

CHROMATOGRAPHIC SEPARATION OF FUNCTIONAL GROUP CLASSES  
FROM PROCESS DERIVED RECYCLE SOLVENTS

by  
G. A. Odoerfer, L. R. Rudnick and D. D. Whitehurst

Mobil Research and Development Corporation, Central Research Division  
P.O. Box 1025, Princeton, New Jersey 08540

INTRODUCTION

To gain a more thorough understanding of the chemistry of coal-solvent interaction in coal liquefaction and to effectively utilize a solvent for this process, detailed information on the chemical composition of the recycle solvent is needed.

The solvent, to be termed a good solvent, must have four critical qualities: it must (1) be able to donate hydrogen to the coal and/or act as a hydrogen transfer agent; (2) function as a physical solvent; (3) prevent char formation; and (4) be chemically stable and be reversibly regenerable to its hydrogen donor form. To identify and quantitatively assess the chemical structures responsible for these actions a chemical characterization method for solvents has been developed.

The development and utilization of this method for separation of a coal derived solvent in terms of different chemical functionalities was our primary objective in this study. The solvent used, Hydrogenated SRC-1 Recycle, is an example of a solvent currently utilized in coal liquefaction studies.

BACKGROUND

Several liquid chromatographic techniques can be found in the literature which potentially could be used for characterization of solvent range coal liquids.

Initially, one such method, the SESC chromatographic procedure (1,2) was employed. This method, based on chromatographic fractionation by sequential elution with specific solvents on silica gel columns, although yielding a good overview of the chemical functionalities present in the samples does not give fine separation of hydrocarbons. This led to the development of the liquid chromatographic technique (RSMC) (3), utilized by us, for the past two years, in the fractionation of coal derived solvents principally of SRC origin.

In the initial portion of this technique, similar to the SARA procedure developed for petroleum liquids (4), fractionation is performed by sequential elution liquid chromatography over basic alumina. The sequence of solvents and chemical species present in each fraction are as follows:

<u>Fraction</u>	<u>Solvent</u>	<u>Chemical Species</u>
1	Petroleum ether*	Saturated hydrocarbons
2	95% Petroleum ether* 5% Benzene	Monoaromatic hydrocarbons with aliphatic substituents (including tetralin and tetralin homologs)
3	85% Petroleum ether* 15% Benzene	Diaromatic hydrocarbons (naphthalene and alkyl derivatives)
4	Tetrahydrofuran; 1% Ethanol	Polyaromatic hydrocarbons Dibenzofuran and other furan derivatives Nonbasic nitrogen compounds
5	Tetrahydrofuran; 10% Water	Phenols and basic nitrogen compounds
6	(Non-eluted)	Polyfunctional Compounds

\* These fractions are now being developed using heptane instead of petroleum ether.

Although this sequence allows good separation of hydrocarbons, and though an improvement over other methods, the technique is not without fault. One difficulty is that phenols, basic components and acidic nitrogen species are sometimes mixed in the same fraction (Fraction 5). Also, polyfunctional molecules, comprising as much as 20% in some process derived solvents (1,3), are generally non-elutable.

To circumvent the problem of non-eluted material a silica column in front of the alumina column could be used to absorb polyfunctional compounds which could then be eluted separately. For the isolation of acidic and basic components, an alternative method is the use of ion-exchange resins as in the SARA procedure.

Two resins, Amberlyst-26 and Amberlyst-15, manufactured by Rohm and Haas, are potentially useful for coal derived solvent separations of this type. The desirability of the Amberlyst type resins is that they are intrinsically porous and can be used for non-aqueous applications as they do not require solvent swelling to become effective. The resin, Amberlyst-26, was used in prior work (5) to isolate the heavy phenol fraction (450°F+), so designated in that it contains no simple single-ring compounds, from a recycle solvent obtained from the Wilsonville, Alabama, Process Demonstration Unit operated by Catalytic, Incorporated for Southern Services, Incorporated. The isolation was quantitative and provided a mixture of phenols and acidic nitrogen compounds (e.g. carbazole). In conjunction with this, reviewing the development of RSMC it was noted that although basic nitrogen and phenols elute in the same fraction (RSMC-5) it appeared that the retention factors were different enough that by introducing an elution solvent of 5% EtOH in THF, separation could be possible.

Considering all past work, a procedure has been developed, using sequential columns of silica, and/or alumina in combination with a strong base ion exchange resin column for separation of a coal derived solvent.

## EXPERIMENTAL

### Sample

The sample used was an Hydrogenated SRC-1 recycle solvent prepared by Conoco Research and Development Corp., and contained 9.67% H. It was initially distilled and the distillation fraction (400-600°F) was used for these studies.

### Material

#### A. Reagents

n-heptane obtained from Aldrich Chemical Company.

Benzene obtained from Fisher Scientific, Fair Lawn, NJ.

Chloroform, Ether(anhydrous) and Methanol were obtained from

J. T. Baker Chemical Co., Phillipsburg, NJ.

Tetrahydrofuran (uninhibited) obtained from Burdick & Jackson.

#### B. Ion-Exchange Resin (Amberlyst A-26)

Skeletal Structure                      Styrene - DVB

Ionic Function                              Quaternary

Porosity (%)                                      27

Surface Area m<sup>2</sup>/g                              28

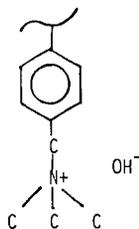
Exchange Capacity:

    meq/g    4.4

    meq/ml    1.0

Stability    in OH<sup>-</sup> form not above 60°C

This resin was rigorously cleaned prior to use by exhaustive washing with MeOH and THF in both Cl<sup>-</sup> and OH<sup>-</sup> forms.



### C. Chromatographic Supports

#### Silica

Preparative - Prep Pack - 500 cartridges (5.7 x 30 cm)  
obtained from Waters Associates.

Analytical - LPS-2 37-53  $\mu\text{m}$  silica gel obtained from  
Whatman Inc., Clifton NJ.

#### Alumina

Basic Alumina Woelm Activity - 1 obtained from ICN.

### PROCEDURE

The overall procedure is shown schematically in Figure 1. The initial separation utilized a modified version of our SESC (1,2) procedure and was performed on a 10 g scale.

The sample, Hydrogenated SRC-1, was dispersed on glass beads (Regular 170/230 mesh) and loaded in a pre-column. Chromatographic separation was then accomplished, using a system similar to the Waters LC/Prep 500 System containing two silica cartridges, at a flow rate of approximately 50 cc/min. The fractions obtained are presented in Table 1.

Each fraction isolated in the initial step was analyzed by analytical SESC, utilizing a stainless steel column (3 x 1000 mm) and 1 cc/min flow rate, to determine the quality of the separation. Vapor-phase chromatograms of each fraction were also obtained on a Hewlett Packard 5750 Research Chromatograph utilizing a Dexsil 300 column (10% on Chromasorb; 1/8" x 10 ft) and programmed at 6°C per minute from 50°C to 350°C.

The hydrocarbons and monofunctional compounds were further fractionated by preparative chromatography over alumina. An Altex analytical glass

column (15 x 1000 mm) equipped with an adjustable plunger and a flow rate of 5 cc/min was used for development of fractions as shown in Figure 1. These fractions were analyzed by vapor phase chromatography.

Both analytical and preparative fractionations were monitored using a Pye 2 Unicam moving wire detector and an Autolab Minigrator. The data from both chromatographic separations are summarized in Table 2.

The chemical and structural nature of the components of each of these fractions are presently being examined by FIMS as well as by other spectral methods and will be the subject of a future publication.

#### RESULTS AND DISCUSSION

The preparative scale chromatography data indicates total recovery of sample from the silica was achieved. Analytical SESC indicates that greater than 90% of the hydrocarbon fraction is saturates and mono, di and polyaromatics. Similar analysis of heterocyclic and functional compound fractions indicate that there is some overlap but that in general the separation obtained appears to be quite good.

Preparative scale separation of both the hydrocarbon and functional compound fractions into sub-groups by RSMC method indicates good separation between chemical groups as outlined in Figure 1. The results, within experimental error, are well in agreement with analytical SESC data and thus give good indication that non basic N, O, S - heterocyclics are contained in fraction B. This fraction may then be further fractionated by ion exchange.

#### CONCLUSIONS

The described fractionation scheme, using sequential columns of silica, alumina and a strong base ion exchange resin, provides separation of process derived coal liquefaction recycle solvents into chemically different fractions containing various hydrocarbons, mono, di and polyaromatics

including sulfur containing heterocycles; furans; non basic N; basic nitrogen species; mono-phenols and polyfunctional compounds.

The combination of fractionation with additional study by elemental analyses, FIMS as well as by other spectral methods leads to a good chemical characterization of each fraction, and the total solvent.

The developed method allows for the circumvention of any problems normally encountered in separating the desired functionalities. The utilization of such method coupled with characterization of the chemical groups obtained allows for the gain of a more thorough understanding of the chemistry of coal-solvent interaction and can lead to a more detailed identification of the chemical composition of recycle solvents.

The latter premise is presently being investigated, for a variety of full range process derived recycle solvents (400-800°F).

#### REFERENCES

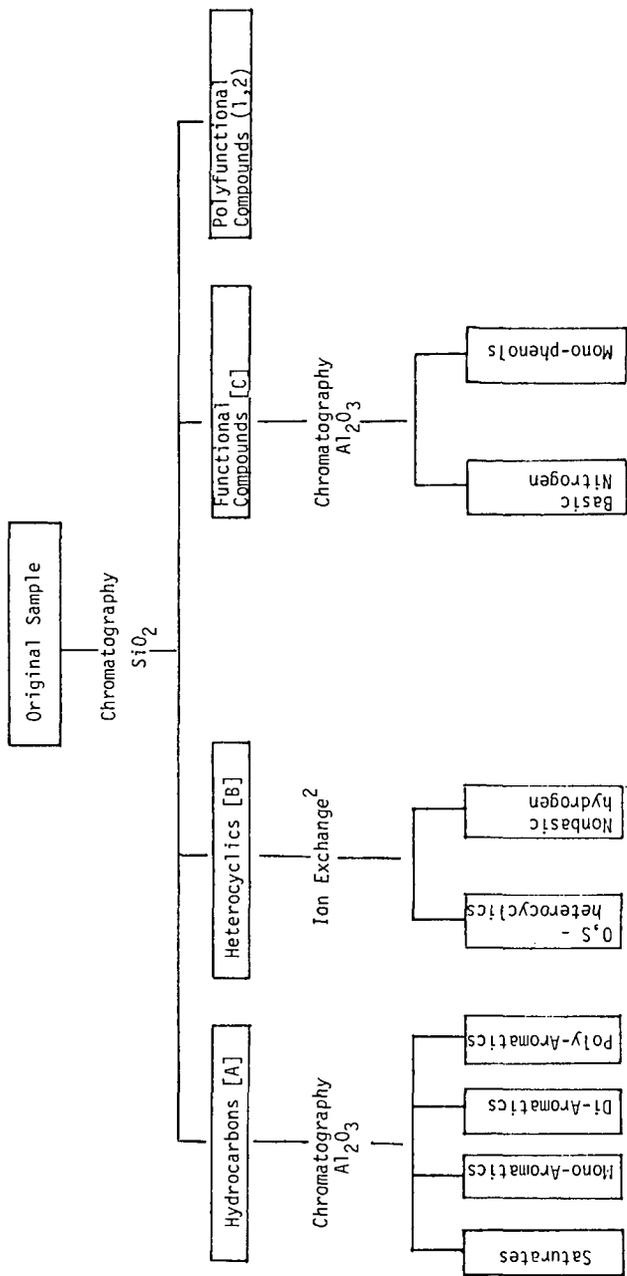
1. D. D. Whitehurst, M. Farcasiu and T. O. Mitchell, "The Nature and Origin of Asphaltenes in Processed Coals," EPRI Report AF-252, First Annual Report Under Project RP-410, February 1976.
2. M. Farcasiu, Fuel, 56, 9 (1976).
3. D. D. Whitehurst, M. Farcasiu, T. O. Mitchell and J. J. Dickert, Jr., "The Nature and Origin of Asphaltenes in Processed Coals," EPRI Report AF-480, Second Annual Report Under Project RP-410, July 1977.
4. E. Lecte, JACS 83, 3645 (1961).
5. D. D. Whitehurst, T. O. Mitchell, M. Farcasiu and J. J. Dickert, Jr., "The Nature and Origin of Asphaltenes in Processed Coals," EPRI Report AF-1298, Final Report Under Project RP-410, Vol. 2, December 1979.

ACKNOWLEDGEMENT

This work was conducted under Electric Power Research Institute (EPRI) Contract No. RP-1655 which is jointly funded by EPRI and Mobil Research and Development Corporation. Mrs. L. F. Atherton is the EPRI Project Manager.

The authors wish to acknowledge Dr. J. Kleinpeter, D. C. Jones, and P. J. Dudt from Conoco Coal Development Corporation for providing the sample used in this study.

Figure 1. Schematic Diagram of the Separation Scheme



1. Fraction was combined with functional compounds for development of the procedure.
2. Actual separation not performed during procedure development. This will be an individual fraction for full range solvent separations.

Table 1  
DATA FROM INITIAL PREPARATIVE CHROMATOGRAPHY

<u>Fraction</u>	<u>Components</u>	<u>Elution Solvent</u>	<u>%</u>
A	Saturates, Mono, Di & Polyaromatics	→ Heptane/ 15% Benzene	~ 80
B	S, O, Heterocyclics and nonbasic N	Chloroform	~ 10
C	Basic Nitrogen & phenols	CHCl <sub>3</sub> /Et <sub>2</sub> O → CHCl <sub>3</sub> /EtOH	~ 10

Table 2  
SEPARATIONS OF INITIAL FRACTIONS

Analytical SESC: (Normal Mode)

	<u>Weight</u> <u>%</u>	<u>Composition</u>	
		<u>Response</u> <u>Factor</u>	<u>Normalized</u> <u>%</u>
Fraction A			
Frac. 1-2	76.4	(1.81)*	90.61
" 3	1.2	(1.30)	1.00
" 4	8.4	(0.52)	2.89
" 5	8.4	(0.42)	2.83
" 6	5.5	(0.87)	3.16
Fraction B			
Frac. 3	59.4	(1.30)	78.2
" 4	28.1	(0.52)	14.8
" 5	8.7	(0.42)	3.7
" 6	3.8	(0.87)	3.3
Fraction C			
Frac. 3	2.1	(1.30)	4.4
" 4	63.6	(0.52)	53.4
" 5	8.3	(0.42)	5.6
" 6-7	21.1	(0.87)	29.6
" 8	2.1	(0.78)	2.6
" 9	2.7	(0.97)	4.2

\* Response factors as determined for solvent 6663. (1,3)

RSMC OF SESC Fractions

<u>Fraction</u>	<u>Fraction A</u>	<u>Fraction C</u>
	<u>%</u>	<u>%</u>
1	27.7	-
1A	8.6	-
2	10.2	-
3	11.4	-
4	15.0	7.0
4A	10.0	42.0
5	10.1	45.0
6	-	~ 5.0*

\* Non-eluted by difference