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ADVANCED DIRECT LIQUEFACTION CONCEPTS for PETC GENERIC UNITS

Quarterly Technical Progress Report for Period October through December 1994

by

University of Kentucky
Center for Applied Energy Research

Sandia National Laboratories

CONSOL Inc.

LDP Associates

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SUMMARY

TASK 1.2 LABORATORY SUPPORT (CONSOL)

Samples of Rosebud coal and Rosebud Syncoal that were received from Western Energy Company were analyzed, tested for liquefaction activity and stored for future use. The Rosebud coal is somewhat less active toward liquefaction than the Black Thunder coal at one set of conditions (THF coal conversion of ~84 wt % vs ~93 wt %); however, the Rosebud Syncoal was much less active at the conditions tested (~66 wt % coal conversion).

TASK 2.1.2.1 PRETREATMENT / DEWAXING - (CONSOL)

Work continued on the solvent extraction method of dewaxing Wilsonville heavy distillate. Approximately 250 g of aromatic-rich material was extracted from Wilsonville Run 262E V-1074 heavy distillate with furfural. Coal conversion in our standard microautoclave test with this furfural extract used as the distillate portion of the solvent was nearly the same as when the original V-1074 was used as the distillate portion of the solvent. Most of the remainder of this furfural extract was sent to Sandia National Laboratory for hydrotreatment.

Thermal dewaxing tests were conducted on Wilsonville heavy distillate. Wilsonville Run 262E V-1074 was heated in the microautoclave to >900 °F for five min. The condensed product is highly aromatic. If, as expected, this material can be hydrogenated to produce an excellent donor solvent, thermal treatment of the distillate stream to eliminate paraffinic components may be an attractive process option.

TASK 2.3.1 IRON BASED DISPERSED CATALYSTS

Impregnated Catalyst Studies

Additional experiments are reported regarding the inhibiting effect of fresh Fe on the activation of Mo. BT coal was liquefied in a hot-filtered Run 258K V-131B from the Wilsonville pilot plant which was essentially free of mineral matter, insoluble organic matter and residual catalyst. During Run 258K at Wilsonville, the Fe catalyst that was being added accumulated in the recycle stream. In the experiments that are reported here catalyst was added to the system using our Vector approach. Catalysts were impregnated onto a portion of the feed coal by an incipient wetness technique at a concentration which would provide the final target metal/dry coal ratio. In the runs reported here, the final metal on dry coal concentrations for the specific metals were: fresh Fe, 0.77 wt %; Mo, 500 ppmw; Ni, 125 ppmw. In these experiments the presence of fresh Fe had decreased the 1050 °F− distillate yield as well as the corresponding resid conversion. In the absence of fresh Fe the distillate yields for both the Mo and Ni/Mo runs were 45 wt % versus 39 wt % when fresh Fe as Fe_2O_3 was present. Resid conversion was roughly 4% higher for the runs with Mo added alone. THF conversion, however, varied. It was nearly the same for the Fe/Mo and Mo runs, differing by less than 1%, but was 3% higher for the Ni/Mo run. This suggests that Ni promotes the dissolution of coal. The promoting effect of Ni on dissolution was reported earlier in experiments using Run 258K V-131B solvent.

When compared with previous run in the Run 258K V-131B that contained residual Fe as pyrrhotite, addition of fresh Fe, as ferrous sulfate, had a negative impact on almost every measure of catalyst activity, with the differences between these two solvents being essentially the same. For example, distillate yields were lower for the freshly added Fe case by ~7% from that observed for the run made in the absence of freshly added Fe. These results indicate that the pyrrhotite has no inhibiting effect on freshly added Mo, whereas the oxide definitely retards its activation.

Liquefaction results using hydrotreated and dewaxed/hydrotreated Run 262E V-1074 distillates that were prepared at Sandia are reported. These are newly prepared solvents that replace the corresponding solvents used in the PST series which were not fully hydrogenated. After preparation of those solvents it was found that the hydrotreating catalysts were only partially sulfided. The newly hydrotreated solvent contained 10.3% versus 9.9 % hydrogen in the original Run 262E V-1074 distillate. The hydrotreated 25% dewaxed Run 262E V-1074 distillate contained 9.8% hydrogen versus 9.2% in the starting blend. The liquefaction experiments were run at 440 °C for 22 minutes on as-received coal without adding any catalyst. The only Fe present in the reaction was recycled pyrrhotite (~1.2 wt% Fe on a full-range recycle oil basis) found in the topped Run 258K V-131B. The results indicate little difference in THF conversion among these solvents. The 25% dewaxed case showed no impact on distillate yield, whereas the hydrotreated solvent showed a 4% increase in resid conversion and a 9% increase in 1050 °F- distillate yield.

Particulate Catalysts

Diphenylether was used to evaluate the influence of promoter metals on deoxygenation. Reactions were carried out in stainless steel, horizontal microautoclave reactors with 800 psig with H_2 at 380 °C. Results indicate that Ni, Co, and lower concentrations (2%) of Mo promoter metals did not display any increase in activity over unpromoted the sulfated hematite. On the other hand, the combinations Ni/Mo and Co/Mo, as well as the 8% Mo, clearly showed an increase in activity. This displays the synergistic effect of the Ni and Co in combination with Mo. Higher Mo concentrations (8%) also worked well. The slow onset of activity for the Co/Mo promoted catalyst was also observed with the Ni/Mo apparently activating more rapidly. Although the Ni/Mo, Co/Mo, and 8% Mo promoted catalysts promotes ether cleavage, the level of deoxygenation is quite low.

Presulfiding runs were made to determined whether the activities of these catalysts could be accelerated. A Co/Mo promoted sulfated hematite catalyst was treated with excess DMDS for 30 minutes at 380 °C. After working up the treated catalyst, it was used in liquefying BT coal in Run 258K V-131B solvent at 440 °C for 22 minutes. At an iron loading of 1 wt % Fe on maf coal the presulfided catalyst resulted in a decrease in THF conversion of ~4 % and a decrease in resid conversion of ~3.5 % compared to the oxide precursor at a loading of 0.8 wt% Fe on maf coal. Presulfiding appears to inhibit rather than improve catalyst activity.

Additional experiments were performed on a 10% Mo on sulfated hematite that had been prepared one year ago. The results in liquefaction experiments indicated a slight increase in activity. Therefore, it appears that large batches of catalyst may be prepared and then stored for extended periods prior to being used without detrimental effects.

TASK 2.4.2 - SOLIDS SEPARATION (CONSOL)

A trial extraction of Wilsonville deashed resid to simulate staged ROSE-SR operation was completed. The "light" and "heavy" resid fractions obtained by this Soxhlet extraction of Wilsonville V-130 deashed resid with cyclohexane were characterized and the material balance was determined to be 100.8 %. Some residual cyclohexane is present in the products, in spite of vacuum drying at an elevated temperature. The light resid fraction represented 44.4 % of the deashed resid. The light resid is lower in phenolic -OH concentration and aromaticity than the heavy resid, but it is higher in aromaticity than the V-1074 distillate. We started additional extractions to generate about 110 g more light resid for testing. This is needed to hydrogenate and test the solvent quality of the material alone, or in a high concentration with distillate (such as 50 wt % light resid), rather than in a low concentration (such as 5 wt % light resid). The extractions were run for two weeks total, and are continuing.

TASK 3.4 PRELIMINARY TECHNICAL ASSESSMENT (LDP ASSOCIATES)

Review of the Bechtel low rank coal study continued during this reporting period. A study was begun on the hydrothermal coal pretreatment step.

Section One

Center for Applied Energy Research
University of Kentucky

TASK 2.3.1 IRON BASED DISPERSED CATALYSTS

Impregnated Catalyst Studies

Interactions of Fe and Ni with Mo in Liquefaction. In the previous quarterly report (DOE/PC/91040-48) experiments were done using Run 258K V-131B as solvent. This solvent contained about 1.2 wt % Fe (full-range solvent basis). In those experiments, evidence was found that the addition of fresh Fe inhibited the activation of Mo giving lower distillation yields. In this report this effect has explored somewhat further by using catalyst combinations of Fe, Ni and Mo. These liquefaction experiments were all run with Black Thunder coal using a filtered Run 258K V-131B. The solvent was prepared by filtering the Run 258K V-131B to remove ash (and with it the Fe that was present as pyrrhotite) and a portion of the IOM. Run experiments in this solvent allowed a measure of the influence of pre-sulfided catalyst (Fe) on the activity of freshly added Mo as well as an evaluation of the activity of freshly added Mo in the total absence of Fe. **Table 1** below summarizes the properties of the new solvent.

Three vector coals, Mo laden (CB-44), Ni laden (CB-45), and Fe laden (CB-46) were prepared individually as described in the previous quarterly report.

Experimental Procedure. Three types of runs were made using three different combinations of catalysts: 1).Fe + Mo added via separate coal vectors, 2).Mo added on a single coal vector, and 3).Ni + Mo added via separate vectors. AR coal and the vector coal(s) were loaded in a proportion such that the final concentrations would give Mo at about 560 ppmw, Ni at 125 ppmw and Fe at 0.80 wt %. Coal weights and the vector fractions were the same as similar experiments that were run during the previous quarter using full-range 258K V-131B. The hot-filtered Run 258K V-131B was added to the reactor in an amount equal to the IOM plus the ash-free resid (i.e., THF soluble resid) used in previous runs (4.5 grams). A constant weight of dimethyldisulfide (DMDS) of approximately 0.0234 grams was added to sulfide the catalysts. When Fe was used, this sulfur addition rate gave a ratio of about 1.6 mol S/mol Fe. This provided an amount of sulfur equal to 140% of the stoichiometric amount to produce $Fe_{0.9}S$. This sulfur addition rate translates to about 39 mol S/mol Mo, including any that might be required for either Fe or Ni. The reaction was carried out for 22 minutes in a standard horizontal 50 mL microautoclave containing 1000 psig H_2 (cold pressure) at 440 °C. After the run, the product gas was collected and analyzed by gas chromatograph using standard methods. The liquefaction products were scraped from the reactor and the materials that were collected were extracted with THF in a Soxhlet apparatus. The THF solubles were then distilled using the standard method described in detail in Quarterly Report DOE/PC/91040-48 to determine the 1050 °F- distillate.

Table 1. Solvent Characterization of Hot-Filtered Run 258K V-131B.

	Solvent Separation Yields wt% maf solvent
Oils	60.5
PA+A	32.4
IOM	7.1
Total	100.0
Mineral	wt % ar solvent
Ash	.25
Fe	0.009
Distillation Yields	wt % ar solvent
1050 °F- Yield	52.4
1050 °F+ Yield	47.6
Total	100.0

Results. As shown in **Table 2,** the presence of fresh Fe had a negative impact on 1050 °F– distillate yield and resid conversion. In the absence of fresh Fe the yields for both the Mo and Ni/Mo runs distillate yields were 45 wt % versus 39 wt % when fresh Fe as Fe_2O_3 was present. Resid conversion was roughly 4% higher for the runs with Mo added alone. For these three runs the gas yields were essentially the same. THF conversion, however, varied. It was nearly the same for the Fe/Mo and Mo runs, differing by less than 1%, but was 3% higher for the Ni/Mo run. This suggests that Ni promotes the dissolution of coal. The promoting effect of Ni on dissolution was reported earlier in experiments using Run 258K V-131B solvent.

Table 2. Vector Coal Runs in Hot-Filtered V-131b.

	Mo vectors		Fe/Mo vectors		Ni/Mo vectors	
		σ		σ		σ
Reaction Temperature	440		440		440	
Run Time(min)	22		22		22	
Coal moisture, wt%	23.3	0.9	22.9	1.1	23.5	0.7
Products, wt% maf coal						
HC Gases	3.5	0.1	3.4	0.6	3.4	0.3
CO_2+CO	6.6	0.3	6.8	0.9	6.4	0.3
Total Gases	10.1	0.4	10.2	1.4	9.8	0.6
1050 °F- Yields	45.8	4.2	39.1	1.4	45.2	0.6
1050 °F+ Yields	44.1	3.8	50.7	2.3	45.0	1.1
Total	100.0		100.0		100.0	
Resid Conversion, % maf resid	28.2	1.8	24.6	1.3	27.7	0.5
H_2 consumed, mg/g maf coal	30	2	27	3	29	3
THF Conversion, % maf coal	87.0	4.5	86.3	1.8	90.2	1.6
Mo conc., ppm mf coal	562	10	594	30	563	8
Ni conc., ppm mf coal	0	n.a.	0	n.a.	125	0
Fe conc., wt% mf coal	0	n.a.	0.83	.01	0	n.a.
mS/mFe or (/mMo)	(39.2)	1.9	1.7	0.1	(37.2)	2.0
Run Numbers	4292-1 4304-1		4292-3 4299-2 4326-1		4303-2 4310-1	
Vector Coals Used	CB-44		CB-46 CB-44		CB-45 CB-44	

Table 3. Comparison of Fe/Mo and Mo Activities in Two Liquefaction Solvents.

Vehicle	Full Range 258K V-131b			Hot-filtered V-131b		
Catalysts added (vector/total feed, %)	Mo (5)	Fe/Mo (10&5)	Δ	Mo (5)	Fe/Mo (10&5)	Δ
1050 °F- Yields	55.1	47.9	(7.2)	45.8	39.1	(6.7)
Resid Conversion, % maf resid	30.3	26.4	(3.9)	28.2	24.6	(3.6)
THF Conversion, % maf coal	107.3	106.2	(1.1)	87.0	86.3	(0.7)
H_2 consumed, mg/g maf coal	38	39	1	30	27	(3)

Data in **Table 3** compares results obtained in Run 258K V-131B both with and without recycled Fe. The addition of fresh Fe, as ferrous sulfate on a coal vector, had a negative impact on almost every measure of catalyst activity, with the magnitude in these two solvents being essentially the same. For example, distillate yields for these two solvents were lower for the freshly added Fe case by ~7% from that observed for the run made in the absence of freshly added Fe. Overall, the presence of recycled Fe did not appear to influence performance. The results reported in the previous quarter in DOE/PC/91040-48 showed that a larger sulfur charge improved conversion and distillate yields, suggesting that Fe may be starving the Mo for sulfur because its rate of uptake of sulfur was much more rapid than Mo thereby preventing the sulfiding of the Mo resulting in a poorly activated form of catalyst. If H_2S partial pressure is important in the Mo sulfidation, the rapid uptake of sulfur may be sufficient to lower the pressure below a level that promotes rapid uptake. Other information available from P. F. Britt at ORNL suggests that Mo has such a thirst for sulfur, it consumes it even at extremely low H_2S partial pressures. It is obvious additional experimental work is necessary to resolve this issue.

Testing of Replacement Hydrotreated and Dewaxed/Hydrotreated Distillates. Upon learning that earlier hydrotreated and dewaxed/hydrotreated Run 262E V-1074 distillates used in the PST series were not fully hydrogenated (due to a partially sulfided hydrotreating catalysts that was inadvertently used at Sandia), two replacement distillates, described below, were prepared for retesting to augment our understanding of hydrotreated distillates in the Advanced Concepts program. Because of the prospect of interference from the large amount of background Mo present in the Run 262E process recycle oil, the earlier PST studies used a modified process oil from Run 258K V-131b, and this resid material is used again here. It had been previously "topped" by CONSOL, where 35.1% of the total recycle oil was removed as a light distillate fraction. This had been done by distilling the recycle oil at 320 °C and 2 Torr. CONSOL's analysis showed the following composition of the topped resid:

Table 4. Composition of Topped R-258K Recycle Oil.

	Ultimate (as determined), %		Proximate (dry), %
C	76.99	Ash (as-is)	15.52
H	5.07	Ash (SO_3-free)	12.72
N	1.04		
Cl	.08		
S	1.21		

The ash numbers translate to a SO_3-free ash concentration of 8.24% on a whole recycle oil basis.

Sandia reran the hydrotreating runs making two new hydrotreated distillates for this study which were supplied to us. These samples were a hydrotreated-only Run 262E V-1074 distillate (HO) and a simulated 25% slipstream dewaxed/hydrotreated Run 262E V-1074 distillate (25% DEW). Both of these were hydrotreated at Sandia at 365 °C over sulfided Shell-324 catalyst under 1400 psig H_2. Details provided by Sandia characterizing the distillates are presented in **Table 5.**

Liquefaction conditions were identical to the PST series (440 °C for 22 minutes) and the first experiment reported here repeats PST Run No. 1. While similar experiments were run in the PST series, there were no exact matches, since much of the earlier work was performed with either the Run 262E V-1074 distillate or a fully dewaxed/hydrotreated Run 262E V-1074 distillate. Also, the runs reported here were made on as-received coal without adding any catalyst. This was done to emphasize the hydrogen-donor properties of the recycle oil. The only Fe present in the reaction was recycled pyrrhotite (~1.2 wt% Fe on a full-range recycle oil basis) found in the topped Run 258K V-131B that was received from CONSOL. There also was a small contribution of the Fe present in the coal. The R-258K V-131B recycle oil was earlier shown to be essentially Mo-free.

Table 5. Properties of Hydrotreated Distillates.

Sample No.	Description	% H	cyclic $\alpha+\beta$	alkyl β
122205	Run 262E V-1074 HO	10.3	32.7	36.3
62205	25% DEW (1621-22-5k)	9.8	37.5	29

The products from these experiments were analyzed using the standard CAER THF extraction method followed by distillation of the soluble portion of the collected products. When the reconstituted R-258K V-131B was used as solvent, the topped Run 258K V-131B was used as the resid, and the appropriate distillate was added in the percentage (35.1%) that had been removed by topping. The mathematical treatment of the data assumes that this reconstitution had no effect on the yield of distillate from the liquefaction solvent in product work-up, or on the IOM content of the original starting Run 258K V-131B (16.48% SO_3-free ash-free basis). This was logical since distillation of the original Run 258K V-131B using the procedure without a temperature hold at the upper temperature showed it to be 46.6% 1050 °F- distillate on a full range solvent basis, much more than the 35% removed by topping.

Data are presented in **Table 6** for the experiments using the recomposited recycle oil with the following three distillates:

1. As-received (AR) R-262E V-1074
2. 25% dewaxed Run 262E V-1074
3. Hydrotreated 25 % dewaxed Run 262E V-1074

Table 6. Product Distribution from Liquefaction of Black Thunder Mine Wyodak Coal at 440 °C for 22 minutes (wt% maf coal, SO_3-free ash basis).

	1050 °F- Distillate Source		
	AR Run 262EV-1074[a]	25% Dewaxed Run 262E V-1074	Hydrotreated 25 % dewaxed Run 262E V-1074
HC Gases	2.9	3.1	2.8
$CO+CO_2$	6.4	6.6	6.2
1050 °F-	38.0	37.6	46.6
1050 °F+	52.7	52.7	44.4
THF Conversion	96.7	98.1	96.4
Resid Conv. , wt% maf resid	22.4	22.3	26.2
mg H_2/g maf coal	27	23	26
Run Number	4333-1 4333-2	4341-1	4341-2
Sandia Sample No.		Sandia 62205	Sandia 122205

The first solvent was run in duplicate, while the other two were single runs. The results indicate little difference in total THF conversion among the coals. The 25% dewaxed case showed no impact on distillate yield (within experimental error), but the hydrotreated 25 % dewaxed Run 262E V-1074 showed a 4% increase in resid conversion and a 9% increase in 1050 °F- distillate yield. The distillate yield in the hydrotreated solvent is nearly the same as observed for the run with 258K V-131B reported in **Table 3**. In that run 0.7 wt % Fe added as impregnated ferrous sulfate and 500 ppm Mo were added as catalyst to the coal. A very big difference in THF conversion exists between those two runs. The run in 258K V-131B gave a THF conversion of 106% while the results with the hydrotreated dewaxed solvent gave only 98%.

Particulate Catalysts

Introduction. Model compounds have been used to try and gain a better understanding of the influence of promoter metals on different reactions that are occurring during coal liquefaction. Model compounds were used that contained bond structures similar to those believed to exist in coal. The use of these type of reactions may help to elucidate the function of the promoter on the sulfated hematite.

Several model compounds were utilized to study various types of reactions. The conversion of naphthalene to tetralin and decalin was used to model the hydrogenation properties of the catalysts. The cleavage of the etheric linkage in diphenyl ether (DPE) was used to model hydrodeoxygenation (HDO) reactions. Similarly, benzothiophene (BZT) and quinoline were employed to study the activity of the catalysts for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions, respectively. The high oxygen content of the Black Thunder coal used in this program tend to suggest that HDO reactions are of particular importance. The results of the model compound experiments reported here will focus on this reaction.

Experimental Model compound reactions were carried out in stainless steel, horizontal microautoclave reactors with volumes of approximately 20 ml. Model compounds were added to the reactors as a 5 wt% solution of the model compound in hexadecane. The model compounds utilized in this study were naphthalene, diphenylether, benzothiophene, and quinoline. In addition to 5 g of the model compound/hexadecane solution, 0.0125 g of catalyst and 0.0176 g of dimethyldisulfide (DMDS), a sulfiding agent, were added to the reactor. The reactors were sealed and then purged and pressurized to 800 psig with H_2. All reactions were carried out at 380 °C in a heated fluidized sand bath in which the reactors were vertically agitated at 400 cycles per minute. All model compounds were tested with each catalyst, and run times ranged from 5-60 minutes.

At reaction completion, each reactor was cooled to room temperature in a cool fluidized sand bath. The gas was vented from the reactor and the products were removed by rinsing with tetrahydrofuran (THF). The spent catalyst was stored with the reaction products to minimize exposure to air prior to XRD analysis. The liquid products were analyzed by gas chromatograph (GC). Reaction products were analyzed to obtain percentage conversion and product distribution. Conversion was defined as rate of disappearance of the model compound rather than rate of formation of other products. Furthermore, desirable products were defined as those in which the heteroatom had been removed.

Results The deoxygenation results shown in **Figure 1** indicate that all of the catalysts showed increased conversion relative to the thermal reaction. However, the Ni, Co, and lower concentration (2%) of Mo promoter metals did not display any increase in activity over unpromoted the sulfated hematite, indicating their utility as promoter metals is negligible. On the other hand, the combinations Ni/Mo and Co/Mo, as well as the 8% Mo, clearly showed an increase in activity over the sulfated hematite. This fact displays the synergistic effect of the Ni and Co in combination with Mo because the conversion at 60 minutes is higher for the Ni/Mo and Co/Mo combination promoter metals than it is for the 8% Mo promoter metal alone. It is also interesting to note the slow onset of activity for the Co/Mo promoted catalyst. While the reason for the delayed onset of activity is still under investigation, it has been reported that, on an alumina support, Ni compounds are more readily reduced than Co compounds. While both catalysts show an initial period of relative inactivity, this may explain the longer time required to activate the Co/Mo promoted catalyst compared to the Ni/Mo promoted catalyst.

While the success of the Ni/Mo, Co/Mo, and 8% Mo promoter metals in cleaving the etheric linkage is evident, their utility for HDO is minimal at these conditions. Product distribution

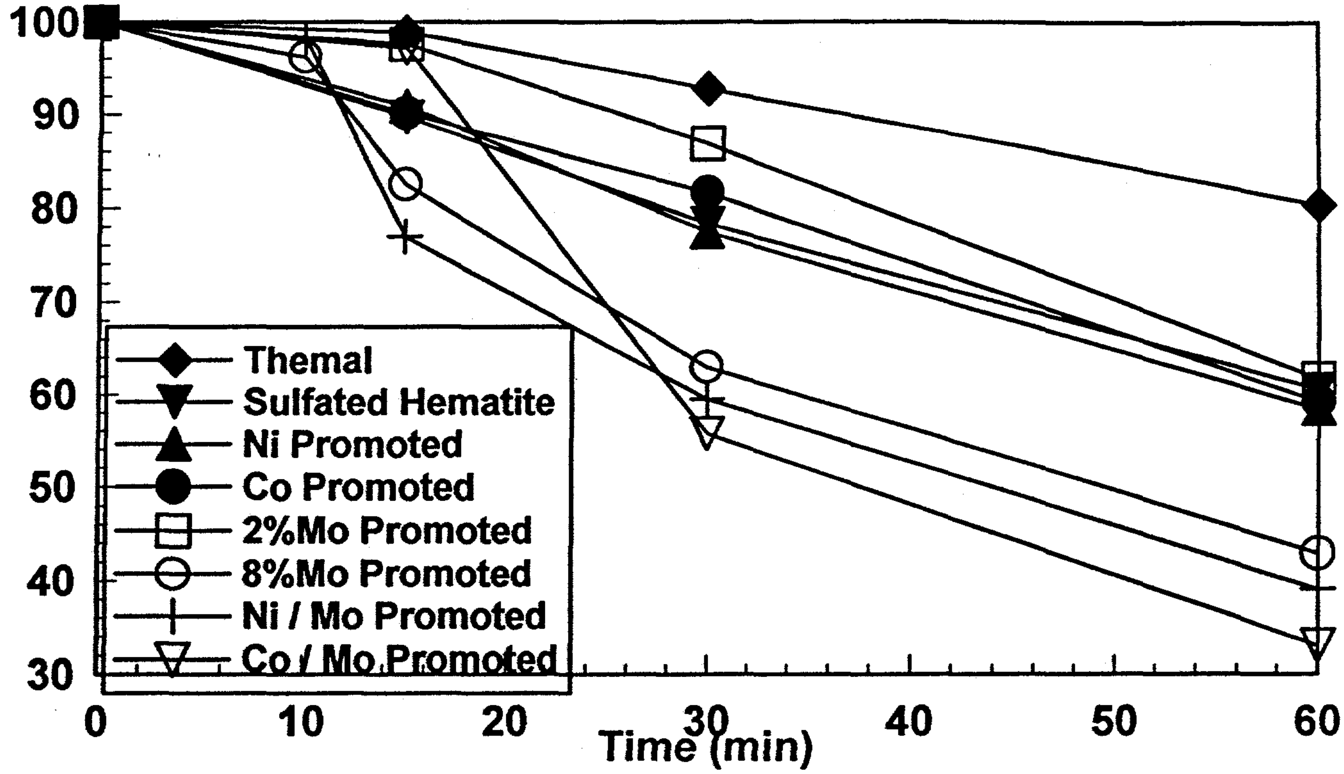

Figure 1. Hydrodeoxygenation of Diphenylether

data from gas chromatography analysis indicated that none of the catalysts were successful in the HDO of DPE, resulting in less than ~10% HDO for even the most active catalysts. This is evidenced by the nearly equal molar ratios of benzene and cyclohexane to phenol and cyclohexanol. Therefore, it appears that the tested promoter metals have little utility in HDO reactions under these conditions. However, other studies have shown that at 475 °C in the presence of added sulfur without a catalyst the amount of oxygen removal was minimal at times less than 4 hours [Sweeny, 1987]. This suggests that more severe conditions may be required for significant oxygen removal.

In sum, Ni and Co alone have no beneficial effect as promoter metals on the sulfated hematite, but display a synergism with Mo to create a relatively high conversion rate. Further, unlike the Ni and Co, Mo alone used at higher concentrations appears helpful in conversion of DPE. However, none of the catalysts displayed an appreciable amount of HDO although substantial cleavage of the etheric bond was observed.

Conclusions. The results of the experiments on HDO of DPE appear to indicate that the catalysts exhibit a period of relative inactivity which may last up to 15 minutes at 380 °C. After this period the catalysts exhibit a very high activity for the cleavage of the etheric linkage. The period of inactivity probably correlates with the conversion of the oxide precursor to the sulfide phase. It has been reported in the literature that pyrrhotite is more active for this reaction than the oxide precursor [Sweeny, 1987]. Further, it has been shown that the activity of the catalyst is related to the partial pressure of hydrogen sulfide in the system which, in turn, is directly related to the stoichiometry of the pyrrhotite. A maximum activity was achieved with a partial pressure of H_2S of 5%. Further increases in H_2S partial pressure up to 10 % yielded minimal increases in activity.

The delayed onset of activity for the promoted sulfated hematite catalyst may therefore be related to this change in phase. However, as shown in **Figure 2**, the XRD analysis of the spent catalyst from the model compound experiments appear to indicate that the phase transformation is complete within 5 minutes. It is important to note that the results of XRD

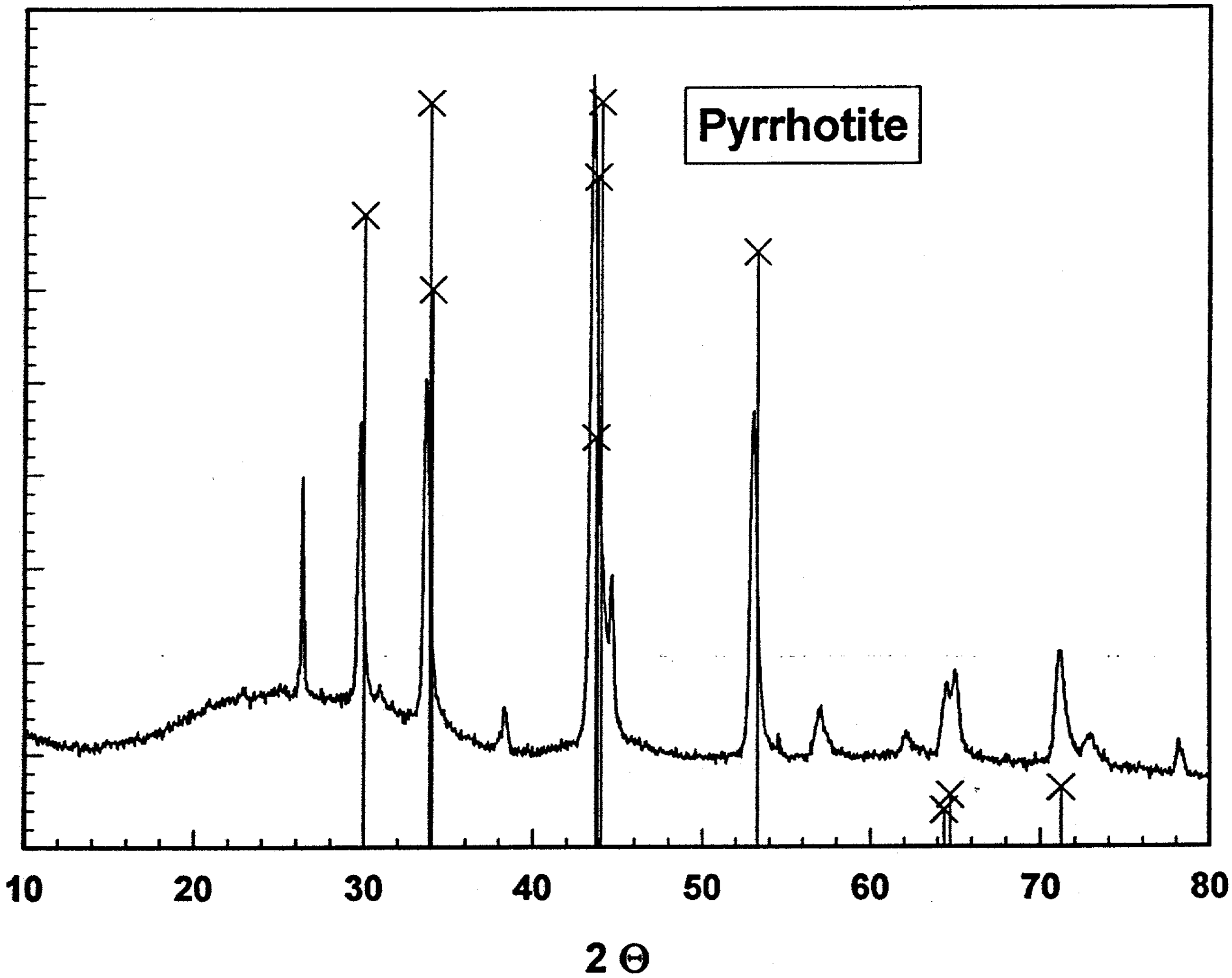

Figure 2. XRD Spectra of Spent Catalyst.

analysis only show the major phases present and do not indicate the completeness of the transformation. Furthermore, it is difficult to determine the stoichiometry of the pyrrhotite from the XRD spectra obtained. The difference between the time of the apparent phase transition and the onset of activity maybe related to a change in the particle stoichiometry.

Particle diameters estimated from these spectra using a Debye-Scherrer relationship indicated no significant increase in particles size during the reaction. It is important to note that this method is useful in estimating the crystallite diameter and may not yield accurate results for these particles during transition. However, SEM micrographs of the spent catalyst appear to be very similar to those of the oxide precursor. As shown in **Figure 3**, both precursor and spent catalyst appear as loose agglomerations of particles below the resolution of the instrument. The agglomerated clusters have diameters of ~ 1 μm. TEM of the spent catalyst will confirm the actual particles size and morphology.

Presulfided Catalyst

The delayed onset of activity displayed by the catalysts in the model compound runs inferred that a similar situation may have occurred in the coal liquefaction experiments. The short reaction times utilized in the coal liquefaction experiments would tend to exaggerate the adverse effects of the delayed activity. However, the effect of an increase in temperature of 60 °C on the phase transformation was unclear. Increasing the temperature may significantly enhance the kinetics of the reaction. Due to pressure constraints it was not possible to repeat the model compound work at the higher temperatures.

A presulfided catalyst was prepared to utilize in the coal liquefaction reactions. The Co/Mo promoted sulfated hematite catalyst was chosen based on the slow activation and high activity of the active phase demonstrated in the model compound reactions. Catalyst presulfidation was carried out in a 20 ml microautoclave. The reactor was loaded with 0.15 g catalyst precursor and 0.35 g DMDS in 5 g of a 5 wt% naphthalene in hexadecane solution. The reaction procedure was identical to that used for the model compound reactions detailed previously. Presulfidation was carried out for 30 minutes at 380 °C. After reaction the

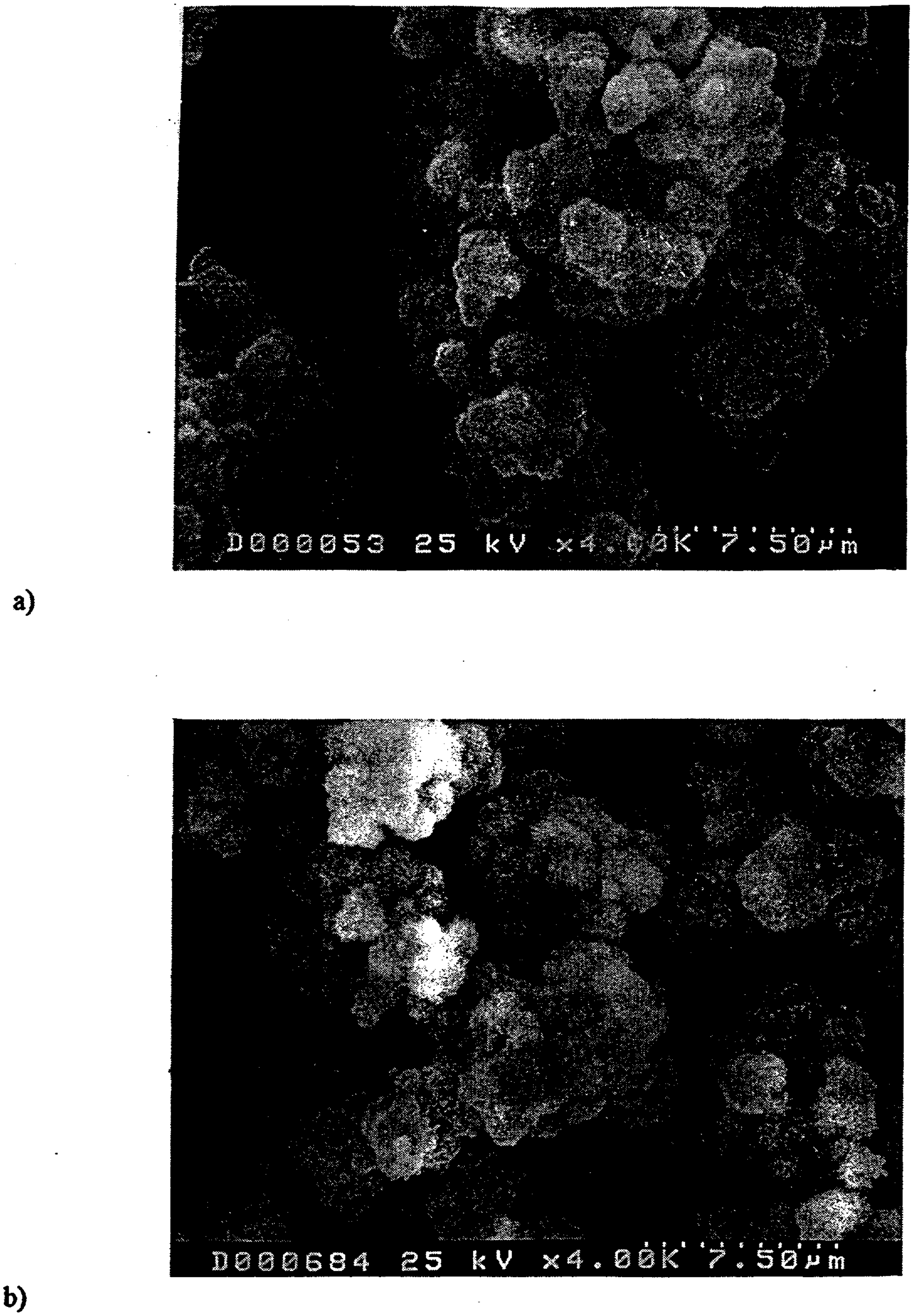

Figure 3. SEM micrographs showing aggoleration of a) fresh catalyst and b) spent catalyst.

gases were vented and the presulfided catalyst was recovered by filtration of the reaction products. The organic products were removed by rinsing with THF and the presulfided catalyst was stored in a vacuum desiccator prior to use.

The details of the coal liquefaction reactions have been detailed in previous reports. Briefly, 3 g Black Thunder coal and 5.4 g V-131B from run 258K were loaded in a ~50 ml microautoclave reactor with ~0.028 g of the catalyst and ~0.06 g of DMDS. This resulted in a catalyst loading of 1 wt % Fe on maf coal for the presulfided catalyst while the oxide precursor had a loading of 0.8 wt % Fe on maf coal. The reactor was sealed, purged and pressurized to 1000 psig with hydrogen. The reactions were carried out at 440 °C for 22 minutes. All runs were done in duplicate to ensure reproducibility. The products were analyzed by THF solubility and by distillation.

Results. **Figure 4** shows the results of the liquefaction experiments. The presulfided catalyst displayed a lower activity than the oxide precursor, despite the higher iron loading. At an iron loading of 1 wt % Fe on maf coal the presulfided catalyst resulted in a decrease in THF conversion of ~4 % and a decrease in resid conversion of ~3.5 % compared to the oxide precursor at a loading of 0.8 wt% Fe on maf coal.

While this catalyst displayed a distinct period of activation in the HDO experiments at 380 °C, the results from this period indicate that presulfidation inhibits rather than improves the catalyst activity. This may be due to faster conversion to the active phase at the higher temperatures used in the coal liquefaction reactions.

Catalyst Aging

Preliminary experiments reported earlier had indicated that the activity of the catalyst may diminish with time. In order to further examine this problem, duplicate runs were conducted over an interval of ~1 year with the same batch of P-2 catalyst. The results of these experiments, shown in **Figure 5**, indicate that the catalyst activity increased slightly. The amount of the increase is dubious since the earlier experiment was not duplicated. During this period, no special precautions were taken to exclude air or moisture from the catalyst. These results indicate that large batches of catalyst may be prepared and then stored for extended periods prior to use in a bench scale unit without detrimental effects..

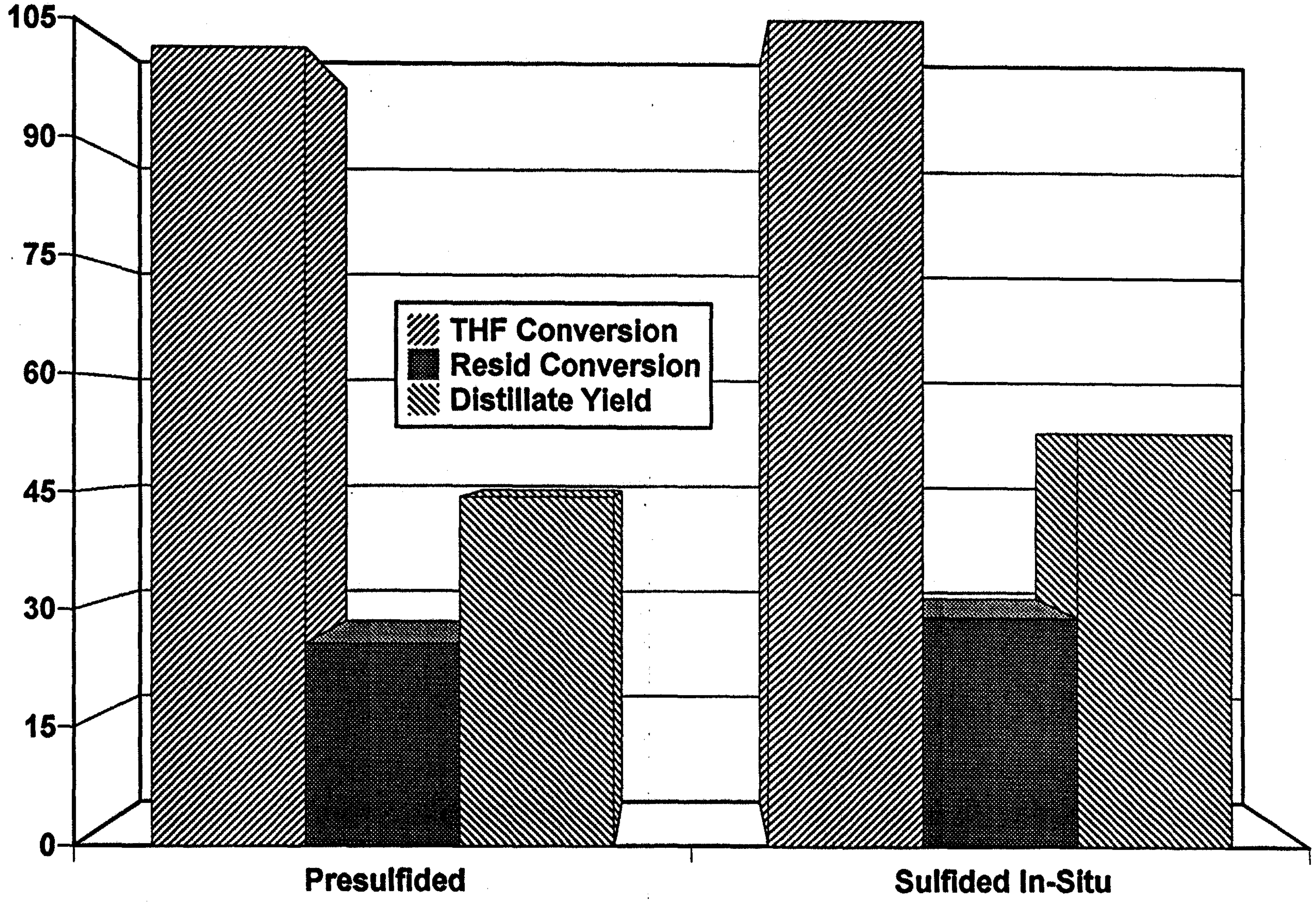

Figure 4. Effect of Presulfiding on the activity of a Co/ Mo promoted Sulfated Hematite

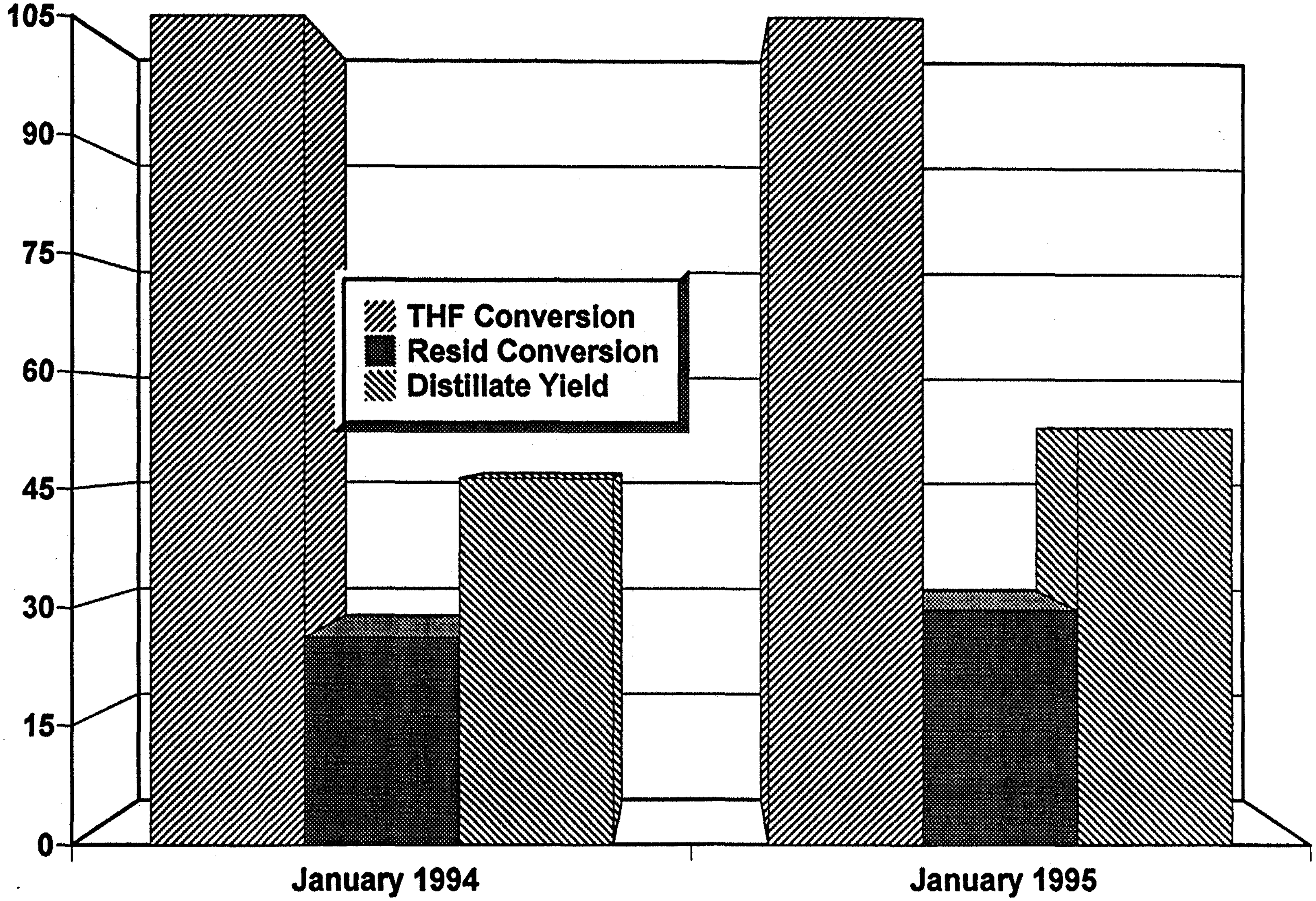

Figure 5. Effect of Catalyst Age on Activity of P-2 in V-131b from Run 258

SECTION TWO

CONSOL Inc.

QUARTERLY PROGRESS REPORT
FOR THE PERIOD OCTOBER 1 THROUGH DECEMBER 31, 1994
SUBCONTRACT No. UKRF-4-25582-92-76

TASK 1.2 - LABORATORY SUPPORT (CONSOL)

Summary

Samples of Rosebud coal and Rosebud Syncoal that were received from Western Energy Company were analyzed, tested for liquefaction activity and stored for future use. The Rosebud coal is somewhat less active toward liquefaction than the Black Thunder coal at one set of conditions (THF coal conversion of ~84 wt % vs ~93 wt %); however, the Rosebud Syncoal was much less active at the conditions tested (~66 wt % coal conversion).

Discussion

Approximately 20 lb each of Rosebud coal and Syncoal were received from Western Energy Company. The Rosebud coal consisted of mostly >2" lumps. The Syncoal sample was very friable and had a top size of ~1". The Rosebud coal sample was coned and quartered to produce two fractions and the entire Syncoal sample was riffled into two portions. Approximately half of each "as received" sample was stored under nitrogen in a triple layer bag. The remaining Syncoal sample was screened at 1", ½", ¼" and 8 mesh to determine its initial size distribution. The results of this screen analysis are shown in Table 1. After screening, the individual size fractions of Syncoal were recombined. The recombined Syncoal sample and the remaining Rosebud coal were ground to -8 mesh and riffled into various quantities. One pound of each -8 mesh material was further ground to -100 mesh and was submitted to CONSOL's analytical laboratory for proximate and ultimate analysis, Btu determination, sulfur forms analysis, ash elemental analysis, and chlorine determination. The results of these analyses are shown in Table 2. In addition to drying the coal, the Syncoal process removed about 1.5 wt % of the ash and lowered the pyritic sulfur content of the Rosebud coal from 0.55 to 0.07 wt % (Table 2). Each of the ground samples were subsequently stored under nitrogen in triple layer bags. The aliquots prepared from both materials are shown in Table 4. These aliquots are available for use by the program participants.

The Rosebud coal and Rosebud Syncoal were tested for liquefaction activity. Both materials were evaluated at the conditions that were used in the baseline test for the Process Simulation Tests (PST), Run 18. These conditions were: 5 min, 824 °F, 1500 psig H_2 (cold), Wilsonville Run 262E solvent, ~1.5 solvent/dry-coal, 1 wt % WIO (Wilsonville iron oxide) and 100 ppm Mo (as MolyVan-L) added on dry coal basis. Coal conversions were determined by THF solubility and are reported on a MAF, SO_3-free basis. The results of replicate microautoclave tests for both samples and the average coal conversion for Black Thunder coal under the same conditions are given in Table 4.

The measured coal conversions for the Rosebud coal, 83.7 and 84.9 wt %, are lower than the coal conversion of Black Thunder coal at the same conditions, 93.3 ±2.5 wt %. The measured coal conversion of the Rosebud Syncoal, 65.8 wt %, is much lower than that of either the Rosebud coal from which it was produced or the Black Thunder coal. This suggests that drying Rosebud coal from its original ~22.5 wt % moisture content to ~2.5 wt % moisture content reduces its suitability as a liquefaction feedstock. It is not clear whether this is a general result of drying or if it is specifically caused by the processing method used to produce Syncoal. We plan to dry an aliquot of the Rosebud coal to ~2.5 wt % moisture content by rotary evaporation at ~70 °C and to subject this dried sample to the same 5-min microautoclave test and compare the results with those from the Syncoal test.

Task 2.1.2.1 - Pretreatment Work at CONSOL - Dewaxing and Solvent Improvement

Summary

Work continued on the solvent extraction method of dewaxing Wilsonville heavy distillate. Approximately 250 g of aromatic-rich material was extracted from Wilsonville Run 262E V-1074 heavy distillate with furfural. Coal conversion in our standard microautoclave test with this furfural extract used as the distillate portion of the solvent was nearly the same as when the original V-1074 was used as the distillate portion of the solvent. Most of the remainder of this furfural extract was sent to Sandia National Laboratory for hydrotreatment.

Thermal dewaxing tests were conducted on Wilsonville heavy distillate. Wilsonville Run 262E V-1074 was heated in the microautoclave to >900 °F for five min. The condensed product is highly aromatic. If, as expected, this material can be hydrogenated to produce an excellent donor solvent, thermal treatment of the distillate stream to eliminate paraffinic components may be an attractive process option.

Discussion

Solvent Extraction

We extracted approximately 500 g of Wilsonville Run 262E V-1074 heavy distillate with an equal weight of furfural to prepare enough aromatic-rich extract for microautoclave testing and for trial hydrotreatment experiments. The V-1074 was extracted in ~20 g batches using the following procedure. The V-1074 and furfural were pipetted into a 125 mL separatory funnel and warmed with a heat gun to ensure that the V-1074 was entirely liquid. After warming and shaking the separatory funnel containing the furfural and V-1074, the funnel was reheated and all the liquid was drawn off into four pyrex centrifuge tubes. A wire with a bent end was inserted in each tube and the tubes were then centrifuged for about 30 min. After centrifugation, the tubes were cooled with dry ice and the hardened aliphatic fraction, which was undissolved in the furfural and which was clearly visible at the top of each tube, was removed from each tube by pulling it out of the tube with the wire. The aliphatic fraction plugs were rinsed with furfural to remove as much non-aliphatic material as possible and the rinse furfural was added to the aromatic oil fraction. The aromatic fraction was then rotary evaporated at ~120 °C under full vacuum. Both the aliphatic and aromatic fractions were then heated for 12 hr at 110 °C in a vacuum oven to remove solvents before ^{1}H-NMR analysis.

The aromatic fraction yield from this extraction was 57 wt % and the total product recovery was 100 wt % (Table 5). These yields are identical to those determined in our trial extractions with furfural.[1] NMR analysis and the phenolic -OH contents of both fractions are also shown in Table 5. The high aromatic proton concentration in the furfural-soluble (aromatic) fraction (over 25%) is also consistent with the trial extractions. The furfural-insoluble (aliphatic) fraction contains nearly 7% aromatic protons. This relatively high aromatic proton concentration in the aliphatic fraction reflects the high yield of this fraction (43 wt %). The phenolic -OH content of the furfural extract, 0.6 meq/g (Table 5) is similar to that of our cryogenically solvent dewaxed distillates (0.55-0.65 meq/g).

The furfural-soluble aromatic fraction was substituted for V-1074 in our standard 5-min microautoclave Black Thunder coal conversion test in order to evaluate it as a donor solvent, Table 6. The measured coal conversions from replicate tests with this furfural extract substituted for V-1074 as the distillate portion of the solvent were 91.8 and 91.3 wt %. This is slightly higher than the conversions measured at the same conditions with the trial furfural extract used as the distillate,[1] 89.0 and 90.2 wt % and about the same as when V-1074 is used as the distillate, 92.0 ±2.4 wt % (Table 5).

Thermal Dewaxing

Trial thermal dewaxing experiments were carried out with V-1074 heavy distillate from Wilsonville Run 262E. Five-gram V-1074 samples were heated in the 45 mL microautoclave for five minutes (including heat-up time) at 900, 925, 950 and 975 °F. The reactor head space was purged with helium before sealing. Gas yields were determined for each run and ^{1}H-NMR proton distributions were determined on the liquids products. The results of these trial experiments are shown in Table 7. Heat-up to maximum temperature required about two min in all cases. Since these runs were trials, no attempt was made to determine the sand bath pre-heat temperatures that were required to attain the desired sample temperatures. Therefore, the desired run temperature and the actual temperature differed by as much as 10 °F, Table 7.

The gas yields, determined as the weight loss on venting after completion of the run, increased with temperature; from 1.4 wt % at 890 °F to 18.6 wt % at 979 °F, Table 7. Coke formation was apparent at the highest temperature. The total aromatic proton concentration (condensed aromatics plus uncondensed aromatics) increased from 15.0% in the original V-1074 to 37.2% in the 979 °F product, Table 7. The effect of heating Wilsonville Run 262E V-1074 for five minutes in a microautoclave under a helium atmosphere on the proton distributions in the liquid product is shown in Figure 1. It appears, from this figure, that as the temperature is increased, compounds that are rich in alkyl beta protons are being depleted and condensed aromatic compounds are created. This may occur through cracking of alkyl side chains on aromatic rings, through naphthene dehydrogenation and through ring condensation reactions. The products of the thermal treatments at 955 °F and 979 °F are among the most aromatic materials that we have obtained from the Wilsonville Run 262E V-1074 distillate by any dewaxing method.

The 925 °F thermal dewaxing run was repeated with a larger sample (15 g vs. 5 g) to determine yields and to obtain enough dewaxed material for solvent quality comparisons. The gas yield, 3.3 wt %, determined as the weight loss on venting after completion of the run, was slightly lower than the 5.6 wt % gas yield calculated for the trial run at 925 °F, Table 7. After venting the gas, the remaining contents of the microautoclave were distilled in the microautoclave at 200 °C, 5-torr (700 °F equivalent) to remove the lighter "cracked" products from the reactor. The procedure for this in-situ distillation was described previously.[2] The results of this test are shown in Table 8. Under these conditions, 19.8 wt % of the product, based on the total weight of original material, was distillable. GC-MS analysis showed that this light distillate had very high concentrations of n-paraffins (C_8 through ~C_{30}). The light distillate (700 $°F^-$ fraction) had a high paraffinic proton content (65.1% alkyl beta plus gamma content compared with 46.9% in the original V-1074) and a low total aromatic proton content (10.5% vs. 15.0% in the original V-1074). The non-distilled (700 $°F^+$) fraction had a very high total aromatic content (31.9%) and correspondingly lower paraffinic content (33.8%). This highly aromatic thermally dewaxed heavy distillate should be upgradable to an excellent donor solvent by hydrogenation.

Short residence time thermal treatment of the heavy distillate stream may be a desirable way to produce an aromatic-rich distillate that can be hydrogenated to produce a superior donor solvent. Two key points that need to be addressed are: the steady state composition of the thermally treated distillate stream and the solvent quality of the hydrotreated distillate.

Task 2.1.2.2 - Pretreatment Work at CONSOL - Agglomeration

No work was performed on this task.

Task 2.3.2 - Catalyst Studies (CONSOL)

No work was performed on this task.

Task 2.4.2 - Solids Separation (CONSOL)

Summary

We completed a trial extraction of Wilsonville deashed resid to simulate staged ROSE-SR operation. The "light" and "heavy" resid fractions obtained by this Soxhlet extraction of Wilsonville V-130 deashed resid with cyclohexane were characterized and the material balance was determined to be 100.8 %. Some residual cyclohexane is present in the products, in spite of vacuum drying at an elevated temperature. The light resid fraction represented 44.4 % of the deashed resid. The light resid is lower in phenolic -OH concentration and aromaticity than the heavy resid, but it is higher in aromaticity than the V-1074 distillate. We started additional extractions to generate about 110 g more light resid for testing. This is needed to hydrogenate and test the solvent quality of the material alone, or in a high concentration with distillate (such as 50 wt % light resid), rather than in a low concentration (such as 5 wt % light resid). The extractions were run for two weeks total, and are continuing.

Discussion

We completed a trial cyclohexane Soxhlet extraction of V-130 deashed resid from Wilsonville period 262E, to simulate "light" and "heavy" resid streams from the ROSE-SR unit. About 30 g of the resid was extracted for 30 days. The extraction was discontinued, although the solvent around the thimble remained light yellow in color, evidently due to freshly extracted material. To remove solvent, both fractions were rotary-evaporated, and then placed in a vacuum oven at 100°C overnight. Material balance was 100.8 wt %, and recoveries of soluble ("light") and insoluble ("heavy") fractions were 44.4 wt % and 56.4 wt %, respectively (Table 9). Analyses of the feed and both fractions by ^{1}H-NMR and by FTIR for phenolic -OH concentration are presented in Table 9. The slightly high material balance and a sharp, characteristic signal in the ^{1}H-NMR spectra at 1.4 ppm indicate that residual cyclohexane is present in both product fractions. As expected, the light resid is lower in phenolic -OH concentration than the heavy resid; additionally, the -OH peak maximum is shifted in a direction to indicate that the light resid is relatively less aromatic. The proton distribution confirms the expected result, that the light resid is much less aromatic and more aliphatic than the heavy resid. However, the light resid is much higher in aromaticity (25.1%) than the V-1074 distillate (15.0%). This indicates that the light resid may be a good candidate for hydrogenation to improve solvent quality.

At the period 262E solvent composition ratios, the proper blend of this component of the deashed resid with V-1074 distillate for hydrogenation would be about 5 wt % light resid and 95 wt % distillate. However, it is also possible to increase the amount of resid which is deashed for recycle in the liquefaction process. Therefore, it is advantageous to test the material alone, or in a high concentration with distillate (such as 50 wt % light resid), rather than in a low concentration (such as 5 wt % light resid). This will provide increased sensitivity to the solvent quality effect of hydrogenating the light resid, and the proportion of light resid can be optimized later.

Because a larger quantity of light resid is required for testing, we started additional Soxhlet extractions of deashed resid with cyclohexane (in triplicate); about 250 g of resid should generate about 110 g more light resid for testing. We expect the extraction time to be 30 days total. The extractions were suspended after one week, and then continued after a preliminary work-up. Preliminary results for the three individual extractions gave 81 to 85 wt % insolubles and 18 to 23 wt % solubles, with balances of 100 to 104 wt %. These results show less soluble material than we obtained in the original extraction (44 wt %, Table 9). This may result from the shorter extraction time (7 vs. 30 days), and perhaps from less-efficient extraction, since a larger quantity of sample was placed in each thimble (ca. 85 g vs. 30 g). Because of the low yield of solubles, we crushed the largest lumps of insoluble material and re-started the extractions. After an additional week of extraction (about two weeks total), the extractions again were suspended, the insolubles were dried of solvent, crushed, and the extractions then were continued.

Task 2.6.2 - Coker Overhead Characterization (CONSOL)

No work was performed on this task.

Task 3.2 - Economic Evaluation (CONSOL)

No work was performed on this task.

References

1. CONSOL Inc., Project Status Report for September 1994, Subcontract No. UKRF-4-25582-92-76 to CONSOL Inc. Under DOE Contract No. DE-AC22-91PC91040, October 1994.

2. Burke, F. P., Winschel, R. A., Lancet, M. S., Second Quarterly Technical Progress Report on DOE Contract DE-AC22-88PC88800, "Stable Carbon Isotope Analysis of Coprocessing Materials", October 1 through December 31, 1988, March 1989.

TABLE 1

SCREEN SIZE ANALYSIS OF ROSEBUD SYNCOAL

Screen Size	wt, g	wt %
+1"	0	0
1" X ½"	130	2.6
½" X ¼"	784	15.4
¼" X 8 mesh	1670	32.9
8 mesh X 0	2494	49.1

TABLE 2

COMPOSITIONS OF ROSEBUD COAL AND ROSEBUD SYNCOAL

	Rosebud Coal	Rosebud Syncoal
Moisture, wt %	22.27	2.65
Proximate, dry wt %		
Ash	10.57	8.82
Volatile Matter	38.86	39.23
Fixed Carbon	50.57	51.95
Ultimate, dry wt %		
Carbon	69.33	70.54
Hydrogen	4.29	4.33
Nitrogen	1.20	1.22
Sulfur	1.02	0.49
Chlorine	0.02	0.02
Oxygen (diff)	13.57	14.58
HHV, dry Btu/lb	11773	11992
Sulfur Forms, dry wt %		
Pyritic	0.55	0.07
Sulfate	0.03	0.01
Organic	0.44	0.41
Ash Elemental, wt %		
Na_2O	0.73	1.15
K_2O	0.34	0.25
CaO	17.95	15.49
MgO	3.85	4.35
Fe_2O_3	5.07	1.38
TiO_2	0.78	0.83
P_2O_5	0.23	0.28
SiO_2	39.49	41.29
Al_2O_3	15.31	18.60
SO_3	16.21	15.55
Total	99.96	99.17

TABLE 3

AVAILABLE FRACTIONS OF ROSEBUD COAL AND A ROSEBUD SYNCOAL

	No. of Individual Bags	
Sample Description	Rosebud Coal	Rosebud Syncoal
"as received" material		
~10 lb bags	1	1
-8 mesh material		
~9 lb bags	1	1
-100 mesh material		
~125 g bags	3	3
~60 g bags	1	1
~8 g bags	7	7

TABLE 4

MICROAUTOCLAVE LIQUEFACTION OF ROSEBUD COAL, ROSEBUD SYNCOAL, AND BLACK THUNDER COAL

Material	THF Coal Conversion, wt %
Black Thunder coal[a]	93.3 ±2.5
Rosebud coal	83.7, 84.9
Rosebud Syncoal	65.1, 66.4

Microautoclave test conditions: 5-min, 824 °F, 1500 psig H_2 (cold), Wilsonville Run 262E solvent, ~1.5 solvent/dry-coal, 1 wt % WIO and 100 ppm Mo (as MolyVan-L) added as wt % dry coal. Results are corrected for SO_3 in the ash.

a) Mean ± standard deviation of results from 9 tests.

TABLE 5

^{1}H-NMR PROTON DISTRIBUTIONS OF FURFURAL EXTRACTION PRODUCTS

			Proton Distribution, %							Phenolic OH Concentration	
Run	Material	Yield, wt %	Condensed Aromatics	Uncondensed Aromatics	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma	Concentration meq/g	ν, cm^{-1}
-	V-1074 feed	---	11.1	3.9	13.9	7.4	15.3	34.9	13.6	0.44	3306
A	Aromatics	57	17.1	8.5	18.8	10	15.2	19.2	11.2		
A	Aliphatics	43	7.5	2.3	8.1	4.9	14.4	47.4	15.3		
B	Aromatics	57	16.6	9.1	18.1	10.6	15.1	18.4	12.2	0.60	3304
B	Aliphatics	43	4.6	2.0	7.6	4.6	14.8	49.5	16.8		

Run A - Trial extraction of 20 g V-1074 with 20 g furfural.[1]
Run B - Extraction of 500 g V-1074 with 500 g furfural in 20 g (V-1074) batches.

TABLE 6

MICROAUTOCLAVE LIQUEFACTION OF BLACK THUNDER COAL

Distillate Component	Conversion, wt %	
	Coal	IOM
V-1074 (Wilsonville Run 262E)[a]	92.3 ±2.4	78.0 ±1.7
Aromatic fraction from furfural extraction	91.8, 91.3	77.4, 78.5

Microautoclave test conditions: 5 min, 824 °F, 1500 psig H_2 (cold), S/C (MF) = 1.5, Wilsonville Run 262E resid and solvent blend ratio used, 1 % WIO and 100 ppm Mo (as Molyvan-L) added as wt % dry coal.

a) Mean ± standard deviation of results from 9 tests.

TABLE 7

TRIAL THERMAL DEWAXING EXPERIMENTS

	V-1074 Feed	Temperature, °F (a)			
		900/890	925/930	950/955	975/979
Gas Yield, wt %	–	1.4	5.6	14.2	18.6
		^{1}H-NMR, %			
Condensed Aromatics	11.1	13.3	18.2	24.9	28.9
Uncondensed Aromatics	3.9	5.2	6.0	9.0	8.3
Cyclic Alpha	13.9	13.1	12.7	12.9	13.2
Alkyl Alpha	7.4	7.5	8.6	10.2	11.7
Cyclic Beta	15.3	13.4	11.6	10.2	10.0
Alkyl Beta	34.9	33.2	28.4	21.5	17.1
Gamma	13.6	14.3	14.4	11.4	10.9

(a) Temperatures shown are the set points and actual temperatures. Heat-up to maximum temperature required approximately 2 min in all cases.

TABLE 8

THERMAL DEWAXING OF WILSONVILLE RUN 262E V-1074 AT 925 °F

	Feed	Gas	700 °F$^-$ distillate	700 °F$^+$ resid
Yield, wt %	100	3.3	19.8	76.1
		^{1}H-NMR, %		
Condensed Aromatics	11.1	–	6.5	23.7
Uncondensed Aromatics	3.9	–	4.0	8.2
Cyclic Alpha	13.9	–	6.2	14.6
Alkyl Alpha	7.4	–	6.8	9.5
Cyclic Beta	15.3	–	11.4	10.2
Alkyl Beta	34.9	–	43.5	23.5
Gamma	13.6	–	21.6	10.3

TABLE 9

MATERIAL BALANCE AND ANALYSES OF SIMULATED LIGHT AND HEAVY DEASHED RESID

Material	Recovery, wt %	Phenolic -OH by FTIR		Proton Distribution, %						
		Concentration, meq/g	Peak Max., cm^{-1}	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
V-130 Deashed Resid (a)	(Starting Material)	0.90	3298	22.7	4.9	19.3	9.3	14.7	19.3	9.7
Light Resid (b)	44.37	0.49	3299	20.1	5.0	14.9	8.5	14.3	25.0	12.1
Heavy Resid (c)	56.45	1.10	3296	26.7	5.1	20.3	9.7	13.9	16.2	8.1
Total	100.82	-	-	-	-	-	-	-	-	-

Notes:

(a) From Wilsonville Run 262, period E; analytical data from the quarterly technical progress report for this contract for the period July 1 through September 30, 1992.
(b) Cyclohexane solubles
(c) Cyclohexane insolubles

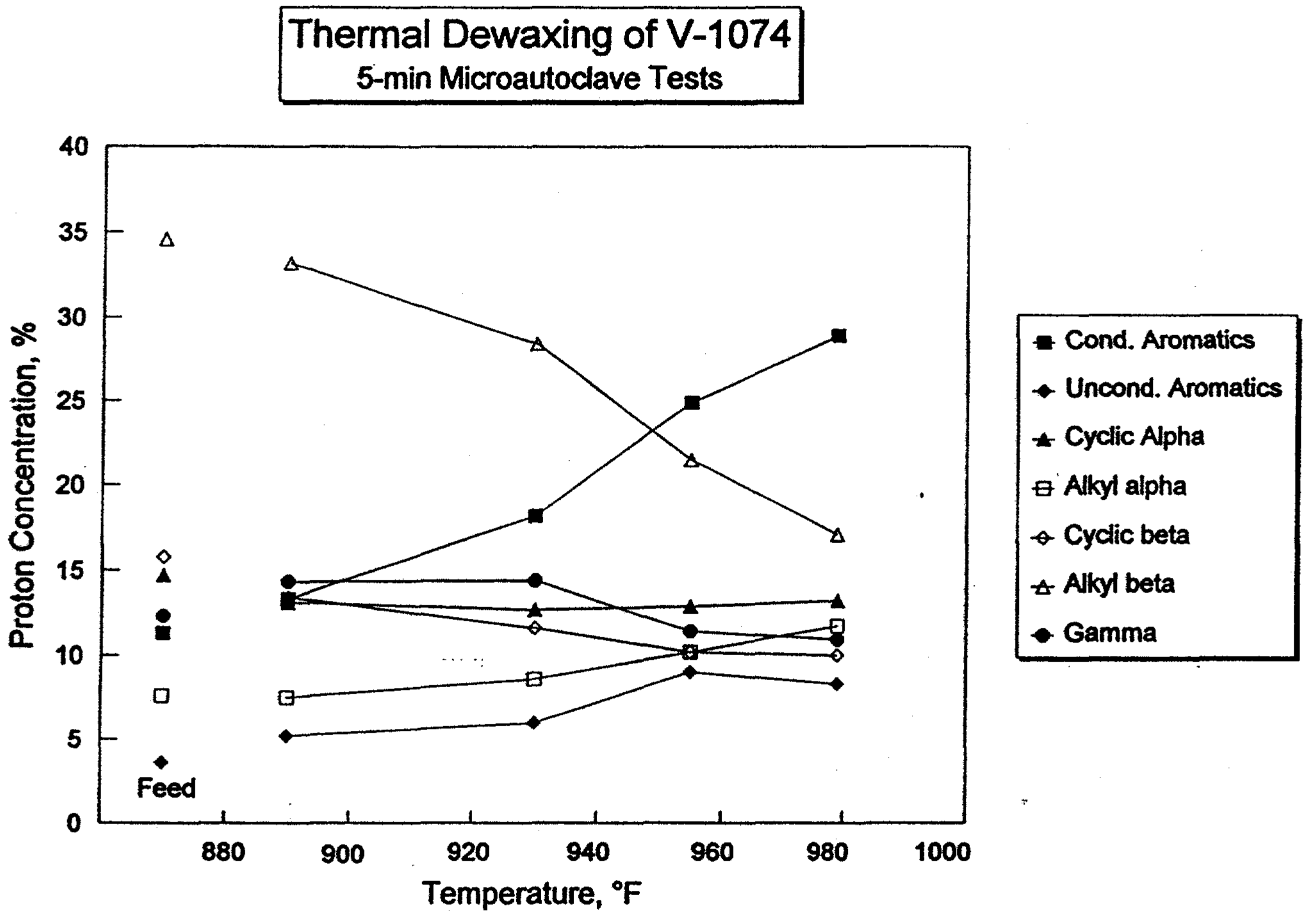

Figure 1. Proton Distributions in Thermally Treated Wilsonville Run 262E Heavy Distillate.

SECTION THREE

LDP ASSOCIATES

LDP ASSOCIATES

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609-586-2301

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

January 20, 1995

Dr. Ed Givens
Center for Applied Energy Research
3572 Iron Works Pike
Lexington, Kentucky 40511-8433

Dear Ed:

Subject: QUARTERLY PROGRESS REPORT FOR OCT. THRU DEC. 1994

For the quarter ending December 31, 1994 the following subcontract services (UKRF-4-25582-92-75) were performed in support of the DOE Advanced Concepts Program (DE-AC22-91PC91040):

BASELINE ECONOMIC ASSESSMENT

A copy of Bechtel's draft report on the Low Rank Coal Study was requested and received from PETC. A review of the report was begun to see its suitability for use as a baseline. Further review is needed to see which, if any, portions of Bechtel's study can be utilized in our required comparative analysis.

ALTERNATE ECONOMIC ASSESSMENT

A case study was begun on CAER's hydrothermal coal pretreatment step based on their latest data.

SOLVENT EXTRACTION OF THE DISTILLATE SOLVENT

The results of CONSOL's batch production tests to produce a 250 gram sample for hydrotreatment was reviewed. SANDIA was contacted in an effort to discuss hydrotreating test conditions.

MISCELLANEOUS

The Phase 2 RFP was received and reviewed. The new stipulation that we directly arrange for the continuous unit testing with a suitable provider led to discussions with potential suppliers. Contact was made with a group led by Al Comolli who are attempting a buyout of HRI's R & D facility. The proposed buyout seems to be progressing, but some issues remain to be resolved.

Marty Poole at Exxon Baton Rouge was contacted on the same subject. Poole requested a brief letter outlining our requirements for continuous bench scale testing (to be prepared & sent by CAER). He would then check with Exxon's management to determine their willingness to work with us.

Very truly yours,

Michael Pel

Michael Peluso
LDP Associates

cc: F. Derbyshire @ CAER
G. Kimber @ CAER
R. Winschel @ CONSOL
F. Stohl @ SANDIA