CHEMICAL RELATIONSHIPS IN ETHANOL AND NON-ETHANOL FUELS

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INTRODUCTION

The U.S. national transportation fuel supply is changing significantly because of environmental pressure to reduce carbon monoxide, ozone, hydrocarbon, and lead emissions. The desire to replace petroleum fuels with alternative fuels because of world shortages and cost has abated but will reappear again as world demand for petroleum approaches supply. The variety of gasoline fuel blends is becoming and will be more varied in the future. The goal of this research is to track changes of the chemical composition of current and emerging transportation fuels by providing: 1) a survey of gasoline chemical composition at the pump from ten sites throughout the U.S., 2) data on seasonal chemical changes in gasoline in a "hot" and a "cold" community, (3) analytical data for tracing actual fuel-related engine problems to constituents in gasoline, and 4) foundational data for tracking changes in chemical composition. This paper deals with the analytical methods being used to "fingerprint" the over 180 fuel samples that will be analyzed in this study.

Gas chromatography (GC) analysis separates volatile organic mixtures into individual compounds depending on GC conditions. This can provide information on the identity of the compounds present as well as quantitative data. Quantitation is complicated by peak overlap and detector response to individual compounds. Whereas most hydrocarbons in petroleum derived fuel have similar response factors, ethanol has a significantly lower response factor and does not elute in the proper boiling point position relative to normal alkanes. These difficulties require a more involved GC method and calculations to analyze fuel blends and to relate them to distillation data.

Proton nuclear magnetic resonance spectroscopy (NMR) provides data on the hydrogen distribution in organic liquids and is relatively easy and fast to obtain on liquid samples. Minimal information is obtained for mixtures of compounds containing similar functional groups. For instance, a mixture of normal alkanes with only $-CH_2-$ and $-CH_3$ groups would give a simple spectrum and no single alkane could be quantified. However, when compounds are present in a bulk mixture that contain protons which resonate in a unique NMR region (such as ethanol or benzene in gasoline), rapid identification of these compounds and their quantitation is possible. Proton NMR, therefore, becomes much more useful for analyzing mixtures that contain a wider variety of functional groups.

EXPERIMENTAL

Gas Chromatography

The gas chromatography (GC) work was done with a Hewlett-Packard Model 5890 GC connected to an HP 3396A integrator with data transfer to an IBM compatible PC.

Ethylcyclohexane (0.1 g) was mixed with 2 grams of the gasoline sample for use as an internal standard. The GC analysis conditions were as follows:

Column:	Supelco Petrocol-DH, 100m x 0.25 mm I.D., 0.5 micron film
Carrier:	H_2, linear velocity of 34 cm/s set at 320°C
Injector:	Injection split ratio: 100:1
Detection:	FID with 30 ml/min of N_2 make-up
Oven Temp.	Prgm: 30 to 35°C at 0.5°/min then 2°/min to 320°C
Critical:	The injector insert (unpacked mixing chamber) was deactivated with HMDS and DMDCS (1).

Proton NMR Spectroscopy

All of the proton nuclear magnetic resonance spectra were determined on a Varian XL200 NMR Spectrometer. Its 47-KGauss magnet has a wide bore and superconducting solenoid that operated at liquid helium temperatures. The proton probe used 5-mm sample tubes and observed the protons at a frequency of 200 MHz while spinning the samples between 25 and 30 Hz. The gasoline samples were prepared for analysis by diluting 40 microliters of the sample with one milliliter of deuterated methylene chloride that contained 0.25% tetramethylsilane as an internal reference standard. The spectra were obtained using a 90 degree flip angle and 5-second delay between pulses for a total of 100 pulses. All spectra are stored on 5.25 inch floppy disks.

RESULTS AND DISCUSSION

Base Gasoline Analysis by GC

The GC system was calibrated with a series of known compounds: methanol, ethanol, n-pentane, 2,2-dimethylbutane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, hexane, benzene, cyclohexane, iso-octane, heptane, toluene, n-octane, ethylbenzene, o-xylene, decane, and naphthalene. Retention index and response factor information was determined for these compounds. It was found that when ethanol content was over 3 wt%, its response factor was non-linear. However, if the sample was diluted, compounds present in small amounts were not detected. A possible solution to this paradox is to use GC to perform a base gasoline analysis (all compounds except ethanol) on a neat sample and to determine ethanol content on a diluted sample, or by using a different method (i.e., NMR spectroscopy).

Figure 1 depicts the computer generated GC profile and simulated distillation curve. Each peak is represented by a line equal to its area% plotted at its relative elution position to the boiling points of normal alkanes (the horizontal scale is 0 to 250°C). One sample (without ethanol) was analyzed five times and the area% standard deviations were calculated for each of 211 peaks. The results are depicted in Figure 2. For peaks under 0.2 area%, the standard deviation was up to 10%, with only a few points off scale above 10%. For peaks of over 0.2 area%, standard deviations of under 3% were obtained. Figure 3 depicts the five overlayed simulated distillation data for these analyses. Essentially one broadened line was obtained. The dotted line is ASTM D86 distillation data. The GC simulated distillation emphasizes the low boiling regions. This is due to a difference in response factors of early and later eluting alkanes for the GC conditions used in the analysis and to early hang-up of material during distillation. A factor, to correct for response factor differences and column influences on the elution position versus boiling point, is planned to enable GC data to better approximate distillation data.

Determination of Ethanol in Gasoline by NMR

Proton NMR observes the hydrogen atoms in a compound. It differentiates them by the functionality they are in and adjacent functionalities. A typical NMR spectrum of gasoline is shown in Figure 4. Differentiation of specific compounds due to the presence of unique protons is evident; primarily ethanol, benzene, and MTBE. If methanol were present it would also be detected by this method.

The proton NMR spectra of a series of gasoline samples spiked with known amounts of ethanol were obtained using the normal proton pulsing sequences. Each spectrum was integrated over each of the integral regions normally used for gasoline samples. The data was reduced after eliminating the baseline regions from 10.00 to 8.15 ppm, 6.60 to 6.00 ppm, 4.60 to 3.75 ppm, and 0.40 to 0.06 ppm from the total area, along with the solvent peak area, 5.36 to 5.25 ppm. The data was then normalized to 100%. The integral region from 3.75 to 3.50 ppm is totally unique to the methylene protons of the ethanol in the gasoline samples, thus the normalized area of this integral should be directly proportional to the concentration of the ethanol. A summary of the ethanol spiked gasoline samples is presented in Table 1. The calculated vol% and calculated wt% data were determined by linear regression analysis of the NMR area% and corresponding ethanol concentration of the standards from 0 to 12 vol% ethanol. The volume % ethanol versus NMR area% gave a regression line described by the formula, $y=0.2822x + 0.02443$, where y is the NMR area% and x is the ethanol vol%. The wt% data gave the line $y=0.26087x + 0.00475$, where x is the wt% ethanol. The error is higher at ethanol concentrations over 13 wt%. Figure 5 shows the data graphically for the samples containing 0 to 13 wt% ethanol.

Determination of Benzene in Gasoline by NMR

The proton NMR spectrum of gasoline gives a single resonance for benzene in the region between 7.31 and 7.42 ppm since benzene contains six equal protons. This region in the gasoline samples was nearly devoid of interfering resonances, which allows calculation of benzene concentrations in the gasoline samples. The standards used were spiked gasoline samples from 0 to 5% added benzene. The spectrum of each standard was integrated and normalized in the same manner as the ethanol standards. Since the base gasoline contained some benzene (the same gasoline was used for each standard), the area of its benzene peak had to be subtracted from the benzene peak areas of standards with added benzene. This added benzene area was then used in the linear regression analysis of the benzene standards presented in Table 2. Here the calculated vol% and wt% data are from the regression lines described by $y=0.50497x + 0.0437$ for the vol% and $y=0.4274x + 0.0284$ for the wt%, where y is the NMR area% and x is the vol% or wt%. From this data, the concentration of benzene in the base gasoline standard can also be calculated. The base gasoline has a benzene area% of 1.6583, which calculates to 3.20 vol% and 3.81 wt% benzene.

Data Base Generation

A computer data base is presently being generated for a suite of samples using the previously described methods containing GC and NMR data. The initial use of the data base is to determine the range of various gasoline blends being used by consumers in the U.S., how gasoline blends vary with additives (BTX and ethanol), and how blends vary seasonally and over shorter time periods. Future work will involve closely integrating the data base to presently used gasoline specification data and to engine performance.

CONCLUSIONS

The preferred method of gasoline analysis for this study is a combined GC and proton NMR analysis. This method will provide an analytical "fingerprint" of gasoline samples for use in determining unique characteristics affecting engine performance. The method encompasses a "neat" analysis of the gasoline sample by GC for identification and quantitation of components, completed by NMR analysis for the determination of functionalities present as well as ethanol and benzene quantitation. All samples in the study are being analyzed by this method and additional research data will be completed on select samples to further define CHN, S, water, lead and solids content, as well as specific gravity and density determinations. Detailed component analysis by GC/FTIR/MS will also be performed.

REFERENCES

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TABLE 1

ETHANOL CONCENTRATION BY NMR

Concentration vol%	Concentration wt%	NMR area%	Calculated vol%	Calculated wt%
0	0.0	0.0736	0.17	0.26
2	2.35	0.5280	1.78	2.01
4	4.39	1.1752	4.08	4.49
4	4.39	1.1118	3.85	4.24
8	8.73	2.3361	8.19	8.94
10	10.92	2.8259	9.93	10.81
12	13.02	3.4089	11.99	13.05
50	52.67	16.3733	57.93	62.75
75	77.77	24.8332	87.91	95.17

TABLE 2

BENZENE CONCENTRATION BY NMR

Concentration vol%	Concentration wt%	NMR area%	Calculated vol%	Calculated wt%
0.0	0.0	0.0	0.04	0.03
0.5	0.61	0.3734	0.65	0.81
1.0	1.23	0.5559	1.01	1.23
1.5	1.84	0.8151	1.53	1.84
2.0	2.39	1.0895	2.07	2.48
2.5	3.02	1.2479	2.38	2.85
3.0	3.62	1.5253	2.93	3.50
4.0	4.73	1.9622	3.80	4.52
5.0	5.92	2.6711	5.20	6.18

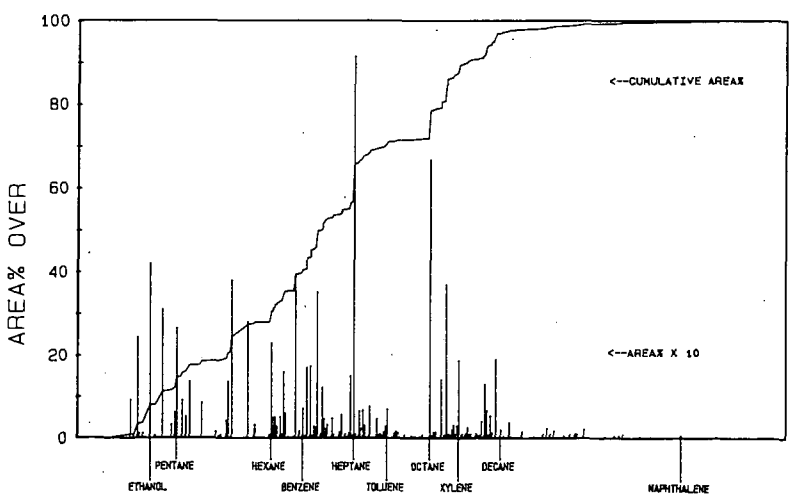

Figure 1. Computer generated GC profile and simulated distillation curve.

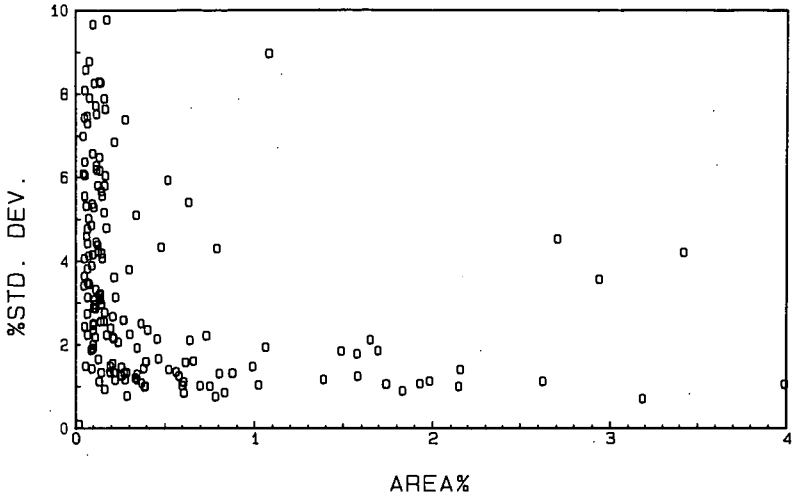

Figure 2. Area percent standard deviations for one gasoline sample analyzed five times by GC.

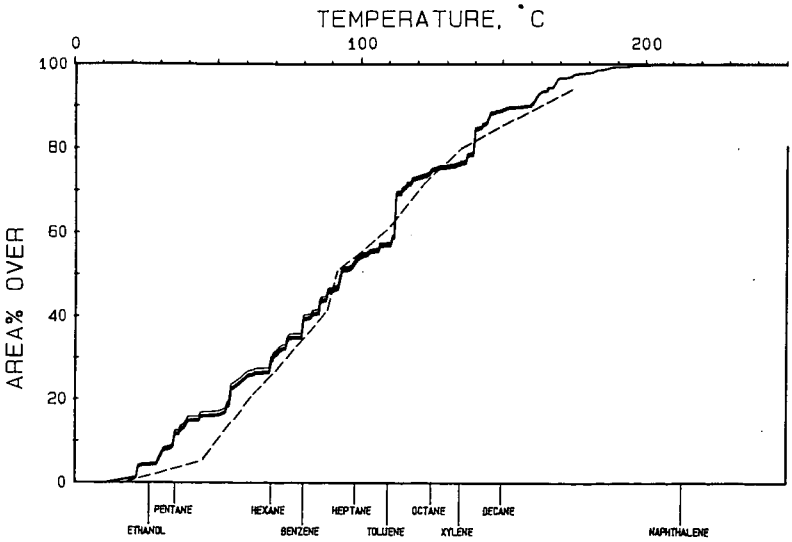

Figure 3. Overlay of five simulated distillation curves for one sample (——), with corresponding ASTM D86 distillation (----).

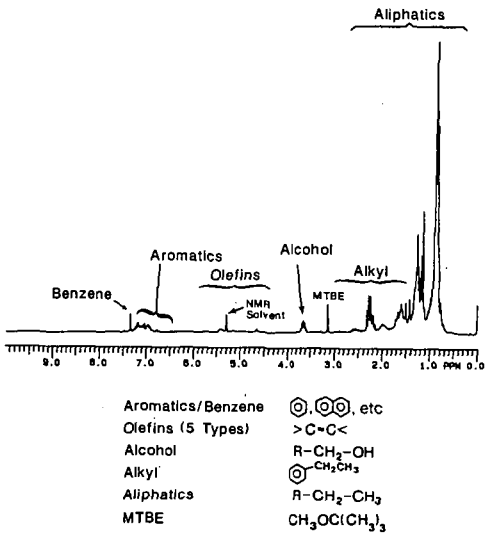

Figure 4. Typical NMR spectrum of gasoline depicting identified components and functional groups.

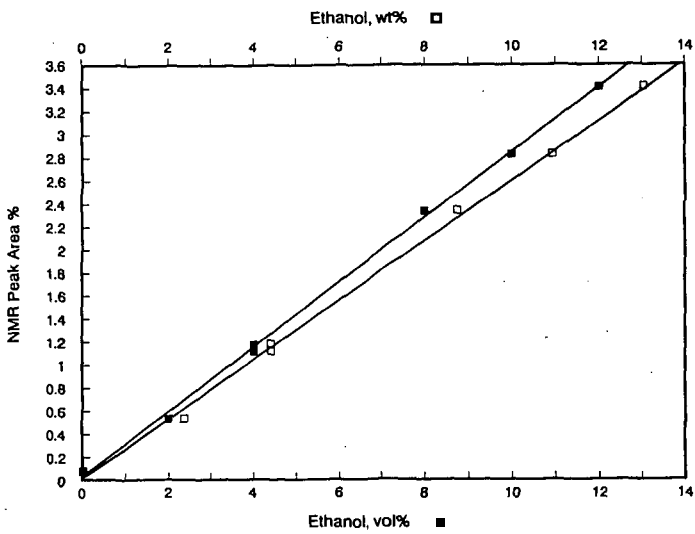

Figure 5. Ethanol content by NMR, vol% and wt%.