Separation of Aromatic Hydrocarbons in Diesel Fuel Using Temperature Programming

Introduction

Aromatic hydrocarbons are a component in diesel fuel. They are quantitated using ASTM method D 6591. This HPLC method is used to quantitate mono-, di- and poly-aromatic hydrocarbons (MAH's, DAH's and PAH's) in the diesel boiling range. It uses refractive index detection, and requires the use of a switching valve to obtain a single peak for the PAH's. It is difficult to achieve baseline resolution betweeen the saturates in the sample and mono-aromatic hydrocarbon components. This work was performed to try to improve the separation between the saturates and mono-aromatic components of interest, and eliminate the need for the switching valve.

Experimental Conditions

Conditions are summarized in Table 1 and Table 2. The HPLC system consisted of an Alltech solvent degasser, Knauer pump and UV detector, an Alcott autosampler, and a Polaratherm Series 9000 Total Temperature Controller. A standard consisting of a mix of saturates (C_6 and C_{30}); toluene, tetralin, and thiophene (MAH's); naphthalene, acenaphthene, benzothiophene, and dibenzothiophene (DAH's); and anthracene (3-ring) and pyrene (4-ring) for the PAH components.

Table 1
Conditions for Analysis of Aromatics in Diesel Using PAC Column

Columns:	Partisil Amino-Cyano (PAC) column, 5um, 250 x 4.6 mm
Mobile Phase:	hexane
Flow:	1.5 mL/min
Detection	Refractive Index
Temperature:	Zero, 30, 60 and 100°C isothermal Various temperature programs. See tables and figures for details.

Results and Discussion

Table 3 shows retention times for the aromatics at four temperatures on the PAC column. Note that there are some selectivity changes of the di-aromatic hydrocarbons with temperature. Figures 1 and 2 show the separation of aromatic standards on the PAC and silica columns. Figures 3 and 4 show the separation of diesel standards on the PAC and silica columns.

Conclusions

Better separation of the saturates from the mono-aromatic hydrocarbons was attained, and the switching valve was eliminated, however run time and overall resolution were not significantly improved. The PAC column provided a better separation than the Econosphere silica column.

Acknowledgement

We are indebted to Frank DiSanzo at Exxon-Mobile for providing the columns and diesel samples used in this work.

Table 2
Conditions for Analysis of Aromatics in Diesel Using Econosphere Silica Column

Columns:	Econosphere silica, 3 um, 150 x 4.6 mm
Mobile Phase:	hexane
Flow:	1.0 or 1.5 mL/min
Detection	Refractive Index
Temperature:	Various temperature programs. Refer to tables and figures for details.

Retention Data for PAC Column
Isothermal Conditions

Analyte	Retention Time			
	0°C	30°C	60°C	100°C
toluene	4.56	4.23	3.89	3.54
tetralin	4.59	4.29	4.00	3.69
thiophene	5.02	4.46	4.08	3.69
naphthalene	6.81	5.69	4.99	4.32
acenaphthene	7.49	5.89	4.92	4.47
benzothiophene	7.81	5.82	5.22	4.49
dibenzothiophene	11.25	8.38	6.73	5.47
anthracene	12.14	9.04	7.30	5.86

Table 3. *Retention time data for PAH standard at four temperature under isothermal conditions. There are some selectivity changes with temperature for the di-aromatic hydrocarbons.*

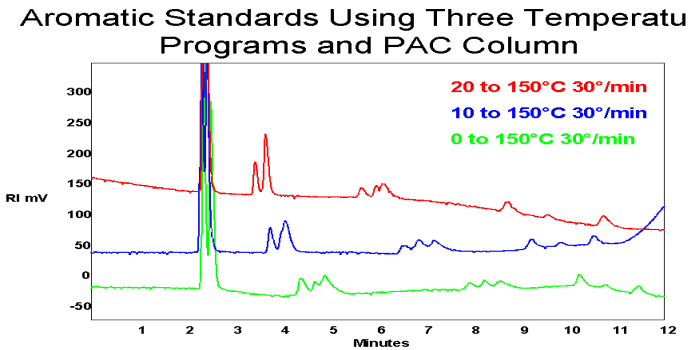

Figure 1. *Aromatic standards using three temperature programs. five minute hold at initial and final temperatures for all runs. Flow rate 1.5 mL/min. Elution order: saturates, toluene, tetralin, thiophene, naphthalene, acenaphthene, benzothiophene, dibenzothiophene, anthracene, pyrene.*

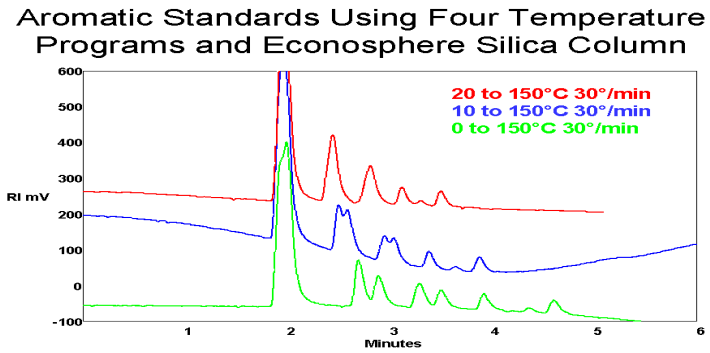

Figure 2. *Aromatic standards using three temperature programs. five minute hold at initial and final temperatures for all runs. Flow rate 1.5 mL/min. Elution order: saturates, toluene, tetralin/thiophene, naphthalene, acenaphthene, benzothiophene/dibenzothiophene, anthracene, pyrene.*

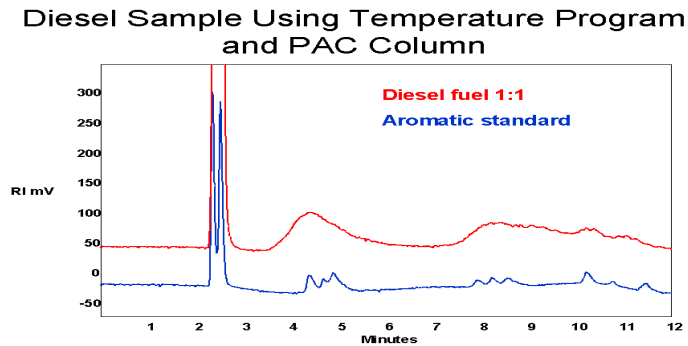

Figure 3. *Diesel sample anlayzed using a temperature program from zero to 150°C at 30°/min. Flow rate 1.5 mL/min. Elution order: saturates, toluene, tetralin, thiophene, naphthalene, acenaphthene, benzothiophene, dibenzothiophene, anthracene, pyrene.*

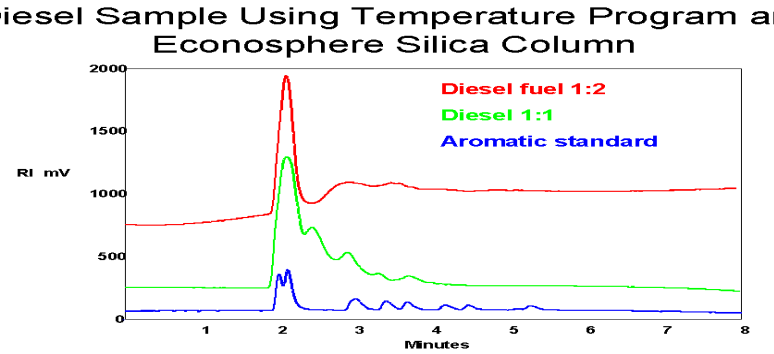

Figure 4. *Diesel sample anlayzed using a temperature program from 20 to 100°C at 30°/min. Flow rate 1.0 mL/min. Elution order: saturates, toluene, tetralin/thiophene, naphthalene, acenaphthene, benzothiophene/dibenzothiophene, anthracene(small peak), pyrene.*