

## Laboratory Batch Liquefaction of Low Rank Coals

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### INTRODUCTION

Laboratory autoclave studies of low rank coals, particularly lignitic coals, have been conducted in the Department of Chemical Engineering at the University of North Dakota over a period of nearly 15 years. Recent research work is focused on providing process support data for the "surviving" liquefaction technologies with particular emphasis on western low rank coals. Early work in the current program was directed to screening several liquefaction solvents. Two solvents were selected for subsequent work; one was a distilled anthracene oil (AOD1 and AOD2) and the second was hydrogenated distilled anthracene oil.

One of the objectives of the research program is to study the effect on liquefaction yields of the identity and quantity of mineral constituents of the coal.

Five North Dakota lignites (Beulah, Gascoyne, Zap, Larson, and Velva), three Montana or Wyoming subbituminous coals (Absaloka, Wyodak, and Decker), and a single Alaska subbituminous coal (Usibelli) were investigated. Analyses of the coals and of the coal ashes are given in Tables 1 and 2, respectively. The elements often considered to be important in liquefaction are iron, calcium, magnesium, sodium, potassium, and sulfur. There is a considerable body of opinion that the various forms of iron sulfides are the primary catalysts in liquefaction. Tables 1 and 2 show that the high ash lignite (BEU 3) and subbituminous (ABS 1) are also high in both iron and sulfur, while the calcium and magnesium contents are in the range of the other coals. The sodium level is relatively high for the Beulah (BEU 3) and Zap lignites, and for the Absaloka coal when it is compared with the other subbituminous coals.

### PRODUCT AND SLURRY ANALYSES

Analyses of liquefaction solvent and of reaction products are largely physical in nature. Solvent and slurry are characterized by vacuum distillation (ASTM-D-1160) and by dissolution of the undistillable portion in tetrahydrofuran (THF). Slurry material not soluble in THF was considered to be unconverted lignite or ash, and the ash was determined independently.

Three distillate fractions were determined in the vacuum (5 torr) distillation. These were the initial boiling point (IBP) to 120°C - light oil; 120°C to 260°C - middle oil; and the fraction distilled above 260°C - heavy oil. The THF soluble, but nondistillable, portion of the product slurry was called soluble residuum. Condensable vapors that were discharged with the reactor gases were collected in cold traps and are also considered to be light oils. It will be noted that the solvents consist primarily of material in the middle oil range. For purposes of data reduction it was assumed the ash was unchanged during the reaction.

### EXPERIMENTAL RESULTS

#### Cold Charge Autoclave

In cold charge autoclave experiments, solvent, lignite, and gas (nominally

an equimolar mixture of CO and H<sub>2</sub>) were charged to the autoclave. The autoclave was heated to the desired reaction temperature at the rate of approximately 3°C/minute. When the maximum temperature was reached the power was immediately shut off. Reactor gases were discharged through cold traps when the reactor temperature dropped to 400 F.

Figures 1 and 2 show the effects of maximum reactor temperature on the product distribution when using Velva lignite in the cold charge autoclave. Distilled anthracene oil (AOD 1) was used as the solvent for the runs presented in Figure 1, while hydrogenated anthracene oil (HAD 29) was the solvent for the data shown in Figure 2. As the temperature exceeds 420°C, the yields of gas and light oil increase, while the heavier distillate yields decrease dramatically and the overall conversion is unchanged or slightly diminished. This indicates that heavier products (soluble residuum and heavier distillates) are converted to lighter products, but some of the solvent or products are polymerized, coked, or charred and thus rendered insoluble in THF. Figures 3 and 4 show the results obtained when using Absaloka subbituminous coal at the same temperatures and with the same solvents. The same general observations can be made although there are some differences apparent between the lignite and the subbituminous coal. The results for the various products of the two types of coal are shown in Figure 5 through Figure 10.

Figure 5 shows that the yield of soluble residuum is high at the lower temperatures, but decreases with increasing temperature for the Absaloka coal, while the soluble residuum yield reaches a maximum at about 420°C for Velva lignite. Additionally, the overall conversion of Absaloka coal is largely unaffected by reaction temperature, but the conversion increases from 69 percent to 89 percent when reaction temperature is raised from 380°C to 420°C for the lignite. Differences in the yields of THF soluble product and of distillate show a greater effect of reaction temperature for the lignite than for the subbituminous coal (Figure 6). The yields of the components of the distillate products follow similar trends although the yield of the middle and heavy oil fraction shows greater variation with temperature changes for the lignite coal (Figure 7).

Figures 8, 9, and 10 show the same general trends when hydrogenated anthracene oil (HAD 29) was the solvent and the same two coals were used.

The highest distillate yield obtained was with Zap lignite using the distilled anthracene oil solvent (AOD 1), while the Larson and Beulah lignites showed the lowest distillate yields. The overall conversion was also highest for Zap lignite. Changing to the hydrogenated solvent (HAD 29) caused a decrease in distillate yield for Beulah lignite, while the yield of gas increased. Overall conversion increased slightly, and the yield of soluble residuum was nearly constant. It appears that distillate (including solvent) was converted to lighter products while other products were unaffected. For the Larson and Velva lignites, the distillate and gas yields and the overall conversion increased, and the yield of soluble residuum decreased.

Comparing the conversion and product yields when using the anthracene oil solvent (AOD 1) for North Dakota lignites and for the subbituminous coals show that the conversion of lignite is generally higher. Correspondingly, the distillate yields are higher for lignite. Changing to the hydrogenated solvent (HAD 29) caused the conversion for the subbituminous coals to increase noticeably; the conversion of lignite increased, but to a lesser extent. Thus, it appears that the presence of a solvent containing greater amounts of hydrogen has a greater effect on the higher rank (subbituminous) coal.

Although the coal screening work has not been completed, results obtained so far do not seem to indicate a positive relation between ash content of the feed coal and overall conversion or production of distillate product. More work will be done

in looking at the effects of the various ash constituents on conversion and yields.

#### Hot Charge Autoclave

Gas (equimolar CO/H<sub>2</sub> mixture) and the solvent/coal slurry were charged to the hot one-gallon autoclave, and periodic samples of both reactor gas and slurry were taken during a run. The same lignites and subbituminous coals and the same solvents were studied. Nominal temperatures were 420°C and 460°C.

Recovery of products on the hot charge system ranged from 88.0 to 96.5 percent, with closure generally in the 92 to 95 percent range. Failures in the runs were generally caused by plugging in the slurry sampling system. In some of the runs, the time samples exhausted the product slurry, so that no end-of-run results were obtained. In other runs, the sampling system plugged so that all of the time samples were not obtained, but end-of-run results could be determined. It is interesting to note that with Decker subbituminous coal and hydrogenated solvent the sampling system plugged each time a run was attempted. However, some end-of-run results were obtained.

The end-of-run data for Beulah, Velve, Larson, and Gascoyne lignites and for Wyodak and Absaloka subbituminous coals are shown in Figures 11 and 12, where yields of distillable oil, soluble residuum, and unconverted coal are plotted against temperature over the range 420° to 460°C. The most obvious difference is the much higher conversion (lower yield of unconverted coal) and much higher yields of distillable oil realized with the hydrogenated solvent HAD 20 as compared with the unhydrogenated anthracene oil, AOD 1 or 2. When comparing results with the different coals, first with the hydrogenated and then with the unhydrogenated solvents, there appears to be little significant difference between any of them. However, the data from the slurry time samples show some differences between lignites and between the two subbituminous coals.

The results of the slurry time sample data were calculated on an MAF coal basis on the assumption that the ash content of the slurry sample is the same as the total ash in the coal charged (this is the so-called "ash-conversion"). This is not strictly accurate, but information on trends was obtained by cross-averaging the data for the three lignites and for the two subbituminous coals for each solvent at each of the two temperatures.

The averaged data are plotted in Figure 13 for the lignites and in Figure 14 for the subbituminous coals. At the lower temperature of 420°C with both solvents and both coals, total conversion (THF solubles and lighter) increases with time, whereas the conversion to distillates and lighter decreases slightly with time. There appears to be no significant difference, considering the scatter of the data, between the lignites and the subbituminous coals. At the higher temperature of 460°C, with the unhydrogenated solvent, total conversion is initially high with the lignites and then decreases, whereas with the subbituminous coals it increases to a maximum and then decreases with time. With the hydrogenated solvent, conversion of the lignites increases with time, whereas conversion of the subbituminous coals is initially high and remains high. The apparent decreasing conversion is the result of repolymerization or condensation reactions to produce THF insolubles occurring to a greater extent than the solubilization reactions.

Here again, future work will be concerned with the effects of the mineral matter constituents on conversion and yield distribution.

TABLE 1  
ANALYSES OF COALS

Mine	S. Beulah	Peerless	Moontan	Velva	Indianhead	Woodak	Absaloka	Decker No. 1	Usibelli
Town	Beulah	Gascoyne	Larson	Velva	Zap	Gillette	Sarpy Creek	Decker	Usibelli
County	Mercer	Bowman	Burke	Hard	Mercer	Campbell	Big Horn	Big Horn	(Nenana Dist.)
State	N. Dak.	N. Dak.	N. Dak.	N. Dak.	N. Dak.	Wyoming	Montana	Montana	Alaska
Abbreviation I. D.	Beu 2	Gas 1	Lar 1	Vel 1	Zap 1	Wyo 1	Abs 1	Dec 1	Usi 1
Grand Forks No.	77-0712	78-4555	78-4867	78-4866	78-4868	78-4467	78-4557	78-4558	
Sample Date	2/77	10/78	11/78	11/78	11/78	7/78	10/78	10/78	
Bin No.	3518	3528	3499	3514	3519	3500	3527	3530	Drum
<u>Proximate Analysis</u>									
<u>As Received</u>									
Ash, Wt %	7.05	7.90	6.71	5.69	8.10	5.82	16.01	4.41	8.03
Moisture, Wt %	25.59	27.81	29.68	32.30	27.19	25.91	19.70	21.05	23.66
Volatile Matter, Wt %	39.47	32.96	31.37	32.94	37.75	38.63	28.94	34.45	
Fixed Carbon, Wt %	27.89	31.33	32.24	29.07	26.96	29.64	35.35	40.09	
Heating Value, Btu/lb	7515	7859	7833	7415	8154	8743	8314	9772	8006
<u>MF Basis</u>									
Ash, Wt %	9.47	10.94	9.54	8.40	11.12	7.86	19.94	5.59	10.52
Heating Value, Btu/lb	10100	10886	11139	10953	11199	11800	10354	12378	10492
<u>Ultimate Analysis</u>									
<u>MAF Basis</u>									
Carbon, Wt %	72.74	65.44	60.81	72.27	68.12		73.84		
Hydrogen, Wt %	5.78	5.14	5.65	4.29	4.29		4.45		
Nitrogen, Wt %	0.66	0.76	0.93	1.08	1.14		0.98		
Sulfur, Wt %	1.05	1.74	0.38	0.63	1.13		0.93		
Oxygen, Wt % (by difference)	20.97	26.92	32.73	21.47	25.32		19.80		
Heating Value, Btu/lb	11157	12223	12314	11957	12807		12933	13111	11726
H/C Ratio	0.96	0.94	1.11	0.76	0.76		0.72		

TABLE 2  
ANALYSES OF COAL ASHES

Mine	S. Beulah	S. Beulah	Peerless	Noonan	Veiva	Indianhead	Wyotak	Abasioka	Decker No. 1	Usibelli
Town	Beulah	Beulah	Gascoyne	Larson	Veiva	Zap	Gillette	Sarpy Creek	Decker	Usibelli
County	Mercer	Mercer	Bowman	Burke	Ward	Mercer	Campbell	Big Horn	Big Horn	(Nenana Dist.)
State	N. Dak.	N. Dak.	N. Dak.	N. Dak.	N. Dak.	N. Dak.	Wyoming	Montana	Montana	Alaska
Abbreviation I.D.	Beu 2	Beu 3	Gas 1	Lar 1	Vel 1	Zap 1	Wyo 1	Abus 1	Dec 1	Usi 1
Grand Forks No.	77-0712	78-4356	78-4355	78-4867	78-4866	78-4868	78-4467	78-4357	78-4558	
Sample Date	2/77	10/78	10/78	11/78	11/78	11/78	7/78	10/78	10/78	10/78
Bin No.		3518	3528	3499	3514	3519	3500	3527	3530	Drum
Ash Content, Mt %	7.18	13.44	7.49	6.60	5.15	8.56	5.76	15.51	4.32	6.15
As Received	10.02	19.95	13.09	9.76	8.25	13.41	8.23	19.72	5.55	27.80
Dry Basis										
Ash Composition										
Oxides as Mt % of Ash										
SiO <sub>2</sub>	6.7	27.6	29.8	31.8	19.6	26.2	33.8	45.9	24.9	31.9
Al <sub>2</sub> O <sub>3</sub>	40.9	14.0	19.4	18.5	12.7	10.7	16.7	21.9	19.5	17.5
Fe <sub>2</sub> O <sub>3</sub>	18.4	14.2	2.0	5.0	5.8	14.0	5.1	11.3	11.9	7.7
TiO <sub>2</sub>	0.2	0.6	0.9	0.9	0.4	0.5	1.0	0.8	1.2	0.8
P <sub>2</sub> O <sub>5</sub>	0.2	0.2	0.2	0.4	0.6	0.4	1.4	0.1	1.7	1.4
CaO	12.1	14.5	22.9	23.2	36.0	16.0	22.5	7.5	15.1	28.3
MgO	3.3	3.9	6.9	6.3	10.2	4.9	6.5	1.7	2.9	4.8
Na <sub>2</sub> O	2.8	5.5	3.3	3.5	2.1	8.0	1.8	2.9	6.5	0
K <sub>2</sub> O	0.1	0.4	0.2	0.4	0.3	0.9	0.3	0.9	0.4	1.0
SO <sub>3</sub>	15.3	19.1	14.4	10.0	12.3	18.4	10.9	7.0	15.9	6.6
Metals as Mt % of MF Coal										
Si	0.31	2.57	1.82	1.45	0.76	1.64	1.50	4.22	0.65	1.27
Al	2.17	1.47	1.34	0.96	0.55	0.76	0.73	2.29	0.57	0.79
Fe	1.29	1.96	0.18	0.34	0.33	1.32	0.29	1.56	0.46	0.46
Ti	0.01	0.07	0.07	0.05	0.02	0.04	0.05	0.09	0.04	0.04
P	0.01	0.02	0.01	0.02	0.02	0.02	0.05	0.01	0.04	0.05
Ca	0.86	2.06	2.14	1.62	2.12	1.53	1.32	1.06	0.60	1.72
Mg	0.20	0.47	0.54	0.37	0.50	0.39	0.32	0.20	0.10	0.25
Na	0.21	0.82	0.32	0.25	0.13	0.79	0.11	0.43	0.27	0
K	0.01	0.02	0.02	0.03	0.02	0.09	0.02	0.14	0.02	0.07
S	0.61	1.52	0.75	0.39	0.41	0.99	0.36	0.55	0.35	0.22

Figure 1  
 Liquefaction of Valva Lignite with Distilled  
 Crowley Chilled Anthracene Oil (ACD 1) 50/50  
 $H_2/CO$  3200 - 4000 psig

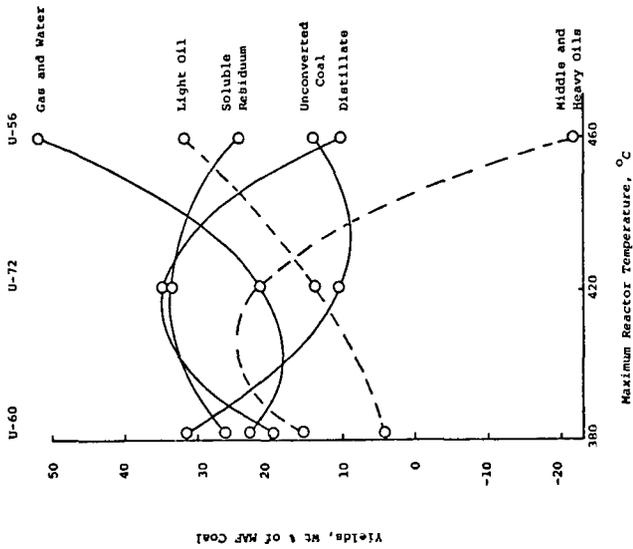


Figure 2  
 Liquefaction of Valva Lignite with Hydrocracked  
 Distilled Crowley Chilled Bathracene Oil (HMD 29)  
 $H_2/CO$  4000 - 4200 psig

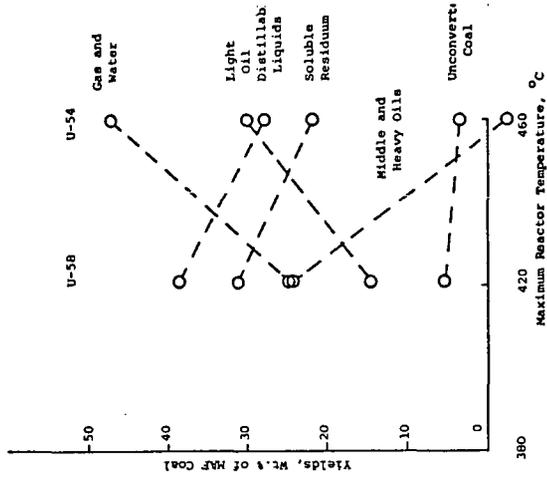


Figure 3

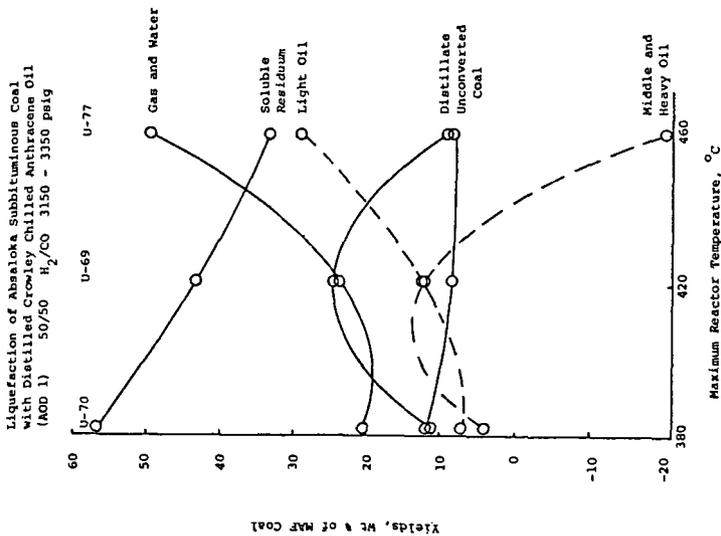
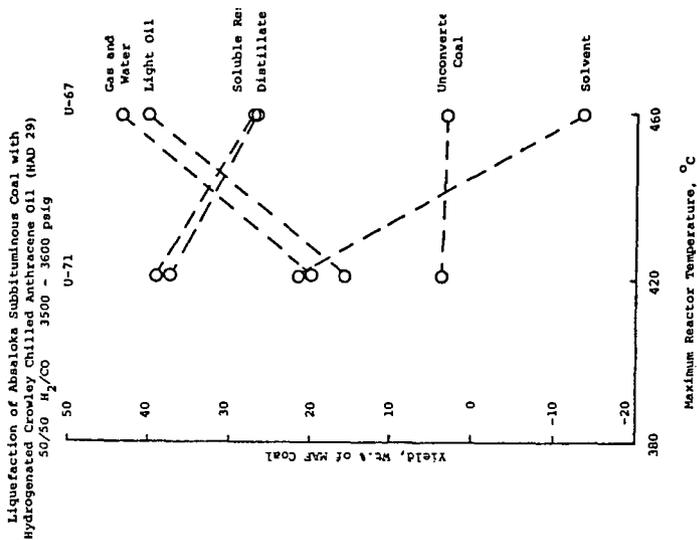


Figure 4



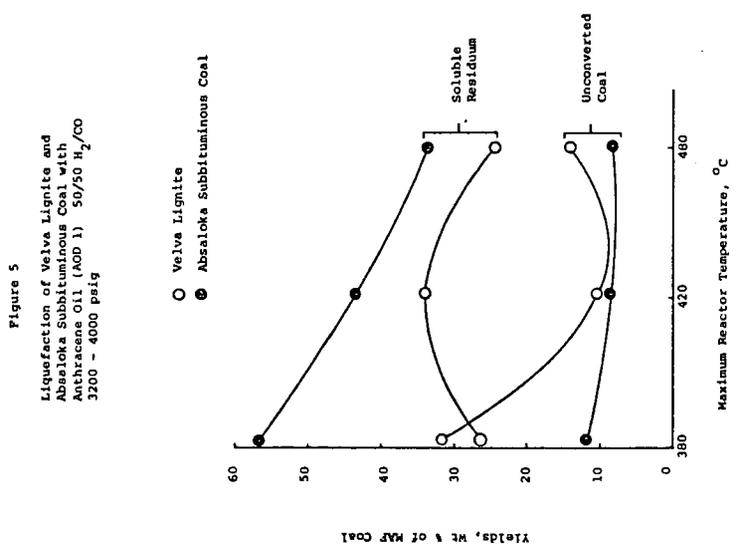
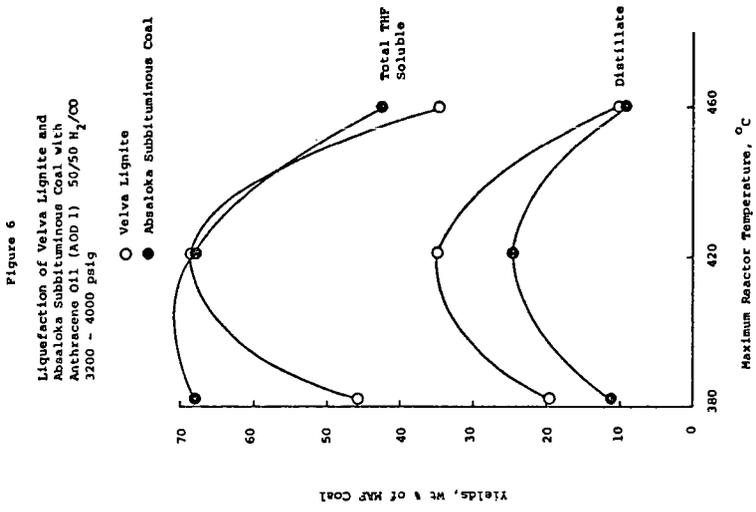


Figure 7  
 Liquefaction of Velve Lignite and Absaloka  
 Subbituminous Coal with Anthracene Oil (MOD 1)  
 50/50 H<sub>2</sub>/CO 3200 - 4000 psig

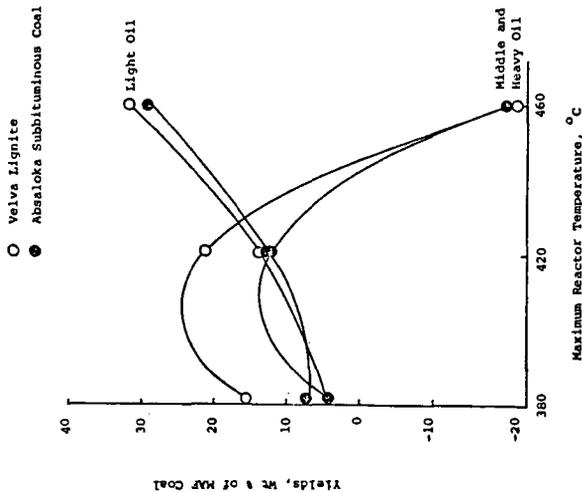


Figure 8  
 Liquefaction of Velve Lignite and Absaloka  
 Subbituminous Coal with Hydrogenated Anthracene Oil (MOD 29)  
 50/50 H<sub>2</sub>/CO 3500 - 4200 psig

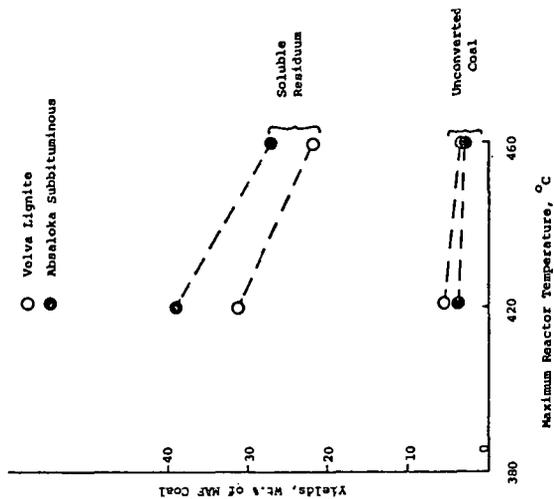


Figure 9

Liquefaction of Velva Lignite and Absaloka Subbituminous Coal with Hydrogenated Anthracene Oil (HAD 29)  
 50/50 H<sub>2</sub>/CO 3500 - 4200 psig

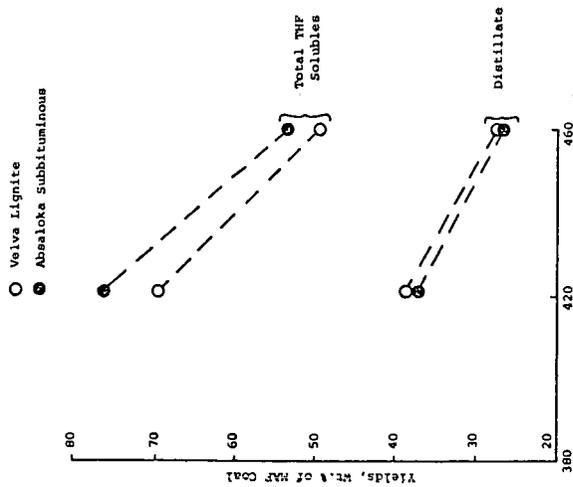


Figure 10

Liquefaction of Velva Lignite and Absaloka Subbituminous Coal with Hydrogenated Anthracene Oil (HAD 29)  
 50/50 H<sub>2</sub>/CO 3500 - 4200 psig

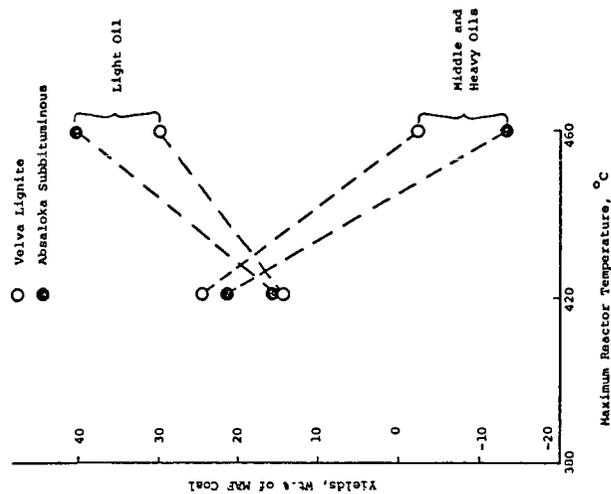


Figure 11

Liquefaction of Beulah, Velva, and Gascoyne Lignites in the Hot Charge Autoclave  
End of Run Results

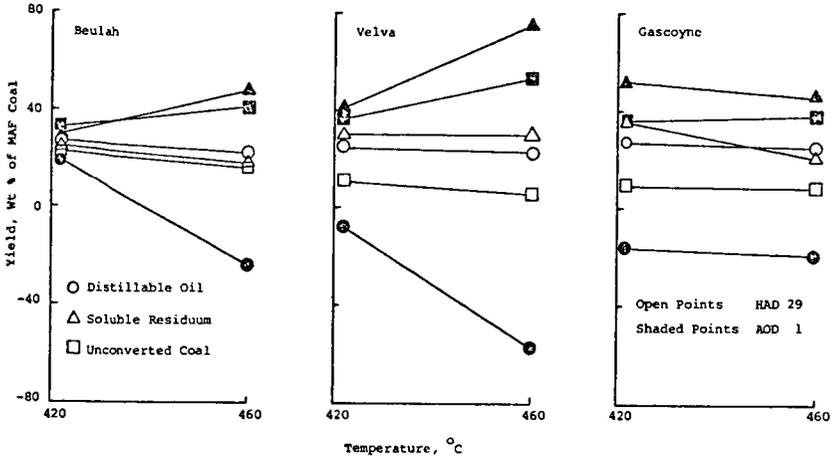


Figure 12

Liquefaction of Larson Lignite and Wyodak and Absaloka Subbituminous Coals in the Hot Charge Autoclave  
End-of-Run Results

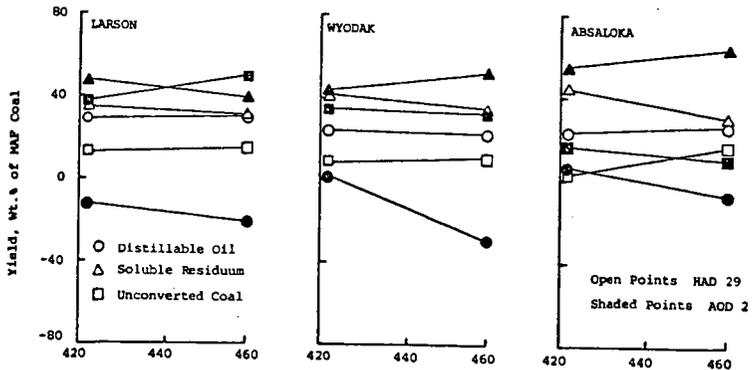


Figure 13

Hot Charge Autoclave Studies with Beulah, Gascoyne, and Valva Lignite, using AOD1 and HAD 29 Solvents at 420 and 460°C. Yields for all coals averaged with each solvent at each temperature.

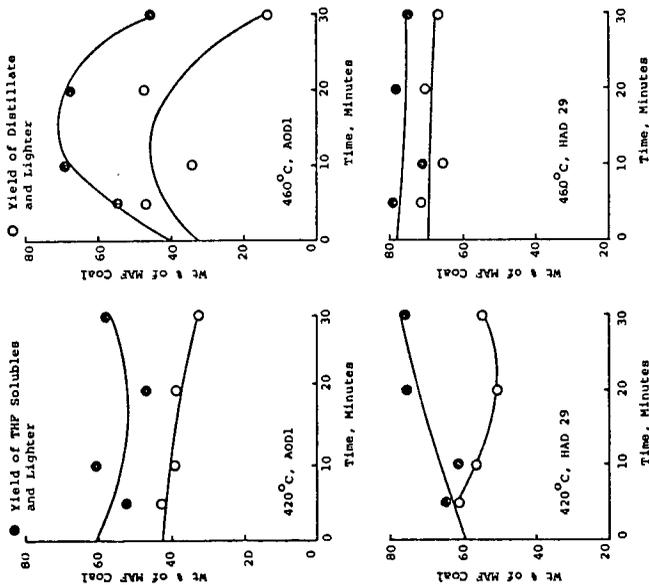


Figure 14

Hot Charge Autoclave Studies with Aberlona and Wyodak Subbituminous Coals using AOD 1 and HAD 29 Solvents at 420 and 460°C. Yields for Both Coals Averaged with Each Solvent at Each Temperature

