

COMPARISON OF SOLVENT REFINED LIGNITES WITH SOLVENT REFINED BITUMINOUS COALS.

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Comparison of SRL and SRC

Introduction

A considerable amount of work is currently being conducted on solvent refining of bituminous coals. The resulting solvent refined coal (SRC) can be used as a boiler fuel or as a feedstock for further refining. A parallel program on lignite coal is being carried out in our Chemical Engineering Department (Project Lignite). Considering the properties of the starting coals, it was initially assumed that SRC and solvent refined lignite (SRL) would be greatly different and, thus, second stage refining reactions and conditions would have to be developed and "fine tuned" for the different feedstocks. As these programs developed, however, it soon became apparent that SRL and SRC were more similar to each other than the starting coals were. In view of these similarities and because of a lack of definitive evidence to the contrary, it has been generally accepted that the second stage reactions and conditions can be simultaneously, rather than separately developed.

In view of the importance of this tentative conclusion to our work, we have set about examining the similarities and differences between a wide variety of SRL and SRC samples. Our preliminary results (1) were consistent with the conclusion that SRC and SRL were nearly the same within the limits of the experiments and samples we were using. We have now obtained more representative samples of both SRL and SRC produced under more commercial conditions and report their comparison here.

Procedure: Samples refined from lignite, sub bituminous and bituminous coals were obtained. (2,3) In addition, as controls, more deeply hydrogenated samples from a COSteam process and from second stage hydrogenation of SRL were included in the comparison. (3) The method of analysis was similar to that used previously (1) using the whole coal samples. Ultimate analyses, including neutron activation oxygen analysis, nonaqueous titrations, uv, mw, nmr and esr spectroscopy were used to examine these samples. A difficulty rapidly developed. Several of the samples contained unreacted coal and ash. Initially we thought a comparison could be made by correcting for these insoluble materials on the basis of pyridine solubility of the sample. Neutron activation (naa) oxygen analysis showed, however, that oxygen by difference and by naa for maf samples were fairly close, but samples containing ash deviated considerably (Table 1). Thus, the variability of oxygen in the ash and unreacted coal led to large errors in the amount of oxygen in the maf material. Because the oxygen content could be critical to a lignite-bituminous coal comparison, we set out to develop an exact, reproducible laboratory deashing procedure. The deashing procedure was based on pyridine Soxhlet extraction, filtration of the eluate and removal of pyridine under standard conditions. The amount of pyridine remaining in each sample was checked by pmr. Several samples were crosschecked by mass spectroscopy. As little as 0.2% pyridine could have been detected. None was found. Table I shows the percentage of each sample found soluble in pyridine with and without 5 μ filtration. The results show the 5 μ sizing procedure seems desirable, especially in view of the variable amounts of materials obtained from different samples by this technique. For laboratory studies we would like to propose this separatory technique as a standard procedure to define an SRC or SRL (cf Experimental Section).

Discussion of Analytical - Spectroscopic Results.

A. NMR: Proton nmr analysis of samples before and after deashing indicates no gross changes in the samples. Nevertheless, small systematic changes did occur. Samples, both SRL and SRC, initially containing ash and unreacted coal had the same $\text{Har}/(\text{H}\alpha + \text{H}\delta)$ ratio within experimental error before and after deashing.

(Table II). Maf samples showed changes of 0.07-0.26 in this ratio, which is outside the precision of the measurements. Another subtle, but consistent trend for nearly all samples was a decrease in the $H\alpha/Ho$ ratio on deashing. This was true for initially maf, as well as samples with ash and unreacted coal. Furthermore, this change in ratio was 0. -0.48 for SRL's and larger, 0.36-1.27, for SRC's. Excluding the Amax sample, the range was 1.17-1.27. The $H\alpha/Ho$ decreased by 0.83-1.17 for two samples when the pyridine insoluble fraction was simply filtered off (nmrs were run with all insoluble material present in non maf material).

Only experience will show if the change in $H\alpha/Ho$ ratio, caused by laboratory deashing, can be used to identify the coal used for SRC or SRL preparation. whether these small changes are caused by material in the ash or by chemical reaction during the deashing process also remains to be investigated. Our experience with FT carbon-13 determined Car/C total (ie fa) ratios are consistent with a recent report (4) that the ratios determined from proton and carbon-13 nmr are very similar. (eg. for MILA Carbon-13 = 0.815+0.009 and from proton fa=0.813).

B. Molecular Weight: The molecular weights (by VPO) of the samples before and after deashing were also measured. The precision on the single determinations before deashing is much less than for the three concentration extrapolated values determined on the laboratory deashed material. Even so, the two values for each sample were either the same within experimental error or very close to each other (with the exception of Tacoma (maf), which increased significantly). The ranges, in general, both before and after deashing are not grossly different, although the SRC's (before 420-597; after 460-620) are marginally higher in mw than the SRL's (before 400-598; after 428-481).

C. Ultraviolet Spectra: The ultraviolet spectra for these samples was run between 270-400nm and is plotted vs $E^{1\%}$ in Fig. 1. These and other such samples have remarkably featureless spectra. All samples thus far examined, fall generally within the range shown. These factors make it unlikely that SRL's and SRC's may be distinguished by such data. Comparison to the COSteam and J-1-11-87 samples, indicates that larger reductive changes, however, can be characterized by uv spectra (Fig. 1). There also seems to be a relationship between the integrated uv absorption and both $H\alpha$ and $H\alpha/Ho$ from nmr data (Fig. 2).

D. Acid base properties: non aqueous titration for acidity gave a range of 1.34-2.80 meq/g for SRL's and 1.45-2.95 for SRC's. The basic titer ranged for SRL's 0.30-0.63, and 0.52-0.84 meq/g for SRC's. Where comparisons can currently be made, the oxygen content is marginally lower for SRL's (despite the fact that initially it was much higher in lignite) than for SRC's. Nitrogen content for SRL's is generally lower than for SRC's. Thus, the acidity and basicity of both SRL's and SRC's seem to parallel roughly the percentage oxygen and nitrogen respectively in the sample.

The percentages of C, H are typical (Amax %C is low and is being checked) of other samples with carbon ranging 85-90% (maf) and hydrogen, 5-6% for SRL and SRC samples. The sulfur content ranges somewhat higher for SRC's. 1.30-3.68% (but only a trace for Amax) than for SRL's, 0.85-1.24; probably a reflection of the sulfur content of starting coal.

E. Electron spin resonance: The esr spectra of the samples was measured, with the results given in Table II. The range of g-values was very small for all samples investigated, 2.0026-2.0028. The g values are in good agreement with those reported for coals having carbon contents over 80%. The linewidths for SRL's ranged 3.8-4.8 gauss; for SRC's 1.7 to 7.6. The linewidth appears marginally lower than that expected for a vitrain of comparable hydrogen content. (5)

Summary of Analytical Comparisons: While the comparisons are not yet complete, the gross makeup of the samples indicate that SRL's and SRC's are quite similar. The variations noted in the uv, molecular weight, esr, and nmr analyses may be more a function of reaction conditions than of starting coal. The percentage composition and acid-base characteristics seem to indicate that the starting coal properties, particularly nitrogen, sulfur and oxygen percentages, may be carried over into the solvent refined products, although they are affected also, to a large extent, by reaction conditions.

Furthermore, in cases which we have investigated thus far, hydrotreating of

SRL and SRC have shown similar trends, in that their reactivities and product distributions depend more on how they are made, stored and treated than on the starting coal.

Assessment of Analytical Procedures: Several difficulties have emerged in these analyses for whole solvent refined samples. A standardized laboratory deashing procedure which we have developed, appears necessary. Oxygen analysis on maf samples by difference may be generally acceptable, but should be checked with neutron activation analysis and is absolutely essential with samples containing unreacted coal and ash. A standardized procedure which we are developing needs to be uniformly applied to pulsed carbon-13 nmr analyses.

Future Work in Analysis of Gross Solvent Refined Coal Samples: Application of Carbon-13 nmr techniques have been applied to coal derived samples, but generally only to that portion of the sample soluble in a "desirable" nmr solvent (CS_2 , $CDCl_3$, etc.). Whole solvent refined samples containing large amounts of preasphaltenes (like SRL and SRC) are not soluble in these solvents. In order to properly characterize whole samples, either new solvents or new techniques have to be developed. We are working on both.

A second area of critical concern to us is the qualitative way comparisons currently must be made. A critical set of standardized measurements needs to be developed (which we have alluded to above). These measurements should then be reduced to a set of critical structural factors, probably through a computerized technique which will allow direct quantitative comparison of samples. While inroads are being made on this approach, (6) better methods need to be developed.

Experimental Section

Analyses were performed by Midwest Micro and Spang Laboratories. Nmr spectra were measured on an EM-390 and analyzed, as previously described. (1) Titrations were conducted, as previously indicated. (1)

Neutron activated analysis was carried out by Intelcom Rad Tech, San Diego, CA. Uv spectra were measured on a Cary 14 in dimethylacetamide. ESR were determined on a Bruker ER 420. Molecular weights were measured by Spang, and with a Corona Wescan 232 VPO in dimethylformamide, the latter at 74.8° at three different concentrations with extrapolation to infinite dilution. Very little association was noted in this solvent.

Laboratory Deashing Procedure: A Whatman no. 1 Soxhlet thimble was shrunk in acetone, dried at $110^\circ C$, cooled in a dessicator and weighed to constant weight. A 3 to 5 g sample of SRL or SRC was weighed into the thimble and extracted with pyridine for 24 hrs under nitrogen. The thimble was dried at 110° for 24 hrs, cooled in a dessicator and weighed. The pyridine solution was filtered through a preweighed 5μ Teflon filter. The sum of the sample in the thimble and on the filter constituted the undissolved sample by definition. Most of the pyridine in the filtrate was removed at 50° (1mm), then at 50° (0.05mm) for 24 hrs. The sample was scraped into a drying boat and further dried at 56° (0.1mm) for 24 hrs. After grinding in a mortar, the sample was redried at 100° (0.1mm) for 24 hrs more. Less than 1% of pyridine could be observed by nmr in hexamethylphosphoramide. Mass spectrometry indicated less than 0.2% pyridine in several samples.

Table I
Comparison of Deashing Techniques

<u>Sample</u>	<u>Simple Extraction</u>	<u>Filtration Extraction</u>	<u>%O by difference</u>	<u>by NAA**</u>
M11-A*	100	96.8	5.80	2.35
Tacoma II*	99.7	95.4	3.81	3.22
Amax*	99.8	94.1	12.36	3.37
M5-C	80.1	84.2	3.88	7.31
M13-A	86.1	77.6	2.91	5.37
M21-A	75.8	68.0	7.04	5.57
Tacoma I	71.8	69.6	10.7	6.53
Wilsonville	76.4	59.3	8.49	7.71

* maf as received
** neutron activation analysis

Table II

	<u>M11-A</u>	<u>Amax</u>	<u>Tacoma (maf)</u>
%C	89.31	80.57	87.19
%H	5.80	5.50	5.45
%N	1.11	1.57	2.25
%S	0.86	< 0.02	1.3
%O(NA)	2.35	3.37	3.22
MW	497+9	585+7	624+19
Acid meq/mole	2.22	2.95	3.35
Base meq/mole	0.30	0.55	0.84
Pyr. sol. (%)	96.80	94.10	95.38
Har/H α +Ho	1.07	1.00	0.826
H α /Ho	2.58	2.22	3.46
fa	0.813	0.797	0.897
σ	0.304	0.399	0.397
Haru/Car	0.707	0.849	0.701
Cl	1.39	1.45	1.29
Ra	5.28	3.41	5.82
Esr $\Delta H(pp)(G)$	4.8		7.6
g value	2.0026		2.0028
<u>Molecular Formula</u>			
C	36.9	39.2	45.3
H	28.8	32.1	34.0
N	0.39	0.66	1.00
S	0.13		0.25
O	0.73	1.22	1.26
Acid eq/mole	1.10	1.72	2.09
Base eq/mole	0.15	0.32	0.52

References

1. N. Woolsey, R. Baltisberger, K. Klabunde, V. Stenberg and R. Kaba, ACS Fuel Preprints, 2 (7), 33 (1976).
2. Samples were generously supplied by Project Lignite, University of North Dakota and the Grand Forks Energy Research Center.
3. Samples are designated as follows:
 - M5-C-(undeashed) Conditions: 2500 psi of 1:1 CO:H₂ at 455°C (max).*
 - M11-A-(deashed) Conditions: 2500 psi of 1:1 CO:H₂ at 479°C (max).*
 - M13-A-(partly deashed) Conditions: 2500 psi of 1:1 CO:H₂ at 453°C (max).*
 - M21-A-(undeashed) Conditions: 2000 psi of 1:3 CO:H₂ at 439°C (max).*
 - Tacoma I (undeashed): Pittsburgh and Midway Coal Co., Merriam, Kansas (a Gulf subsidiary). From a Kentucky no. 9 and no. 14 blend of bituminous coal from the Colonial Mine. Conditions: PDU, continuous flow, 1500 psi of H₂ (85% min), 450°C (max), using recycle solvent; product not filtered and stored in the open.
 - Tacoma II (deashed): Same as Tacoma I except product filtered before solvent distilled. (maf)
 - Amax-Southern Services, Inc., Birmingham, Alabama (an ERPI contractor). From a sub-bituminous coal from the Bel Air Mine in Wyoming. Conditions: continuous flow, 2500 psi of H₂ and recycle gases, 460° (max) using recycle heavy in phenols with 1, 2 and 3 ring aromatics.
 - Wilsonville-Prepared essentially by the procedure for Amax.
 - J-1-11-87: Reduction fraction of KC-SRL. Conditions: batch autoclave, 4500 psi (max) of H₂ at 450° for 2 hrs. using presulfided HT-100 (NiMo) catalyst b.p. 110-180°C (0.4 mm) followed by removal of solid which precipitated on standing in the freezer for ca. month.
 - COSTeam: Pittsburgh Energy Research Laboratory (an ERDA Lab). N. D. Lignite treated in a tubular reactor with synthesis gas under COSTeam conditions. Conditions: continuous flow, 4000 psi of CO:H₂. Whole product chromatographed on alumina. This fraction eluted with toluene (aromatics fraction). 126-2 (Separation done in Grand Forks Energy Research Laboratory)
4. H. L. Retcofsky, F. K. Schweighardt and M. Hough, Analytical Chem., 49 (4), 585 (1977).
5. H. L. Retcofsky, G. P. Thompson, R. Raymond and R. A. Friedel, Fuel 54, 126 (1975) and papers cited therein.
6. M. Oka, H.-C. Chung and G. R. Gavalas, ibid., 56, 3 (1977).

* Solvent refined N.D. lignite by Project Lignite of the University of North Dakota. PDU operation, FS-120 as make up solvent during recycle operation using ca. 1.8:1 solvent to coal.