DOE/PC/91040-104

ADVANCED DIRECT LIQUEFACTION CONCEPTS
for PETC GENERIC UNITS
Phase II

Quarterly Technical Progress Report
for Period July through September 1998

by

University of Kentucky
Center for Applied Energy Research

CONSOL Inc.

Hydrocarbon Technologies, Inc.

LDP Associates

February 2000

Prepared for
The U. S. Department of Energy
Under Contract No.
DE-AC22-91PC91040

Disclaimer

ABSTRACT

The results of Laboratory and Bench-Scale experiments and supporting technical and economic assessments conducted under DOE Contract No. DE-AC22-91PC91040 is reported for the period July 1, 1998 to September 30, 1998. 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 project has been modified to include an investigation into the production of value added materials from coal using liquefaction based technologies.

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EXECUTIVE SUMMARY

TASK 2 LABORATORY SUPPORT (UK/CAER)

Dispersed Catalyst Studies.

Studies into the development and characterization of ‘novel’ dispersed catalyst systems continued during this quarter, particular emphasis was placed on the characterization of Vanadium based catalyst systems.

TASK 2 LABORATORY SUPPORT (CONSOL)

During this quarter, the design and construction of a pilot scale unit for the production of oil agglomerated coal was completed. The unit is currently undergoing performance evaluations and a set of safety/operating instructions are being drafted prior to shipment to the HTI site.

TASK 3. CONTINUOUS OPERATIONS

A planning meeting was held at the CAER on July 28, involving all participants. At this meeting, a tentative schedule for the commencement of Run ALC#3 was agreed upon and a discussion document was circulated between all participants for comment.

ALC#3 was planned to be carried out in two distinct stages, the first stage would be the ‘advanced’ stage using 1000 ppm Mo impregnated from Phosphomolybdic Acid onto Black Thunder Coal mixed with oil agglomerated coal in a 1:9 ratio to give a final catalyst loading of 100 ppm. The 2nd stage would seek to replicate the ‘baseline’ conditions employed in ALC#1 to confirm the initial yields measured during ALC#1.

1. SECTION ONE

UNIVERSITY OF KENTUCKY
CETER FOR APPLIED ENERGY RESEARCH

TASK 2. LABORATORY SUPPORT (UK/CAER)

Introduction

Work at the CAER continues into the synthesis and characterization of novel catalytic materials utilizing vanadium and molybdenum precursors. All parties met at the CAER on July 28 in order to commence planning for run ALC #3.

Dispersed Catalyst Studies

Studies into the development and characterization of 'novel' dispersed catalyst systems continued during this quarter. Four thiomolybdenum precursors have been prepared, including di- and tri-molybdenum cluster compounds, with the objective of determining the critical reaction pathways and conditions required for their transformation into an active state. The sulfur-molybdenum atomic ratios for these compounds ranged from two to six. The UV spectra of all these compounds dissolved in water were observed to change, though at widely different rates. This indicates some reaction was taking place with the ADTM and ATTM ultimately forming the oxomolybdate, which was observed in the ^{95}Mo NMR spectra. Changes were observed in the UV spectra of Mo_2S_{12} and Mo_3S_{13}, though continued absorption in the UV region suggests that Mo-S bonding continue to exist. The structures of the resulting compounds are unknown. The precursors were sufficiently soluble in water to be impregnated onto coal from an aqueous solution, except for Mo_3S_{13}, which was soluble in 0.05 N NaOH solution. The previous liquefaction studies of coals impregnated with these precursors suggest that all, except ADTM, were sufficiently stable to be deposited on the surface of the coal. The species on the surface of the coal impregnated with ADTM was probably oxomolybdate. Upon liquefaction coal and resid conversions have been shown to increase significantly in the presence of H_2S and were essentially the same as obtained with AHM impregnated coals. The low conversions without added H_2S demonstrate that combined sulfur is not adequate to activate the precursors fully. The only effect of the preformed Mo-S bonds was the very slight increase in activity of the catalyst for coal conversion without H_2S. Although all these compounds form MoS_2 in H_2 at temperatures from 350-400^{o}C, the active catalyst probably involves partial substitution of oxygen into the structure forming an oxothiomolybdate, which is the active form of the catalyst. In coal systems, the source of oxygen to affect this reaction is the water generated during the initial stages of the coal dissolution process. There is clearly no advantage for using any of these thiomolybdates over AHM, since their activities after activation are the same. The presence of bound sulfur does not preclude the necessity of adding H_2S, or some other source of sulfur, to fully activate these precursors.

The effect of varying the S content in a series of thiomolybdate precursors on coal and resid conversion was previously reported (1,2,3). Coals impregnated with catalyst precursors including ammonium dioxodithiomolybdate (ADTM), ammonium tetrathiomolybdate (ATTM), ammonium polythiomolybdate (APTM), Mo_3S_{13} and Mo_2S_{12}, were assessed. Ammonium heptamolybdate (AHM) was used for comparison. Results showed that at catalyst loadings of 100 and 300mg Mo/kg dry coal, resid. conversions increased with increasing S/Mo ratio while coal conversions were almost unchanged, (summarized in Table 1.). It appeared that the excess internal sulfur associated with the precursors did not provide any benefit to coal conversion, although the catalysts thus generated may have been transformed into a more active state. These tests were carried out in the presence of an external source of sulfur (H_2S). With no added H_2S, both coal and resid conversions increased with increasing S/Mo ratio, although by a smaller amount. In this case, although there was a positive response to increasing S/Mo ratios, it was not sufficient to reproduce the conversions observed when H_2S was present. Thus, none of these precursors provided an enhancement in activity that might suggest that adding sulfur into the structure of the Mo precursors would be beneficial to the process.

Table 1 - Summary of Coal and Resid. liquefaction Data

	Catalyst Precursor												
	none	**AHM**			**ADTM**			**ATTM**			**Mo_3S_{13}**		
Mo, mg/kg dry coal	none	100	300		100	300		100	300		100	300	
H_2S added¶	no	yes	yes	no	yes	yes	no	yes	yes	no	yes	yes	no
524 $^{o}C^{+}$ Resid Conver$^{\underline{n}}$ wt.% maf coal	51	74	80	60	74	83	59	78	83	62	76	83	62
Coal Conversion, wt.% maf coal	60	86	91	70	86	91	71	87	91	76	89	92	79
HC Gases, wt.% maf coal	9.1	11.3	9.9	5.8	9.3	11.1	8.8	8.8	7.2	9.0	9.5	7.6	6.1
CO_x, wt.% maf coal	8.6	8.3	7.4	9.8	8.5	13.1	9.5	8.3	8.2	8.9	9.2	8.6	5.8
Coal and resid conversion data were very similar for Mo_3S_{13} & Mo_2S_{12}¶ H_2S added at approx. 5.6wt% dry coal.													

Another approach to enhance the activity of the Mo catalysts was to pretreat the precursor with H_2S in H_2 over a range of temperatures. Coal conversions were not affected by this treatment although resid conversions showed a noticeable increase at the 100mg Mo/kg dry coal concentration, equivalent to 300mg Mo/kg fresh Mo. This suggests that pretreatment is very effective for converting the precursor into an active catalyst.

At typical liquefaction operating conditions, catalyst precursors can undergo two types of competing reactions, thio-substitution and decomposition. When the rate of ammonia loss due to decomposition is greater than the rate of thio-substitution, the resultant Mo compounds are more difficult to sulfide. However, the complete conversion of the precursor to the final active catalyst is possible through sulfidation via gas phase interactions with the H_2S and/or intramolecular rearrangement within the precursor. For different sulfur-containing precursors, there may be a difference in their decomposition mechanisms and kinetics. The chemical form and the number of active sites may be different as reflected by the activities towards resid conversions. In addition, in the presence of water, oxidation reactions can convert the Mo catalyst to a less active or even inactive form. The observation that resid conversion increases with S/Mo ratio may be attributed to these effects.

To gain a better understanding of the mechanisms by which these catalysts are converted to the active phase, their stability in aqueous solutions (5% Na_2CO_3 in D_2O) has been assessed using ^{95}Mo NMR spectroscopy. The chemical shifts that may be expected for the various combinations of oxide and sulfide Mo ions are shown in Table 2. ADTM is quite reactive in water at ambient temperatures undergoing hydrolysis accompanied by thiolation to form $MoOS_3^{2-}$ and MoS_4^{2-}. All of the thio monomolybdate ions, including tri- and tetrathiomolybdate ions, were observed in ^{95}Mo NMR scans of the ADTM. Within 24 hours, 75% of the starting material had reacted with the displaced sulfur from the $MoO_2S_2^{2-}$ ion being incorporated into the tri- and tetrathiomolybdates, (Table 2). After 27 days the di-thio ion concentration had decreased by an additional 50% and the S/Mo ratio had decreased from two in the parent ion to 0.8 in the monomolybdate ions. MoO_4^{2-} and MoO_3S^{2-} were the dominant ions observed in the scans. The rate of decomposition of ATTM in aqueous solutions was somewhat less, one of the main absorption peaks (at 470nm) showing a 16% decrease in intensity after 4days at ambient temperature. However, this band had essentially disappeared after 7 days, suggesting autocatalysis of the decomposition. A half-life of 50h has been reported for the first-order hydrolysis of ATTM in an aqueous solution buffered at a pH of 9 (4).

Table 2 - ^{95}Mo NMR Chemical Shift Data & Decomposition of $(NH_4)_2MoO_2S_2$ in 5% Na_2CO_3/D_2O (pH 13).

	Chemical Shift, ppm		**Relative Concentration, %**		
	Experimental	**Literature***	**Initial**	**1 day**	**27 days**
MoO_4^{2-}	0.0	0	-	13	52
MoO_3S^{2-}	497.5	497	-	18	26
$MoO_2S_2^{2-}$	1066.4	1067	100	25	11
$MoOS_3^{2-}$	1653.0	1654	-	41	7
MoS_4^{2-}	2253.2	2259	-	3	4
S/Mo atomic ratio in ions			2	2.0	0.8

* Minelli, M., et al., *Chem. Rev.* 1985, 68, 169.

Comparing these time scales with the time taken to prepare the solutions and impregnate the coal, the slower hydrolysis rate observed for ATTM implies that it may remain intact after being deposited onto the surface of the coal. In contrast, the faster reacting ADTM may be expected to form molybdate ions and depending on the time and temperature used in the impregnation process, a range of different thio molybdates. Since ADTM is moderately soluble in methanol, this was evaluated as an alternative to impregnating from an aqueous solution. However, analysis of the solutions using UV spectroscopy showed similar decomposition reactivities: the prominent absorption peaks at 312 and 398nm soon faded into the baseline and a new band appeared at 444nm. Over a five-day period the absorption at 470nm disappeared while one at 320nm decreased and merged as a shoulder on broad absorption peaks below 300nm. Thus, the ADTM would appear to have been transformed into other species.

At low concentrations, ~0.01wt%, Mo_3S_{13} is slightly soluble in water. However, it is more soluble (1wt%) in 0.05N NaOH, which was used for impregnating the coal in the test program. Mo_2S_{12} was sufficiently soluble in water to be impregnated onto coal from a 0.2wt% aqueous solution. Using this large excess of water required that the coal be dried before use. The UV spectra of these two materials are indistinct with absorption bands in the 350-450nm region steadily increasing at the shorter wavelengths. The spectra changed over a 2-day period with the absorption for the 350nm band of Mo_3S_{13} nearly doubling while absorption for Mo_2S_{12} at the same position showed a smaller increase. Since these spectra change more slowly than the spectrum of ADTM, their original structures are more likely to remain intact upon the surface of the coal after impregnation.

It is thus apparent that all of the Mo-sulfide compounds used here react in water, though at widely different rates. This introduces some uncertainties into the form and chemical structure of the species actually deposited on the coal surface. Once deposited, they will continue to transform by reacting with water and other reactive functional groups present in the coal. ATTM and ADTM ultimately form the completely oxygenated molybdate, whereas the final and intermediate products from hydrolysis of Mo_2S_{12} and Mo_3S_{13} have not been defined. The liquefaction results suggest that all of the impregnated precursors remained largely intact except for ADTM.

Neither the active catalysts nor the pathway by which these precursors are transformed into active catalysts are known. However, studies reported on the thermal conversion of all the precursors show that they will either thermally decompose or, in the presence of H_2, react to form MoS_2. When ATTM is heated in either an inert atmosphere or H_2, it forms ammonia, H_2S and MoS_3 with the maximum rate of formation being at 220°C (5). Upon further heating, amorphous MoS_2 is formed (6,7). In H_2, MoS_2 is formed at 400°C whereas in an inert atmosphere it forms over a range of temperatures up to a maximum of 800°C. In H_2 the surface area generated in the MoS_2 increases with increasing heating rate (5,8). The reaction of Mo_2S_{12} in either an inert atmosphere or H_2 at temperatures up to 400°C forms MoS_3 along with ammonia and H_2S. At 410°C in an inert atmosphere, MoS_3 is converted rapidly to MoS_2 via an oxidative-reductive reaction with the elimination of S_2(9). In H_2, MoS_2 forms at a slightly lower temperature of 394°C. Mo_3S_{13} behaves differently in that it does not form MoS_3 but initially forms Mo_3S_{12}. In H_2, it produces MoS_2 over a temperature range from 330 to 440°C(9). In an inert atmosphere this transformation to MoS_2 occurs at temperatures slightly in excess of 400°C. ADTM decomposes in a similar manner to ATTM forming an intermediate presumed to be $MoOS_2$ (7), which subsequently decomposes to MoS_2 (10). Thus, at typical liquefaction temperatures, around 400°C, all of the precursors are eventually transformed into MoS_2, although this material is not the active catalyst.

Thus, H_2S is necessary to produce an active form of the catalyst from all of the precursors, regardless of whether the selected catalyst is already in its fully sulfided state. This is supported by evidence from the catalytic processing of residual petroleum feeds where it was shown that treating ATTM with H_2S in the presence of H_2 produced a more active catalyst (11). Here it was suggested that the active catalyst is not MoS_2 but an undefined molybdenum oxysulfide. It was also found that the activity of a commercial MoS_2 catalyst, which performed quite poorly, compared with ATTM, improved when H_2S was added. The activity of both commercial MoS_2 and ATTM improved when water was added along with H_2S. If the active form of the catalyst is molybdenum oxysulfide, then a source of oxygen is necessary for the transformation. With coal present in the reaction mixture, a source of water is already present and adding more does not affect the reaction. In contrast, for petroleum feedstock processing there is much less oxygen present, and the addition of water improves the conversion efficiency. In this study, the only evidence that the presence of Mo-S bonds in the precursor facilitates formation of active catalysts is the slightly improved coal conversions found without H_2S. The decrease in conversion for these precursors suggests that the Mo sulfide formed in the decomposition has been over oxygenated through reaction with the water and left in a state that has only partial activity. The H_2S formed from the sulfur displaced from the Mo sulfide precursors is too small to reverse the reaction and re-sulfide the intermediate. Only by addition of more H_2S can the over oxygenated form be reversed to an active form.

Continuous Operations

A planning meeting was held at the CAER on July 28th, involving all participants. At this meeting, a tentative schedule for the commencement of Run ALC#3 was agreed upon and a discussion document was circulated between all participants for comment. ALC#3 was planned to be carried out in two distinct stages, the first stage would be the ‘advanced’ stage using 1000ppm Mo impregnated from Phosphomolybdic Acid (PMA) onto Black Thunder Coal mixed with oil agglomerated coal in a 1:9 ratio to give a final catalyst loading of 100ppm. The 2nd stage would seek to replicate the ‘baseline’ conditions employed in ALC#1 to confirm the initial yields measured during ALC#1.

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2. SECTION TWO

CONSOL, INC.

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 - October 31, 1998

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

SUBCONTRACT OBJECTIVES: No change

TECHNICAL APPROACH CHANGES: None

SUMMARY OF TECHNICAL PROGRESS – OVERALL

The major effort for the 3rd quarter of 1998 was focussed upon the planning fro run ALC#3. A planning meeting was held in Lexington on July 28 where plans for a shortened run ALC#3 were discussed and tentative operating conditions were formulated.

SUMMARY OF TECHNICAL PROGRESS – BY TASK

TASK 2. LABORATIRY SUPPORT (CONSOL)

During this quarter, the design and construction of a pilot scale unit for the production of oil agglomerated coal was completed. The unit is currently undergoing perfromance evaluations and a set of safety/operating instructions are being drafted prior to shipment to the HTI site.

The Black Thunder Mine coal received from HTI as an agglomeration feedstock was re-analyzed; these results are described in detail below. The initial analyses were reported in June; the complete set of initial and repeated analyses as reported here was included in the April-June quarterly report. This coal was used in laboratory agglomeration tests, and will be used in testing of the 18-gallon agglomeration unit for Run ALC-3. Analyses of the new Black Thunder Mine coal (analyses designated “initial” and “repeated”) are compared in Table 1 with the analyses of the coal samples used in lab and production agglomeration runs for ALC-1. The initial determination of ash content of the new coal was lower than expected. The lower carbon content, higher oxygen by difference content, and lower heating value of the new coal suggested that it may be oxidized relative to the ALC-1 coal samples. If the new and ALC-1 samples are from the same batch of coal at HTI, it is possible that oxidation may be taking place in long-term storage at HTI. The initial analysis of the new coal showed more volatile matter and less fixed carbon than did the Run ALC-1 samples. Because of the ash and volatile matter differences and the possibility that the coal was oxidized, CONSOL repeated the ultimate and proximate analyses on the new coal to check these results.

The repeated analyses agreed with the previous (initial) set on most properties (Table 1), including the carbon and oxygen concentrations that indicate that the coal may be oxidized. However, the repeated analysis indicated that the initial volatile matter content reported for this sample was incorrect. The initial analysis was high, and the repeated one is in line with analyses of several prior samples of Black Thunder Mine coal. The repeated analysis will be taken as correct. The initial ash elemental composition on an SO_3-free basis is in good agreement with that of a previous coal sample.

We obtained water analyses from agglomeration tests A131-A135 made with total water recycle (reported in the January-March 1998 quarterly report), but have not fully evaluated them. The analyses obtained were pH, acidity as $CaCO_3$, and concentrations of aluminum, calcium, total iron, magnesium, manganese, potassium, sodium, and sulfur as sulfate. The data will be evaluated with regard to trends in analytical properties with increasing number of recycles, and with dilution from rinsing.

TASK 3. CONTINUOUS OPERATIONS

Aspects of the agglomeration unit and proposed operating approach were discussed with Theo Lee of HTI prior to the July 28 meeting. The oil agglomeration plans were discussed by phone with Dave Tanner and Walt Karolkiewicz at HTI after the meeting. Photographs of the oil agglomeration unit were provided to HTI to assist them in planning for operation of the unit on-site. HTI recommended using a slurry mix tank to prepare four-hour feed batches (instead of the proposed two-hour feed batches) to increase operator efficiency and avoid possible problems with slurry drying of wet agglomerates.

The project schedule and unit modifications (mainly the motor and screen pan) were discussed with CONSOL's Mechanical Services personnel, who will prepare a quotation for fabricating an inner screen pan. We also requested that spare screen cloth be obtained for back-up purposes during Run ALC-3 operations. A 1.75 hp air-driven motor was ordered for stirring the unit; this motor is inexpensive, compact, explosion-proof, and can be varied over 300-3000 rpm.

The 1.75 hp air motor was received and installed on the agglomeration unit. However, a stirring test with water indicated only that the stirring speed was too low (estimated to be ~200 rpm). Attempts to increase the airflow did not substantially improve the performance. In light of the inadequacy of the 1.75 hp air motor, we estimated the power and torque requirements in more detail. In doing this, we found that stirring power (measured as electrical current) data collected during agglomeration for Run ALC-1 proved invaluable. The torque requirement for the 18-gal agglomerator was estimated, as described below. Motor horsepower is related to stirrer speed and torque by the equation

$$1 \text{ hp} = 63{,}025 / (\text{speed in rpm} * \text{torque in in-lb}).$$

When the 50-gal agglomerator was run in 1996,[1] a measurement of the electrical current was used to determine that the power used in agglomeration was 0.87-1.08 hp/ft^3 of slurry volume (the power depended on the stage of the run). Typically, 465 rpm was used, but in one experimental (non-production) run, 520 rpm was used. Using the equation, and 0.87 hp @ 520 rpm, the minimum torque used then is estimated to be 105 in-lb. For 1.08 hp @ 465 rpm, the maximum torque used then is estimated to be 146 in-lb. For the 18-gal agglomerator, the slurry volume will be approximately 1 ft^3 (ca. 20 L of water + 5 kg coal + 2 kg heavy oil), and the required rpm was estimated to be ca. 1100 rpm. The required torque estimate ranges from 49.8 in-lb (0.87 hp @ 1100 rpm) to 61.9 in-lb (1.08 hp @ 1100 rpm). Technical data for the 1.75 hp air motor indicate that with 80 psi air supply, it can provide about 28-44 in-lb of torque (ca. 39 in-lb @ 1100 rpm). At 1100 rpm, the motor would operate at only 0.7 hp with an 80 psi air supply. That motor is indeed undersized.

Options considered were to obtain a 2:1 speed reducer to increase the motor torque output, to obtain a 4 hp or 5 hp air motor, or to obtain a geared variable speed electrical drive. The latter was much more expensive, and was too bulky to mount to the existing frame. The speed reducer offered less flexibility, since the existing air motor would have to be run at the high end of the speed range. A larger air motor offered easy mounting and operating flexibility; the 5 hp motor provided an extra margin of torque over the 4 hp motor with little additional cost. Because of the problems encountered to this point, we decided to obtain a continuously reading tachometer for use on the unit.

CAER and HTI were kept apprised of our progress in preparing the 18-gal agglomerator.

The 5-hp air motor, a panel-mounted tachometer, and pH electrodes were obtained for use in the agglomeration work. The revised inner screen pan was completed. The air motor and tachometer were installed and tested. The 5-hp air motor has enough power to operate at about 1200 rpm with water only. The tachometer sensor (capable of sensing from about three feet away) will be relocated to the frame, away from the vicinity of the motor. The operating procedure and safety checklist for the 18-gal oil agglomeration unit is being typed.

TASK 4. TECHNICAL ASSESSMENT

CAER's preliminary run plan for Run ALC-3 was reviewed, and comments were provided (Appendix A).

The Run ALC-3 oil agglomeration plan was presented at the review/planning meeting in Lexington, KY, on July 28, a summary of discussions is provided in Appendix B.

CONSOL's Quarterly Technical Progress Report for January through March 1998 was issued. Comments were provided to UK/CAER on their draft Quarterly Technical Progress Report for January through March 1998.

CAER requested our ideas for new work on this project. CAER personnel are planning to meet with CONSOL and DOE personnel on September 16 or 17 to discuss ideas for new project directions.

CONSOL personnel met with DOE and CAER personnel at FETC on September 16 to discuss new project directions. A follow-up conference call was held to discuss CAER's outline for a white paper to describe new directions that would be explored. CAER would explore solvent processing approaches to making heavy products, and would concentrate on pitch products for making carbons. CONSOL would explore thermal processing approaches to making light products, and would concentrate on making chemicals and transportation fuels. The two organizations would exchange materials made by different routes for evaluation for the different markets. CAER will write their portion of a short justification paper, and will send it to us for addition of our sections, and for review of their portion.

APPENDIX A

CONSOL Comments on Run Plan for HTI Run ALC-3

Draft Run Plan dated July 17, 1998

1. A flowsheet or other description of stream flows should be provided as part of the run plan.

2. The In-Line Hydrotreater should be used in Condition 2.

3. For the best comparison with Condition 1, we may want to continue the use of the vacuum still in Condition 2.

4. The reduced-pressure still (RPS) should replace CAS in the run plan.

5. Space velocity for Condition 2 should be 561 kg/hr/m^3 as in Condition 1; the rationale follows. At the end Condition 1 of ALC-1, a downward adjustment in space velocity was being made, because the 850 °F$^+$ yield was too high. Also, LDP's recent re-analysis indicates that there was a high resid yield at SV = 670 kg/h/m^3.

6. Toluene extraction should be used to reduce the amount of carbon rejected in the bottoms, but the arrangement should be that used in ALC-1, not that used in ALC-2 (extraction of PFC worked well in ALC-1, but extraction of vacuum still bottoms did not work in ALC-2). HTI can comment on any change in extraction procedures that may improve extraction efficiency and speed.

7. Instead of specifying coal flow rate and recycle flow rate as shown, we recommend that the charge of coal to agglomeration and vector catalyst addition, recycle oil to agglomeration, and recycle oil and recycle solids to liquefaction slurry preparation be specified for Condition 1. In Condition 1, the net coal charge will be 10% vector treated coal, and 90% agglomerated coal. CONSOL is recommending that the charge to agglomeration be quantified, and that it be assumed that 100% of the agglomeration charge (minus any samples) is charged to liquefaction. This is because of uncertainty in determination of the moisture content of wet agglomerates. Drying of the wet agglomerates will take place in the liquefaction slurry.

8. The recycle streams will not contain DW-HT (dewaxed, hydrotreated) VSOH in ALC-3, although there will be hydrotreated VSOH or a similar stream. Exact recycle mix will depend on back-end configuration (not specified in draft run plan). With use of toluene extraction of PFC, there would be no PFC recycle, but toluene extracted oil would be a recycle stream.

9. Molyvan A will not be used in Condition 1 with vector addition of catalyst. Catalyst selection will be discussed at the meeting. Catalyst type for the baseline condition should also be the subject of discussion. If possible, TNPS should be used in K-2 instead of K-1, in order to minimize its contribution to yields.

10. A sampling plan would be finalized after the run plan is completed. Sampling of agglomeration streams would be included.

APPENDIX B

PILOT PLANT RUN ALC#3
PLANNING MEETING

9:00 AM, July 28, 1998
Ben Bandy Conference Room
Center for Applied Energy Research (CAER)
2540 Research Park Drive
Lexington, KY

Thirteen scientists from the CAER, DOE, CONSOL, LDP Associates and HTI gathered to plan for ALC#3.

The first speaker was Xiaodong Zhan of the CAER. He presented coal liquefaction results for the ammonium based Mo precursors: AHM, ATTM, APTM and for the non-ammonium based Mo precursors MoVL, PMA, KMo and NiMo. Zhan made the following conclusions supported by his results: 1) similar liquefaction activities were found for sulfur-free Mo precursors as long as they undergo decomposition under the reaction conditions 2) sulfur incorporated into precursor molecules improved their activity 3) pre-sulfidation of the catalyst precursor improved resid conversion 4) no significant benefit for liquefaction was found for Mo concentrations higher than 300 ppm. For ALC#3, he recommended that either Ammonium molybdate(AHM) at 100 ppm Mo in the reactor be used as precursor along with H2S/H2 pre-sulfidation at 120, 250 and 360 degrees centigrade or else Ammonium tetrathiomolybdate(ATTM) at 300 ppm Mo in the reactor.

Following the presentation, pretreatment was discussed in terms of ALC#3. Pretreatment would be done to only the coal impregnated with 1000 ppm Mo. The pretreated coal would then be mixed with agglomerated coal in ALC#3.

The use NiMo in ALC#2 was discussed. It was differentiated from the NiMo presented. The NiMo presented was from Nickel Molybdate which fails to decompose under the reaction conditions; therefore, the active Mo species does not form and thus leads to poor liquefaction. The NiMo from ALC#2 was derived from Nickel Sulfate and thus decomposes to an active Mo specie.

The second speaker was Belma Demirel of the CAER. She presented liquefaction results for the Mo precursors MoO3, Molyvan A, Molyvan L and PMA. Belma presented results of the precursors added directly to the coal mixture and also upon either impregnating all or just spiking 10% of the coal. She made the following conclusion supported by her results: 1) Molyvan A had the highest activity of the studied precursors for liquefaction 2) PMA when impregnated onto coal yielded higher conversions 3) the resid conversions for spiked coals were about 3% lower than when precursor was impregnated onto all feed coal 4) coal conversions were nearly the same whether all or just 10% of the feed coals were impregnated with the precursors. Belma presented results on the sulfiding of PMA. Results of impregnating the sulfided PMAs onto coal yielded in all cases a lowering in coal liquefaction. She then presented liquefaction results using the phosphomolybdic precursors, PMA, NiPM, CoPM and KPM, which were impregnated onto coal and studied in coal liquefaction. She made the conclusions supported by presented results that: 1) all exhibited high coal and resid conversions 2) PMA yielded the highest coal conversion 3) NiPM yielded the highest resid conversion. For ALC#3, Belma recommended Nickel Phosphomolybdate(NiPM) due to its high water solubility, ease in coal impregnation with pretreatment and high activity in liquefaction.

The low cost of PMA was discussed as well as its salt NiPM. Comments were made of PMA's use for high coal conversion and NiPM for high resid conversion. It was reiterated that the PMA and NiPM precursors are easily impregnated onto coal and were very active in coal liquefaction.

The third speaker was Howard Van Woert of the CAER. He presented liquefaction results for the Mo precursors, AHM, ADTM, ATTM, Mo3S13 and Mo2S12. Howard concluded that both molybdates and thiomolybdates exhibit the same activity in coal dissolution and resid conversion. He concurred with the recommendations of Zhan for use of either ATTM or AHM with pretreatment for ALC#3.
Howard then reported on the synthesis and testing in liquefaction of vanadium containing phosphomolybdic acids(VPMA). V2O5 was said to have greater dehydrogenation properties than MoO2.

The fourth speaker was Gary Robbins of CONSOL. He presented the methodology of coal agglomeration, its integration into the liquefaction process and benefits for increasing coal conversion and distillate yield in ALC#3. Tentative dates for the equipment construction, training and run were presented.
The oil used in agglomeration was discussed by Nowak, Winschel and Lee as well as the PSI Program. The amounts of coal water, temperature and treatment for ALC#3 were discussed. Winschel, Lafferty and Robbins discussed the use of pH paper for acidity monitoring during the run. Detailed steps and material amounts of coal agglomeration were discussed. Slurry drying in relation to normal operations at HTI was discussed. The existence if foaming in the mixing tank was discussed. Kimber and Jacques commented on slurry foaming and slurry pumping.

The fifth speaker was Theo Lee of HTI. He presented the equipment and unit operations of the pilot plant. Theo described problems in run conditions of ALC#2. An itemized cost estimate for ALC#3 was then presented.

The sixth speaker was Mike Peluso of LDP Associates. He presented problems encountered in ALC#1 Condition #1. Then, he presented a revised mass balance for ALC#1 Condition #1. Mike made the following conclusions: 1) the reference case in ALC#1 is approximated at a 20% lower space velocity distillate and resid yields using oil agglomerated coal (conditions 2&3) 2) the distillate and resid yields at 38% lower space velocity with oil agglomerated coal (condition 4) are better than the reference case 3) the distillate and resid yields at 31% lower space velociy with solvent dewaxing and hydrotreating are better than in the reference case. In conclusion, he requested that project team members review current assessments and ask if a rerun of the reference condition needs to be made in ALC#3.

A general discussion was held. PMA was chosen to be the catalyst for ALC#3. It was confirmed that two conditions would be run in ALC#3. In Condition 1, NiPM would be the used catalyst run which would be impregnated onto HTI coal at 10% concentration. This impregnated coal would be mixed with 90% HTI agglomerated oil. In Condition 2, Mol. with no Fe would be the used catalyst for reproducing the baseline for ALC#1.