to the start of the run. This was done at HTI during October and early November. A preliminary description of the method used to impregnate the coals was included in the previous quarterly report. (DOE/PC/91040-72, page 1-2). Batches of coal were prepared using a ribbon mixer that could handle approximately 136 kg (~300 lb) of wet coal per batch. Aqueous salt solutions that contained the precursor salts were sprayed onto the coal using a reservoir/sprayer apparatus that used motive air to feed the salt solution to the coal. Based on a series of preliminary trial runs, the sprayer was set up to deliver solution to the mixer at a rate of ca 1500 g/hr while operating with air pressure of 0.15 MPa (7 psig) on the liquid reservoir and 0.27 MPa (25 psig) on the nozzle. Although lower impregnation rates were possible, the higher air pressures that would

have been required at these lower rates tended to atomize the solution at the nozzle and fluidize the coal in the mixer freeboard which would have resulted in loss of coal from the mixer.

During the preparations, after the specified amount of impregnating solution had been sprayed onto the coal, the coal was agitated for an hour to insure uniform mixing. In cases where more than one reservoir volume of solution was required, the coal was agitated for one hour between charges. Since metal salts were never mixed to avoid any complications due to precipitation of insoluble salts that would form, i.e., FeMoO_4 or NiMoO_4 , Ni was always added before Mo and Mo before Fe. After the impregnation was complete, eight samples of the prepared coal were taken from the mixer and three were submitted to the lab for analysis. Each sample was analyzed for Ni, Mo, Fe, moisture and ash. The finished impregnated coals were stored in plastic bags and sealed in barrels, each of which held about 68 kg (150 lb). The recipes that were used for each of seven coal preparations are presented in Table 9.

Unit Configuration

The equipment configuration for ALC-2 up to the O-3 flash vessel remained essentially the same as in ALC-1 except that the volume of the slurry mix tank was increased in order to have at least a 4 hr capacity and have the capability of heating the slurry to approximately 200 °C (400 °F) to facilitate mixing, if necessary. Also, addition of sulfiding agents to the two reactors was changed such that H_2S was fed to the pretreater at a rate of 2 w% S on dry coal and DTNPS was fed to the 2nd stage reactor at a rate of 0.5 w% S on dry coal. Major changes were made to the downstream separation sections. During Conditions 1-3, the effluent from the O-3 separator underflow accumulator vessel, O-6, was drained every 2 hours into an intermediate holding vessel and transferred to the CVS feed tank. The CVS overhead distillate fraction (CVSOH) was collected and combined with O-7A LP overhead receiver bottoms, O-4A vent gas K.O., and O-5A flare K.O. and passed to the RPS that provided an overhead product (RPSOH) having a final cut point that was initially set at 398 °C (750 °F). Early in the run RPSOH was passed to the on-line hydrotreater K-3. However, later in the run, this was discontinued and the fraction was drummed as product. From the CVSB, a fraction containing the amount of solids to be removed from the system was separated and sent to the toluene extraction unit. The remaining CVSB was returned to the slurry mix tank. The toluene extracted solids (TES) were drummed and the toluene extract distilled to recover toluene as distillate and toluene extracted oil (TEO). TEO was recycled to the slurry mix tank.

The on-line hydrotreater was operated throughout ALC-2 under conditions that were essentially the same as in ALC-1. Early in the run the total overhead product from the RPS was combined with the 2nd-stage O-1 hot separator overhead and fed to the on-line hydrotreater to produce a low nitrogen and sulfur product. Because it was difficult to maintain a steady flow of feed to this unit due to demands further back in the product handling system, this was discontinued later in the run. Thereafter, RPSOH was drummed as product without further treatment.

Operation

The run lasted for 30 days in which 4 conditions were tested. The unit initially started up on about 20 November and went on coal on the 23rd. However, a leak occurred at the TNPS inlet line to K-2

and the unit had to be shut down to repair the leak. Following repair, the unit started up on 26 November but a plug occurred in the preheater so the unit had to be again shut down and the preheater coil replaced. After these initial problems, the unit was put on stream on the 27th and onto coal on Friday, 29 November. The unit operated satisfactorily for three periods but a plug developed in the O-2 cold separator overhead line from the on-line K-3 hydrotreater on 2 December and the unit had to be shutdown for repair. The unit was restarted and brought on coal on 5 December continuing with Condition #1, Period 4. Thereafter the unit operated continuously until completion of Condition #4 Period 21 at 0400 on 23 December.

Run Conditions

The process conditions for the run are given in Table 10. Because of equipment problems, there were only 21 days of actual run time during this run. Originally, six different conditions were to be tested over a 30 day period, each condition scheduled to last for 5 days. In the first five conditions, five different metal-impregnated coal compositions were to be tested. In the sixth condition, the effect of catalyst accumulation in the recycle solvent was to be tested. Because of a number of factors including the shortened on-stream time, only four conditions were actually run. It was recognized before the run started that in order to assure that good data representative of each of the impregnated coals were obtained, the accumulated solids in the reaction system during the balance period had to be representative of solids derived from the test coal. Although solids turnaround time in the unit wasn't known at the beginning of the run, it was expected that the turnaround time would be no more than 14 hours. Within this time period, it was estimated that 90% of the solids accumulated in the system from a previous coal should be replaced by the 4th day of the condition. It appears now that the turnaround time was about 12 hours which was a combination of the approximate 90 min residence time in the two reactors, 2 hour accumulation time in the O-6 bottoms separator, 2 hour drawdown of the CVSB, 4 hour hold time in the mix tank plus time associated with handling and weighing of materials. Preliminary analysis of the metals concentration in the CVSB solids, however, shows that the solids in the system clearly did not follow this pattern due to the inability to effectively remove solids during the run.

Selection of "Conditions" - Since the main objective of this run was to evaluate several different metal-impregnated precursors. The selection of the precursors and processing conditions that were followed for each are summarized in Table 11 and discussed below:

In Condition #1, coal impregnated with ammonium molybdate (100 ppm Mo) and ferrous sulfate (2500 ppm Fe_2O_3) was tested at base conditions to define operability of the new unit configuration and to provide a direct comparison with ALC-1 Condition #1. Since Fe was thought to affect unit operability by influencing the properties of the resid-containing stream, it was run in the first condition to minimize any problems associated with start up of the CVS and the toluene extraction unit. The Fe concentration, though somewhat high versus earlier runs at HTI, was chosen based on the low cost associated with this level of Fe-addition (< 15¢/bbl gasoline) and the desire to insure sufficient Fe is present to have an effect.

In Condition #2, an ammonium molybdate-impregnated coal containing 100 mg Mo/kg

dry coal was tested. The absence of Fe would show if any operability problems arose related to viscosity buildup in the resid-containing fractions. If operability problems had arisen, an alternative Fe-impregnated coal "vector" would have been added to spike the feed coal at a level of 0.25 wt% Fe_2O_3 on total dry coal in order to overcome the problem. Although the Mo make-up rate would have dropped to 90 ppm, this concentration level would be sufficient to allow comparison with Condition #1. During the run, there appeared to be no indication of any operability problems related to handling or distilling the bottoms containing stream so the feed was not modified to inject Fe during this condition.

In Condition #3, a coal impregnated at a level of 100 ppm Mo added as ammonium molybdate and 50 ppm Ni added as nickel sulfate was run. Although lower concentrations of Ni have been found to be effective in microautoclave tests, this test was run at the higher 50 ppm level to increase the probability that an effect would be observed. At the 50 ppm level the cost is still quite low (8 ¢/bbl gasoline).

In Condition #4, coal impregnated with 100 ppm Mo as phosphomolybdic acid (PMA) was tested. The use of phosphoric acid offers a low cost method for solubilizing MoO_3 and provides an alternative to using ammonia for this purpose. Microautoclave tests have shown PMA to be quite active which may be related to complexes that exist between Mo and P in these systems.

In all these conditions the target solids level in the feed slurry was 0.30 w% dry coal. During the Condition #1 balance period 7, the recycle solids/dry coal ratio in the feed slurry reached only approximately 0.21. During this time 65-70% of the CVSB was being. As the run proceeded it was decided to drop the recycle solids/dry coal feed ratio target to the 0.2 level and keep the CVSB recycle/solids separation split at a 2/1 ratio. As time progressed, however, the solids continued to accumulate with the recycle solids/dry coal ratio reaching approximately 0.25 during Period 12, the balance period for Condition #2. With this happening, it was apparent that solids were accumulating and the amount being removed from the unit was less than expected. Throughout this time the quinoline insolubles in the TES remained inordinately low, as shown in Table 12, indicating that a large amount of quinoline soluble material was being rejected with the solids rather than being recycled. Concomitantly, as it became apparent later, solids were contained in the TEO that was being recycled to the coal slurry tank. During Condition #3, Period 15, solids separation by filtration was started when toluene extraction was abandoned. Filtration seemed to operate satisfactorily for 20 hrs after which the efficiency for removing solids dropped dramatically. After being unable to make filtration effective, it was abandoned after completion of the material balance period for Condition #3. Starting in Period 18, CVSB was vacuum distilled to an end point of approximately 535 °C (1000 °F) to initiate a more effective solids removal method. Presently work is continuing in the laboratory to understand the unusual behavior of these solids-containing streams and why solids removal did not function as expected.

Deferred Conditions - In anticipation of being able to evaluate more coals, several additional metal-impregnated coals were prepared. Those coals and the specific conditions under which they

were to have been evaluated is discussed below. The option remains of examining these impregnated coal and particular deferred conditions in a subsequent run. The deferred conditions are described here:

The vector approach, wherein the precursor was impregnated onto only a portion of the feed coal, was to be tested with a coal that was sequentially impregnated with Ni and Mo salts. The coal was prepared by impregnating coal with ammonium molybdate, at a level of 1000 ppm Mo, and nickel sulfate, at a level of 500 ppm Ni. One part of impregnated coal was then mixed with 9 parts of starting coal to give a final mix having a loading of 100 mg Mo and 50 mg Ni per kg dry coal. The purpose of the test was to determine if impregnating the precursor metals onto a portion of the coal performs in a manner equivalent to impregnating all of the coal. This will confirm that impregnation can be handled quite simply without the need for additional coal handling facilities.

A coal impregnated with ammonium tetrathiomolybdate at a Mo concentration of 100 mg/kg dry coal was prepared and was available for testing if time had permitted. This material represents an advanced stage of sulfided Mo which has performed satisfactorily in microautoclave tests. The purpose of the test was to determine if the level of sulfur incorporation in the precursor would impact on the ultimate performance of the catalyst formed in the reaction system.

In the original plan, the effect of running at a lower accumulated catalyst level in the recycle stream was to be tested with a coal impregnated with ammonium molybdate to a level of 100 mg Mo/kg dry coal in the final condition. Since running at a high solids to coal feed ratio results in displacing some of the coal that can be fed to the unit, the objective was to determine if running at a coal concentration of 35% in the feed slurry along with a 0.03 recycle solids/dry coal ratio (Condition #2) was justified relative to running at the same coal space rate with a feed slurry containing 41% coal and a 0.10 recycle solids/dry coal ratio.

Run Status - HTI is continuing analysis of the samples taken from the unit plus accumulating the data developed during the run. Following completion of the analysis of the data a draft report will be prepared and circulated for comment. It is anticipated that the report will be available during late February or early March. Simultaneously, work is continuing on trying to understand the unusual behavior of the solids contained in the products from all of the conditions. Before further runs are made a method of removing this solids must be identified and verified to insure that these materials can be handled. It will also be desirable that an alternative method be developed in case the prime separation fails to operate.

Simulated Distillation - (R. Anderson)

This section reports the results of simulated distillation (SIMDIS) laboratory support work for ALC-2, and discusses the background of proposed directions for ongoing work to improve the

interpretation of SIMDIS GC data. Two issues related to simulated distillation have been discussed in previous technical review sessions and are addressed here: 1) the aromaticity of the boiling point calibrant; and 2) the correlation of SIMDIS data to different types of distillations. CAER began operating SIMDIS equipment for this project in the spring of 1996. The method used is a High Temperature Extended ASTM Method D2887 (also known as HT 750), using proprietary software developed by AC Analytical Controls and Hewlett Packard. The basis for this method, ASTM D2887, "Boiling Range Distribution of Petroleum Fractions by Gas Chromatography", is a GC method used for fully eluting samples with a final boiling point of 538 °C (1000 °F), corresponding to a carbon number of ca 44. HT 750 extends this analysis range to a final boiling point of 750 °C+ (1380 °F+, to C-120) and accepts partially-eluting samples.

Selected samples from the four balance periods of ALC-2 [eg, Separator Overhead (SOH), Continuous Vacuum Still Bottoms (CVSB), Continuous Vacuum Still Overheads (CVSOH), Reduced Pressure Still Overheads (RPSOH), and Reduced Pressure Still Bottoms (RPSB)] were delivered to the CAER for SIMDIS, as well as other analyses. As a representative sampling, results for CVSB, RPSB, and RPSOH streams are shown in Figures 9-14 where those samples were provided. The CVSB is typically a full range, ash-containing resid, while both the RPSB and RPSOH are mid-boiling range aromatic materials, containing little ash. The simulated distillation data presented appear in each figure as a nearly continuous series of either circles or squares. The squares are SIMDIS data using *n*-paraffins as a boiling point vs retention time calibrant. The circles are the same data "corrected" by a method described in a previous report,²² using an aromatic calibrant. For comparison, the D1160²³ distillation data determined by HTI are shown on the graphs as triangles.

Aromaticity of the BP vs Retention Time Calibrant For highly paraffinic and low boiling range liquids, SIMDIS methods are well documented and standardized, and are therefore not the subject of the discussion here. Rather, this would address high boiling resids, containing varying amounts of aromatics. D2887 recognizes and cautions against the potential boiling range distribution errors arising from the presence of non-normal paraffin hydrocarbons and multiple-ring aromatics due to their propensity to elute faster than paraffins of the same boiling point from silicone rubber columns. For samples in the applicable boiling range of D2887, there is scarcely any effect. However, for samples in the target range of HT 750, the difference between actual and reported boiling range may be as much as 56 °C (100 °F). To accurately determine boiling cut points of coal derived liquids around 566 °C (1050 °F), researchers at CAER developed an aromatic standard and attendant correction procedure that would be applicable to the compounds present in those liquids. The retention time data that forms the basis of this correction is shown in Figure 15.

The data presented for the ALC-2 samples allow us to address the aromaticity of the calibrant that is used to determine boiling range from the gas chromatograph. For petroleum derived materials, the paraffinic mixtures have been shown to provide the best calibrant. As can be seen from this sequence of figures, for light coal liquids with a 50 wt% distilled (d_{50}) boiling point below 300 °C, the paraffinic calibrant is likewise satisfactory. For samples with a d_{50} above 600 °C, the aromatic calibrant is best. In between, say for the RPSB materials here, some calibrant between the two

extremes would seem to be in order.

Figure 16 shows the process flow relationship among the SIMDIS samples discussed here, and it is evident that for representative samples collected at steady state, plots of boiling range vs percent mass distilled should flow smoothly from the lightest cut (RPSOH), to the middle RPSB cut, and finally to the highest boiler (CVSB). This should apply to both physical and simulated distillation data. Distillation data from Period 17 along with mass flow rates during that period were used to check the consistency between the three distillation cut. Figure 17 shows the HTI D1160 data along with SIMDIS data using the *n*-paraffin calibrant. Figure 18 shows the HTI distillation data with the SIMDIS data using the aromatic correction.

The HTI distillation data are seen to be the most consistent, giving a smooth curve from 0 to 100%. The paraffinic correlation is not as good, readily showing a mismatch between the CVSB and RPSB curves. The aromatic correction to the SIMDIS data also shows this inconsistency, but with the data shifted to a higher boiling range. However, the full range, ashy continuous vacuum still bottoms are more accurately characterized with the aromatic correction. This inconsistency in boiling curves had also been observed from time to time in earlier SIMDIS data, but from microautoclave sized samples separated in microdistillation apparatus.

What Distillation is Simulated? There are generally two types of distillation methods that are of interest in laboratory analyses:

- Low efficiency (also referred to as either simple or single tray), typified by ASTM Methods D86 and D1160. This analysis is relatively easy and economical to perform, and allows comparisons with typical plant data.
- High efficiency [alternately referred to as multi-tray, fractional distillation, or True Boiling Point (TBP)], typified by ASTM Method D2892. This data is more descriptive and therefore more useful for economic evaluations since it better approximates distillation operations in a fractionator, and may allow comparisons with a larger variety of data in the literature.

Daubert²⁴ illustrated the relationship between these distillation types in 1994, as shown in the Figure 19. As can be seen, SIMDIS inherently approximates a TBP distillation, and ASTM D2887 documents the accuracy that SIMDIS results of petroleum fraction samples match their corresponding TBP distillations.

Several correlations and graphical techniques are available to translate chromatographic results to physical distillation data, including the reference above and both API and ASTM publications. Presently, all CAER sample SIMDIS data are translated to ASTM D1160 (vol %) using one of those correlations, ASTM Special Technical Publication 577²⁵, and the relevance of that information will be evaluated in future runs.

Conclusions and Future Work

While the purely aromatic boiling range calibrant correction method has worked well in determining boiling ranges of the high boiling coal derived resids, and thus is an accurate, *ad hoc* tool for the

present catalyst activity studies, the data is clearly not as accurate for lighter boiling materials and some improvement could extend the range of application of SIMDIS analyses. Whether this is due to the reduced aromaticity of the lighter samples, or some needed change in calculation method/application of technique will be examined in future work. Initially, this could be done using the d_{50} paraffinic standard boiling point as an aromaticity correlation parameter for the coal derived resids (with light materials assumed to be more paraffinic and heavier materials assumed to be more aromatic), ultimately using a correction factor based on TBP data for coal derived materials. While commercially prepared boiling range standards derived from petroleum derived materials are readily available, coal derived ones are not. We are presently obtaining coal derived liquids from ALC-1 whose TBP data have already been determined, along with similar materials from other sources for use in the revised correlation.

With regard to the type of distillation that is to be simulated, we believe it is preferable to continue to report data which has been correlated to the TBP method, which provides more valuable information. In general, correlation of GC data to a physical distillation was generally viewed as a stop-gap approach while ASTM chromatographic methods were refined and implemented. Certainly in this program, developing laboratory methods based on actual coal derived materials characterized with a single cut point from a simple physical distillation method have been useful. But comparisons of the SIMDIS data with D1160 data from HTI show much more important differences (shift to higher boiling range) due to aromatic correction than type of distillation, where the shapes of the curves are similar, if not identical in some cases, suggesting our focus should remain on improving the accuracy of the TBP simulations. Moreover, correlation of GC data to physical distillation data for lighter boiling ranges has been extensively studied for petroleum derived materials, and those interested in that type of data could select the most appropriate and applicable correlation technique starting with the references cited.

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Table 1. Effects of Moisture on Coal on Liquefaction with Mo and Fe Catalysts (Metal loadings: 100 mg Mo/kg dry coal and Fe at 1.0 wt% Fe ₂ O ₃ on dry coal)									
Solvent source	Wilsonville Run 262e					Wilsonville Run 258a-b			
Moisture on Dry Coal (%)	0	9	20	59	0	9	20	59	
Products (% maf coal)									
CO+CO ₂	7.7	11.3	8.7	7.5	8.0	8.4	8.5	10.2	
HC Gases	8.9	11.1	9.8	7.8	8.4	11.0	8.0	9.1	
1050- °F for R262 (975- °F for R258)	64.7	55.2	55.1	58.9	41.2	38.3	36.7	31.6	
1050+ °F for R262 (975+ °F for R258)	18.7	22.3	26.4	25.7	42.4	42.3	46.8	49.1	
THF Coal Conv. (%)	91.3	92.1	92.0	90.2	91.4	92.1	93.2	90.7	
Resid Conv. (%)	39.5	36.9	35.7	35.9	26.8	25.6	24.8	23.6	
Resid Conv. (% maf coal)	82.4	78.8	74.7	75.4	58.7	58.8	54.3	52.0	
a.	Liquefaction experiments were carried out at 440 °C, and 7.0 MPa (1000 psig) (cold H ₂ , 3% H ₂ S) for 30 minutes, using 3 g BT/HTI dry coal, 1.8 g of V-1074 heavy distillate, and 3.6 g of V130 deashed resid from the Wilsonville Runs 262e and 258a-b. The cut point of liquid product was 565 °C (1050 °F) for Run 262 material and 524 °C (975 °F) for Run 258 material. The 565 °C (1050 °F-) cut for the products obtained with Run 262e solvent was obtained by difference and contains 565 °C- (1050 °F-) oil, water, and losses. The 524 °C- (975 °F-) cut for the products obtained with Run 258a-b solvent was obtained by difference and contains 524 °C- (1050 °F-) oil, water, and losses.								
b.	The catalysts were impregnated on coal using ammonium heptamolybdate ((NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O) and ferrous sulfate (FeSO ₄ ·7H ₂ O) as precursors.								

Table 2. Effects of Coal Slurry Pretreatment on Liquefaction of Mo and Fe Impregnated Coals in Run 262e Solvent (Metal loadings: 100 mg Mo/kg dry coal and Fe at 1.0 wt% Fe ₂ O ₃ on dry Coal)											
Pretreating Gas	H ₂						H ₂ S				
Moisture on Dry Coal (%)	9			20			59			9	
Pretreating Pressure, MPa (psig)	0.1 (0)	3.5 (500)	7.0 (1000)	0.1 (0)	3.5 (500)	10.0 (1500)	0.1 (0)	3.5 (500)	10.0 (1500)	0.1 (0)	3.5 (500)
Products (% maf coal)											
CO+CO ₂	8.3	7.7	7.9	10.9	9.5	10.0	10.6	7.9	9.2	7.9	8.5
HC Gases	9.3	8.1	9.0	8.4	10.2	10.7	11.4	8.7	10.1	7.4	9.2
1050- °F	55.1	61.9	73.9	56.6	56.7	57.7	60.2	50.6	59.7	60.1	58.5
1050+ °F	27.2	22.2	9.2	24.2	23.6	21.5	17.8	32.8	21.0	24.6	23.8
THF Coal Conv. (%)	91.5	92.5	93.3	90.7	92.8	92.7	91.9	91.8	91.9	89.8	91.6
Resid Conv. (%)	35.4	37.7	44.0	36.8	37.0	37.9	39.7	32.7	38.3	36.6	36.9
Resid Conv. (% maf coal)	73.9	78.9	91.9	76.9	77.5	79.6	83.3	68.3	80.1	76.5	77.3
<p>a. Liquefaction experiments were carried out at 440 °C, and 1000 psig (cold H₂, 3% H₂S) for 30 minutes, using 3 g BT/HTI dry coal, 1.8 g Wilsonville Run 262e V-1074 heavy distillate, and 3.6 g Wilsonville Run 262e V-130 deashed resid. The cut point of liquid product was 565 °C (1050 °F). The 565 °C- (1050 °F-) cut was obtained by difference and contains 565 °C- (1050 °F-) oil, water, and losses.</p> <p>b. The catalysts were impregnated on coal using ammonium heptamolybdate (NH₄)₆Mo₇O₂₄·4H₂O and ferrous sulfate (FeSO₄·7H₂O) as precursors.</p> <p>c. Prior to reaction, the coal slurry was pretreated in a furnace for 30 minutes at 200 °C and pressures ranging from 0.1-7.0 MPa (0 to 1000 psig). The pretreating gas was either pure H₂ or 8 vol% H₂S in H₂ with a flow rate of 200 cc/m.</p>											

Table 3: Sulfur Concentration in PMA treated with 8 vol% H ₂ S in H ₂						
Treatment Temperature, °C	H ₂ S treat as S/Mo for 4 hrs, g atoms S/g atom Mo					
	0.3 S/Mo (1 hr) (10 g sample)			1.2 S/Mo (10 g sample)	12.3 S/Mo (1 g sample)	122.8 S/Mo (1 g sample)
	S, wt%	Mo, wt%	S/Mo, g atoms S/g atom Mo	S, wt%	S, wt%	S, wt%
125	1.48	60	0.07	-	4.08	4.37
150	2.13	62	0.1	-	4.24	-
200	1.21	62	0.06	-	3.3	-
300	2.21	-	-	5.93	3.12	-
450	4.20	70	0.18	8.89	19.1	-

Table 4. Activity of precursors added directly to reaction mixture				
Precursor	Mo conc, mg/kg dry coal	THF Conv	524 °C+ resid conversion, w% maf coal	Run Numbers
None	none	66.3	28.1	B6-149-1
PMA	325	80.7	42.7	B6-149-3
MoO ₃	245	73.0	41.8	B6-212-1
Molyvan L	294	85.4	57.0	B6-241-1
Molyvan A	330	91.2	60.7	B6-128-1 B6-276-1 B6-311-1
Conditions: BT Wyodak coal with 8.9% moisture.				

Table 5. Activity of coals impregnated with PMA at 300 mg Mo/kg dry coal				
Impregnated Coal	moisture, w%	THF Conv	524 °C+ resid conversion, w% maf coal	Run Numbers
PM-1	none	90.0	64.6	B6-163-1
PM-2	1.8	95.0±0.7	70.2±4.9	B6-270-1 B6-278-1 B6-295-1
PM-3	3.9	91.1±2.1	61.1±4.8	B6-207-1 B6-228-1 B6-253-1 B6-257-1 B6-297-1
PM-4	11.3	91.5±1.4	64.7±0.9	B6-268-1 B6-295-2
All samples		92.3±2.4	64.5±5.4	N=11

Table 6. Activity of 10% spiked coals				
Spiked Impregnated Coal	moisture, w%	THF Conv	524 °C+ resid conversion, w% maf coal	Run Numbers
PM-1-10C	8.0	90.8	70.4	B6-166-1
PM-2-10C	9.3	93.1±1.9	62.0±2.9	B6-277-1 B6-284-1 B6-303-1
PM-3-10C	8.0	89.1±1.6	57.9±3.5	B6-197-1 B6-226-1 B6-260-1 B6-306-1
PM-4-10C	11.3	93.6±2.8	61.9±1.8	B6-269-1 B6-283-1 B6-303-2
All samples		91.6±2.7	61.2±4.4	N=11

Table 7. Activity of PMA Impregnated Carbons @ 300 mg Mo/kg dry coal				
Spiked Impregnated Carbon	moisture, w%	THF Conv	524 °C+ resid conversion, w% maf coal	Run Numbers
PM-5AC	none	82.2	62.2	B6-344-1
PM-10AC	none	80.9	64.6	B6-331-1
PM-CC	2.8	93.5	65.8	B6-351-1
PM-CC-10C	2.3	92.7	61.7	B6-351-2

Table 8.					
Precursor	Mo Conc, mg/kg dry coal	vol% H ₂ S in H ₂	THF Conv	524 °C+ resid conversion, w% maf coal	Run Numbers
PMA	476	0	66.9	29.3	B6-262-1
PMA	325	3	80.7	42.7	B6-149-1
Molyvan L	344	0	77.5	34.1	B6-264-1
Molyvan L	294	3	85.4	57.0	B6-241-1
Molyvan A	295	0	76.7	35.1	B6-199-1
Molyvan A	330	3	91.2	60.7	B6-128-1 B6-276-1 B6-311-1

Table 9. Impregnated Coals Prepared for Continuous Bench Scale Testing							
HTI Drum Nos	ALC-2 Condition & Description	Metals Content mg metal/kg dry coal	Wet Coal kg/batch	Impregnating Solution Composition			Impregnating Solution added to coal, g per batch
				#	salt, g/batch	DI water, g/batch	
L-902 L-903	#1 Fe-Mo	100 Mo 1748 Fe	136	1.	37.4 M	2043	1441
				2.	1814 F	4086	4085
L-904, L-905, L-912, L-913	#2 Mo	100 Mo	136		37.4 M	4086	2855
L-906, L-907 L-916, L-917	#3 Ni-Mo	100 Mo 50 Ni	136	1.	68.9 N	2043	1386
				2.	37.4 M	2043	1366
L-910 L-911	#4 PMA	100 Mo	136		35 PMA	3715	2706
L-914, L-915	ATTM	100 Mo	136		45 ATTM	4500	3665
L-908 L-909	Ni-Mo Vector [†]	1000 Mo 500 Ni	136	1.	360 N	10,675	10,162
				2.	180 N	5338	3762
				3.	280 M	15,295	13,651
L-918	15% Fe Vector (Backup Fe Source)	11,981 Fe	125.8 kg (276.8 lbs)		8000 F	17,222	23,738
Abbreviations: N is ammonium nickel (II) sulfate purchased from JT Baker and Aldrich; M is ammonium heptamolybdate purchased from JT Baker; PMA is phosphomolybdic acid purchased from Aldrich; ATTM is ammonium tetrathiomolybdate prepared at CAER; and F is ferrous sulfate purchased from Aldrich. [†] dried to 12-15% water							

Table 10. ALC-2 Operating Conditions		
Reactor volumes		
Pretreater	200 cc	
K-1 and K-2	2000 cc ea	
Coal feed rate		
kg/hr/m ³	640	
lb/hr/ft ³ per reactor	40 ea	
Gas feed rate, w% dry coal		
H ₂ total	20 ^a	
H ₂ S (pretreater & 1st stage)	2	
H ₂ S (2nd stage as TNPS)	0.5	
Temperatures, °C/°F		
1st reactor	440/825	
2nd reactor	450/840	
Inlet pressure, psig	2500	
Distillation cut points, °C/°F	Periods 1 to 5	Periods 6 to end
RPS, atmos equiv	357/775	315/600
CVS, atmos equiv	412/775	427/800
a. 66% to pretreater-K-1 and 33% to K-2.		

Table 11. ALC-2 Run Summary				
Condition	#1	#2	#3	#4
Periods	1-7	8-12	13-17	18-21
Catalyst Precursor	AM/Fe	AM	AM/Ni	PMA
Coal feed drum numbers	L-902 L-903	L-904 L-905	L-906 L-907	L-910 L-911
Metal conc, mg/kg dry coal				
Mo Make-up rate	100	100	100	100
Fe Make-up rate	3500	-	-	-
Ni Make-up rate	-	-	58	-
Target feed slurry composition, w%				
Dry coal	35			
Solvent, solids free	55			
Solids	10			
a. 66% to pretreater-K-1 and 33% to K-2.				

Table 12 Ash and quinoline insoluble in solids concentrate from ALC 2		
	Condition #1 Period 7 Toluene extracted solid	Condition #2 Period 12 Toluene extracted solid
ASTM ash, wt%	14.43	19.21
QI, wt%	22.98	31.16

Figure 1 Effect of Moisture Concentration on Coal (wt% dry coal) on the Liquefaction Results with Mo-Fe Catalyst
(Mo: 100 mg/kg dry coal, Fe_2O_3 : 1.0 wt% dry coal)

Figure 2 Effect of H_2 Pretreatment on Coal Liquefaction with R262 Solvent
(Catalyst: 100 mg Mo/kg dry coal and 1.0 wt% Fe_2O_3 on dry coal,
Pretreatment Condition: 200 °C, 30 min., and 200 STD $cm^3/min H_2$)

Figure 3 Effect of H_2S/H_2 (8 vol% H_2S) Pretreatment on Coal Liquefaction with R262 Solvent (Catalyst: 100 mg Mo/kg dry coal and 1.0 wt% Fe_2O_3 on dry coal, Pretreatment : 200 °C, 30 min., and 200 STD cm^3/min H_2S/H_2)

Figure 4. TG/MS spectra of PMA in He

Figure 5. TG/MS spectra of PMA in H_2 .

Figure 6. TG/MS spectra of PMA in $\text{H}_2\text{S}/\text{H}_2$.

Infrared spectra of (a) PMA, (b) PMA sulfided at 125°C, (c) PMA sulfided at 150°C, (d) PMA sulfided at 200°C, (e) PMA sulfided at 450°C

XRD spectra of (a)PMA (b) PMA sulfided at 125°C, (c) PMA sulfided at 150°C, (d) PMA sulfided at 200°C and (e) PMA sulfided at 450°C.

High-Temp Sim Dist Analysis

Period 7 RPSB

High-Temp Sim Dist Analysis

- Aromatic correction
- Paraffinic standard
- ▲ HTI D1160 data

Figure 9. Simulated distillation data for ALC-2, Period 7 samples.

Period 7 RPSOH

High-Temp SIMS Analysis

Period 12 CVSB

High-Temp SIMS Analysis

- Aromatic correction
- Paraffinic standard
- ▲ HTI D1160 data

Figure 10. Simulated distillation data for ALC-2, Period 12.
Period 12 RPSB

High-Temp SIMS Analysis

Period 12 RPSOH

- Aromatic correction
- Paraffinic standard
- ▲ HTI D1160 data

Figure 11. Simulated distillation data for ALC-2, Period 12.

High-Temp SimDist Analysis

Period 17 CVSB

High-Temp SimDist Analysis

Figure 12. Simulated distillation data for ALC-2, Period 17.

Period 17 RPSB

Period 17 RPSOH

- Aromatic correction
- Paraffinic standard
- ▲ HTI D1160 data

Figure 13. Simulated distillation data for ALC-2, Period 17.

High-Temp SIMDS Analysis

Period 21 RPSB

High-Temp SIMDS Analysis

Figure 14. Simulated distillation data for ALC-2, Period 21.
Period 21 RPSOH

Figure 15. Comparison of retention times for the CAER n-paraffin and aromatic calibrants.

Figure 16. HTI's continuous vacuum still process flow scheme.

H11 D1160 Data vs SIMDISn-Paraffin Calibrant

Figure 17. Period 17 D1160 distillation data compared with CAER SIMDIS results (paraffinic standard).

H11 D1160 Data vs SIMDIS Aromatic Calibrant

Figure 18. Period 17 D1160 data compared with CAER SIMDIS results (aromatic correction).

Figure 19. Daubert's illustration of distillation types.

SECTION TWO

CONSOL, INC.

March 4, 1997

Report Period: October 1 - December 31, 1996

SUBCONTRACT TITLE AND NUMBER:

Subcontract UKRF-4-25582-92-76 to CONSOL Inc.

Under DOE Contract No. DE-AC22-91PC91040, "Advanced Coal Liquefaction Concepts for the PETC Generic Bench-Scale Unit"

SUBCONTRACTOR NAME:

CONSOL Inc.

Research & Development

4000 Brownsville Road

Library, PA 15129

SUBCONTRACT PERIOD: November 26, 1991 - February 28, 1997 (future extension to September 30, 1998, expected)

PRINCIPAL INVESTIGATORS: R. A. Winschel, G. A. Robbins

SUBCONTRACT OBJECTIVES: No change.

SUMMARY OF TECHNICAL PROGRESS - OVERALL

CONSOL provided on-site support during Run ALC-2 from November 30 to December 2. Support for the remainder of the run was conducted by fax and phone.

Process oil samples from Runs ALC-1 and ALC-2 were characterized under DOE contract DE-AC22-94PC93054. The characterization of samples from Run ALC-1 was completed. Plans were made for CONSOL to provide rapid turn-around analyses to determine catalyst concentrations during Run ALC-2, but operating problems during the run disrupted the plan. CONSOL submitted a request for routine process oil samples from Run ALC-2 to HTI. The seventeen samples from Run ALC-2 received this quarter are now being characterized.

Analyses were partially completed on the hydrotreating samples received from Sandia. The results will be reported after all the analyses are completed in January.

Activities planned for next quarter include: completion of the elemental and material balances for the agglomerate production runs, completion of the characterization of the Sandia hydrotreating samples, characterization of the process samples from HTI Run ALC-2, evaluation of methods to integrate catalyst addition with oil agglomeration, and initial

planning for Run ALC-3.

SUMMARY OF TECHNICAL PROGRESS - BY TASK

Task 2 - Laboratory Support

Characterization of Run ALC-1 samples

The characterization of process oil samples collected during Run ALC-1 was completed by CONSOL this quarter under DOE Contract DE-AC22-94PC93054.

Elemental Balances for Run ALC-1 Agglomeration Runs

Ash elemental balance calculations were begun for the production agglomeration runs made for Run ALC-1.

Laboratory Support for Run ALC-2

It was determined that HTI would not be able to provide timely determinations of the catalyst metal concentrations within each run condition for Run ALC-2. Therefore, CONSOL made arrangements to provide analyses of ash, major elements, Mo and Ni in daily toluene-extracted solids samples. HTI was to ship samples from each day of a 5-day run condition by overnight express to CONSOL at the end of each run condition. CONSOL was to provide an analysis turnaround time of about two working days for each sample set. This would allow the determination of the solids equilibration time and possibly permit the shortening of later run conditions and the addition of an optional test period. Operating problems during the run disrupted this plan. However, four toluene-extracted solids (TES) samples were received from Condition 1 of HTI Run ALC-2. The samples were submitted for determination of moisture, ash, major ash elements, and Mo and Ni in the ash. The NMR spectra (obtained on samples dissolved in deuterated pyridine and filtered) showed that most samples retained a modest amount of toluene as a contaminant. However, the sample from Period 6, which was received as a liquid (the rest were solids), contained a large amount of toluene. The samples were found to contain 34-82% THF-solubles (including toluene), 8-41% IOM, and 7-21% ash.

Thirteen additional samples were received this quarter from HTI Run ALC-2 for characterization under DOE Contract DE-AC22-94PC93054. At HTI's request, a small quantity of one sample will be sent back to them.

Characterization of Sandia Hydrotreating Samples

A set of eight hydrotreating samples was received from Sandia. The samples were submitted for C, H, N, and S determinations, and they were characterized for proton distribution and phenolic -OH concentration. J. Miller of Sandia supplied background information on the samples. The results will be reported when the analyses are completed in January.

Task 3 - Continuous Operations

Run ALC-2 Sample Request

Sampling and support issues related to Run ALC-2 were discussed with HTI and LDP. CONSOL submitted a request for samples from Run ALC-2 to HTI.

Support For Run ALC-2

G. Robbins provided on-site support for Run ALC-2 from November 30 to the major shutdown on December 2. Support for the remainder of the run was conducted by fax and phone.

Formulation of Plans for Run ALC-3

Various issues related to early planning for Run ALC-3 were discussed with LDP Assoc.

Task 4 - Technical Assessment

R. A. Winschel made a presentation entitled "Testing of Advanced Liquefaction Concepts in HTI Run ALC-1: Coal Cleaning and Recycle Solvent Treatment" at the U.S./Japan Joint Technical Workshop in State College, PA, on October 2.

R. A. Winschel and G. A. Robbins attended the Run ALC-2 planning meeting in Lexington, KY, on October 8 and made presentations on some ALC-1 results and ideas for possible implementation in Run ALC-3.

An abstract for a paper "Oil Agglomeration at Low pH as a Pretreatment for Liquefaction of Wyoming (USA) Subbituminous Coal" was submitted to the 9th International Conference on Coal Science.

R. A. Winschel

SECTION THREE

LDP Associates

LDP ASSOCIATES

Michael Peluso, Proprietor
609-586-2301

32 Albert E. Bonacci Dr.
Hamilton Square, N.J. 08690

February 11, 1997

Subject: QUARTERLY PROGRESS REPORT: OCTOBER - DECEMBER 1996

For the quarter ending December 31, 1996 the following subcontract services (UKRF-4-25582-92-75) were performed in support of the DOE Advanced Concepts Program (DE-AC22-91PC91040):

ALC-1 ANALYSIS

At the Quarterly Review Meeting in Lexington the molybdenum balance calculated for each condition of the run was reported. The results indicated that the moly leaving the unit was much greater than the reported moly input. The reason for this apparent inconsistency was investigated by CONSOL.

ALC-2 RUN PLAN

The comparative costs of catalysts to be used in this run were presented at the Quarterly Review Meeting. As a follow up to a question raised by Ed Klunder of PETC at the above meeting, the feed flowrates to the toluene extraction unit were compared for the proposed ALC-2 run conditions of 0.1 and 0.3 recycle solids to coal feed ratio.

A prerun meeting (Nov. 14) was attended at HTI to review the detailed run and execution plans. HTI also discussed their revised material balance procedure. Comments and suggestions on the above items were discussed with HTI at the prerun meeting and at a followup meeting on November 20.

ALC-2 OPERATIONS

ALC-2 operation was interrupted twice during the first week due to a leak in a sulfiding line and a plugged vapor overhead line. Comments on the restarts of ALC-2 were discussed with CAER, CONSOL and HTI. ALC-2 operation was resumed on December 5 and was completed on the morning of December 23 after 18 consecutive operating days. All facets of the run were monitored onsite. Activities included run planning, data analysis, suggestion of back end distillation system operating conditions, solid-liquid separation system performance evaluation and troubleshooting and co-ordination with CONSOL and CAER.

ALC-2 ANALYSIS

An elementally balanced material balance for Condition #1 (Iron & Moly catalysts) was prepared and transmitted to CAER (see Table 1). Due to a poor ash balance the standard normalization procedure of first adjusting the solids-rich stream rate could not be used. Instead, the rates of all carbon containing output streams and components was normalized to close the carbon balance. This appears to be a reasonable approach as only a small adjustment to the output stream rates was required (as-is carbon balance= 98.2%). Nitrogen, oxygen and sulfur balances were then closed using the standard procedure.

The result is a material balance which reflects the yields at that particular point in time, but is not representative of true steady state operations as the amount of ash removed from the unit was only 56% of the ash entering the unit with the coal feed. Distillate and resid yields were also affected by the solids imbalance. The main reason for this poor ash (& solids) balance appears to be deposition of solid material within the unit. In addition, the solids balance was adversely affected by the inability of the Toluene Extraction Unit to effectively separate solids from the system. As a result the normally solids free toluene extracted oil (TEO) stream (part of the recycle solvent) contained a significant amount of solids which were recycled to the front end of the unit. The contamination of the TEO stream with solids was not discovered until well after Condition #1 operation had been completed.

Elementally balanced material balances will also be prepared for the three other run conditions as the required analytical data becomes available.

REACTOR MODELING

No activity.

ECONOMIC ASSESSMENT

No activity.

Michael Peluso

LDP Associates

TABLE 1: CAER ADVANCED CONCEPTS, ALC-2, CONDITION #1 (Period 7) MATERIAL BALANCE

BALANCED OUTPUT STREAMS	Grams	C	H	O	N	S	SO3-Free Ash
H2O Net	0.00	0.00	11.19	88.81	0.00	0.00	0.00
H2S	0.00	0.00	5.92	0.00	0.00	94.08	0.00
NH3	0.00	0.00	17.76	0.00	82.24	0.00	0.00
CO	479	42.88	0.00	57.12	0.00	0.00	0.00
CO2	1591	27.29	0.00	72.71	0.00	0.00	0.00
C1	1198	74.86	25.14	0.00	0.00	0.00	0.00
C2	1142	79.98	20.02	0.00	0.00	0.00	0.00
C3	1427	81.86	18.14	0.00	0.00	0.00	0.00
C4	794	82.86	17.14	0.00	0.00	0.00	0.00
C5+ Gas	1355	84.12	15.88	0.00	0.00	0.00	0.00
HTU Liq. Product	10874	86.58	13.17	0.24	0.00	0.00	0.00
RPSOH	5063	85.47	9.75	4.55	0.13	0.10	0.00
RPSB	14629	88.34	9.01	1.93	0.52	0.20	0.00
ASH-FREE CVSB	36546	85.34	6.10	6.30	0.94	1.32	0.00
ASH	5375	0.00	0.00	0.00	0.00	0.00	100.00
Total w/H2O,H2S,NH3	85288.42	63269.36	7129.96	7560.51	678.87	1274.41	5375.30
Total exH2O,H2S,NH3				4273.90	425.18	516.99	
O BALANCE		N BALANCE		S BALANCE		H BALANCE	
IN	7560.51	IN	678.87	IN	1274.41	OUT	7129.96
OUT - H2O	4273.90	OUT - NH3	425.18	OUT - H2S	516.99	IN	5090.55
O IN H2O	3286.61	N IN NH3	253.69	S IN H2S	757.43	CONSUMED	2039.42
H2O OUT	3700.72	NH3 OUT	308.47	H2S OUT	805.09	Wt.% MF Coal	6.81

12/22/96 : ESTIMATED SO3-Free ASH IN MF COAL

TABLE 1 : CAER ADVANCED CONCEPTS, ALC-2, CONDITION #1 (Period 7) MATERIAL BALANCE

	GROSS YIELDS	Wt.% MF Coal INPUTS	NET YIELDS		Wt.% MAF Coal NET YIELDS
H2O	12.36	0.00	12.36		13.15
H2S	2.69	2.67	0.01		0.02
NH3	1.03	0.00	1.03		1.10
CO	1.60	0.00	1.60	COx	7.36
CO2	5.31	0.00	5.31		
C1	4.00	0.00	4.00	C1-C3	13.38
C2	3.81	0.00	3.81		
C3	4.76	0.00	4.76		
C4	2.65	0.00	2.65		2.82
C5+ Gas	4.53	0.00	4.53		4.82
HTU Liq. Product	36.32	0.80	35.52		37.78
RPSOH	16.91	2.00	14.91		15.86
RPSB	48.85	52.88	-4.02		-4.28
ASH-FREE CVSB	122.05	85.37	36.68		39.02
ASH-FREE TEO	0.00	22.34	-22.34		-23.77
ASH	17.95	11.95	6.00		6.38
External Moly	0.00	0.00	0.00		0.00
External Fe	0.00	0.00	0.00		0.00
Total	284.83	178.02	106.81		113.63
		H2 Consumed	6.81		7.25
		H2 for TNPS	0.04		0.04
		Net H2 Cons'd	6.77		7.21

12/22/96 : ESTIMATED SO3-Free ASH IN MF COAL

Abbreviations and Acronyms

AHM	Ammonium heptamolybdate
ALC	Advance liquefaction concepts
API	American Petroleum Institute
APTM	Ammonium polythiomolybdate
ASOH	Atmospheric still overhead
ASTM	American Society for Testing Materials
ATTM	Ammonium tetrathiomolybdate
BT	Black Thunder Mine
CAER	Center for Applied Energy Research
CAS	Continuous atmospheric still
CMSL	Run designation used by HTI
CST	Catalyst screening test
DAF	Dried and ash free
DW-HT	Dewaxed-hydrotreated
DW-HT	VSOH Dewaxed hydrotreated vacuum still overhead
DW-VSOH	Dewaxed-vacuum still overhead
EO	Extracted oil
EOVSB	Extracted oil vacuum still bottoms
ES	Extracted filter cake
FBP	Final boiling point
FS	Ferrous sulfate
GC	Gas Chromatograph
HC	Hydrocarbon
HTI	Hydrocarbon Technologies, Inc.
HTU	Hydrotreater unit
IBP	Initial boiling point
IOM	Insoluble organic matter
J-1	Charge pump
J-2	Charge pump
K-1	First stage reactor
K-2	2nd-stage reactor
K-3	In-line hydrotreater
L-814	End-of-run makeup oil in Tank #4 from HTI's POC-02 run
MAF	Moisture and ash free
O-1	2nd-stage hot separator
O1-A	1st stage hot separator
O-2	2nd stage cold separator
O-2A	1st stage cold separator
O-3	2nd stage hot separator bottom flasher
OA	Oil agglomerated
P-2	Feed tank

PFC	Pressure filter cake
PFL	Pressure filter liquid
PMA	Phosphomolybdic acid
POC	Proof of concept
QI	Quinoline insolubles
SIMDIS	Simulated distillation
SOH	Separator overhead
TBP	True boiling point
TBP	True boiling point
TE	Toluene extraction unit
TEO	Toluene extracted oil
TES	Toluene extracted solid
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TNPS	Ditertiarynonyl polysulfide
UK	University of Kentucky
VSB	Vacuum still bottoms
VSOH	Vacuum still overhead