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"FUNDAMENTAL STUDIES OF RETROGRADE REACTIONS IN DIRECT LIQUEFACTION"

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ABSTRACT

We have tried to get definitive structural information on the C-C-O polymers from a variety of analytical techniques. However, in all cases the results were not conclusive. This lack of confirmation has bothered us. In view of the need for a better characterization of the model polymers before drawing definitive conclusions from liquefaction or pyrolysis results, we have reexamined some of the previous analyses and have conducted further characterization of the C-C-O polymers by elemental analysis and FT-IR spectroscopy.

Liquefaction experiments were repeated at 400°C, 10 minutes for the three raw coals. For the Zap and Illinois coals, the results at 10 minutes were significantly different when compared to the first set of experiments. Since all of these experiments were done shortly before the heater elements failed in the Fluidized Sand Bath (FSB), it was thought that this may have been a contributing factor, since the reproducibility in the past has been quite good for the 30 minute experiments ($\pm 3\%$). The FSB was rebuilt and liquefaction experiments were repeated for a second time at 400°C, 10 minutes for the three raw coals. The results were now in general agreement with the results of the previous set. Consequently, it appears that the results from the first set of experiments were likely affected by the deterioration of the heating elements in the fluidized sand bath (which has since been rebuilt) and these results will not be used.

Work continued on using the AFR FG-DVC liquefaction model to predict the results of the experiments on coals and modified coals from this program. Once the data for the 10 and 20 minute experiments had been verified, as discussed above, we were still left with the problem that the FG-DVC liquefaction model generally overpredicted the yields at short times, but was in good agreement with the 30 minute data. We decided to simulate some literature data which included both time resolution and mixing. Good agreement was obtained with the data of Prasad et al. (1986) for two Australian coals which are similar to Illinois No. 6 and with the data of Foster et al. (1985) on Liddell coal (similar to Pittsburgh No. 8) over a wide range of residence times and temperatures. Consequently, the conclusion is that the yields from our 10 minute experiments are probably mass transfer limited. We will do some additional experiments with shaking of the reactor to verify this.

"FUNDAMENTAL STUDIES OF RETROGRADE REACTIONS IN DIRECT LIQUEFACTION"

**SEVENTH QUARTERLY REPORT
CONTRACT NO. DE-AC22-88PC88814**

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I. INTRODUCTION AND SUMMARY

Introduction

Most of the proposed processing schemes for improving liquefaction yields involve favoring bond-breaking and radical stabilization reactions over the retrograde reactions. The retrograde reactions are often encountered before liquefaction temperatures are reached. The goal of this program is to elucidate and model the retrograde reaction chemistry in direct coal liquefaction through the application of experimental techniques and theoretical models which have been successfully employed at Advanced Fuel Research (AFR) and SRI International (a subcontractor) to understand and predict coal reaction behavior. The program will necessarily include studies of bond-breaking reactions, since these are intimately related to the retrograde reaction chemistry. The information from this program could be used to control and/or optimize liquefaction processes. The program would take advantage of AFR's and SRI's unique and complementary approaches to coal conversion experiments and modeling. The proposed program has two major elements, as described below.

1. Unique Probes - At AFR, Fourier Transform Infrared Spectroscopy (FT-IR) has been used to analyze coals and coal conversion products both for stationary samples and as an on-line diagnostic. At SRI, Field Ionization Mass Spectrometry (FIMS) has been used for direct measurement of the molecular weight and chemical class distributions of coal liquids. Both FT-IR and FIMS have been invaluable tools for following the progress of the thermal reactions in coal conversion systems.

2. Multi-System Approach - We propose to study retrograde reactions by an integrated approach using extensive characterization of the liquefaction chemistry of three kinds of systems: 1) model polymers; 2) coal; and 3) modified coals. Each system has advantages as well as drawbacks. The experience of AFR has primarily been in studying the reaction behavior of coal and model polymers, mainly under pyrolysis conditions, to identify global reactions and transport effects. The experience of SRI has primarily been in studying thermal reactions of model compounds from a chemical mechanism perspective, mainly under liquefaction conditions. Each organization has developed specialized experiments, techniques, and models required to examine, elucidate and describe these systems. The combination of these resources offers a unique opportunity to try to reconcile the often conflicting observations which have been reported from experiments with model compounds and coal.

The results of the experiments in the proposed program will lead to an improved mechanistic understanding of retrograde reaction mechanisms in liquefaction, that can be used

to explore improved process concepts designed to minimize retrograde reactions and, thus, to improve liquefaction yields.

Summary of Work During Seventh Quarter

We have tried to get definitive structural information on the C-C-O polymers from a variety of analytical techniques. However, in all cases the results were not conclusive. This lack of confirmation has bothered us. In view of the need for a better characterization of the model polymers before drawing definitive conclusions from liquefaction or pyrolysis results, we have reexamined some of the previous analyses and have conducted further characterization of the C-C-O polymers by elemental analysis and FT-IR spectroscopy.

Elemental analysis of the poly(4-allylphenol) showed the presence of substantial amounts of nitrogen. FT-IR analysis of the sample also showed the presence of DMF, along with some nitromethane. If we ascribe all of the nitrogen to DMF, the discrepancy between the observed and predicted carbon and oxygen contents is somewhat improved. If we ascribe the nitrogen to nitromethane, the solvent in which the polymerization was conducted, and correct for it, the C, H, and O content of the polymer works out in good agreement with the calculated value.

A second sample of poly(4-allylphenol) was examined which had been phenol terminated. This did not have the same problem with nitrogen contamination, but there was an excess of oxygen which seemed consistent with the incorporation of trifluoroacetic acid during the synthesis procedure. This would explain the production of CO₂ during pyrolysis of the sample in TG-FTIR analysis.

Liquefaction experiments were repeated at 400°C, 10 minutes for the three raw coals. Experiments were also done at 20 minutes with the same set of coals. For the Zap and Illinois coals, the results at 10 minutes were significantly different when compared to the first set of experiments. Since all of these experiments were done shortly before the heater elements failed in the Fluidized Sand Bath (FSB), it was thought that this may have been a contributing factor, since the reproducibility in the past has been quite good for the 30 minute experiments ($\pm 3\%$). The FSB was rebuilt and liquefaction experiments were repeated for a second time at 400°C, 10 minutes for the three raw coals. The results were now in general agreement with the results of the previous set. Consequently, it appears that the results from the first set of experiments were likely affected by the deterioration of the heating elements in the fluidized sand bath (which has since been rebuilt) and these results will not be used.

The liquefaction system is being modified to allow the reactor to be shaken during the experiment. This will allow the assessment of the presence of heat and/or mass transport effects which may be important, particularly in the short contact time experiments. We are also planning to do additional liquefaction experiments with calcium loaded Zap lignite to examine the effects of calcium on the retrogressive reactions.

Work continued on using the AFR FG-DVC liquefaction model to predict the results of the experiments on coals and modified coals from this program. Once the data for the 10 and 20 minute experiments had been verified, as discussed above, we were still left with the problem that the FG-DVC liquefaction model generally overpredicted the yields at short times, but was in good agreement with the 30 minute data. We decided to simulate some literature data which included both time resolution and mixing. Good agreement was obtained with the data of Prasad et al. (1986) for two Australian coals which are similar to Illinois No. 6 and with the data of Foster et al. (1985) on Liddell coal (similar to Pittsburgh No. 8) over a wide range of residence times and temperatures. Consequently, the conclusion is that the yields from our 10 minute experiments are probably mass transfer limited. We will do some additional experiments with shaking of the reactor to verify this.

II. TASK 1 - WORK PLAN

This task has been completed.

III. TASK 2 - STUDIES WITH POLYMERIC MODEL COMPOUNDS

A paper on the synthesis, characterization, and liquefaction of the C-C-O bridged polymers was presented at the ACS National Meeting in Boston. This presentation provided an opportunity to re-examine the data collected thus far (either at SRI or at AFR) and summarize our current understanding. Some important observations regarding conversion of the C-C-O bridged polymers include the following:

- Only small amounts of oligomers are produced during pyrolytic characterization in FIMS or in a TGA.
- FI-mass spectra are dominated with peaks due to simple alkylated phenols and catechols.
- TGA-FTIR analysis shows production of CO₂ although the polymers contain no carboxyl groups.
- CO₂ production correlates with oligomer production but not with catechol production; catechol production correlates with H₂O production.
- Liquefaction of these polymers in a potent donor solvent like dihydrophenanthrene results in very little hexane-solubles, in contrast to bibenzyl polymers.

From our study, we conclude that:

- The C-C-O bridged polymers are very reactive, but because of crosslinking, they are not easily converted.
- The formation of phenols and catechols, as opposed to larger oligomeric products, are consistent with the great proclivity of these polymers to undergo crosslinking, but the result is not quantitatively rationalizable.

We suspect that the differing behavior of the polymeric models and phenyl phethyl ether (PPE), which undergoes facile cleavage to phenol and styrene, may lie in the extra oxygen that is present in the polymers and whether or not it is present as a free hydroxy or an ether. At the ACS meeting, Dr. Klein informed us of his recent work on lignin models, in which he noted preferential cleavage of the PPE-bridges when there was an extra hydroxyl group present.

We have tried to get definitive structural information on the C-C-O polymers from a variety of analytical techniques. However, in all cases the results were not conclusive. This lack of confirmation has bothered us. In view of the need for a better characterization of the model polymers before drawing definitive conclusions from liquefaction or pyrolysis results, we have reexamined some of the previous analyses and have conducted further characterization of the C-C-O polymers by elemental analysis and FT-IR spectroscopy.

With regard to the elemental composition, our problem lies with the inability to purify the polymer products. For both of the C-C-O bridged polymers, we observed a substantially greater oxygen content than expected from the respective formulas. Polymers that are prepared in solvents often give erroneous elemental analyses because of the difficulty of removing all the solvent. In our case, the polymers were soluble only in DMF, which is particularly hard to remove. Elemental analysis of the poly(4-allylphenol) showed the presence of substantial amounts of nitrogen. FT-IR analysis of the sample also showed the presence of DMF, along with some nitromethane. If we ascribe all of the nitrogen to DMF, the discrepancy between the observed and predicted carbon and oxygen contents is somewhat improved. If we ascribe the nitrogen to nitromethane, the solvent in which the polymerization was conducted, and correct for it, the C, H, and O content of the polymer works out in good agreement with the calculated value:

	<u>C</u>	<u>H</u>	<u>O</u>	<u>N</u>
Observed	69.04	6.12	20.05	4.75
Corrected (for CH ₃ NO ₂)	81.85	6.43	11.72	
Calculated	80.59	7.46	11.94	

A similar analysis for the poly(eugenol) sample results in only a marginal improvement, which basically means that there might be other contaminants. Consequently, we focused on the further analysis of a phenol-terminated poly(4-allylphenol) because of its solubility in many solvents. The sample analyzed was 8874-25, which was also studied by AFR using TG-FTIR. The elemental analysis of the sample 8874-25 (oxygen by direct determination) as such, and after dissolution in methanol followed by precipitation with ether and rigorous drying were found to be as follows:

	<u>C</u>	<u>H</u>	<u>O</u>	<u>N</u>
8874-25	71.80	6.07	13.79	0.75
8874-25 Washed	71.19	6.01	14.48	0.65
Calculated	80.59	7.46	11.94	

There is very little nitrogen in these samples compared to those found in the other sample of poly(4-allylphenol), discussed above. However, there is some excess of oxygen and the observed CHNO values add up to only about 92%. There was no residue, thus the missing 8% is not due to a metal; it could be halogen, possibly fluorine from incorporation of trifluoroacetic acid. Trifluoromethane has been seen in TG-FTIR, a fact that further supports this hypothesis. By assuming 8% fluorine in the sample, we can calculate the frequency of incorporation of trifluoromethyl residues to be approximately one every five monomers. If we further assume that fluorine was incorporated as trifluoroacetate groups, the fractional weight of carboxyl functions (CO_2) in the polymer calculates out to about 3.5%, a number that is not inconsistent with the weight of CO_2 observed in TG-FTIR.

IV. TASK 3 - STUDIES WITH COALS AND MODIFIED COALS

Liquefaction experiments were repeated at 400°C, 10 minutes for the three raw coals. Experiments were also done at 20 minutes with the same set of coals. For the Zap and Illinois coals, the results at 10 minutes were significantly different when compared to the first set of experiments. Since all of these experiments were done shortly before the heater elements failed in the Fluidized Sand Bath (FSB), it was thought that this may have been a contributing factor, since the reproducibility in the past has been quite good for the 30 minute experiments ($\pm 3\%$). The FSB was rebuilt and liquefaction experiments were repeated for a second time at 400°C, 10 minutes for the three raw coals. The results were now in general agreement with the previous set (± 3 wt.%), which were significantly different when compared to the first set of experiments. The results of the repeats of the 10 minute experiments with the three raw coals have now been added to Table IV-3 of the Sixth Quarterly (replacing the original 10 minute data), which is included as Table IV-1 in the current report. Consequently, it appears that the results from the first set of experiments were likely affected by the deterioration of the heating elements in the fluidized sand bath (which has since been rebuilt) and these results will not be used.

There is still more variation with the 10 minute experiments than with the 30 minute experiments. This is likely due to the fact that the former experiments are more sensitive to temperature fluctuations. The short time experiments would also be more sensitive to mass transfer effects. For this reason, the liquefaction system is now being modified to allow the reactor to be shaken during the experiment. This will allow the assessment of the presence of heat and/or mass transport effects which may be important, particularly in the short contact time experiments.

Samples of calcium-loaded demineralized Zap lignite were prepared under our other program (Fundamental Studies of Water Pretreatment of Coal). Surprisingly, the calcium addition did not reduce the tar yield from TG-FTIR analysis, which was the case for the calcium-loaded ion-exchanged coal. It is possible that the severe (HCl/HF) demineralization process changes the coal such that the calcium cannot be put back in the same way. Additional characterization of the calcium-loaded Zap by FT-IR analysis is planned.

We do not currently have enough of the calcium loaded samples to do liquefaction experiments. An additional shipment of the Argonne Zap coal has been ordered for this purpose. We are also planning to do liquefaction experiments with calcium loaded (mild) acid washed Zap to see if the severity of the demineralization process has an effect on how the calcium goes onto the coal.

TABLE IV-1 - LIQUID AND GASEOUS PRODUCT YIELDS FROM LIQUEFACTION EXPERIMENTS
IN DHP DONE AT SHORT TIMES (10 MIN.)

(All Product Yields are DAF wt.%)

Coal Preparation	Total	T _s	Oils	T _i	P _s	P _i	Gas	D _H	H ₂	C ₂ H ₂	C ₂ H ₄	CH ₄	C ₂ H ₆	C ₂ H ₈	C ₂ H ₁₀	H ₂ S
Zap																
fresh																
a)	11	9	87	19	79	2.1	0.055	0.00	1.99	0.08	0.00	0.00	0.00	0.00	0.00	0.00
b)	7	4	90	21	77	2.5	—	0.03	2.29	0.15	0.00	0.01	0.00	0.00	0.00	0.00
vacuum dry	9	7	89	16	82	2.4	0.041	0.02	2.24	0.13	0.01	0.01	0.00	0.00	0.00	0.00
ion-exchanged (new)	22	1	76	53	45	2.5	0.038	0.01	2.24	0.14	0.33	0.06	0.01	0.00	0.00	0.00
demineralized	14	1	84	43	56	2.6	0.061	0.03	2.31	0.19	0.01	0.04	0.00	0.00	0.00	0.00
methylated	23	9	76	59	40	1.1	0.015	0.00	0.99	0.07	0.05	0.00	0.00	0.00	0.00	0.00
Wyodak																
fresh																
a)	11	7	89	24	76	0.7	0.034	0.00	0.65	0.03	0.00	0.00	0.00	0.00	0.00	0.00
b)	17	10	81	43	54	2.5	0.056	0.03	2.26	0.12	0.00	0.06	0.00	0.00	0.00	0.00
vacuum dry	2	0	97	15	85	0.8	0.057	0.00	0.75	0.03	0.00	0.00	0.00	0.00	0.00	0.00
ion-exchanged (new)	2	0	97	10	89	0.6	0.067	0.00	0.61	0.03	0.00	0.00	0.00	0.00	0.00	0.00
demineralized	24	16	74	58	40	2.5	0.030	0.03	2.20	0.21	0.03	0.07	0.00	0.00	0.00	0.00
methylated	31	11	68	88	11	1.2	0.014	0.03	0.88	0.09	0.16	0.05	0.00	0.00	0.00	0.00
Illinois No. 6																
fresh																
a)	12	5	88	62	38	0.1	0.033	0.00	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.06
b)	12	3	88	80	19	0.4	0.066	0.02	0.27	0.02	0.06	0.00	0.00	0.07	0.01	0.00
vacuum dry	10	3	89	46	54	0.4	0.022	0.00	0.05	0.00	0.00	0.06	0.00	0.32	0.00	0.00
ion-exchanged (new)	27	15	72	95	4	0.7	0.023	0.03	0.17	0.02	0.00	0.06	0.01	0.00	0.00	0.47
demineralized	10	1	89	11	89	0.2	0.029	0.00	0.16	0.01	0.00	0.00	0.00	0.00	0.00	0.06
methylated	34	14	65	95	4	1.3	0.025	0.09	0.15	0.03	0.61	0.11	0.01	0.01	0.00	0.34

Notes: Experimental conditions: 400°C, 10 min.

* Asphaltene fraction only

T_s = Toluene Solubles
T_i = Toluene Insolubles
P_s = Pyridine Solubles
P_i = Pyridine Insolubles
D_H = Hydrogen Transfer Index = 2 DHP/180/T_s

V. TASK 4 - DATA EVALUATION AND REPORTING

Work continued on using the AFR FG-DVC liquefaction model to predict the results of the experiments on coals and modified coals from this program. Once the data for the 10 and 20 minute experiments had been verified, as discussed under Task 3 (Section IV), we were still left with the problem that the FG-DVC liquefaction model generally overpredicted the yields at short times, but was in good agreement with the 30 minute data. We decided to simulate some literature data which included both time resolution and mixing. Good agreement was obtained with the data of Prasad et al. (1) for two Australian coals which are similar to Illinois No. 6. These comparisons are shown in Fig. V-1. The data were taken over a range of residence times from 100 to 3600 s and over a range of temperatures from 380 to 420°C. Equally good agreement was obtained with the data of Foster et al. (2) on Liddell coal (similar to Pittsburgh No. 8) over a range of residence times from 100 to 1200 seconds and temperatures from 380 to 420°C. These comparisons are shown in Fig. V-2. Consequently, the conclusion is that the yields from our 10 minute experiments are probably mass transfer limited. We will do some additional experiments to verify this.

A simulation was also made of the data of Derbyshire and Whitehurst (3) on the conversion of coals of a wide range of ranks to pyridine solubles in a non-donor solvent system. The predictions followed the correct trend with rank but were somewhat lower, as shown in Fig. V-3 (solid triangles). This would suggest that the model is not as good in non-donor solvent systems and/or there were some other conditions present in these experiments that the model does not account for.

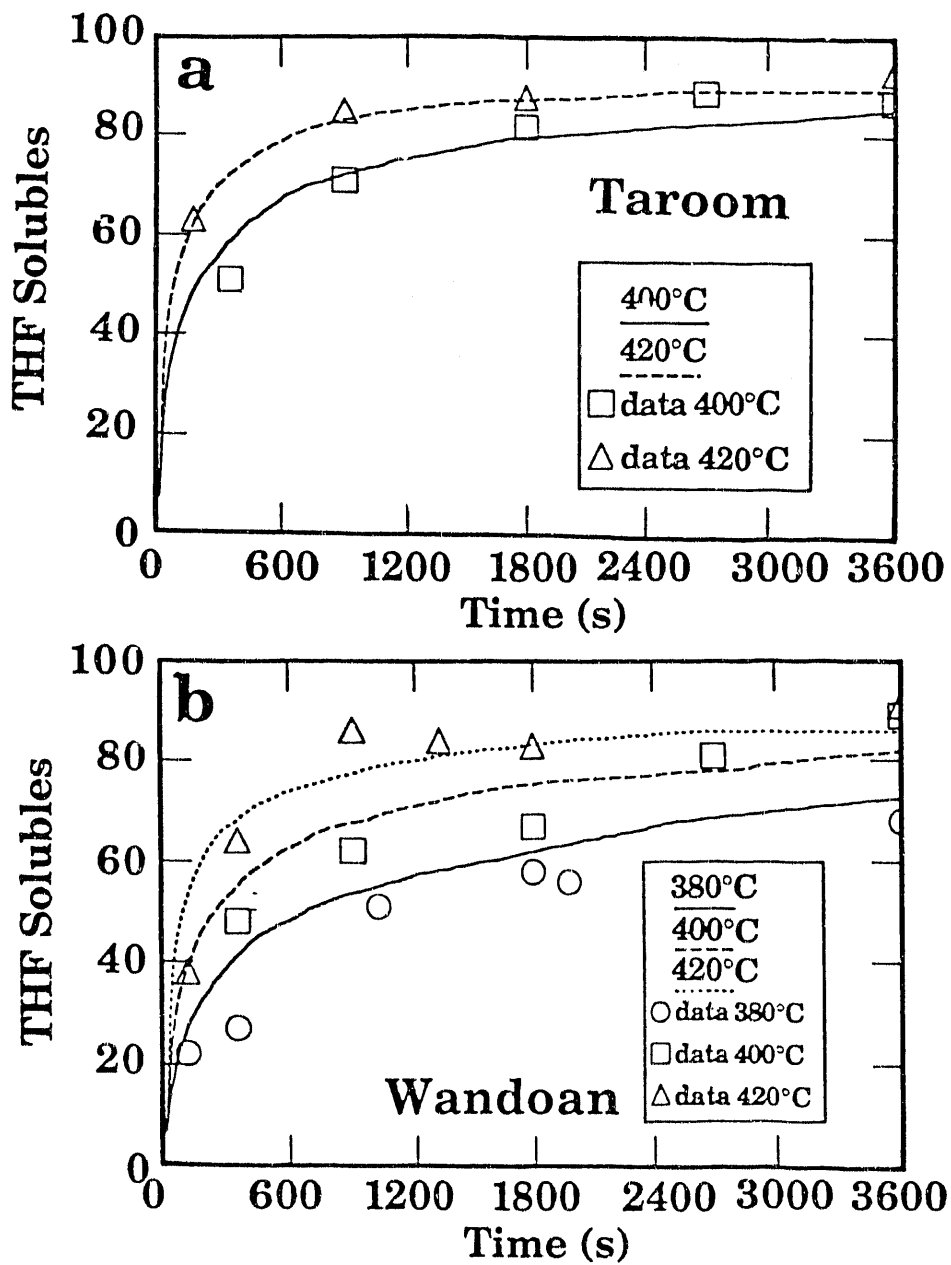


Figure V-1. Comparison of FG-DVC Liquefaction Model Predictions with Literature Data for Two Australian Coals. Data from Ref. 1.

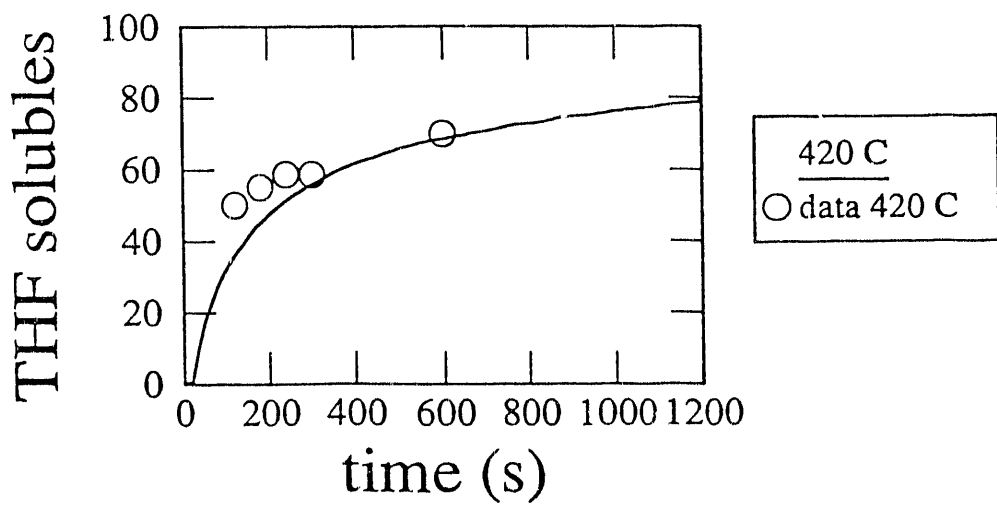
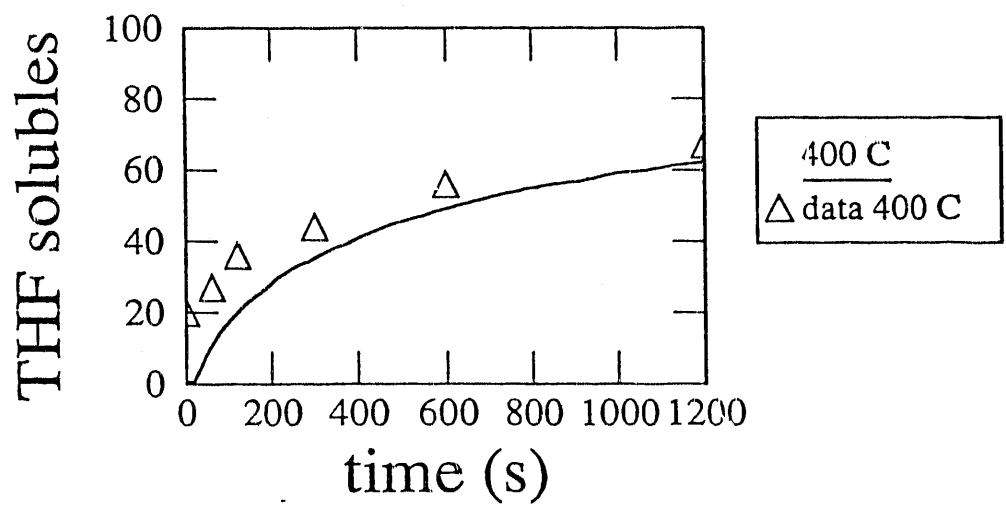
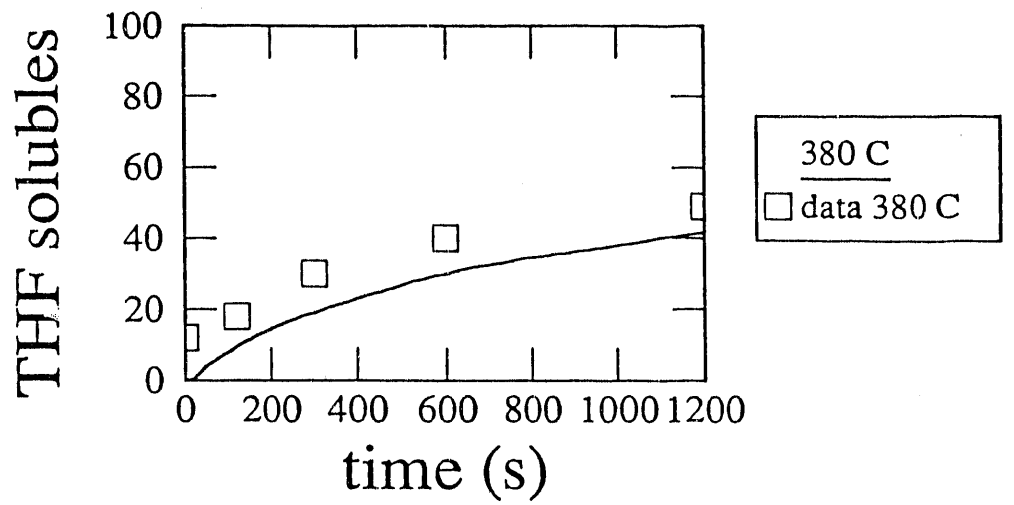


Figure V-2. Comparison of FG-DVC Liquefaction Model Predictions with Literature Data for Liddell Coal. Data from Ref. 2.

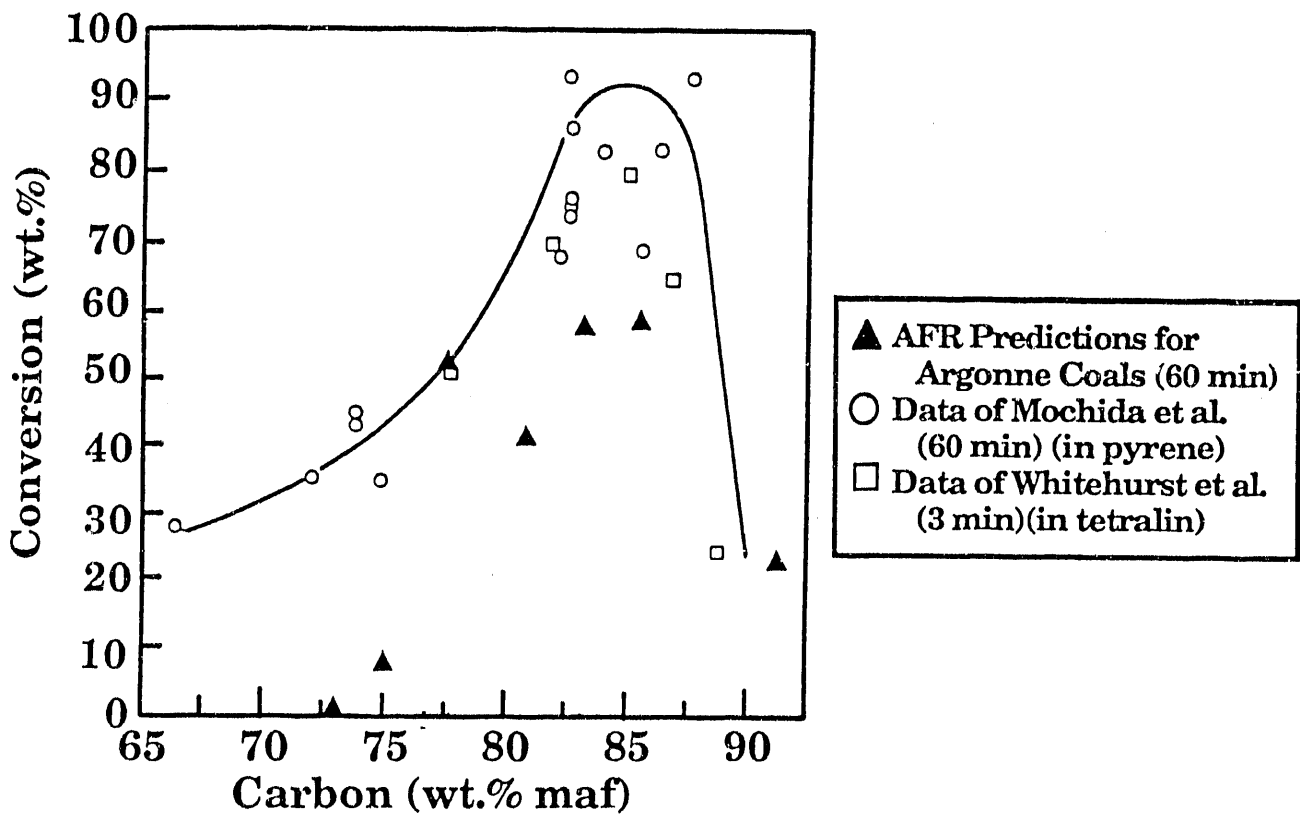


Figure V-3. Coal Conversion to Pyridine Solubles in a Non-Hydrogen Donor Solvent. Figure adapted from Ref. 3.

VI. PLANS FOR EIGHTH QUARTER

The plans for the Eighth Quarter are as follows:

- Produce a lower MW fraction of one of the C-C-O polymers, poly(4-allylphenol), by fractional precipitation. Characterize to verify structure and subject to liquefaction experiments.
- Do selected liquefaction experiments on coals and modified coals which include shaking.
- Do selected liquefaction experiments on calcium loaded Zap lignite starting from demineralized, acid washed, and ion-exchanged coal.
- Complete work on a sensitivity analysis of the FG-DVC liquefaction model.
- Complete work on modeling coal liquefaction results including literature data.
- Evaluate our data and literature data on the effect of minerals in promoting retrogressive reactions.
- Try to explain the role of CO₂ evolution, carboxyl group decomposition, and ion-exchanged cations in retrogressive reactions during liquefaction of low rank coals.

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