

Fuel Oil Compatibility Probed

J.W. HOLMES,
Bryan Research & Engineering, Inc.,
Bryan, Texas

J.A. BULLIN,
Texas A&M University,
College Station, Texas

ABSTRACT

A severe case of incompatibility occurred when three residual fuel oils were shipped as a blend. The oils were blended as they were being loaded. During transport, a tar-like precipitant formed, settled to the bottom and partially solidified. These fuel oils were analyzed in an attempt to predict future potential incompatibility problems and to investigate the known case of incompatibility.

Hydrocarbon Processing September 1983: 101-103.

[Bryan Research & Engineering, Inc.](#)

Visit our Engineering Resources page for more articles.

A severe case of incompatibility occurred when three residual fuel oils were shipped as a blend. The oils were blended as they were being loaded. During transport, a tar-like precipitant formed, settled to the bottom and partially solidified. These fuel oils were analyzed in an attempt to predict future potential incompatibility problems and to investigate the known case of incompatibility.

Several studies on the chemical and physical characteristics of heavy fuel oils and on handling problems have been reported in the literature.¹⁻¹⁸ An excellent summary of the handling problems has been presented by Martin.¹⁹ As distinguished by Martin, "instability" refers to the tendency of a residual fuel to produce a deposit by itself. "Incompatibility" is the tendency of a residual fuel to produce a deposit when blended with other fuel oils. Two fuels, each stable in itself, may be incompatible when mixed. Although a case of incompatibility is easily recognized after it has occurred, prediction of potential incompatibility is not so simple.

This study showed that major incompatibility problems occur when an oil with an asphaltene content greater than three to five percent is blended with other oils which are primarily paraffinic. This improper blending caused the precipitation of the tar-like material in the known case of incompatibility.

Better tests needed. Since the composition of these fuel oils is very complex, their characterization is generally limited to meeting specifications as defined by the American Society for Testing and Materials (ASTM). These usually include API gravity, viscosity, distillation temperature, and flash point. The composition of the heavy oil depends on the origin of the crude as well as the refining scheme. These specifications are not indicative of the oil composition. Since heavy fuel oils contain a very large number of different hydrocarbon compounds, their composition is generally specified in terms of three main classes: paraffinic, aromatic and naphthenic. The aromatics can include some very heavy compounds in the molecular weight range of 1000 to 20,000, which are known as asphaltenes.¹ When fuel oils with a significant asphaltene content are mixed with oils of primarily paraffinic content, the asphaltenes might precipitate.

Small amounts of asphaltenes commonly precipitate out of residual fuel oils during storage over periods of

several months. The resulting sludge can often be remixed with the oil so the mixture is pumpable. However, aromatic No. 6 oils, when sufficiently heated and aerated, will produce increasingly heavier asphaltenes until transformed into tar or asphalt, usable in roofing and road surfacing.

In the present work, the results from an investigation of a severe case of incompatibility between heavy fuel oils are presented. As a part of the investigation, samples of heavy fuel oil from several suppliers in the Gulf Coast area were obtained and analyzed. The ASTM spot tests, the ASTM test for asphaltene content, gel permeation chromatography (GPC) and other tests were used to evaluate the incompatibility of two or more fuel oils.

Analytical methods for this study. Samples of several heavy fuel oils and mixtures thereof were analyzed using one or more of the following methods.

The only compatibility test listed in the ASTM Index of Tests is ASTM D2781 entitled "Compatibility of Fuel Oil Blends by Spot Test."²⁰ The technical description states that this test is valid to predict the compatibility between a residual fuel oil and a specific distillate fuel oil, such as a No. 1 or No. 2 fuel oil. In the test, equal volumes of the two oils are blended at 140 to 145°F and a drop of the blend is allowed to spread on chromatographic paper of a specified grade. The compatibility of the two oils is rated by comparing the spot to a series of reference spots.

A telephone survey of several heavy fuel oil suppliers in the Gulf Coast area revealed that this test is the only test commonly used for compatibility of two or more heavy fuel oils. This test is used even though the method specifically states that it is for a residual fuel oil and a specified distillate fuel oil.

Another test related to heavy fuel oils is ASTM D3279 for the determination of weight percent asphaltenes.²¹ In this method, a sample is dispersed in n-heptane by gentle refluxing. The mixture is cooled and filtered. The insoluble material is washed, dried and weighted to determine the weight percent of n-heptane insolubles. These are called asphaltenes. The method is tedious and requires several hours to perform. In addition, only one gram of sample is used and since the precipitated asphaltenes are transferred from a flask to a filter, several errors can enter into the analysis.

A gel permeation chromatograph (GPC) was also used to analyze the heavy fuel oils. The GPC separates molecules on the basis of linear molecular size and the samples elute in decreasing order of molecular length. The samples were prepared by dissolving the oil in tetrahydrofuran and filtering. A Waters Associate Model ALG/GPC 202 liquid chromatograph equipped with a Model R401 refractometer was used. Straight chain alkanes from Applied Science and polystyrene standards from Waters Associates were used for the molecular size calibration of the GPC. A detailed discussion of the application of GPC for the analysis of heavy fuel oils has been presented by Philip, et al.²² They showed that the asphaltenic, paraffinic and light aromatic content of heavy fuel oils can be easily determined by GPC. A chromatogram showing the molecular sizes and relative amounts of each hydrocarbon group is presented in Figure 1.

Selected samples of different fuel oils were also mixed with varying amounts of n-heptane at room temperature. These mixtures were visually inspected for precipitants. The ASTM spot test was also performed on some of these mixtures.

Samples tested. The fuel oil samples used in the present work are identified as samples A through E. Sample F is a portion of the solidified material resulting from an incompatible mixture of samples A, B and C.

Sample I.D.	Asphaltenes by ASTM	Asphaltenes by GPC	Paraffins by GPC	Light Aromatics by GPC
A	17	14	39	47
B	0	NIL	84	16
C	0	NIL	60	40
D	0	NIL	82	18
E	0	NIL	60	40
F	42	36	45	19

The results from the asphaltene tests by ASTM D3279 are shown in Table I along with some of the results from

the GPC analyses. From the five oils from suppliers represented by samples A through E, the only one with any appreciable asphaltene content was oil A. The GPC can also be used to estimate the asphaltene content of fuel oils. As can be seen in Table I, the GPC results agreed closely with the asphaltene content by ASTM D3279.

A GPC chromatogram for oils A and C are presented in Figures 1 and 2, respectively. As determined by Philip, et al²², the asphaltenes in oil A are the hydrocarbons with a molecular weight above about 2,900. This corresponds to compounds with linear molecular sizes greater than $n\text{-C}_{44}\text{H}_{80}$. The paraffins are primarily those compounds with linear molecular sizes between $n\text{-C}_{44}\text{H}_{80}$ and $\text{C}_{12}\text{H}_{26}$ while the light aromatics are those compounds with linear molecular sizes smaller than $n\text{-C}_{12}\text{H}_{26}$. The estimated paraffinic and light aromatic content of oils are included in Table I.

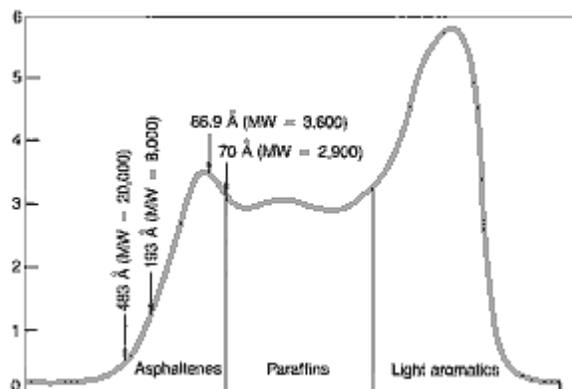


Figure 1. GPC chromatogram, Sample A.

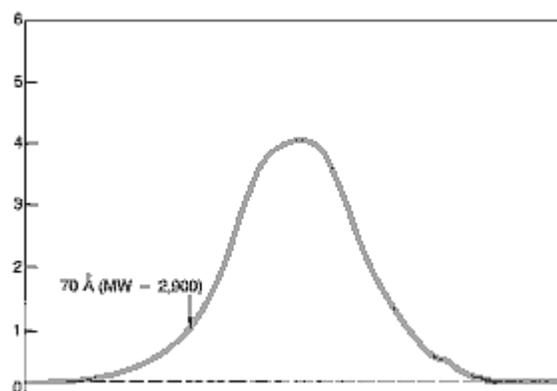


Figure 2. GPC chromatogram, Sample C.

The GPC gives both leading and trailing tails to the peaks. Thus, when determining the asphaltene content, a definite peak should exist in the molecular weight range above 2,900. In Figure 2, a slight leading tail above 2,900 molecular weight can be seen. However, no indication of a peak is evident and the oil contained no asphaltenes as verified by ASTM D3279. If there were any doubt about the asphaltene content, the ASTM test could be performed even though it requires several hours compared to about 30 minutes for the GPC analysis.

Previous blending of one of the fuel oils (sample A) is indicated by the GPC analysis. The GPC chromatogram for oils B, C, D and E showed a smooth curve with hydrocarbon molecular weights primarily in the paraffin range. The chromatogram shown in Figure 2 for oil C is representative for oils B, D and E. This can be contrasted to the chromatogram for oil A in Figure 1, which shows major peaks in the asphaltenic, paraffinic and light aromatic areas. The large light aromatic content suggests that light aromatics were added to the fuel oil to dissolve the asphaltenes, to keep them in solution and to ensure that the oil would meet the specifications for No. 6 fuel oil. If oil A is kept segregated, the light aromatics should keep the asphaltenes in solution and few problems should occur. However, when oil A is blended with other oils of high paraffinic content, such as oils B through E, the asphaltenes can be precipitated. The only difference between the precipitation caused by these paraffins and by n-heptane used in ASTM D3279 is that lighter paraffins will precipitate more of the asphaltenes.

Another related series of tests consisted of mixing varying proportions of the fuel oil samples and n-heptane at

room conditions. As expected, since no asphaltenes were present, oils B through E mixed readily with the n-heptane in all proportions and caused no problems. However, when n-heptane was mixed with oil A which contained about 15% asphaltenes, a fine brown precipitant formed at heptane/oil A ratios up to about 1.7:1. This fine precipitant dispersed easily into the oil and probably would not have caused any pumping problems. However, at heptane/oil A ratios near 2:1, a tar-like substance was formed almost immediately in the mixture. The amount of the tar-like substance was about 5 to 10% of the mixture volume. Combined with the fact that no previous asphaltene deposit had occurred in various blends of oils A, B and C, the heptane/oil blending tests indicate that rather precise mixtures of the oils would be required to produce the tar-like deposit. These tests are summarized in Table II.

Blends	Observations
A -- B -- C	Severe incompatibility. Tar-like precipitant (Sample F) settled and partially solidified during shipping.
A -- B A -- C A -- D A -- E	Severe incompatibility possible
n-heptane -- A	Fine brown precipitant formed at ratios up to about 1.7:1 for heptane/oil. Precipitant dispersed easily. No pumping problems anticipated. At ratios near 2:1 heptane/oil, tar-like substance formed that was about 5% to 10% of the mix, although no change was exhibited by the spot test.
n-heptane -- B n-heptane -- C n-heptane -- D n-heptane -- E	No precipitant. Blends mixed readily in all proportions.

The spot test for compatibility. (ASTM D2781) was performed on some of the heptane/oil mixtures. The heptane did not influence the spot rating of 1 for oils B through E. In the heptane/oil A mixture of about 2:1 where the tar-like substance was formed, a spot rating of 1 was also obtained. This was apparently because the tar-like deposit formed very quickly and any incompatibility in the remaining liquid was eliminated by the deposit. Thus, the ASTM D2781 spot test may be helpful in predicting light asphaltene precipitation which might cause clogging of fuel burners and perhaps deposit or sediment over several months of storage, but it is not a reliable tool to predict major asphaltene deposits in blends of heavy fuel oils.

When blends of different fuel oils are needed, laboratory blends in the proper proportions could be made for visual inspection of incompatibility. However, since most of the heavy fuel oils are black, visual observations through the fluid are impossible. Close inspection with a stirring rod or spatula would reveal major deposits but could easily miss minor or nonagglomerating deposits.

In summary. Gel permeation chromatography (GPC) can be used to characterize heavy fuel oils into asphaltenic, paraffinic and light aromatic groups. The asphaltenic content by GPC and ASTM D3279 were found to agree within about 15%. The GPC results can give an indication of previous blending of a fuel oil. The heptane/fuel oil blends showed that if asphaltenes are present in a fuel oil, a fine precipitant can be formed and, at certain heptane/oil ratios, a tar-like deposit can be formed. The ASTM spot test for compatibility, designed for blending a light distillate oil with a heavy fuel oil, was found unreliable as a test for compatibility of two or more heavy fuel oils.

ACKNOWLEDGMENTS

Special thanks are extended to Drs. C. V. Philip, R. G. Anthony and L. E. Mohrman of the Chemical Engineering Department at Texas A&M University for their contributions to the work. The financial support of the Texas Engineering Experiment Station and the Center for Energy and Mineral Resources at Texas A&M University is very much appreciated.

LITERATURE CITED

1. Long, R. B., "The Concept of Asphaltenes," ACS Symposium Series, Chemistry of Asphaltenes, Vol. 24, No. 4, 1979.
2. Ancillotti, F., Pescarello, E., "Fuel Blends Create Solubility Problems," Hydrocarbon Proc., 11, pp.295-299, 1977.
3. Dieker, E. V., "Two Years Experience in Handling and Burning No. 6 Low Sulfur Fuel Oil," Combustion, 1, pp.34-36, 1972.
4. Exley, L. M., "A Practical Review of Residual Oil Firing Problems and Solutions," Combustion, 3, pp.16-23, 1970.
5. Harbert, W. D., "Jug Gives Online Bottom Blends," Hydrocarbon Proc., 58, pp.139-140, 1979.
6. Knepper, J. I., Hutton, R. P., "Blend for Lower Pour Point," Hydrocarbon Proc., 9, pp.129-136, 1975.
7. Kyriacopoulos, G. B., "Blending Oil for Viscosity Index," Hydrocarbon Proc., 9, pp.137-138, 1975.
8. Robertson, W. N., "Fuel Oil Handling Systems for Glass Furnaces," Ceramic Bulletin, 57, pp.1,028-1,031, 1978.
9. Siegert, L. D., "Residual Oil Handling and Burning for Modern Cement Kilns," Rock Products, July, p. 72, 1971.
10. Yen, T. F., "Structural Difference Between Petroleum and Coal-Derived Asphaltenes," ACS Symposium Series, Chemistry of Asphaltenes, Vol. 24, No. 4, 1979.
11. Speight, J. G. and W. E. Moschopedis, "Some Observations on the Molecular Nature of Petroleum Asphaltenes," ACS Symposium Series, Chemistry of Asphaltenes, Vol. 24, No. 4, 1979.
12. Hall, G. and S. P. Herron, "Size Characterization of Petroleum Asphaltenes and Maltenes," ACS Symposium Series, Chemistry of Asphaltenes, Vol. 24, No. 4, 1979.
13. Hernandez, J. O. and E. Choren, "Thermal Stability of Asphaltenes," ACS Symposium Series, Chemistry of Asphaltenes, Vol. 24, No. 4, 1979.
14. Fuel Oil Manual, P. F. Schmidt, Industrial Press, New York, N.Y., 1951.
15. McKay, J. F., P.J. Amend, P. M. Harnsberger, T. E. Cogswell and D. R. Lathem, "Separation and Analyses of Petroleum Residues," Laramie Energy Research Center, Energy Research and Development Administration, Laramie, Wyo., pp.52-57.
16. "How to Deal with Heavy Fuel Residues," *Chemicals*, September 1979.
17. Petroleum Refinery Handbook, 4th ed., W. L. Nelson, McGraw-Hill Books, New York, N.Y., 1958.
18. Petroleum Products Handbook, 1st ed., V. B. Guthrie, ed., McGraw-Hill Books, New York, N.Y., 1960.
19. Martin, C. W. G., "The Stability and Compatibility of Fuel Oils," Proceedings Third World Petroleum Congress, Section VII, pp.66-75.
20. American Society for Testing and Materials, Test Method ANSI/ASTM D2781.
21. American Society for Testing and Materials, Test Method ANSI/ASTM D3279.

22. Philip, C. V., J. A. Bullin and R. G. Anthony, "Separation of Heavy Fuel Oils by Gel Permeation Chromatography," submitted for publication in Fuel Processing Technology, June 1983.

copyright 2001 Bryan Research & Engineering, Inc.