CHANGES IN ASPHALTENES AND PREASPHALTENES WITH REACTION CONDITIONS AND EFFECTS ON COAL STRUCTURE

C.L. Knudson, R.J. Baltisberger, N.F. Woolsey, and W.G. Willson

University of North Dakota Energy Research Center
Box 8213, University Station
Grand Forks, North Dakota 58202

Asphaltenes (A) and preasphaltenes (PA) have broad chemical compositions because they are solubility fractions. Detailed separations by Baltisberger, et al. (1) of the A and PA fractions and detailed analyses (over 100) of samples produced at 12 different liquefaction conditions have provided a better definition of what chemical parameters most affect their solubility. Relating the A and PA changes to coal liquefaction operating conditions indicates that a key factor in upgrading these materials is to decrease their phenolic content. The changes in hydrogen content and distribution in asphaltenes observed when operating with H_2 or CO-H_2 (syngas) indicated CO was more effective in hydrogenating aliphatic positions in asphaltenes than H_2 gas. The change in hydrogen distribution has implications concerning coal structure (both lignites and bituminous coals) and initial coal decomposition mechanisms.

Experimental

The continuous process unit (CPU) used to produce the A and PA material has been described elsewhere (2). The A and PA fractions were separated from samples obtained from twelve different continuous process unit (CPU) tests performed at the University of North Dakota Energy Research Center (UNDERC). Nine tests were made with Beulah (B3) lignite, one with Big Brown (BB1) Gulf Coast lignite, and two with Powhattan (POW1) bituminous coal. Five tests were single-pass with coal and solvent; three of these five tests were at 400°, 440° and 460°C operating temperatures and a gas flow rate of 0.5 scfm of syngas using a continuous stirred tank reactor (CSTR) while two were at gas flow rates of 0.5 and 1.1 scfm at 460°C using an open tubular reactor. Seven tests were bottoms recycle tests at nominally 460°C and at operating pressures of 2000 to 4000 psi. Operating conditions have been previously reported (1). During CPU operation, a coal-solvent slurry (preheated to 200°C) and reducing gas (preheated to 300°C) was fed to a continuous stirred tank reactor (CSTR) or an up flow open tubular reactor (OTR). Thus, most of the heating to reaction temperatures occurred in the reactor. The redistribution of the feed to product streams is depicted in Figure 1. All streams were sampled after each bottoms recycle pass (4 h) or single pass test period (6 to 12 h) and extensively analyzed. In single pass operation a 40% coal and solvent slurry was passed once through the system. In bottoms recycle, the major portion of product slurry (PS) and usually the light oils (LO) were recycled as solvent for the next pass. Total insolubles including ash and insoluble organic matter (IOM) increase. These remain nearly constant after about ten passes due to the removal of PS not required for use as solvent. The amount of coal fed was 30 wt% of the feed slurry (FS). Only product slurry analyses will be considered in this paper.

Product Slurry Analysis. Product slurry was collected in a 1 gallon can during the last hour of a test period or pass. The contents of the can were shaken in a paint mixer (single pass) or transferred to a Waring blender and blended (bottoms recycle). After mixing, the material was rapidly split into small sample containers and the remainder returned to storage. Settling was not a problem except when distillate solvents were employed in a single pass run. The validity of analysis techniques using microgram quantities was verified by repeated analyses. Samples

were analyzed in duplicate or triplicate to define major product fractions. Water was usually 1% to 3% of the PS and was determined by Karl Fischer titration. Tetrahydrofuran (THF) insolubles were determined by dissolution of a sample in excess THF at ambient conditions and filtration through a 0.5 micron, Teflon, Millipore filter. Distillation residue (MDR) was determined by microdistillation of less than 0.5g at 250°C, 1 Torr for 0.5 h. Ash was determined by initially driving off volatile organics at about 200°C followed by ashing at over 800°C in a muffle furnace. The THF soluble portion of the MDR defined the soluble residue (SR) yield. The quality of the SR was routinely determined by high pressure liquid chromatography (HPLC) gel permeation chromatography (GPC) of the THF soluble fraction of the MDR (3). GPC provided the molecular weight (MW) distribution profile of the SR. Also, the GPC ratio of the absorbance at 254 nm of the exclusion peak or shoulder near 950 MW to the absorbance at 250 MW provided an index value to the amount of high MW material in the SR.

Asphaltenes. The product slurry stream samples were separated into A and PA fractions by exhaustive extraction using toluene and THF. Then each fraction was separated by molecular weight (MW) using Bio Beads -Sx-3 into narrower MW fractions (1). The MW fractions were each analyzed for carbon, hydrogen, nitrogen, sulfur, and phenolic hydroxyl (OH) content. The average MW was determined by vapor phase osmometry. Proton NMR analyses were performed to determine the hydrogen distribution as:

H_{ar} - hydrogens attached to aromatic carbon atoms,
H_a - hydrogens attached to carbons which are attached to an aromatic ring (benzylic hydrogen), and
H_o - hydrogen on carbon at least one carbon atom away from an aromatic ring or in an alphatic hydrocarbon (aliphatic hydrogen).

Single Pass Solvents. The CPU once through tests with the CSTR used an anthracene oil (AO1) purchased from Crowley Tar Products spiked with 10% tetralin while tests with the OTR used AOD1 solvent, which was a distillate fraction of AO1. The solvent analyses have been presented elsewhere (4, 5). Neither AO1 or AOD1 solvent contained any THF insolubles and would therefore not interfere with the preasphaltene analysis unless incorporated into that fraction during processing. The amount of hexane insolubles in the single pass solvents was only 1.28 wt%. In addition, this portion showed a uniform low absorbance value from 2000 to 100 g/mole as indicated in Figure 2. Assuming the low absorbance is consistent with a small concentration there should be no major contribution to the average molecular weight determined by VPO analysis of the asphaltene fractions of the SR samples.

The MDR of AO1 amounted to 8.05 wt% and was entirely soluble in THF. The GPC MW distribution of this material was bell shaped (Figure 2) with minimum values at 950 and 250 MW and therefore would have little influence on the GPC ratio determined for an SR.

Results

Coal Analysis and Reactions. Ultimate and Fischer-Schroeder Assay data (provided by the Alberta Research Council) for the coals are presented in Table I. The 18 to 21 maf wt% oxygen content of the lignites was considerably higher than the 8.6 value for the bituminoua coal. For the B3 lignite about 74% of the total sulfur was retained in the ash as sulfate due to its high molar Ca/S ratio. This increased the apparent ash resulting in the calculated maf oxygen value being low. POW1 and BB1 exhibited sulfur retention of 5% and 84%, respectively. Ignoring the effects of sulfur retention, most of the oxygen in the B3 lignite was observed during 500°C assay as CO_2 and chemical water (51% and 37% for B3, respectively). For the bituminous coal, 58% of the oxygen was observed in chemical water and only 22% in CO_2. Chemical water is water produced in excess of coal moisture (cf. Table I). Typical values depending on rank have been reported for many coals (6). For 200g of

Table I. Coal Analysis

A. Elemental

Rank	Coal[a]	Moisture %AR	Ash %MF	Ultimate, wt% maf C	H	N	O	S
Lig	B3	28.90	16.32	70.10	34.50	1.04	21.60	2 76
Lig	BB1	26.51	12.57	74.05	5.42	1.32	18.09	1.11
Bit	POW1	4.80	10.61	79.96	5.74	1.39	8.59	4.31

B. Fischer-Schroeder Assay Yields, wt% maf[b,c]

Coal	Char	Total Gas	Chemical Water[d]	Tar	Light Oil
B3	66.41	18.85	8.95	4.65	1.83
BB1	63.03	16.25	8.71	9.83	1.04
POW1	69.56	7.97	5.62	15.74	0.12

Coal	Gas	H_2	CO	CO_2	H_2S	C_1-C_6	CH_4	C_2H_6
B3	18.85	0.07	1.49	15.23	0.38	1.61	0.92	0.18
BB1	16.25	0.05	1.79	11.83	0.23	2.34	1.19	0.28
POW1	7.97	0.05	0.52	1.68	1.10	4.54	2.52	0.70

[a]Dry pyritic sulfur contents were 0.63, 0.16, and 0.91, respectively.
[b]Analyses provided by the Alberta Research Council Canada, M. Selucky and M.P. duPlessis.
[c]Dry ash values were 16.75, 11.35, and 10.00, respectively.
[d]Water produced in excess coal moisture under pyrolysis conditions.

B3 coal, CO_2 evolved rapidly prior to reaching 400°C in batch autoclave tests with coal only (7). Similar rates of chemical water and CO_2 production from this coal at various temperatures was observed by Solomon (7). In coal-CO-water-solvent autoclave tests rapid CO_2 production initiated at about 360°C coincident with CO consumption and some H_2 production (8, 9). However, in slurry dried coal CO tests CO_2 was observed with CO consumption but minimal H_2 gas was observed. In rapid heat up tests with about 150g of maf lignite (triple the normal amount) to 3 moles of CO, 98% of the CO was rapidly converted to CO_2. The amount of CO consumed was found to be proportional to the amount of coal charged.

In continuous process unit operation at the UNDERC with H_2 gas, the water and CO_2 yields are similar to the assay CO_2 and chemical water yields of the coal being processed. When CO gas was present the molar amount of CO consumed approximated the quantity of feed water (coal moisture plus chemical water) consumed. In summary, the chemical water was produced rapidly at temperatures above 360°C without consuming gaseous hydrogen but rather abstraction of coal hydrogen which reduces the net available hydrogen in the coal. Loss of this hydrogen in chemical water would increase aromatization during the initial coal reactions. This net available hydrogen has been found to correlate with liquefaction conversion and pyrolysis tar yields (10). The CO results indicated that CO reacted with the chemical water or

its functional group precursor to result in the net hydrogenation of the coal structure. This necessitates the presence in coal of functional groups that can thermally decompose to produce water at temperatures as low as 360°C.

Temperature Effects - Single Pass CPU Runs. The reaction temperature has a large effect on the characteristics of the SR, PA, and A fractions and on yield structures. Conversion values of coal increased with temperatures from 400° to 460°C but decreased at 480°C for these tests. The yield results at 480°C are solvent dependent. The SR fraction exhibited a rapid and then slower decrease in over 950 MW material with increasing temperature (Figure 3) as was observed in batch autoclave tests (3). The preasphaltene fraction indicated a similar decrease in the magnitude of the exclusion peak with temperature (Figure 4). The individual PA-MW fractions all exhibited uniformly decreased hydrogen content with increasing temperature as seen in Figure 5. The range of molecular weights for the PA-MW fractions compressed from 200-3000 to 400-2000 to 500-1000 with increasing temperature (see Figure 5). This indicated that the PA material became more refractory 500-1000 MW material through the loss of lower MW material. Solvent incorporation into the lower MW PA could also result in an upward shift in MW especially at 480°C since at this temperature coal conversion decreased relative to conversion at lower temperatures.

The A-MW fractions (not depicted) obtained at 480°C had higher hydrogen content than those obtained at 460°C indicating that hydrogen rich solvent had been incorporated. The phenolic contents of both A- and PA-MW fractions obtained at 400°C changed in a parallel manner but were higher than those obtained at 460°C and 480°C. The exception was the 460°C PA-MW fractions which were even higher then the values obtained at 400°C.

Pressure Effects During Bottoms Recycle. The relationship of A and PA material can be better understood by consideration of the effects of pressure on their hydrogen and phenolic OH content. Figure 6 presents the data for the hydrogen content changes with MW for the A- and PA-MW fractions of the bottoms recycle Runs 46 and 41 at 2000 and 4000 psi, respectively. The hydrogen content of both the A- and PA-MW fractions increased at any particular MW for the higher pressure indicating the greater hydrogenation which occurs at higher pressures was similar for both A and PA material. The OH content of the PA-MW fractions was higher and parallel to those of the A-MW fractions. However, as seen in Figure 7, the OH content for the PA-MW fractions of the same MW was higher when operating at 4000 psi than at 2000 psi (the A-MW fractions behaved similarly with pressure). The higher operating pressure increased the hydrogen content, as well as the phenolic content. At higher pressures the yield structure changed, as indicated in Figure 8. At 4000 psi operation, insoluble organic matter (IOM) was less (conversion was higher), and the amounts of A and PA produced were less than at 2000 psi operation. However, increased conversion due to increased operating pressure resulted in producing A and PA that had a higher OH content. The molecular weight distribution of the SR was also higher when operating at 4000 than at 2000 psi. The phenolic content of distillates also increased with conversion (12). The higher operating pressure increased 1) conversion, 2) the hydrogen content of the A and PA, 3) the phenolic content of the A and PA, and 4) the GPC molecular weight distribution of the SR fraction.

Effect of CO on Hydrogenation of Lignite and Bituminous Coal. The influence of CO on the hydrogenation of asphaltenes derived from lignite or bituminous coal indicated that CO preferentially hydrogenated the H_o position. Table II presents the operating conditions, conversions, and SR yields for four bottoms recycle tests with and without CO for two coals. CO-H_2 was somewhat more effective at converting lignite while H_2 was more effective for converting bituminous coal. SR yields also varied. The GPC-MW distributions were essentially identical for the two coals when

Table II. Effect of CO on the Hydrogenation of Asphaltenes

Coal	Lignite, B3		Bituminous, POW1	
CPU Run[a]	41	45A	69	53
Feed Gas	$CO-H_2$	H_2	$CO-H_2$	H_2
Total Pressure, psi	3841	1990	2633	2006
Partial Pressure, pH_2	1563	1707	1225	1907
pCO	1604	--	1291	--
pH_2O	600	270	71	98
pLO	58	13	47	0
Flow Rates:				
Feed Gas, scfh	44	55	38	32
Feed Slurry, kg/h	2.18	2.28	2.47	2.36
Ratio, PS/FS[b]	0.782	0.793	0.787	0.832
Yield, wt% maf coal:				
Conversion	92	88	87	92
SR	21	14	22	16
Asphaltene	12.0	10.5	15.6	--
Preasphaltene	6.0	5.5	6.3	--
Ratio PS/FS[c] H/C	0.996	1.022	0.981	1.028
Light Oil H/C	1.503	1.602	1.420	1.473
Asphaltenes:				
VPO MW, g/mol	372	384	347	336
H/C	0.911	0.865	0.809	0.765
% H_{ar}	37.4	43.8	48.9	54.5
% H_a	34.1	35.4	31.7	30.0
% H_o	26.1	18.3	17.8	13.7
% H_{OH}	2.4	2.5	1.6	1.8
Preasphaltenes:				
VPO MW, g/mol	671	676	702	701
H/C	0.727	0.740	0.636	0.676
% H_{ar}	43.5	43.3	52.1	53.9
% H_a	28.3	29.2	23.9	23.3
% H_o	24.7	23.4	21.6	19.6
% H_{OH}	3.5	3.4	2.4	3.2

[a]CPU bottoms recycle operation with light oil add back except in Run 52. The light oil partial pressure in the gas phase is expressed by pLO.

[b]The ratio of flow rate of the product slurry (PS) to the feed slurry (FS).

[c]The ratio of the H/C ratio of the product slurry to that of the feed slurry.

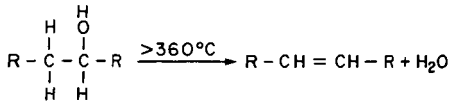
only H_2 gas was present. When the same start up solvent was used, the MW distribution of the SR was distinctly lower over the entire run when operating with CO than without CO and seen in the B3 runs.

The partial pressures of hydrogen were higher in the runs that used H_2 gas. This resulted in greater over all hydrogenation as indicated by somewhat higher H/C values for the light oil product and for the ratios of the (H/C ratio of the product slurry) to the (H/C ratio of the feed slurry). The A and PA data on Table II indicate great similarities when operating with and without CO except when comparing the H content and the hydrogen distribution of the asphaltenes. The asphaltene fraction from each coal showed a significant increase in the H content (also the H/C ratio) and in the H_o (aliphatic hydrogen) content when CO was used. The preasphaltenes had slightly lower H content but were slightly higher in H_o content. These results indicate a tangible benefit to the presence of CO on the hydrogenation of the asphaltene fraction.

Conclusions

Asphaltene and preasphaltene data have been presented to demonstrate the effect of temperature, pressure, and reducing gas composition on their hydrogen and phenolic content. The previous paper by Baltisberger (1) showed how the hydrogen and phenolic content of the A and PA defined whether or not a coal derived product will be classified as such. The influence of processing parameters as discussed in this paper indicates that reduction in the number of phenolic functional groups and cracking are required to further convert asphaltene and preasphaltene material to distillates.

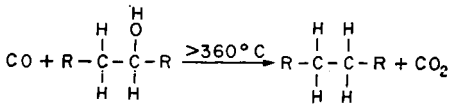
The influence of CO on the H_o positions of asphaltene along with the previously discussed data on CO and water reactions has a significant effect on models postulated for the original coal structure and on possible initial steps in coal decomposition. Large numbers of hydroxyl functional groups must be present in the coal which will decompose to water as low as 360°C. However, the hydroxyl groups must be primarily in aliphatics or alkyl side chains on aromatics to satisfy the increase in H_o observed in reactions where CO was present. This suggests that a dewatering reaction occurs thermally (with or without H_2 gas) as indicated in Equation 1.



1)

Some phenolic functional groups may also decompose to water. However, hydrogenation at this position would not result in an increase in H_o content.

With carbon monoxide present, the overall reaction to hydrogenate the coal structure (without observing H_2 gas and less water products) would occur as in Equation 2.



2)

The R-groups would need to activate dewatering since typical alcohols such as cyclohexanol do not decompose thermally to cyclohexene at 375°C (13). Glycols such as those found in cellulose, do decompose to water at about 360°C (14). Coal models

do not include water producing functional groups (15,16). However, these models were prepared to represent a coal model that would predict observed products (17) and are valid for reactions in H_2 gas. Also, cellulose is reported to decompose and therefore is considered to be absent. Indeed, only 0.01% cellulose was obtained by the direct extraction of a Beulah lignite (18). The presence of humic acids in coals is well documented (19). However, residual fragments of cellulose or humic acids incorporated into the coal structure may account for the presence of alcohol functional groups.

That alcohol groups are present in aromatic bridging structures was indicated in the data in this report by the decreased MW of SR when processed with CO present since after hydrogenation an aliphatic bridge would cleave easier. The rapid thermal cleavage of biphenylethane (bibenzyl) relative to the stability of biphenylethylene at liquefaction temperatures (20) is an analogous situation. The increased aliphatic hydrogen content in the asphaltene fraction when reacted with CO may also indicate that some alcohol groups were initially in the aromatic bridges. The presence of alcohol groups in long chain aliphatics has been indicated because increased yields of long chain alkanes were observed when CO was present (12).

In conclusion, the previous data has shown how operating conditions such as pressure and temperature affects the hydrogen content, phenolic content, and molecular weight range of asphaltene and preasphaltene fractions. The effects are reflected similarly in individual MW fractions of both A and PA material. The presence of alcohol groups in original coal (both lignites and bituminous coals) was strongly suggested. The preferential reaction of these alcohol groups with CO gas (but not H_2) to increase the hydrogen content of the asphaltenes, to reduce the overall MW distribution of coal, and to increase yields of alkanes indicates the beneficial effects of CO as a reductant of these functional groups which are present in both lignites and bituminous coals.

Acknowledgments

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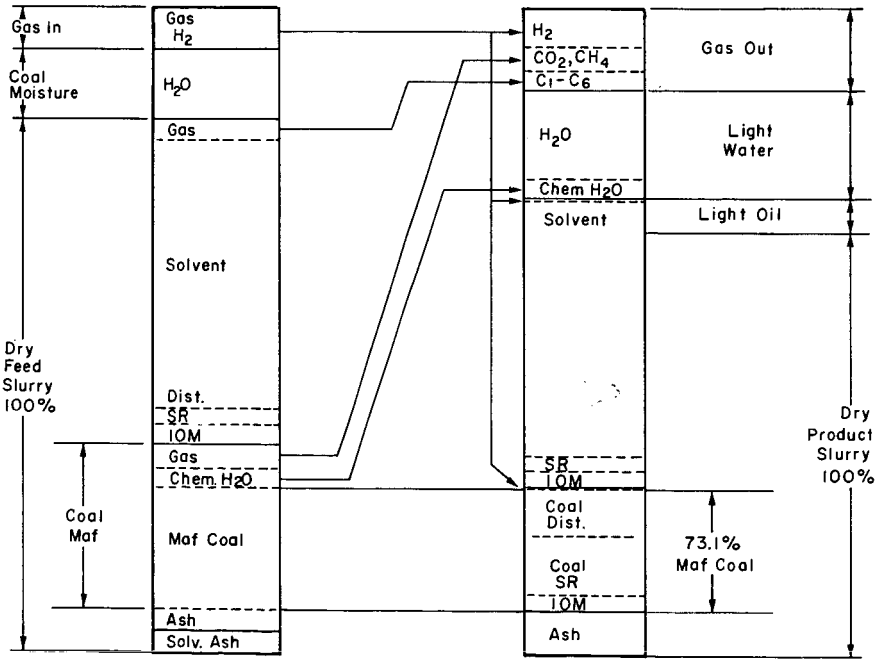

Figure 1. Redistribution of Continuous Process Unit feed streams to product streams.

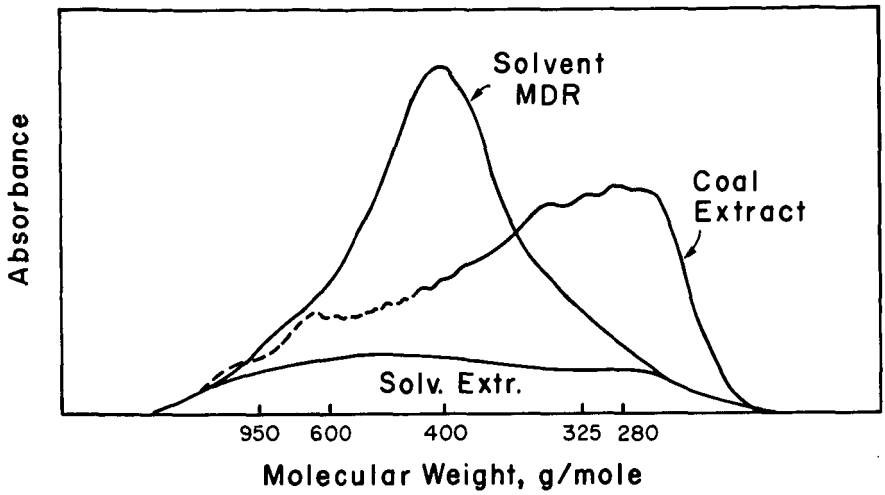

Figure 2. HPLC-GPLC molecular weight distribution of SR (Solvent MDR) and asphaltene fraction (solvent extract) of the solvent A01. Asphaltene extracted from a coal-solvent slurry (coal extract) is also depicted.

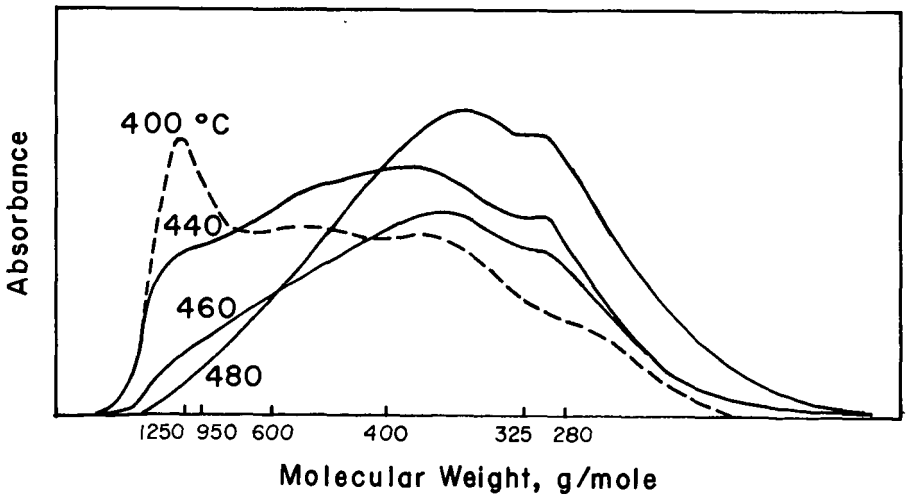

Figure 3. Changes in the MW distribution of SR with CPU operating temperature.

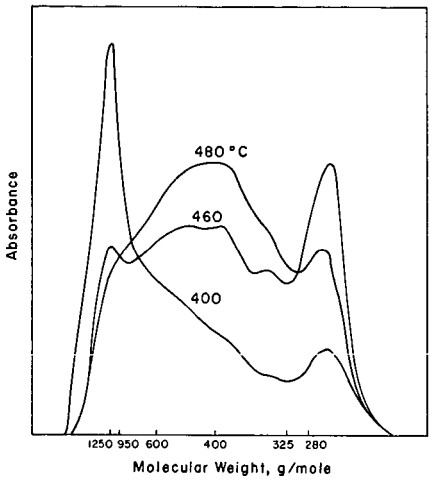

Figure 4. Changes in the MW distribution of the preasphaltenes with CPU operating temperature.

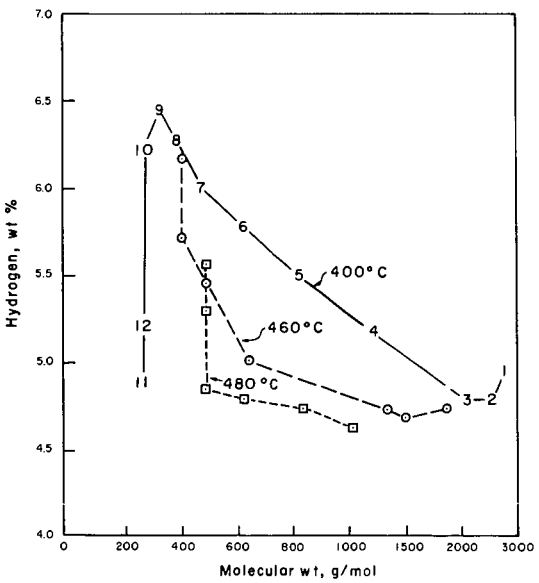

Figure 5. Changes in the hydrogen content of preaaphaltene MW-fractions with CPU operating temperature.

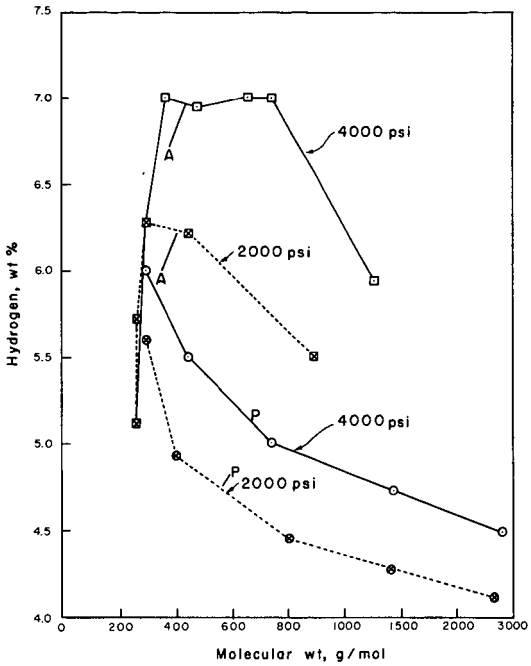

Figure 6. Effect of operating pressure on the hydrogen content of asphaltene and preasphaltene-MW fractions. Data for unseparated samples is indicated by A for asphaltenes (⊡,⊠) and P for preasphaltenes (⊙,⊗).

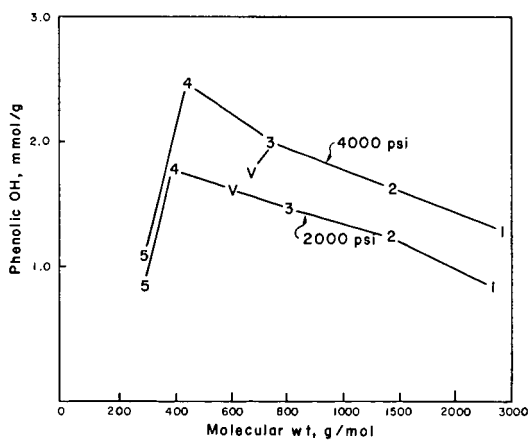

Figure 7. Effect of operating pressure on the OH content of preasphaltene-MW fractions. Unseparated sample data is represented as V.

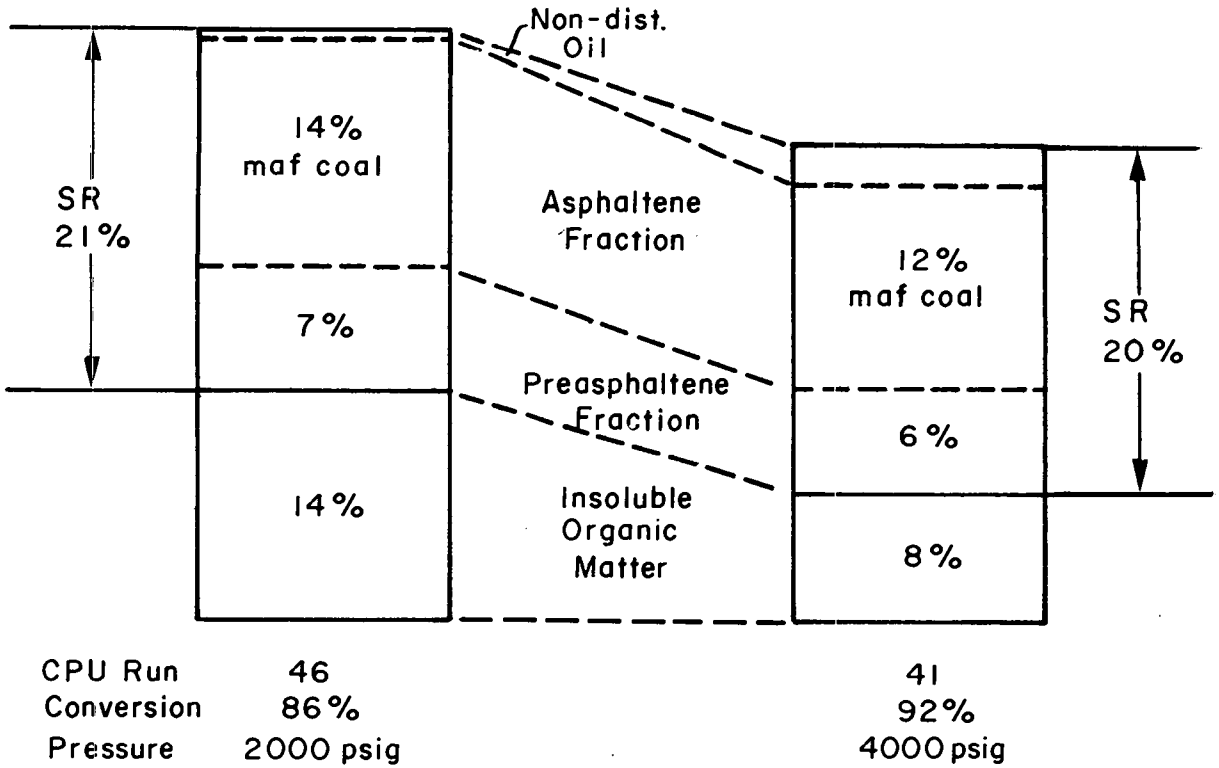

Figure 8. Effect of operating pressure on the yield structure.