

COMPARISON OF METHODS FOR THE DETERMINATION OF
ASPHALTENES, OILS AND INSOLUBLES - PART II

Hyman Schultz and Margaret J. Mima

U. S. Department of Energy
Pittsburgh Energy Technology Center
4800 Forbes Avenue, Pittsburgh, PA 15213

INTRODUCTION

According to Sternberg et al., asphaltenes are high molecular weight compounds which affect the viscosity of products from coal conversion processes (10) and may be the intermediaries in the formation of oil from coal (3, 6, 12). Asphaltenes have traditionally been defined by their solubility properties. A knowledge of the concentration of asphaltenes in coal-derived oil is often helpful to the engineer in evaluating hydrotreating processes. Studies of coal hydrogenation at DOE's Pittsburgh Energy Technology Center (formerly Pittsburgh Energy Research Center, Bureau of Mines) over the years often depended on the determination of asphaltenes (5, 11, 12). However, there is no standard method for the determination of asphaltenes in the products from coal conversion, nor is there any known relationship between asphaltene values produced by the analytical methods currently in use. Therefore, one cannot with any degree of confidence compare the asphaltene content of coal derived liquid fuels that are analyzed by different methods. At present, every laboratory has developed its own procedure for determining asphaltenes in coal-derived materials.

In order to ascertain if the different methods used to determine asphaltenes in coal-derived materials produce significantly different results, a study was initiated at the Pittsburgh Energy Technology Center aimed at objectively comparing five different methods currently used to analyze such

materials for asphaltenes, oils and insolubles. Part I of the study involved the use of a hydroliquefaction product of intermediate asphaltene content as a test material and was reported previously (7). Part II of the study is reported herein and involves the use of a high asphaltene containing substance as the test material.

EXPERIMENTAL

The experimental methods used were the same as those employed in Part I (7). A solid product from the Solvent Refined Coal (SRC) plant of Fort Lewis, Washington was chosen for the "standard" material. A large sample of the SRC was provided by the Combustion Division at PETC and was subsequently ground to pass through a 60-mesh screen. After thorough mixing, the SRC was divided into five portions which were stored under nitrogen in sealed, dark glass bottles until used.

The analytical procedures used were outlined previously (7) and will be described in greater detail in a future publication.

Method A has been in use by the Analytical Chemistry Branch at PETC for years for routine, high volume work and requires only inexpensive equipment (5). No attempt is made to keep the sample or the various fractions from contact with the air since chemical characterization of the fractions was not a consideration in the design or use of this method.

Method B was developed in the Molecular Spectroscopy Branch at PETC to give rapid results with a small number of samples and to produce fractions for further study (8).

Method C was designed in the Process Sciences Division at PETC as a means of studying the conditions for precipitation of asphaltenes and for preparing fractions for further study (2, 9).

Method D was developed at ARCO as a means of preparing fractions for further study (4).

Method E was designed at EXXON Research and Engineering Company as a preparative method (1). Due to the limited amount of sample available and after consultations with the originators of the method, a 25 gram sample size was employed instead of the 50 gram sample originally specified.

RESULTS AND DISCUSSION

The results of the study are shown in Table 1. After replicating method C a number of times it became apparent that the results varied so widely that the method was not working well enough to warrant continued replication. It was concluded that the probable cause of the observed variation was the passing of fine particles through the extraction thimble in a non-reproducible way. The results for method C were therefore left out of Table 1.

The averages vary over almost a factor of 2 for insolubles and asphaltenes and almost a factor of 15 for the oils. The ranges for the relative standard deviations were 4 to 9% for the insolubles, 6 to 15% for the asphaltenes and 4 to 40% for the oils.

The sums of the average values of insolubles, asphaltenes and oils for methods B, D and E (the oils are calculated by difference in method A) add up to more than 100%. While the difference between the sums of the average values and 100% are not statistically significant at the 95% confidence interval for methods B and D (it is for method E), the fact that all three methods show sums of greater than 100% can be interpreted as evidence of solvent retention in the fractions (the use of nitrogen in these methods would make oxidation an unlikely explanation).

In order to determine in an objective manner if significant differences exist between the results obtained from the various methods, Student's "t" test was applied. The results obtained with methods A, B, D and E were compared two at a time and in all cases statistically significant differences were found.

Based on the experience gained during this study the analysts involved made estimates for each method of the elapsed time and man-hours necessary to complete a determination and of the expected production rate. They concluded that in all cases these were not as favorable as those for the medium asphaltene material in Part I of the study (7). The differences were mainly due to the difficulties encountered in removing solvents from the insoluble material and, in some cases, the oils.

CONCLUSIONS

This study has shown that materials high in asphaltenes are more difficult to analyze for their asphaltene content than materials of moderate asphaltene content. Indeed, one of the test methods failed completely to work with the test sample. As authors of the method report (9) successfully applying the method to an SRC-I material, it was concluded that our results were caused by either of two things. First, although the specifications spelled out in the method were met, the Soxhlet thimbles were obtained from a different manufacturer than used by the originators and therefore may have been of a different porosity allowing fine particles through. Second, the SRC used was different than that reported on and may have been ground to a different average particle size.

Four of the methods worked but were less precise, required more effort and produced analyses at a lower rate than they did with the more tractable medium asphaltene material. In spite of all the above, methods A, B, D and

E could be used to analyze high asphaltene materials but each will produce different results with the same material. Clearly a standard method is called for but whether one method can be devised that will be usable with coal derived materials of widely varying asphaltene content is problematical.

REFERENCES

1. Aczel, T., R. B. Williams, R. J. Pancirov, and J. H. Karchmer. Chemical Properties of SYNTHOIL Products and Feeds, Anal. Proj. Rept. BRD.1BA.76, EXXON Research and Engineering Company, Baytown, Texas.
2. Bockrath, B. C. PETC/DOE, personal communication, May 1977.
3. Husack, R. and C. Golumbic. J. Am. Chem. Soc. 73, 1567 (1951).
4. Kutta, H. W. and E. H. Burk. Investigations on the Nature of Preasphaltenes Derived From Solvent Refined Coal Conversion Products, Atlantic Richfield Company, Harvey Technical Center, 400 E. Sibley Boulevard, Harvey, Illinois.
5. Mima, M. J., H. Schultz, and W. E. McKinstry. Method for the Determination of Benzene Insolubles, Asphaltenes, and Oils in Coal-Derived Liquids, PERC/RI-76/6.
6. Pelipetz, M. G., E. M. Kuhn, S. Friedman, and H. H. Storch. Ind. & Eng. Chem. 40, 1259 (1948).
7. Schultz, H. and M. J. Mima. American Chemical Society, Division of Fuel Chemistry, Preprints of papers presented at Anaheim, California, March 12-17, 1978, Volume 23, No. 2, pp. 76-78.
8. Schweighardt, F. K. PETC/DOE, personal communication, January 1977.
9. Steffgen, F. W., K. T. Schroeder, and B. C. Bockrath. Anal. Chem 51, 1164 (1979).
10. Sternberg, H. W., R. Raymond, and F. K. Schweighardt, Science 188, 49 (1975).
11. Weller, S., M. G. Pelipetz, and S. Friedman. Ind. & Eng. Chem. 43, 1572 (1951).
12. Weller, S., op.cit., pp. 1575-79.

Table 1. Average of 20 replicate analyses of a sample of SRC.

<u>Method</u>	<u>% Insolubles</u> <u>± 1S</u>	<u>% Asphaltenes</u> <u>± 1S</u>	<u>% Oils</u> <u>± 1S</u>
A	37 ± 3	52 ± 3	12 ± 2
B	58 ± 5	43 ± 6	1.5 ± 0.6
C	<u>See Text</u>		
D	64 ± 3	27 ± 4	14 ± 2
E	49 ± 2	34 ± 2	22.0 ± 0.8