

THE ROLE OF SOLVENT IN DIRECT LIQUEFACTION OF LOW-RANK COAL

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Direct liquefaction of low-rank coals by high pressure, high temperature processes usually utilizes a process-generated solvent to disperse the coal as a slurry and to act as an H-donor during reaction. The role played by the solvent is, therefore, a central one. The selection and evaluation of start-up solvents, changes in the solvent with processing, changes in the recycle material with approach to reactor equilibrium, changes in solvent character in response to changes in process variables and mechanisms of solvent-coal interactions are important in direct liquefaction.

The effect of solvent on the yield structure and operability during low-rank coal liquefaction is often very large. The changes the solvent undergoes during passage through the reactor in continuous processing units or during batch autoclave reactions may make the determination of true yield structures very difficult. These effects are the result of solvent instability and changes under processing conditions as well as varying solvent interactions with the coal. Some examples of these effects and of how they alter yield structure during low-rank coal CPU operation have been reported (1).

The criteria for evaluating low-rank coal solvents may conveniently be divided into six categories: 1. physical properties, including viscosity, specific gravity, solvent mixing properties, and boiling point distribution; 2. thermal stability; 3. potential H-donor ability; 4. phenolic content; 5. coking tendency; and 6. compound type distribution.

This paper discusses some of the changes in compound type distribution for passes one through fourteen for two liquefaction runs which were started up with different solvents.

EXPERIMENTAL

Direct liquefaction was carried out in the Grand Forks Energy Technology Center's 4.5 kg slurry/hr continuous processing unit operating in the bottoms recycle mode (1). The operating conditions and net yields for the runs discussed are summarized in Table 1.

The startup solvents and recycle slurry ASTM D-1160 distillates from each run were characterized by multi-method analysis. The separations were effected using silica gel column chromatography and solvent extraction. Determination of the fraction components was by 50 MHz ^{13}C , 200 MHz ^1H NMR spectrometry and capillary GC as previously reported (2). Selected fractions were analyzed by capillary GC-mass spectrometry.

The solvent-extraction nonpolar fraction of the ASTM D-1160 distillate was divided into $(\text{CH}_3)_2\text{SO}$ soluble and $(\text{CH}_3)_2\text{SO}$ insoluble portions as described in the reference (2) to simplify interpretation of the ^{13}C NMR spectra. The $(\text{CH}_3)_2\text{SO}$ soluble fraction contained aromatic hydrocarbons with two or more rings and aromatic ethers. The $(\text{CH}_3)_2\text{SO}$ insoluble fraction contained mainly alkanes, alkyl benzenes and tetralins. There was compound overlap between these two fractions. The concentration of some components of the $(\text{CH}_3)_2\text{SO}$ soluble and insoluble fractions were determined by quantitative 50 MHz ^{13}C NMR spectrometry. A weighed amount of the sample to be examined was combined with a known weight of internal standard dioxane and relative peak intensities were used to determine the concentrations of the components. The weight percent of each component was calculated after calibra-

tion with a standard. Figure 1 shows an example of the ^{13}C NMR spectra obtained and the resonance lines used to determine dibenzofuran, phenyl ether, acenaphthene, fluorene, fluoranthene, tetralin, phenanthrene and 2-methylnaphthalene. The component concentrations were calculated for both fractions, weighted for fraction size and summed.

DISCUSSION

The start up solvents used in the two liquefaction runs of Beulah, North Dakota (B-3) lignite reported here were quite different in composition. The solvent HAOb1 was the vacuum bottoms portion of an anthracene oil (AO1 from Crowley Tar Products Co.) which had been hydrotreated over a commercial Co-Mo catalyst in the GFETC trickle bed reactor. The 200 MHz ^1H NMR shown in Figure 2 indicates that HAOb1 was a highly alkylated mixture of heavy aromatics. This is indicated by the large Ho signal at 2.5 to 3.1 ppm caused by protons on carbons adjacent to aromatic rings. The other solvent was a blend of AO4, a highly aromatic anthracene oil (Crowley Tar Products Co.), and SRC II process middle distillate. The ^1H NMR of AO4 illustrated in Figure 2 indicates 70% aromatic hydrogen signals and a small amount of non-aromatic hydrogens. The AO4 consisted of 2 and 3 ring aromatic structures. The alkane analysis was carried out gravimetrically by silica gel column chromatography. Both oils have low enough alkane concentrations to minimize solvent cracking above 460°C.

The two anthracene oils have nearly identical elemental analyses and H/C ratios; however, as was seen from the ^1H NMR spectra, they are very different chemical mixtures. Both of these oils were adequate start-up solvents for direct liquefaction. In the studies reported here, the HAOb1 was used directly (Run 45) and the AO4 was mixed 60/40 by weight with an SRC II middle distillate, (SRCMD, Table 2), to simulate a lined-out recycle solvent (Run 65).

During direct liquefaction processing, a constant aromatic-aliphatic carbon ratio of the slurry ASTM D-1160 distillate oils was obtained after 9-10 passes through the reactor. Figure 3 shows a plot of the fraction of aromatic carbon, fa, against the pass number. The start-up mixture of AO4 and SRCMD (60/40) had an aromatic carbon fraction, fa, of 0.79. After 9-14 passes the value had dropped to 0.70 and leveled off.

The change in concentration of some components with the number of passes through the reactor was conveniently followed by ^{13}C NMR spectrometry. These changes are presented in Figures 4 and 5. Fluoranthene, phenanthrene, acenaphthene, and dibenzofuran change most rapidly during the 14 passes through the reactor, dropping to 1/10 to 1/3 of their first pass concentrations. These components are not formed from the lignite as rapidly as they are being displaced from the recycle pass slurries by the product formation. Other components determined showed gradual changes in concentration and appeared to be approaching constant composition. During this same time the concentration of phenols increased from 13.0% after pass 1 to 17.0% after pass 14. The changes seen in the concentrations of these components in addition to reflecting dilution as the solvent is replaced by lignite-derived products, also represents a balance between degradation and production of each component.

Figure 6a and 6b show the ^{13}C NMR spectra of the $(\text{CH}_3)_2\text{SO}$ soluble fraction of the recycle slurry distillate from two runs with North Dakota Beulah-3 (B3) lignite. Figure 6a shows the spectrum for pass 12 when HAOb1 was used as the start-up solvent (Run 45); while Figure 7b shows the spectrum from pass 14 when a mixture of AO4 and SRCII middle distillate was the start-up solvent (Run 65). The $(\text{CH}_3)_2\text{SO}$ soluble portion of the AO4/SRCMD is shown for comparison in Figure 7c. When a comparable liquefaction run is started with a different solvent, analyses of the products are different after 14 passes. Many of the same components were found in each of the liquids but there are some components that are not common to both. The ethers, dibenzofuran and phenyl ether, introduced with the AO4/SRCMD are one of the most prominent features of the ^{13}C NMR spectra of all the liquids for which this start-up solvent was used. In Run 65, the concentrations of these ethers level off at 20 to

40% of their initial concentration in the start-up material (Figure 5). This indicates some production of ethers from the coal or from other components of the solvent is taking place. In Run 45, which was started with HAOB1, both of these ethers are absent in the products.

Multi-method analysis of the two slurry ASTM distillates is given in Table 3. The percent of the ASTM distillate characterized ranged from 45 to 48%.

It may be concluded that:

1. A new technique for determination of selected major components of the vacuum distillate fraction of lignite liquefaction product was developed using 50 MHz ^{13}C NMR analysis preceded by simple analytical separations.
2. While average molecular properties such as fa values may appear constant, some components of the vacuum distillate of a recycle slurry continue to change in concentration while others appear to be nearing constant composition.
3. Certain unique components such as dibenzofuran and diphenylether were only present in products of runs where they were present in the start up solvent.
4. Concentration differences were noted among the compounds determined in the multi-method analysis of vacuum distillates of recycle slurries started up with different solvents. Additional differences were observed in examination of the whole sample by NMR, suggesting further variations among the 52-54% of the sample not identified by the multimethod analysis.

REFERENCES

1. Willson, W.G., Knudson, C.L., and Baker, G.G., *Ind. Eng. Chem. Prod. Res. Dev.*, 1979, 18, 297-310.
2. Farnum, S.A. and Farnum, B.W. "Determination of Low-Rank Coal Liquefaction Light Oils by Chromatography and Nuclear Magnetic Resonance Spectrometry." Analytical Chemistry, in press.

TABLE 1
CONTINUOUS PROCESS UNIT - SLURRY RECYCLE TESTS

CPU Run No.	45	65
Coal	B3	B3
Coal moisture, wt %	29.5	2.8
Additive	Lt oil	Lt oil
Gas	H ₂	H ₂ ^a
Start-up solvent	HAOB1	SSOL ^a
<u>Run Conditions:</u>		
Temperature, °C	460	460
Pressure, psig	2000 ^b	2600
Reactor	OTR ^b	OTR
<u>Summary Data (wt % maf coal):</u>		
Net distillate	45.4	47.9
Net SRL + distillate	61.2	67.6
Overall maf coal conversion	91.5	90.1
No. passes through reactor	12	14

^aSSOL = A04/SRCMD, 60/40 by weight (see Table 2).

^bOTR = 1½ inch by 5 foot open tubular reactor.

TABLE 2
PROPERTIES OF SOLVENT COMPONENTS

Oil	C	H	N	S	H/C	Ash	Proton NMR				Alkane	Phenols
							H _{ar}	H _α	H _O	H _{phe}		
^{a,b} HAOB1	90.49	5.87	0.85	0.53	0.78	0.0	24.3	32.5	43.2	--	9	--
^a A04	90.84	5.98	0.85	0.49	0.79	0.0	70.0	19.5	10.5	--	2	--
^c SRCMD	88.53	6.88	0.85	3.28	0.93	0.0	58.0	22.0	10.0	5	8	32

^aAnthracene oil obtained from Crowley Tar and Chemical Company.

^bHydrogenated anthracene oil bottoms (Co-Mo catalyst, 420°, 3500 psi), note--originally A04 and unhydrogenated AOB1 were very different.

^cSRC middle distillate from Ft. Lewis, Washington, SRC Pilot Plant, Powhatan No. 5, ASTM D-86.

TABLE 3
 DETAILED MULTI-METHOD ANALYSIS OF B3 LIGNITE-DERIVED RECYCLE SLURRY ASTM D-1160 DISTILLATES (WT. %)

Compound	Run 45	Run 65	Compound	Run 45	Run 65
n-alkanes					
C-9		--	2,7-,2,6-dimethylnaphthalene	0.50	0.53
C-10	0.02	0.001	1,4-,2,3- and 1,5-dimethylnaphthalene	0.18	0.01
C-11	0.09	0.03	acenaphthene	0.21	1.1
C-12	0.14	0.10	1,3-dimethylnaphthalene	0.10	0.004
C-13	0.24	0.17	dibenzofuran	0.001	1.40
C-14	0.28	0.22	6-ethyltetralin	0.19	0.03
C-15	0.33	0.27	5-ethyltetralin	0.02	0.003
C-16	0.35	0.24	phenanthrene	3.32	5.20
C-17	0.32	0.24	3-methylphenanthrene	1.46	0.31
C-18	0.26	0.18	2-methylphenanthrene	2.11	0.34
C-19	0.25	0.16	4-methylphenanthrene	0.29	0.20
C-20	0.25	0.13	1-methylphenanthrene	0.28	0.06
C-21	0.20	0.11	1,2,3,4-tetrahydrophenanthrene	0.34	0.19
C-22	0.18	0.09	octahydrophenanthrene	0.09	--
C-23	0.16	0.09	3,6-dimethylphenanthrene	0.36	--
C-24	0.07	0.08	pyrene	1.15	--
C-25	0.28	0.10	2-methylpyrene	3.23	1.15
C-26	0.07	0.08	4-methylpyrene	2.53	0.40
C-27	0.07	0.08	dihydropyrene	0.15	--
C-28	0.17	0.05	fluorene	0.68	0.12
C-29	0.05	0.04	9,10-dihydrophenanthrene	0.54	2.32
C-30	0.03	0.03	anthracene	0.25	0.41
C-31	0.03	0.01	fluoranthene	0.03	--
C-32	0.02	0.01	2-methylfluorene	0.60	0.28
C-33	--	0.008	1-methylfluorene	0.22	0.39
C-34	--	0.004	4-methylfluorene	0.36	0.51
C-35	--	0.002	1,2- and 2,3-benzofluorenes	0.19	0.16
pristane	0.10	0.05	3,4-benzofluorene (?)	0.44	0.12
phytane	--	0.008	benz(a)anthracene	0.12	0.07
tetralin	0.24	0.85	chrysene	0.79	0.13
1-methyltetralin	0.43	1.57	6-methylchrysene	0.36	0.06
2-methyltetralin	0.06	0.015	phenyl ether	--	--
5-methyltetralin	0.11	0.03	biphenyl	0.49	0.48
6-methyltetralin	--	0.009	2-methylbiphenyl	0.13	1.04
2,7-,2,6-dimethyltetralin	0.47	0.65	Phenols	14.9	17.0
2-methylnaphthalene	0.20	0.03	Bases	2.1	3.4
1-methylnaphthalene	1.69	3.40			
2-ethylnaphthalene	0.23	0.14			
	0.61	0.60			
Subtotals	8.13	9.73			
TOTALS				37.49	38.44
				45.62	48.17

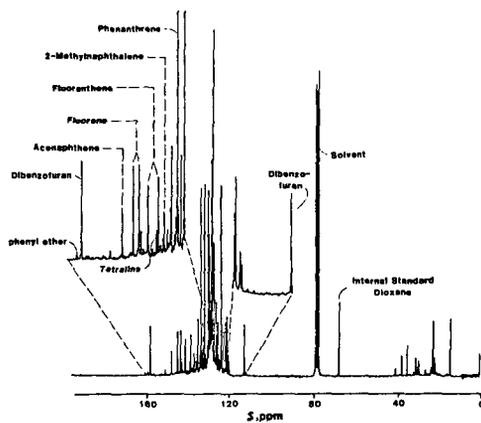


FIGURE 1. - ^{13}C NMR analysis of Run 65 (pass 3) DMSO soluble hydrocarbon fraction by the method of internal standards.

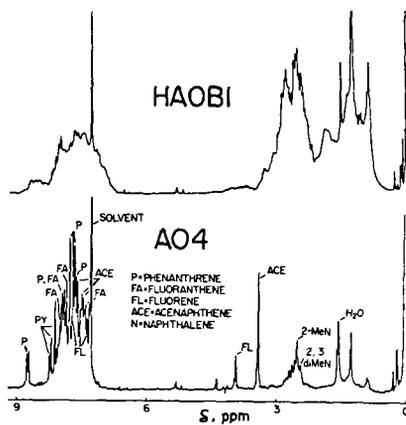


FIGURE 2. - Comparison of anthracene oils by 200 MHz ^1H NMR.

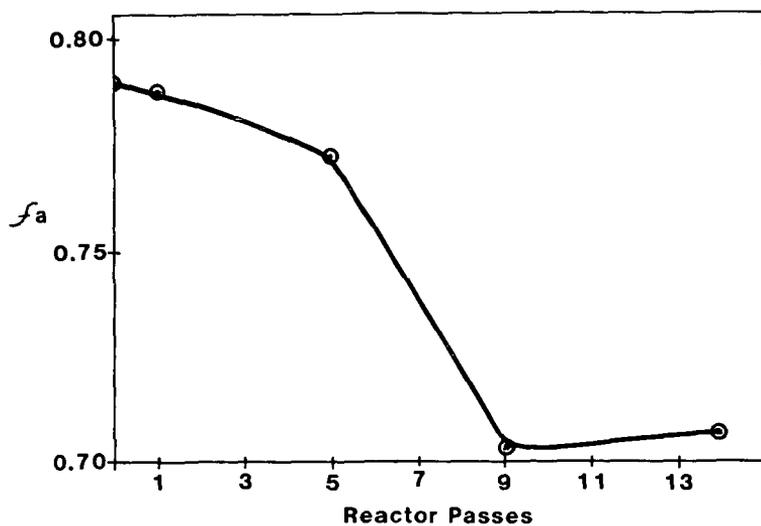


FIGURE 3. - Variation in fraction of aromatic carbon, f_a , for slurry distillate with number of reactor passes, Run 65.

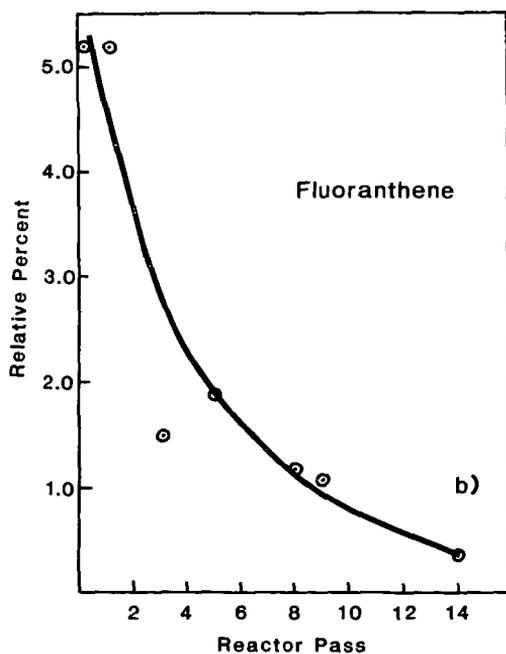


FIGURE 4. - Variation in concentration of fluoranthene with pass number, Run 65.

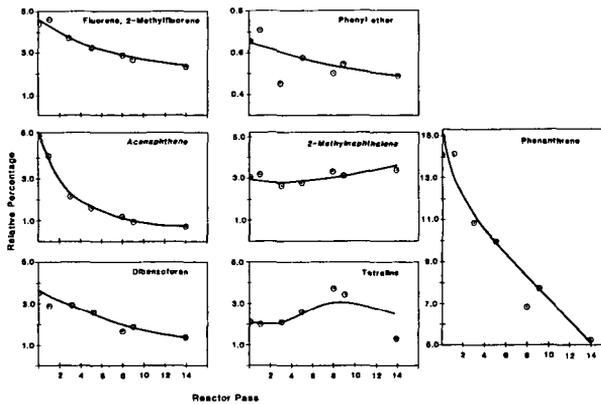


FIGURE 5. - Variation in component concentration with pass through the reactor, Run 65.

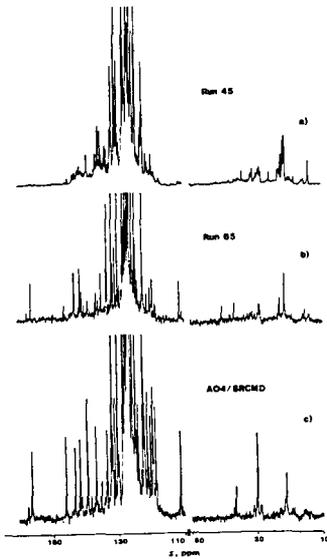


FIGURE 6. - DMSO soluble aromatic hydrocarbon fractions of two 83 ligite liquefaction runs and of the startup solvent for Run 65.