



TRC0804

**Verifying and Simplifying Tests for
Presence of Air Blown Asphalt**

John R. Hardee

Final Report

2008

Final Report

TRC 0804

Verifying and Simplifying Tests for the Presence of Air Blown Asphalt

by

John R. Hardee

conducted by

Department of Chemistry
Henderson State University

in cooperation with

Arkansas State Highway and Transportation Department

Henderson State University
Arkadelphia, Arkansas 71999-0001

October 2008

Acknowledgements/Disclaimer

The content of this report reflects the views of the author who is responsible for the facts and accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the Arkansas State Highway and Transportation Department. This report does not constitute a standard, specification, or regulation.

Abstract

Three laboratory tests (identified in MBTC 2076 and MBTC 2049) for the presence of air-blown asphalt were evaluated using asphalt from 15 feedstocks. Tests involving relative viscosities of toluene solutions of asphaltenes and diffuse reflectance Fourier Transform spectroscopy could not reproducibly predict the presence of air-blown asphalt. Refractive index measurement of toluene solutions of asphalts also proved to be of no value in this regard. A solubility test involving asphaltenes in a heptane-toluene solution accurately predicted the presence or absence of air-blown asphalt in all 15 samples. The detection of a precipitate was simplified by eliminating a centrifuging step. Gel permeation chromatography proved also to be useful and accurately predicted the presence or absence of air-blown asphalt in all samples tested.

Introduction

Chemical and physical properties of air-blown asphalt blends were reported in MBTC 2049. Following this study, the characteristics of air-blown blends from three different feedstocks were described in MBTC 2076. Based on three different asphalt sources, the following differences between air-blown and non air-blown blends were observed:

1. Relative viscosities (relative to the solvent toluene) for solutions of asphaltenes from air-blown blends are the same at 30° and 45°C, while differences in relative viscosities for solutions of asphaltenes from non air-blown blends were observed at these temperatures.
2. From relative viscosity data it appears the concentration at which asphaltene aggregation occurs is lower for air-blown asphaltenes than it is for non air-blown asphaltenes.
3. Refractive index data show that when heptane is added to toluene solutions of asphaltenes, non air-blown asphaltenes precipitate before air-blown asphaltenes. This provides evidence that even though air blown asphaltenes are more polar than non air-blown asphaltenes, the structure of aggregates of air-blown asphaltenes must be more open and less tightly packed than aggregates of non air-blown asphaltenes.
4. Precipitation of non air-blown asphaltenes at lower heptane volumes was directly observed by titrating toluene solutions with heptane and centrifuging solutions.
5. Diffuse reflectance infrared Fourier Transform (DRIFT) spectroscopy indicates air blowing oxidizes carbon-nitrogen, carbon-sulfur, and carbon-oxygen bonds. The peak responsible for C-N, C-S, and C-O stretching ($1070-960\text{ cm}^{-1}$) diminishes as the percent air-blown blend in the binder increases.
6. In MBTC 2049, gel permeation chromatography results indicate an increase in molecular weight when asphalt is air-blown. This results in a “front end tailing” of higher molecular weight material in air blown blends that is not present with non air-blown blends.

These six observations offer the potential for the development of laboratory tests that may distinguish between air-blown and non air-blown asphalt blends. The purpose of this study is to determine if the above observations hold true for a larger number of feedstocks and, if possible, develop in simplest form, one or more laboratory tests to identify the presence of air-blown asphalt.

Experimental

Iatroscan Analysis

Samples were first deasphalted in accordance with ASTM D3279 to yield maltenes. The maltenes were adsorbed on 5 micron silica-gel and fractionated by upward elution on silica-gel coated glass rods using pentane to separate saturates, and then a toluene/chloroform solution to separate resins from the aromatics. The three separated fractions were then burned from the chromarods using flame ionized detection (FID) and flame thermionic ionization detection systems.

Air Blowing

Air-blown asphalts from Ergon and Marathon were prepared by blowing at 490-500F for 4.5 hours with an air rate of 1.11 gal/min. The air-blown material was blended with the base asphalt (for Ergon asphalt this was a flux and for Marathon asphalt this was a PG 52-28) to an ODSR at 67° C of 1.3 kPa. Based on experience from contacts in industry, both materials should pass PG67-22 specifications. The weight percent air-blown is 50% for the Ergon blend and 27% air-blown for the Marathon blend.

A third air-blown asphalt was prepared by air-blowing a flux from Lion Oil which had a viscosity of 555 saybolt fural seconds, a softening point of 100° F, and a penetration value of 280/10 at 77° F. A hard asphalt with a softening point of 160° F and a penetration value of 7mm/10 at 77° F was prepared by propane extraction of the flux. Air-blown asphalt was prepared by air blowing the flux for 6.5 hours in a 1.59 gallon container at a temperature range of 490 to 500° F and an air flow rate of 1.1 ft³/min. The resulting air-blown asphalt had a softening point of 219° F and a penetration value at 77° F of 14mm/10. The flux from Lion Oil was blended with 39 wt % air-blown asphalt to a PG64-22.

Separation of Asphaltenes

Asphalt was mixed with heptane at a concentration of 10% (w/v). The mixture was refluxed for 2 hours and then left to settle 12 to 16 hours. The heptane insolubles were recovered on a Buchner funnel over an Erlenmeyer flask connected to an aspirator. The filtrate was washed on the filter paper three times with 50 mL portions of heptane and then placed in a beaker and stirred in excess heptane for 4 hours. The heptane insolubles were filtered again, washed three times with heptane, and then dissolved in toluene. The asphaltene toluene solution was stirred overnight and then filtered. Toluene was evaporated slowly in a hood leaving the purified asphaltenes. Asphaltenes were heated to 150° C and evacuated for 2 hours to remove any remaining toluene.

Gel Permeation Chromatography

Gel Permeation Chromatography (GPC) was performed on a Hewlett-Packard 1050 HPLC. A TSK-GEL^RG4000H_{HR} column and a TSK-GEL^RG3000 column were used in series. An H_XL² guard column was placed in line before the two GEL^R columns. 0.1 g of sample was dissolved in 10 mL of tetrahydrofuran (THF) and then stirred with a magnetic stirrer for 30 minutes. The resulting solution was passed through a 0.45 μ filter. Analysis was performed on a 25 μL injection. Tetrahydrofuran was used as the solvent at a flow rate of 1 mL/min. The columns were maintained at a temperature of 35°C and a refractive index detector was used.

Viscosity

Viscosity measurements were made using a Cannon glass capillary viscometer. Solutions were prepared and stirred overnight. The viscometer was placed in a constant temperature bath for 15 minutes before measurements were made. For each solution the viscosity was measured at least three times and an average of the readings was reported.

Refractive Index

Solutions of asphaltenes were prepared at concentrations of 8 g/L and were stirred overnight. An ATAGO refractometer equipped with a digital thermometer was used at a constant temperature of 25.6 Celsius degrees.

Solubility Experiments

Asphaltene solutions were prepared by dissolving 0.100 g in 2.00 mL of toluene at 25°C. Solutions were stirred from 12 to 15 hours to ensure equilibrium was achieved. Heptane was then added with vigorous stirring using a micropipette. Stirring was stopped and solutions were left undisturbed for 10 to 12 hours. Precipitates were noted by direct observation of drops on filter paper.

Diffuse Reflectance

Approximately 0.05 g of asphaltenes were ground with an agate mortar and pestle and physically mixed with 0.200 g of KBr. and. One cup was filled with this mixture, while another cup was filled with KBr in a Pike diffuse reflectance apparatus. A Midac Series M infrared spectrophotometer was aligned and then the background was established using pure KBr. One hundred scans were run at a resolution of 8 cm⁻¹ for the background. The asphaltene-KBr mixture was then placed in the path of the IR beam and scanned 50 times at a resolution of 8 cm⁻¹.

Results

Iatroscan Analysis

Compositions of asphalt blends are shown in Table 1.

Table 1. Iatroscan Analysis

Sample	Performance Grade	Wt % Asphaltenes	Wt % Resins	Wt % Aromatics	Wt % Saturates
Newell Resin		0.25	5.82	76.04	17.89
Hunt	67-22	17.82	11.86	64.25	6.07
Valero-Ardmore*	64-22	10.4	13.9	69.94	5.75
Venezuela		15.72	20.78	60.08	3.41
Suncor Heavy Resid		26.27	7.92	58.87	6.94
BP Amaco		15.49	14.26	62.5	7.76
Sinclair Wyoming		17.66	13.48	60.63	8.23
Exxon-Mobile Baytown		17.89	13.95	64.52	3.64
China 2710	70-22	10.97	26.94	50.68	11.1
China 2770	58-22	7.79	24.27	52.16	15.78
Staatsolie	58-22	3.6	17.9	70.9	7.5
Afganistan	58-22	9.15	9.43	80.56	0.86
Lion Oil	58-22	7.8	22.9	61.5	7.8
Ergon	67-22	10.6	68.6	14.0	6.8
Marathon	67-22	14.2	67.3	12.5	5.6

*later found to be an air blown blend

Results in Table 1 indicate a good variety of asphalts were used in this study. Asphaltene levels vary from a low of 0.25 wt % to a high of 26.27 wt %. A high asphaltene content (>20 wt %) can sometimes be an indication of an air blown blend. Even though it is a good idea to be suspicious of an asphalt with a high asphaltene content, Suncor Heavy Resid had 26 wt % asphaltenes and all evidence indicated it was not air blown. On the other hand, the Valero-Ardmore blend was found to be air-blown with only a 10 wt % asphaltene content.

Solubility Experiments

Differences in solubility behavior of asphaltenes were observed in heptane-toluene solutions in MBTC 2076. When heptane was added to toluene solutions of asphaltenes, it required more heptane to precipitate asphaltenes from air-blown asphalt than it did asphaltenes from non air-blown asphalt. Precipitation of asphaltenes from non air-blown asphalt at a concentration of 50.0 g/L in toluene occurred when the volume percent heptanes reached 46 volume percent. This procedure was repeated with 14 of the 15 asphalts listed in Table 1. The low asphaltene content of the Newell Resin prevented the isolation of a sufficient amount of asphaltenes to be used in the solubility test. Initial results were disturbing in that precipitation was not observed for the majority of the asphaltene solutions. Even the asphaltenes from non air-blown blends used in MBTC 2076 would not precipitate. The problem appeared to be that the test was run on asphaltenes that were 2 to 4 months old. Even though samples were stored in the dark in amber bottles, enough oxidation occurred for the majority of asphaltenes to appear as if they came from air blown blends.

Fresh asphaltenes were isolated from 14 of these asphalts along with asphaltenes from three known air blown blends. Heptane was added to toluene solutions of asphaltenes (50.0 g/L) with stirring until the heptanes concentration reached 46 volume percent. Stirring was stopped and the samples were left undisturbed for 10 hours. Precipitation was observed in 13 of the samples, while asphaltenes from the Valero-Ardmore blend and the three air-blown blends remained in solution. Further investigation revealed the Valero-Ardmore blend was actually air-blown.

Samples were not centrifuged in order to observe a precipitate. Instead, a drop of solution was placed on filter paper and the presence of a precipitate was confirmed by the appearance of a dark inner circle surrounded by a lighter circle which formed as the solvent diffused through the filter paper.

There are four conditions that must be met in order for this solubility test to accurately detect the presence of air-blown asphalt: (1) asphaltenes must be properly washed, (2) asphaltenes must be fresh, (3) toluene solutions must be stirred for at least 10 hours before titrating with heptanes, and (4) after heptanes addition, solutions must be left undisturbed for 10 hours before testing for precipitates.

In an attempt to circumvent asphaltene separation, asphalt samples were dissolved directly in toluene and titrated with heptanes. No trend in precipitation was observed with these solutions and it appears that this test must be carried out with asphaltene solutions.

Diffuse Reflectance Spectroscopy

Infrared and diffuse reflectance infrared Fourier Transform (DRIFT) spectroscopy have been used to study weatherability of coating asphalts (1) and to study structural features of resins, asphaltenes, and kerogen (1). Figure 2 shows a typical DRIFT spectrum for an asphaltene from an asphalt used in this study.

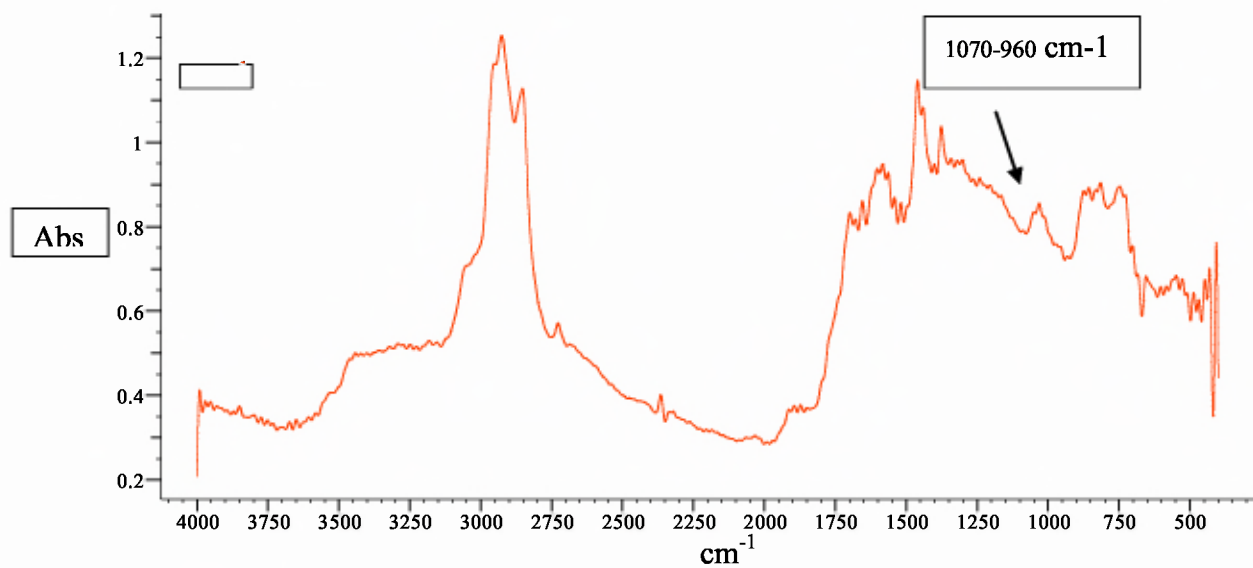


Figure 2. DRIFT of an asphaltene from an air blown blend plotted as absorbance versus wavenumber.

Table 2 shows peak assignments for this spectrum.

Wavenumber (cm ⁻¹)	Type of Functionality
3100-3000	Aromatic stretch
2950 shoulder	Asymmetric CH ₃ - stretch
2925	CH stretching
2855	CH stretching
1820-1650	Aldehyde, ketone and acidic carbonyl
1600	Aromatic C=C
1460	C—CH ₃ and —CH ₂ — asymmetric stretch
1375	Symmetric C—CH ₃ bend
1070-960	C—N, C—S, C—O stretch
880-790	Aromatic C—H stretch

Table 2. Peak assignment for DRIFT spectra.

After studying several spectra in MBTC 2076, it appeared that the area of the peak from 1070 to 960 cm⁻¹ (shown under arrow in Figure 2) was smaller for asphaltenes from air-blown blends. This seems reasonable in that C—N, C—S, and C—O groups can be oxidized. Oxidation at these sites during air blowing would decrease the area from 1070 to 960 cm⁻¹. To put this decrease on a quantitative basis, an internal standard was used. KCN was chosen because it has a peak at 2150 to 1990 cm⁻¹ that does not interfere with asphaltene spectra and KCN has no peak that interferes in the 1070 to 960 cm⁻¹ range. Equal weights of KCN and asphaltene were mixed and ground in a mortar and pestle. After thorough mixing, a small amount was physically mixed with 0.200 g of KBr. A diffuse reflectance cup was filled with this mixture and spectrum was obtained. The spectrum in Figure 3 shows the cyanide peak in an asphaltene spectrum.

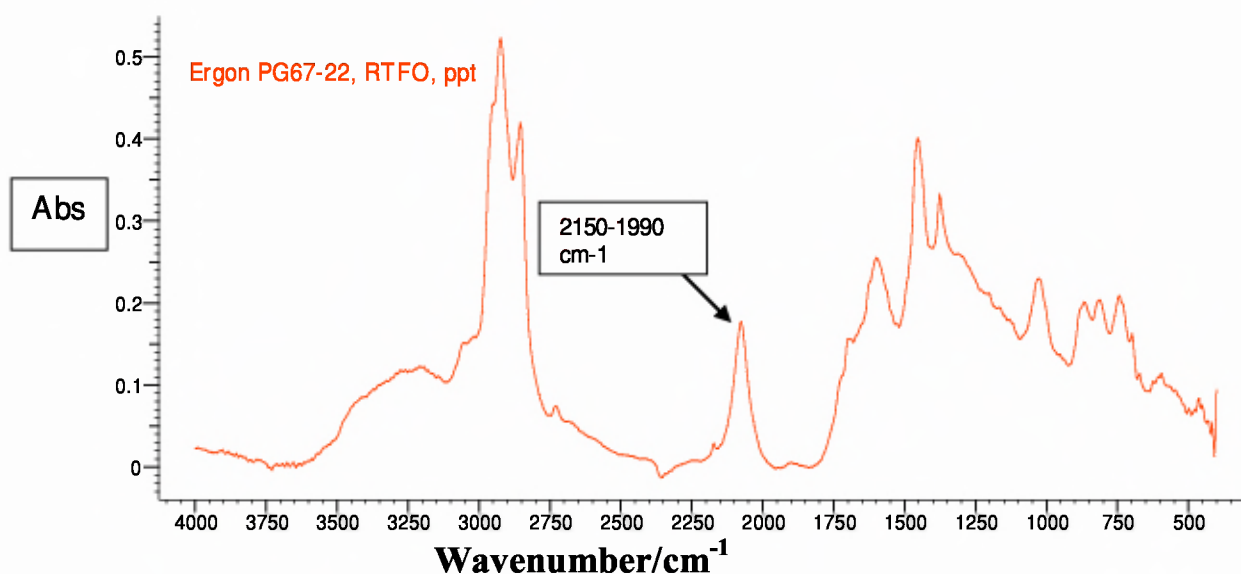


Figure 3. DRIFT spectrum of asphaltene with CN⁻ present as an internal standard.

Table 3 shows integration values for the cyanide peak (2150-1990 cm^{-1}), for the carbon-heteroatom stretch (1070-960 cm^{-1}) and for the carbonyl area (1820-1650 cm^{-1}). With the limited number of asphalts studied in MBTC 2076, it appeared that the carbon-heteroatom site was oxidized by air-blowing and that the ratio of the 1070-960 area to the 2150-1990 cm^{-1} would be greater than 0.15 for asphaltene derived from non air-blown asphalt blends. It is now apparent that this ratio depends on the asphalt source. Asphaltenes derived from a feedstock high in nitrogen and sulfur will give ratios of these areas greater than 0.15, but asphaltenes from feedstocks with low nitrogen and sulfur content will give ratios below 0.15, even if they are not air-blown.

The carbonyl areas of these asphaltene spectra were compared using the cyanide internal standard and there appears to be no observable trend. Asphaltenes from the non air-blown Exxon-Mobil asphalt has larger carbonyl area than asphaltene from the air-blown Marathon asphalt. It has been shown that air-blowing increases the carbonyl region of the IR spectrum (2), but this does not provide a way to distinguish between air-blown and non air-blown blends.

Asphalt	Area from 2150-1990 cm^{-1}	Area from 1820-1650 cm^{-1}	Area from 1070-960 cm^{-1}
Afganistan	6.6	2.94	1.16
Amaco	4.61	2.56	0.511
Marathon (air-blown)	7.22	2.39	0.803
Marathon (non air-blown)	3.66	2.87	0.699
Valero	5.88	2.40	0.639
Venezuela	6.7	2.26	0.551
Suriname	4.9	2.96	0.66
Exxon-Mobil	5.63	7.08	0.984

Table 3. Areas from IR spectra of asphaltene.

Asphalt	Area 1070-960/area 2150-1990	Area 1820-1650/area 2150-1990
Afganistan	0.18	0.45
Amaco	0.11	0.56
Marathon(air-blown)	0.11	0.33
Marathon(non air-blown)	0.19	0.78
Valero	0.11	0.41
Venezuela	0.11	0.41
Suriname	0.12	0.60
Exxon-Mobil Baytown	0.17	1.26

Table 4. Area ratios of IR regions of interest in spectra of asphaltenes.

Gel Permeation Chromatography

Gel permeation chromatography (GPC) is a form of size-exclusion chromatography. The smallest molecules pass through bead pores, resulting in a relatively long flow path while the largest molecules flow around beads, resulting in a relatively short flow path. The chromatogram in a GPC experiment shows detector response versus time or elution volume with the largest molecules appearing first on the chromatogram.

Referring to Figure 4, the three samples without air blown components can be distinguished from the air-blown blend by the absence of the highest molecular weight compounds. A signal from these blends is not observed until about 14 minutes. Observation of this front end tailing on a Gel Permeation Chromatogram appears to be a viable method for determining the presence of air blown asphalt. Additional work using air blown roofing asphalts indicates the greater the extent of air blowing, the more pronounced front end tailing and the greater the area under the high molecular weight region of the GPC chromatogram. GPC analysis of polymer modified asphalt indicated the presence of polymer does not interfere with the detection of high molecular weight compounds in air blown asphalt.

Asphalt GPC Data

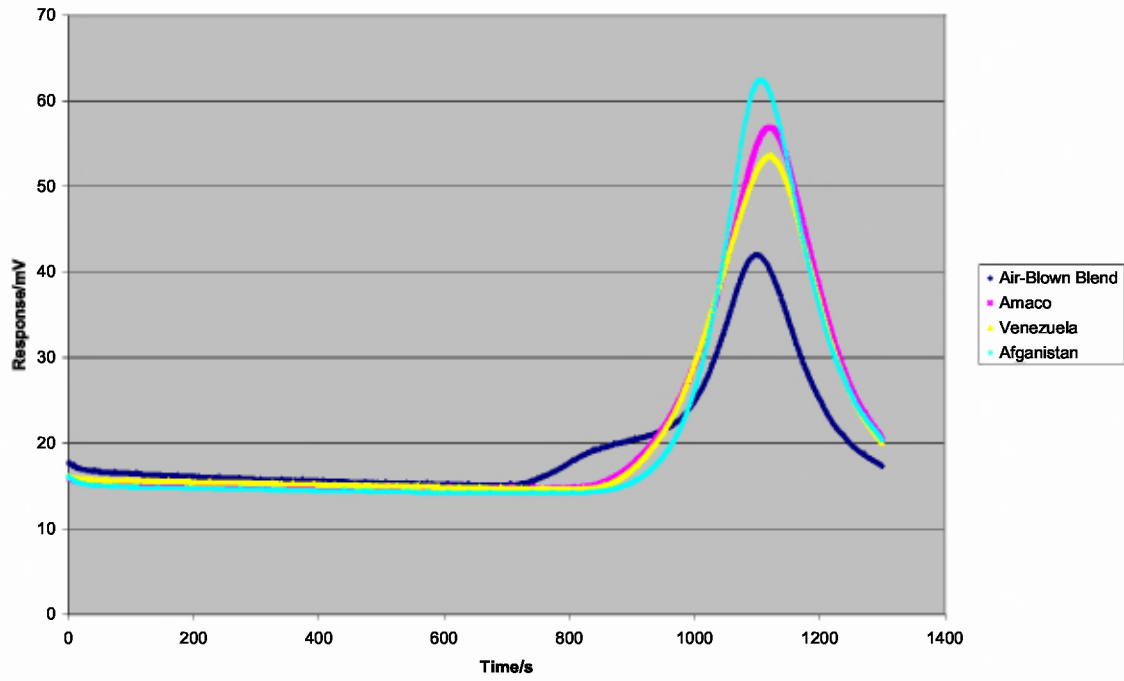


Figure 4. GPC results of Amaco, Venezuela, and Afganistan asphalts compared to an air-blown blend.

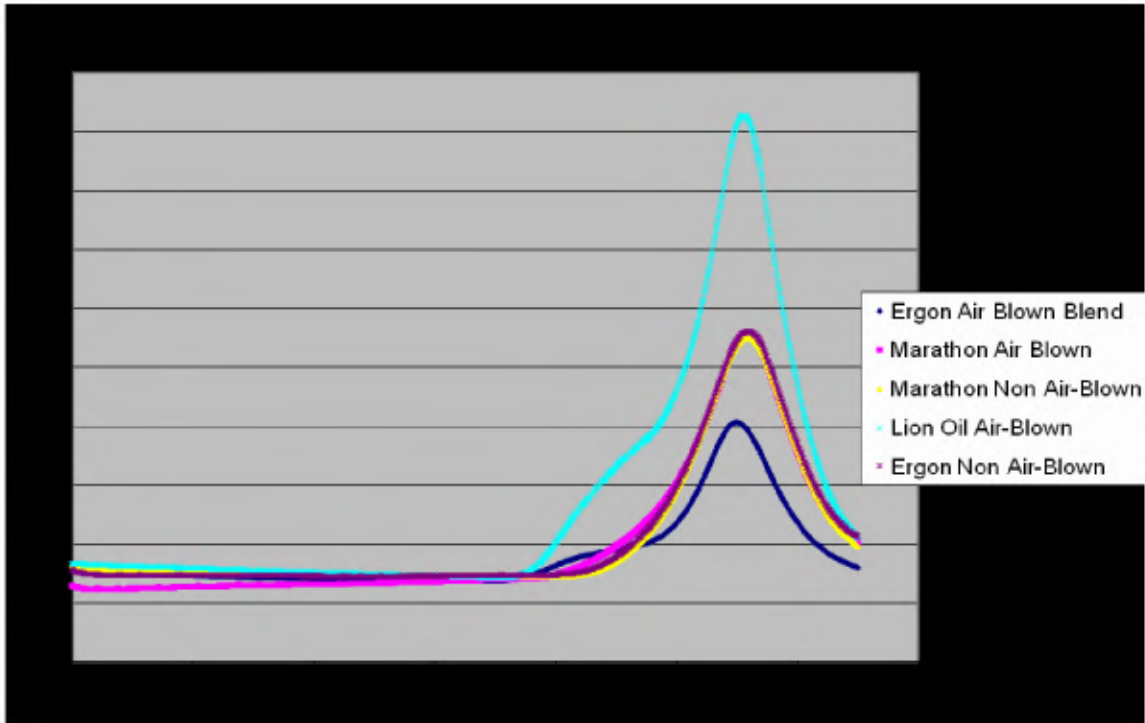


Figure 5. Comparison of Ergon and Marathon non air-blown blends to three air-blown blends

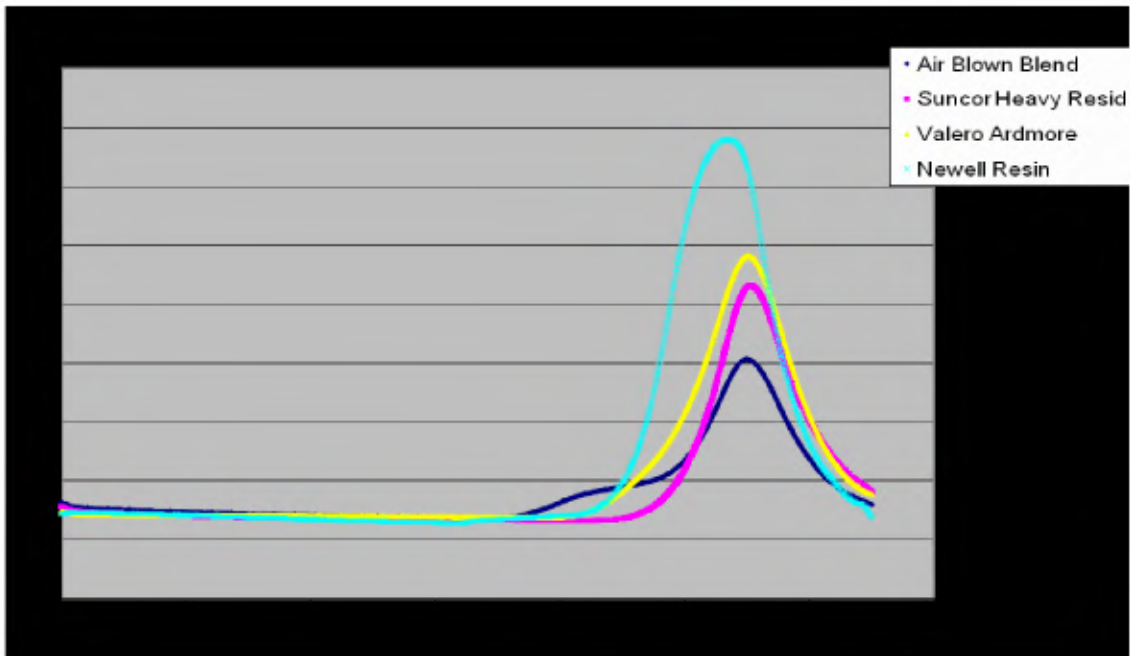


Figure 6. GPC results for Suncor, Valero, and Newell Resin compared to that of an air-blown blend.

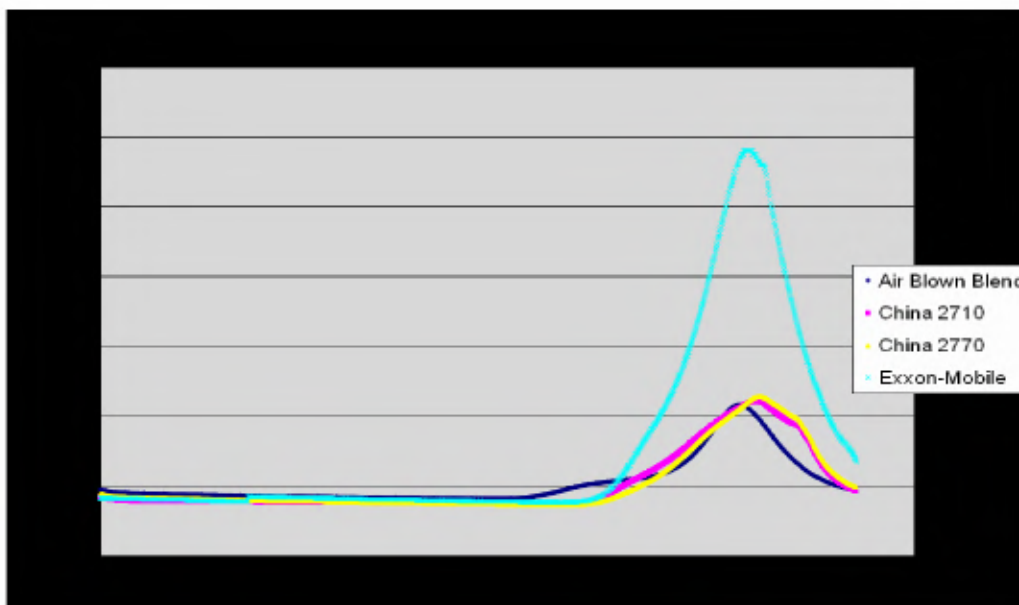


Figure 7. Comparison of GPC results for China 2710, China 2770, and Exxon-Mobil Baytown to that of an air-blown blend.

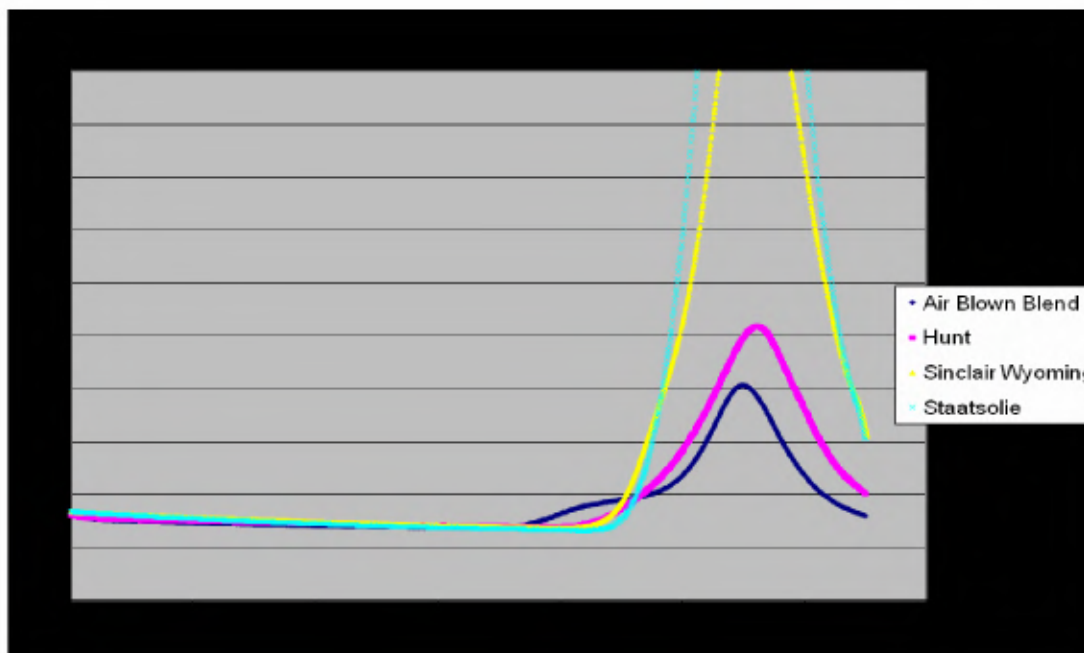


Figure 8. Comparison of GPC results of Hunt, Sinclair Wyoming, and Staatsolie blends to that of an air-blown blend.

Figures 4 through 8 compare GPC results of the asphalts of this study to GPC results of air-blown blends. GPC results clearly show front end tailing for air-blown blends is not present in non air-blown blends. There is slight front end tailing in Valero Ardmore asphalt. This is an air-blown blend, but the small amount of tailing could be a result of relatively mild air-blowing. This asphalt gave a positive result for the presence of air-blown asphalt in the solubility test. This may be due to it being very soft asphalt with a low asphaltene content before air-blowing. Another possible cause may be that the asphalt was not blown as severely as the type IV air-blown asphalts used in this study. Regardless, GPC is a useful tool and can be used in conjunction with the solubility test to help identify the presence of air-blown material.

Refractive Index Measurements

In an attempt to simplify test methods, refractive index measurements and viscosity measurements were made on asphalt solutions rather than asphaltene solutions. Refractive index measurements were made on toluene solutions of non air-blown and air-blown blends of asphalt. Reproducible differences in refractive indexes were not observed.

Differences in refractive index were observed between heptol solutions of asphaltenes from air-blown and non air-blown asphalts. The discontinuity at 50 % heptane for the asphaltenes from non air-blown asphalt is due to the precipitation of asphaltenes. It is these data that suggested the solubility test. The refractive index measurement is more time consuming and would not be preferred over the solubility test.

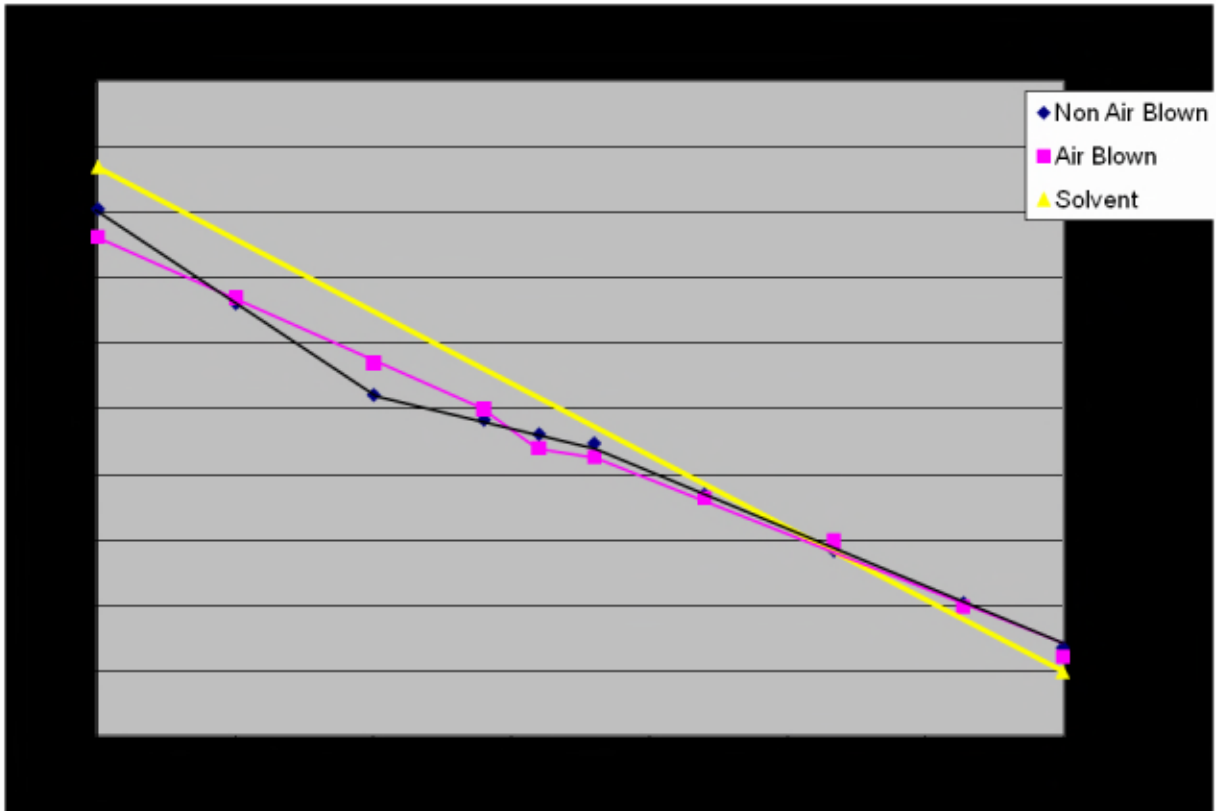


Figure 10. Refractive indexes of heptane-toluene solutions of asphaltenes.

Viscosity Measurements

Differences in viscosities were not observed between toluene solutions of air-blown and non air-blown asphalts. In addition, the small differences in the viscosities at 30°C and 45°C of toluene solutions of asphaltenes from non air-blown blends were not confirmed in this study. This does not appear to be a reliable test for the presence of air-blown asphalt.

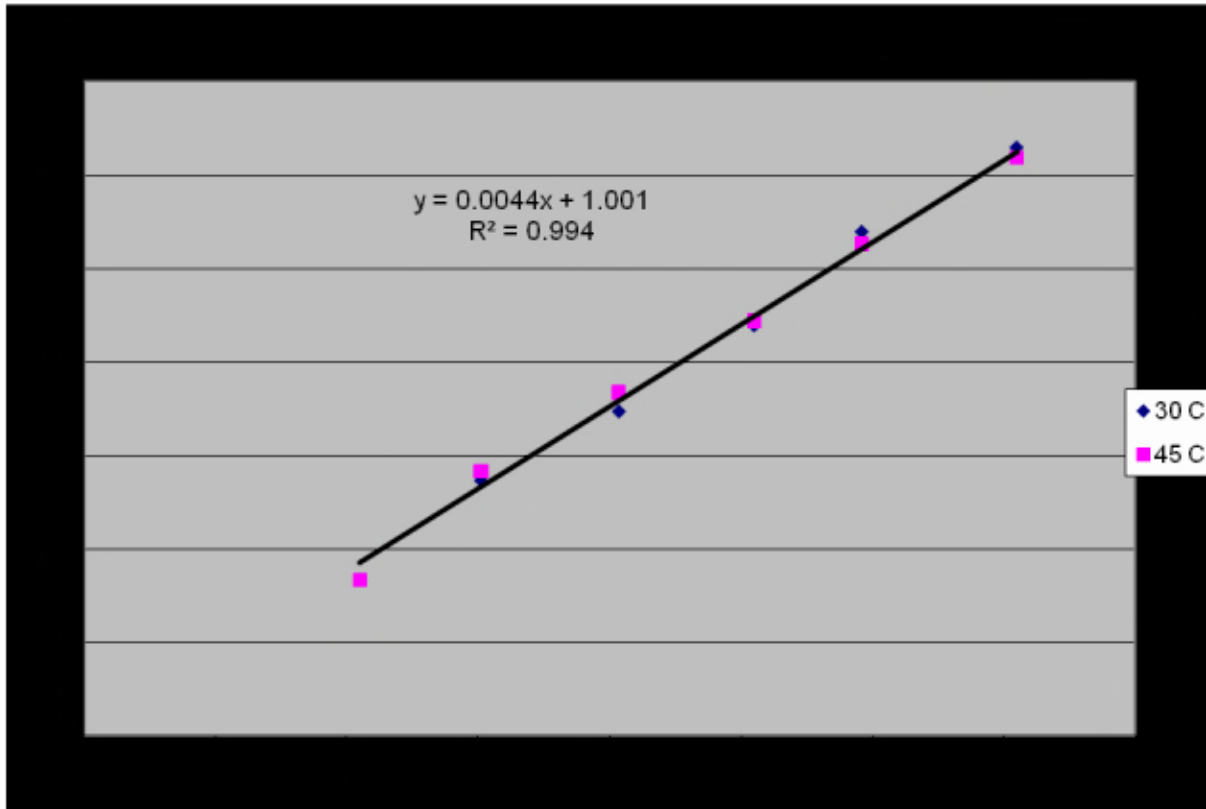


Figure 11. Relative viscosities of toluene solutions of asphaltenes from non air-blown blends at 30° and 45° C.

Conclusions

1. Laboratory tests involving relative viscosities of toluene solutions of asphaltenes and diffuse reflectance Fourier Transform spectroscopy could not reproducibly predict the presence of air-blown asphalt.
2. Refractive index measurement of toluene solutions of asphalts proved to be of no value predicting the presence of air-blown asphalt.
3. A solubility test involving asphaltenes in a heptane-toluene solution accurately predicted the presence or absence of air-blown asphalt in from 15 different feedstocks. Four conditions must be met in order for this solubility test to accurately detect the presence of air-blown asphalt: (1) asphaltenes must be properly washed, (2) asphaltenes must be fresh, (3) toluene solutions must be stirred for at least 10 hours before titrating with heptanes, and (4) after heptanes addition, solutions must be left undisturbed for 10 hours before testing for

precipitates. The detection of a precipitate was simplified by eliminating a centrifuging step. This test is simple and inexpensive.

4. Gel permeation chromatography proved to be useful and accurately predicted the presence or absence of air-blown asphalt in the samples tested. This test requires an High Performance Liquid Chromatograph but it offers the advantage that tests can be run directly on asphalts and does not require asphaltene separation.

References

1. Christy, A., Dahl, B., and Kvalheim, O., *Fuel*, **1989**, *68*, 430-435.
2. Lui, M., Lunsford, K.M., Davison, R.R., Golver, C.J, and Bullin, J.A., *AICHE Journal*, **1996**, *42*, No. 4, 1069-1076.