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CHEMICAL AND PHYSICAL CHARACTERISTICS OF TEST FUELS IN CANMET'S RESIDENTIAL OIL HEATING PROGRAM

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**CHEMICAL AND PHYSICAL CHARACTERISTICS OF TEST FUELS IN CANMET'S RESIDENTIAL OIL
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by

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ABSTRACT

The chemical and physical characteristics of a number of various light and heavy distillate fuels are given and intercorrelated. These fuels are being evaluated for an experimental combustion program on residential oil furnaces at CANMET. Properties being examined are related especially to the combustion characteristics of these fuels, i.e., aromatics by FIA, aniline point, NMR aromaticity, PNA by mass spectroscopy, carbon/hydrogen ratio, viscosity, etc.

The various analytical methods to measure hydrocarbon types are described and the intercorrelations of results using these methods are shown. This paper attempts to illustrate the application of the methods for hydrocarbon type analysis, i.e., to correlate the combustion properties of the fuels in the test program and to emphasize the need for rapid and extensive hydrocarbon type analyses.

RÉSUMÉ

Les propriétés physiques et chimiques de plusieurs combustibles de distillats légers et lourds sont présentées ainsi que les corrélations qui existent entre elles. Une évaluation de ces combustibles est présentement en cours et faisant partie d'un programme d'essai de brûleurs de fournaies domestiques aux laboratoires de CANMET. Les propriétés qui retiennent l'attention sont celles reliées à la combustibilité, soit: FIA, point aniline, les composés aromatique par RMN et par SM, le rapport hydrogene/carbone, etc.

Les méthodes analytiques sont résumées et les résultats obtenus pour déterminer les différentes familles d'hydrocarbure sont comparés. L'exposé se propose de démontrer l'utilité de différentes méthodes pour déterminer les familles d'hydrocarbure lors du programme d'essai; soit de permettre d'établir une corrélation entre la combustibilité d'un combustible et de sa composition.

On espère ainsi démontrer le besoin de méthodes analytiques rapides pour le dosage de différentes familles d'hydrocarbure.

INTRODUCTION

CANMET's Energy Research Laboratories respond to R & D objectives in bitumen, heavy oil and synthetic crude upgrading; coal combustion, gasification and liquefaction; and energy conservation including improvements to domestic heating systems. The research projects in these areas usually involve bench-scale or pilot plant experiments on combustion, upgrading, liquefaction, and other processes. These experiments are normally multi-parameter and are designed so as to vary the many factors involved over a working range, either singly or jointly. For this reason, any research project will entail a great number of experimental runs, for which many variables must be determined.

Among these are the physical and chemical characterization of the feeds and products and perhaps also of intermediate products. Such experiments thus require important support from an analytical laboratory. However, the analyses must be meaningful if the experiments are to be valid, i.e., the analyses must meet the following conditions:

1. Analyses must be readily available at a reasonable cost.

- This implies routine analyses which can be done on a regular basis on many samples.

Automated or instrumental laboratory methods are the most efficient means to meet this condition.

2. Analyses must be informative.

- The analyses must provide measurements of all of the important variables. This requires continuous consultation between the researchers and analysts to develop analyses which will meet the needs of the experiments.

3. Analyses must be of good quality.

Analyses of doubtful quality are meaningless thus so is the experiment.

These conditions are equally important to ensure good R & D project completion.

Research at the Energy Research Laboratories (ERL) deals essentially with hydrocarbon fuels. Invariably, analyses of hydrocarbon types in fuels, feeds and products are necessary for each project. The characterization of hydrocarbon types is very complex - in fact it is difficult to define what is meant by hydrocarbon types. Generally one is satisfied to define types on the basis of saturates and aromatics and attempt to determine a few sub-classes. However, the determination always depends on the analytical method.

A number of different methods for hydrocarbon type analyses are used at ERL. Some are standard industry-wide methods such as ASTM D-1319 (FIA), while others were developed in-house. One of the research projects which requires these methods is the residential oil heating program which involves combustion performance study of middle distillate fuels.

This project is continuing at ERL in cooperation with major oil companies to determine the effects of lower fuel quality and high aromatic fuels on oil burner performance, in order to free up more distillates for the diesel market. Fuels containing properties exceeding both low and high ends of specifications are being tested with particular emphasis on viscosity, gravity, and aromatic content.

Experimental programs are designed so that test data provide combustion characteristics of each fuel such as burner ignition behaviour, particulate emissions, concentrations of combustion products in flue gas (carbon monoxide, carbon dioxide, nitrogen oxides, oxygen) excess air levels and temperatures including that of the fuel, ignition, flue gas, and differential between cold air intake and warm air. These characteristics are carefully monitored and studied for transient start-up, shut-down phases and steady state operations.

Data from the combustion test program are being interpreted and correlated with the physical and chemical properties of the fuels. It is intended to develop a system to rate fuel/burner performance, to predict performance from fuel property information and to guide refiners on satisfactory fuel characteristics to enable maximum use of the crude oil. Equipment such as different combustion heads and nozzles, new burner designs and preheaters which could improve the performance of problem fuels are to be tested soon.

TEST FUELS AND ANALYTICAL METHODS

Various fuels were obtained for evaluation (either as received or for blending) under the residential oil heating program. These include No. 2 fuel oils from different refineries normally used to fire domestic furnaces, diesel fuels, synthetic tar sand fuels, and various refinery middle distillate streams. The availability of this variety of different products allowed the analytical section to evaluate various hydrocarbon type analysis methods and to determine the correlation between the different methods.

Tables 1 and 2 list the test fuels and give results of the various analyses. The analytical methods are described below:

Density

Determined using a Parr DMA40 meter.

Heat of Combustion

Determined according to method ASTM D-240 using Parr adiabatic calorimeters with model 1720 controller.

Simulated Distillation

Method ASTM D-2887 using a H.P. 5880A gas chromatograph equipped with a H.P.7671A auto sampler.

Flash Point

ASTM D-3828 (Setaflash)

Viscosity

ASTM D-445

Pour Point

ASTM D-97

Sulphur

PGT 100 Analyzer

Carbon/Hydrogen

Perkin Elmer PE 240 elemental analyzer.

F.I.A.

ASTM D-1319.

Aniline Point

ASTM D-611

Aromaticity

Determined by Brown and Ladner technique using ^1H NMR on a Varian CFT-20. The aromaticity is given by the equation:

$$f_a = [C/H - H^*_{al}/(H_{al}/C_{al})]/C/H$$

where f_a is calculated from the carbon to hydrogen atomic ratio (C/H) and from the concentration of aromatic and aliphatic hydrogen groups, determined by ^1H NMR. H^*_{al} is the fraction of total hydrogen present as aliphatic groups and H_{al}/C_{al} is the atomic H/C ratio for the aliphatic groups. A value of 2 was used for H_{al}/C_{al} assuming that the aliphatic hydrogen averages out to be methylene groups, CH_2 .

MASS SPECTROSCOPY (PONA)

The relative amounts of hydrocarbon types (paraffins, naphthenes, aromatics) (P,N,A) were determined by mass spectroscopy. A Finnigan 4500 GC/MS was used. The samples were separated using a 1.83 m column (3% Dexil 300 on acid-washed Chromosorb W) from 60°C to 300°C at 8°C/min. Chemical ionization (methane) mass spectra were acquired continuously during the g.c. separation on a 3-s cycle. The series of peaks characteristic of each given class of compounds (P,N,A) is summed continuously. Summations of the series of peaks which are used to characterize the classes are given in Table 3. The olefin content determined previously by NMR is used to correct the appropriate peaks with which it interferes. The NMR and mass spectrometric techniques developed at the Energy Research Laboratories are described elsewhere (1).

RESULTS AND DISCUSSION

The combustion properties of the various test fuels and blending stocks are of prime importance in the residential oil heating program. It is expected that the properties affecting combustion performance are related to the hydrocarbon type content. These are hydrogen/carbon ratio, FIA, aniline point, NMR aromaticity and PNA by mass spectroscopy.

The intercorrelations of these properties are shown in Fig. 1 to 5 and the correlation coefficients are given in Table 4.

FIA

The FIA test for determining hydrocarbon types is used extensively. However, it has many limitations, and in the present case its applicability has been pushed somewhat into a higher boiling range. For a number of samples, it was difficult to properly determine the concentrations of each hydrocarbon type due to imprecise zone boundaries and considerably long (up to 24 h) elution times. The correlation of FIA aromatics with aniline point, MS aromatics and NMR aromaticity is good. However the limitations of the FIA test, especially its limited applicability to dark and higher boiling range products, makes the test less useful in correlating combustion properties with hydrocarbon types.

ANILINE POINT

The aniline point test has served for many years to characterize the aromaticity of hydrocarbons. The aniline point shows excellent correlation with the aromatic content as measured by the other methods. Its disadvantage, however, is that it does not directly measure aromatic content. Problems in determining aniline point can occur with samples which are very dark and have a high boiling point. However, its range of applicability is much wider than that of the FIA test.

HYDROGEN TO CARBON RATIO

The ratio of hydrogen atoms to carbon atoms is a direct measure of the average carbon-hydrogen bonding. A totally aliphatic hydrocarbon will have a ratio

of 2.0 or slightly higher whereas pure benzene, or totally monoaromatic hydrocarbon will have a ratio of 1.0. If the hydrogen/carbon ratio is to be used as a measure of aromatics bonds certain assumptions must be made. First that the olefins are negligible and that the multicyclic compounds (whether aromatics or alkanes) are also present in minor proportions. In either case the result will be a bias towards greater aromaticity, e.g., if the ratio for polynuclear aromatics is less than 1.0 this will decrease the overall ratio.

Nevertheless, the hydrogen/carbon ratio is an excellent indicator of aromaticity. This is shown in the very good correlation with NMR aromaticity in Fig. 3. The hydrogen/carbon ratio can be readily determined using existing instrumentation (especially the Newport analyzers on samples with low heteroatom content) and is a cost-effective and accurate, although limited, measure of hydrocarbon type.

NMR AROMATICITY

The aromaticity as determined by NMR is a direct measure of the aromatic content on an atom-by-atom basis. The advantages of NMR methods are the ease and the accuracy with which the determinations may be made in the presence of heteroatoms which will affect other methods. Also, proton NMR, as used here, is much less costly and considerably faster than ^{13}C NMR, although it provides less information. The applicability of the NMR technique to the full range of compounds from very light to very heavy is another asset.

The correlation between aromatics content as measured by mass spectroscopy and that determined by proton NMR is shown in Fig. 4. The correlation is shown to be excellent and as expected, the aromaticity measured by NMR is lower than that obtained by mass spectroscopy. NMR aromatics content is determined on an atomic basis, while that of MS is determined on a molecular basis.

AROMATICS CONTENT BY MASS SPECTROSCOPY

Mass spectrometric techniques determine hydrocarbon types on a molecular basis. The aromatics content measured by MS should therefore be directly comparable to that measured by FIA. Fig. 5 compares those samples on which it was

possible to perform an FIA test. The relationship is indeed one-to-one as expected.

The MS technique is therefore equivalent to the FIA and offers considerably more advantages. It is easier to conduct, has the potential to provide much more information on the individual hydrocarbon types and as mentioned previously is not limited with respect to the FIA test for heavy oil samples.

However, the MS technique has certain limitations. The method, as used in our laboratory on a quadrupole GC/MS, cannot adequately handle oil samples at boiling ranges much beyond 400°C. The possibilities of heteroatom interferences exist. As stated before, olefins cannot be determined directly. Finally, the instrumentation is expensive and requires high-cost professional support.

CONCLUSIONS

Research into the processing of hydrocarbon base stocks into fuel products and research into their performance demands accurate, informative and cost-efficient analyses. With the increasing variety of possible base stocks, e.g., heavy oils, tar sand bitumen, coal liquids, biomass, and oil shales analytical methods must be much more sophisticated. The simple mainly physical tests used previously to characterize fuel products when the base stock consisted only of light crude oils are not sufficiently discriminating.

Performance tests based on octane and cetane numbers are still the criteria by which the usefulness of the products are determined. However, probing tests into the chemical make-up of fuel products are now required to relate the performance to chemical composition and hopefully will assist research towards the goal of extending the supply of base stocks which will meet performance specifications.

This challenge can only be met by fully using powerful instrumental techniques and by developing standardized methods which will provide a maximum of information on chemical structure at a reasonable cost. NMR and GC/MS are only two of such techniques illustrated here. Others exist and their potential should also be developed fully. This is one of ERL's objectives.

ACKNOWLEDGEMENTS

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Table 1 - Test Fuels: Properties

	Density		Heat of Combustion MJ/kg	Sim. Dist. (°C)		Flash Point (°C)	Viscosity (c St)		Pour Pt. (°C)
	S.G.	API		5%	95%		100°F	210°F	
A - Cat. Crak. LGO	0.884	28.6	44.03	160	334	57	1.69	0.80	-40
B - No. 2 FO	0.863	32.5	45.80	143	355	43	2.07	0.93	-42
C - 1990 Diesel	0.880	29.4	44.79	160	387	62	2.91	1.15	-39
D - No. 2 FO (Tar Sand)	0.860	33.0	46.22	188	357	64	3.04	1.17	-29
E - LGO	0.860	33.0	46.79	211	351	88	3.26	1.24	-26
F - Blend of C & G	0.922	22.0	44.58	189	421	67	3.42	1.24	-52
G - LCO	0.953	17.0	42.48	199	402	82	3.45	1.35	-54
H - GO	0.939	19.2	43.12	211	383	92	4.56	1.48	-37
I - GO	0.912	23.7	44.15	208	427	90	10.07	2.29	-42
J - HGO	0.890	27.5	45.80	293	380	135	9.19	2.28	-8
K - HGO	0.896	26.4	45.86	234	446	76	10.76	2.53	-8
L - Furnace oil	0.864	32.3	43.96	190	404	62	2.68	1.10	-18
M - LCO	0.926	21.3	42.91	221	359	114	3.60	1.28	-13
N - Winter Diesel	0.845	36.0	44.31	196	357	62	2.09	0.94	-30
O - LCO	0.950	17.5	42.44	179	309	87	2.82	-	-24
P - LCO	0.935	19.8	43.16	184	316	101	2.82	-	-27
Q - No. 2 FO	0.846	35.8	45.53	172	363	63	2.59	1.08	-29
R - Jet Fuel	0.801	45.2	46.22	121	220	48	1.28	-	< -51
S - Kerosene	0.806	44.1	46.13	128	230	54	1.32	-	< -51
U - Naphtha	0.765	53.5	48.22	81	166	2	0.68	-	< -55

Table 2 - Test Fuels: Component Analysis

	Sulphur (wt%)	Carbon/Hydrogen (wt%)			FIA (Vol%)			Mass Spectroscopy (wt%)				Aromaticity NMR %	Aniline Point (°C)
		C	H	H/C Mole Ratio	A	O	S	P	(O)**	N	A		
A - Cat. Crak. LGO	0.58	87.7	11.3	1.54	-	-	-	23	6	20	51	37	15.8
B - No. 2 FO	0.30	86.8	12.2	1.68	38.7	1.5	59.8	27	1	30	42	23	47.4
C - 1990 Diesel	0.51	87.3	12.2	1.68	44.6*	2.8	52.6	24	0	34	42	23	45.4
D - No. 2 FO (Tar Sand)	0.22	86.4	12.8	1.78	-	-	-	29	0	38	33	17	59.8
E - LGO	0.66	86.2	13.3	1.85	22.6	11.1	66.4	32	0	43	25	12	60.8
F - Blend of C & G	0.93	88.4	10.7	1.45	-	-	-	21	0	26	53	39	31.4
G - LCO	1.35	88.3	10.2	1.39	73.0	2.0	25.0	11	0	9	80	46	18.5
H - GO	1.09	88.2	10.5	1.43	-	-	-	16	0	15	69	42	33.8
I - GO	1.49	86.5	12.2	1.69	-	-	-	21	0	57	22	19	53.7
J - HGO	1.22	86.1	12.9	1.80	44.8*	2.3	52.9	25	0	53	22	14	66.9
K - HGO	1.25	86.3	12.8	1.77	54.9*	0.9	44.2	28	0	46	26	17	65.7
L - Furnace oil	0.39	87.6	12.6	1.73	37.8	1.0	61.2	29	0	36	35	21	55.2
M - LCO	0.34	89.4	10.8	1.44	70.7*	0.9	28.4	15	0	20	65	41	25.5
N - Winter Diesel	0.28	86.5	13.0	1.80	28.6	1.0	70.4	33	0	37	30	15	56.6
O - LCO	1.47	88.7	9.7	1.32	77.6	1.5	20.9	10	0	14	76	51	5.4
P - LCO	0.42	89.1	10.1	1.36	77.7	0.6	21.7	13	0	13	74	48	6.7
Q - No. 2 FO	0.32	86.6	13.0	1.81	27.7	1.3	71.0	32	0	41	27	13	60.5
R - Jet Fuel	0.00	86.3	13.7	1.90	19.9	0.2	81.9	37	0	40	23	9	55.9
S - Kerosene	0.00	86.5	13.7	1.89	20.5	0.2	79.3	35	0	38	27	10	56.2
U - Naphtha	0.00	86.0	14.1	1.97	17.6	0.7	81.8	35	0	35	30	8	46.4

* FIA test difficult, results may be in error.

** Olefins by NMR.

Table 3 - Summations of mass spectroscopic peaks

<u>Components</u>	<u>Summation equation</u>
Saturated hydrocarbons	$71 = H_{71} + H_{85} + \dots$
Monocyclic saturated hydrocarbons	$69 = H_{69} = H_{83} + \dots$
Dicyclic saturated hydrocarbons	$67 = H_{109} + H_{123} + \dots$
Monoaromatics	$79 = H_{79} + H_{93} + \dots$
Naphthalenes	$129 = H_{129} + H_{143} + \dots$
Polyaromatics	$179 = H_{179} + H_{193} + \dots$
	$203 = H_{203} + H_{217} + \dots$
	$229 = H_{229} + H_{243} + \dots$
Benzocycloparaffins	$117 = H_{117} + H_{131} + \dots$
	$119 = H_{119} + H_{133} + \dots$

Table 4 - Correlation Coefficients

	Aromatics (FIA)	Aniline Point	H/C Ratio	Aromaticity NMR	Aromatics MS
Aromatics (FIA)	1	-0.795	-0.951	0.942	0.876
Aniline point	-	1	0.873	-0.916	-0.917
H/C ratio	-	-	1	-0.992	-0.921
Aromaticity (NMR)	-	-	-	1	0.960
Aromatics (MS)	-	-	-	-	1

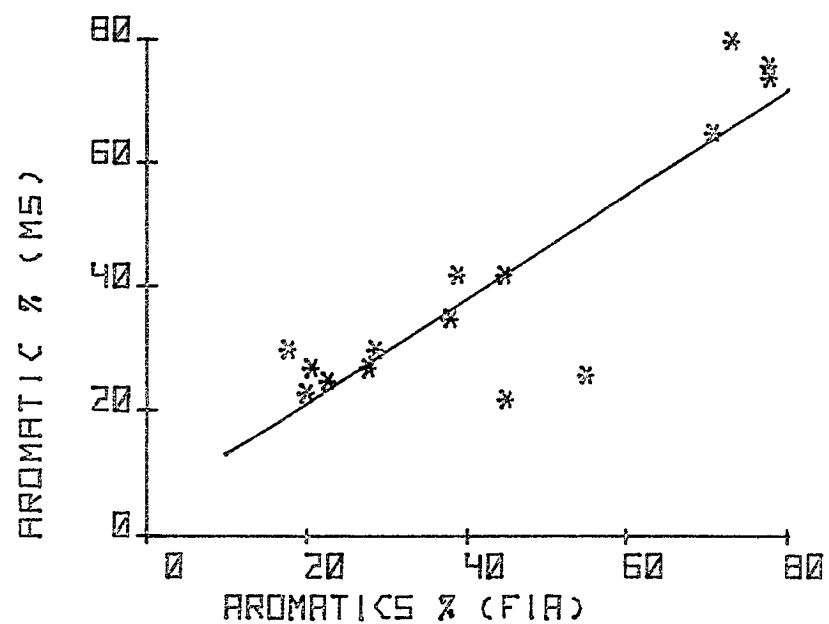
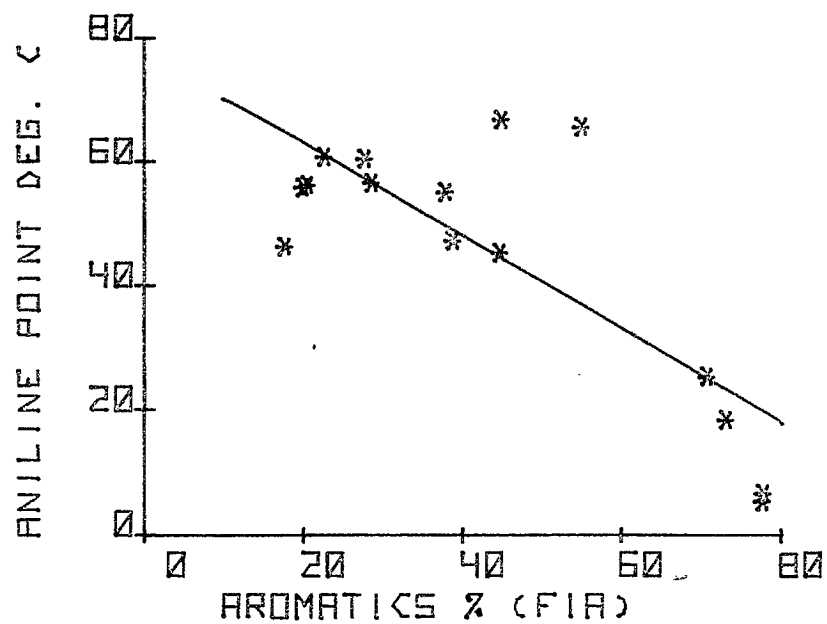
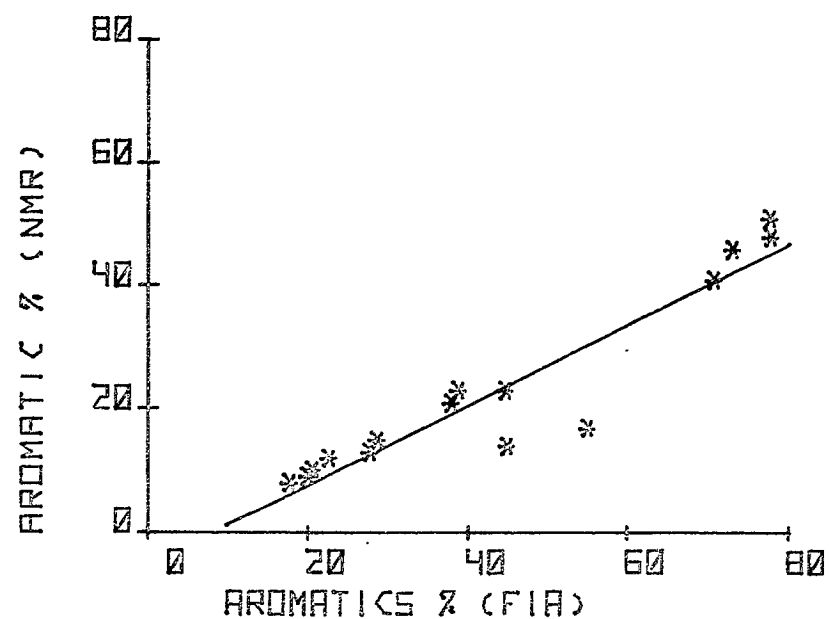
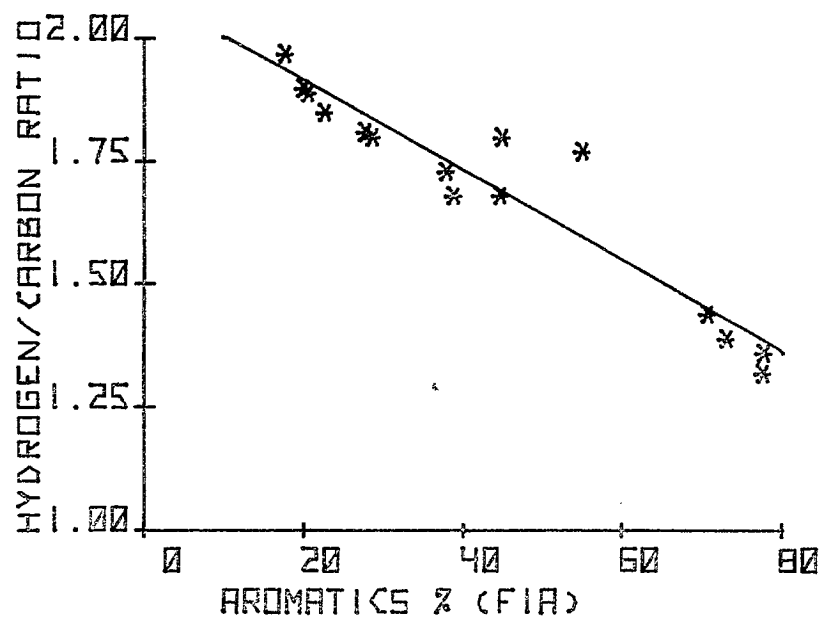


FIGURE 1

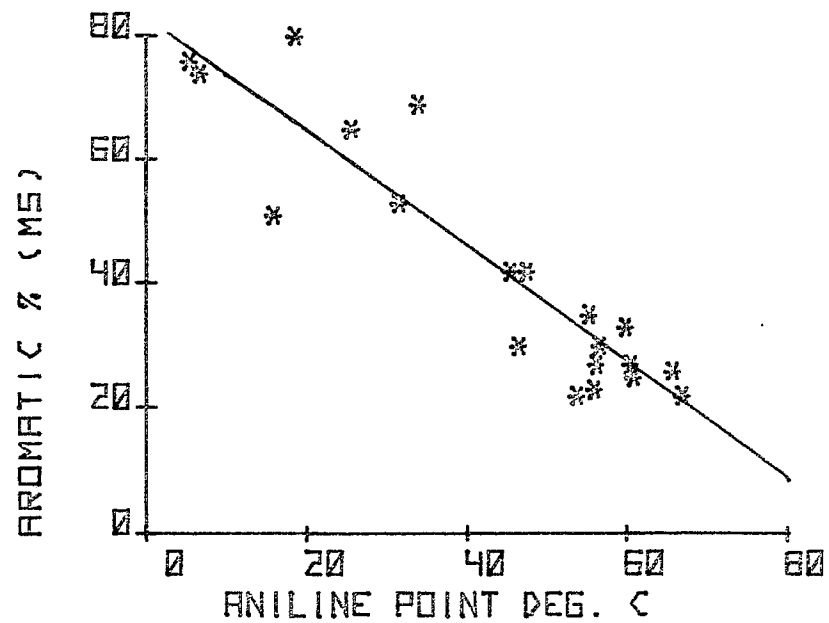
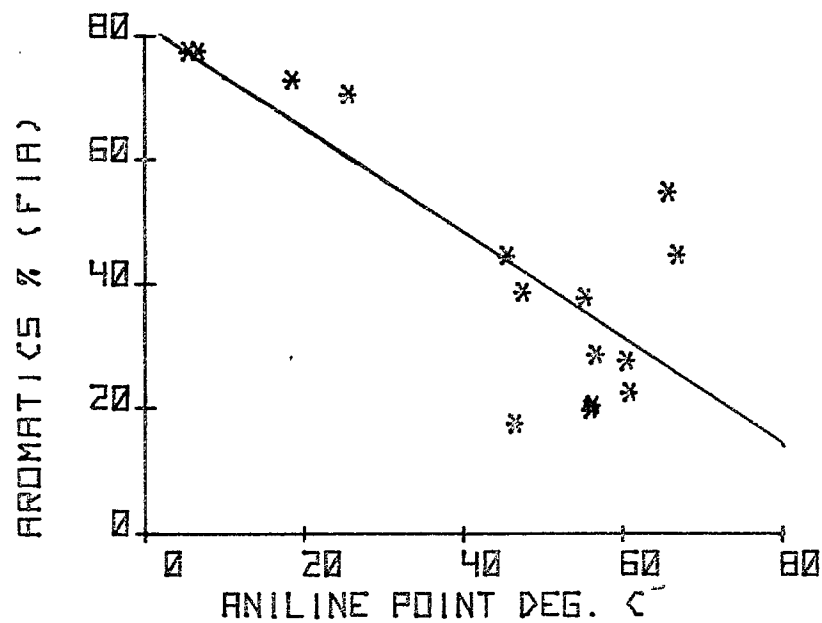
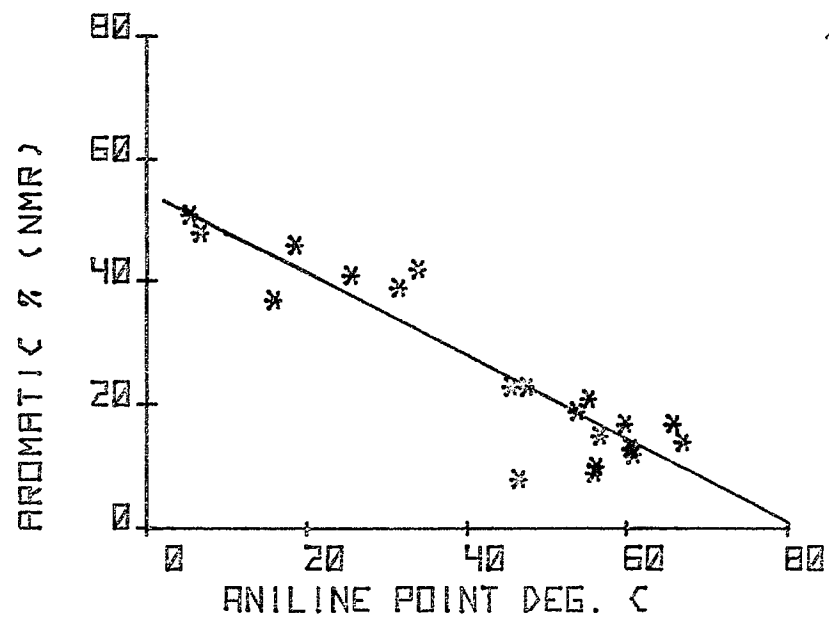
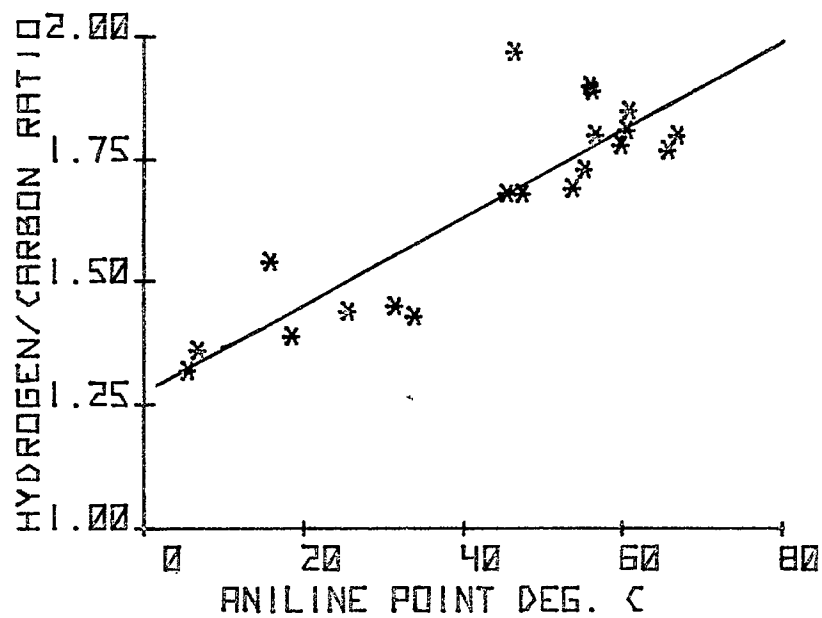


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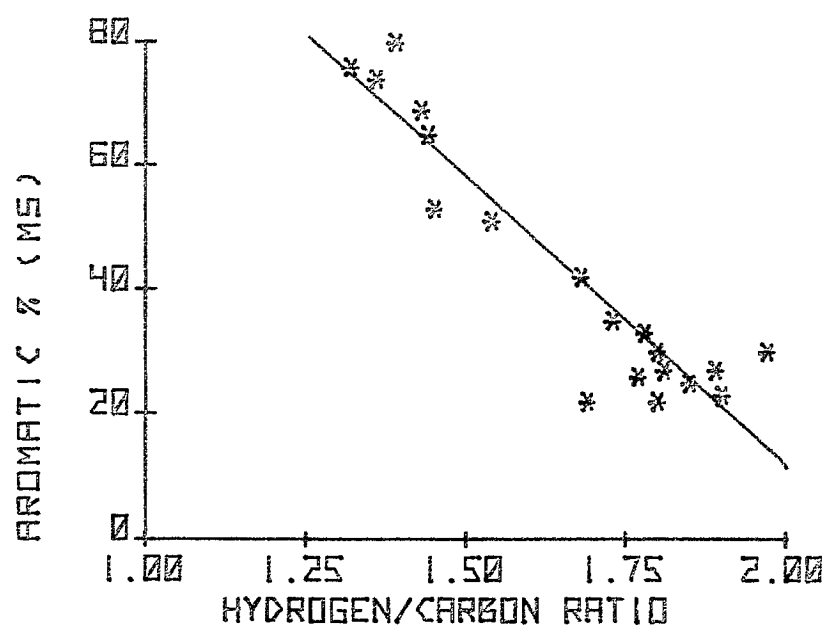
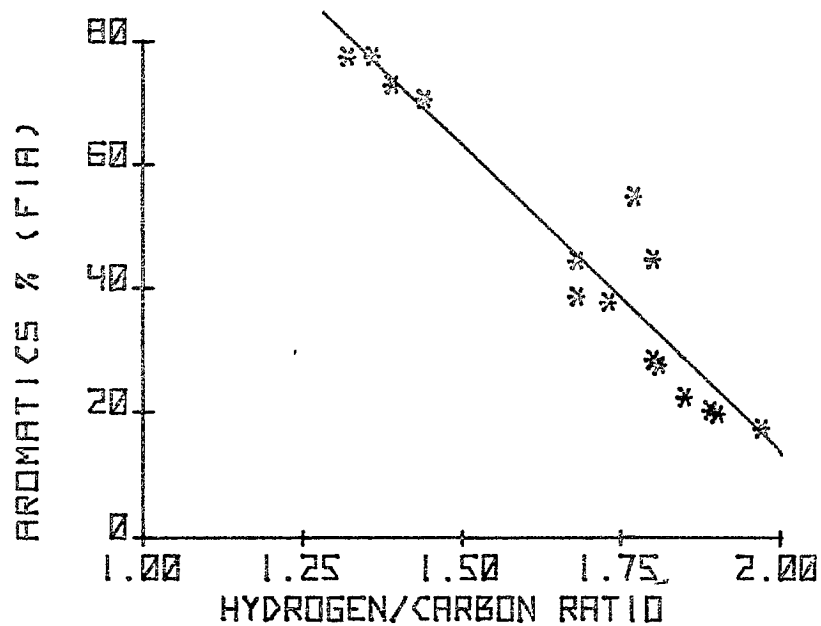
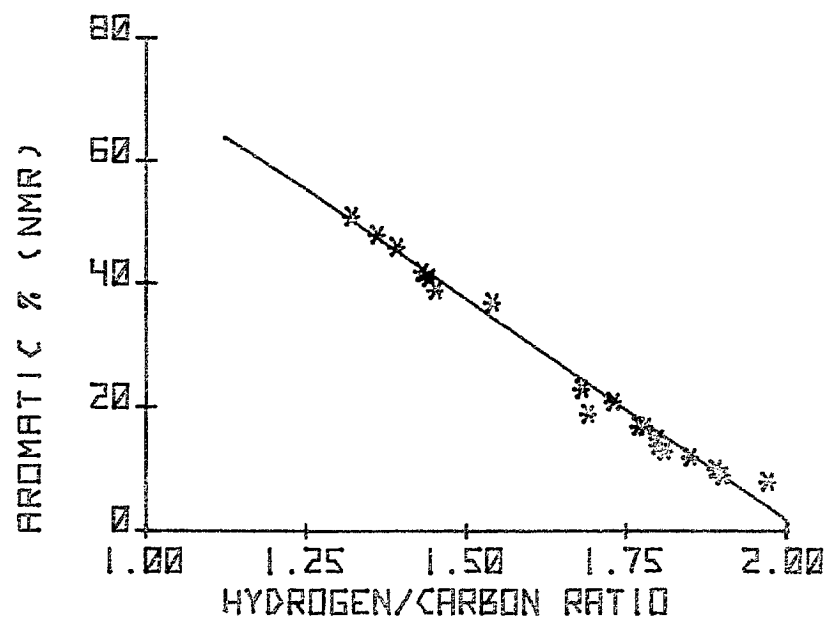
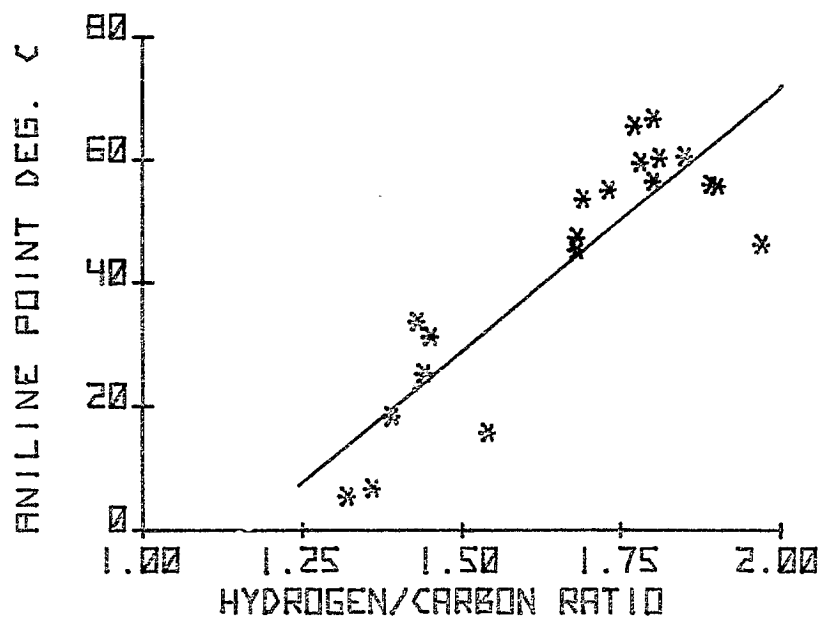


FIGURE 3

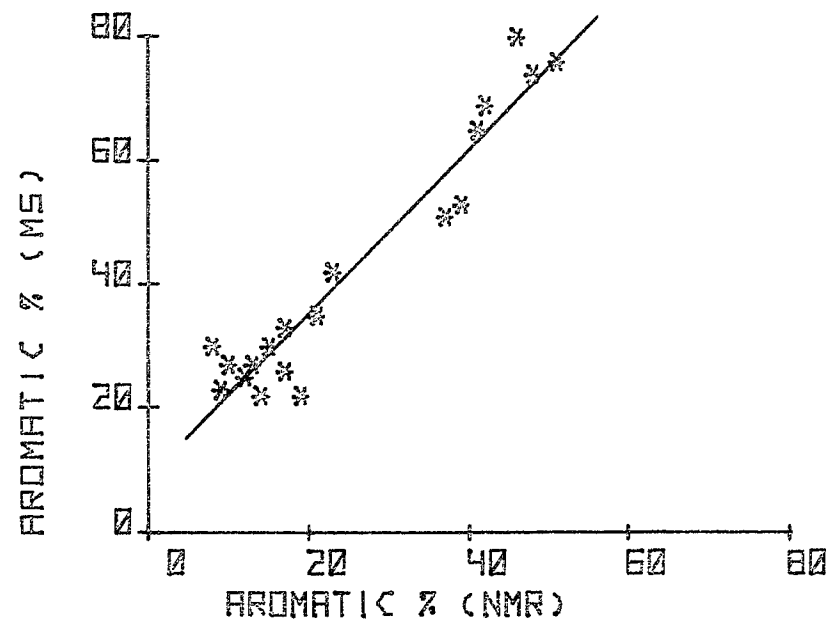
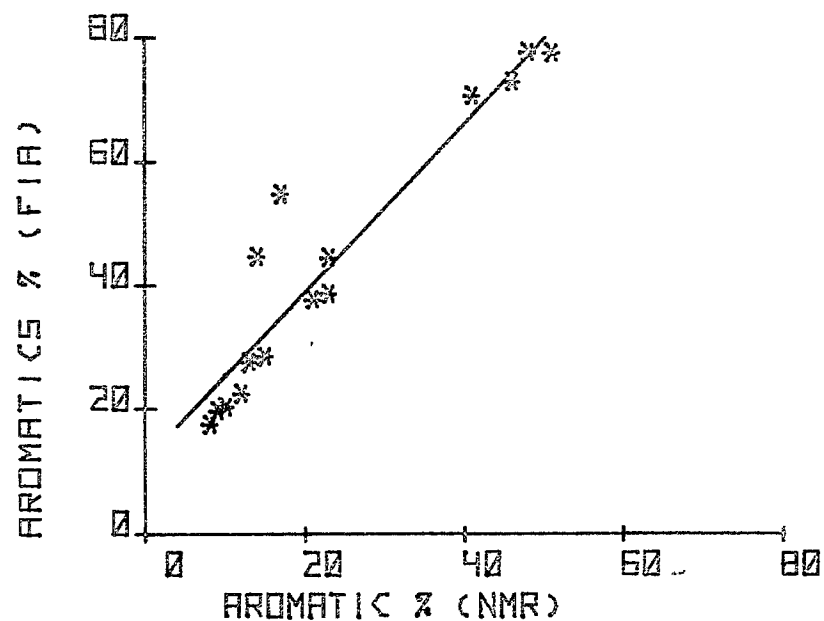
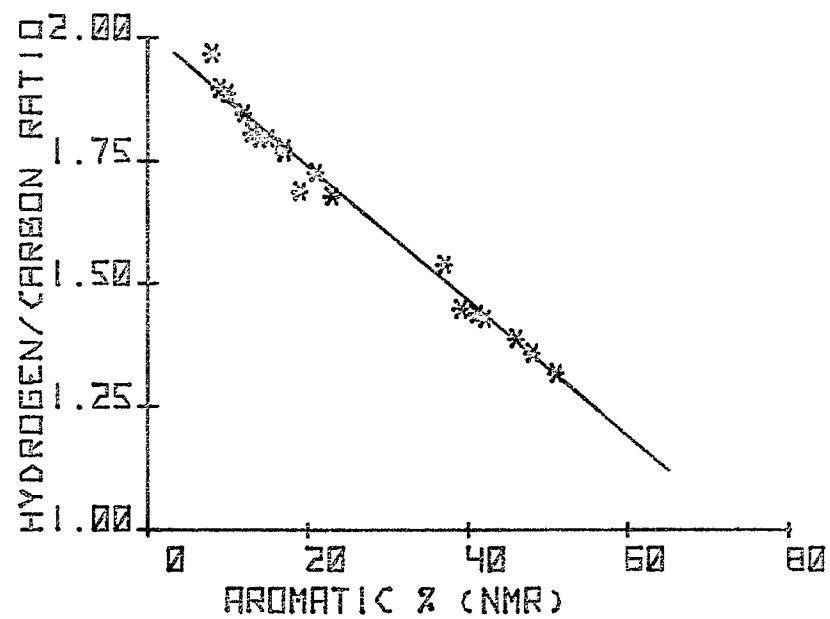
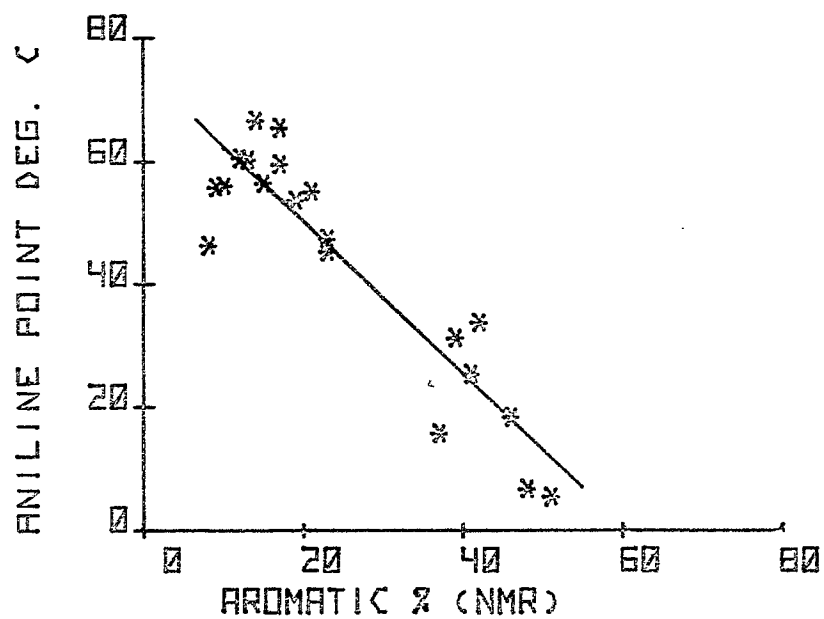


FIGURE 4

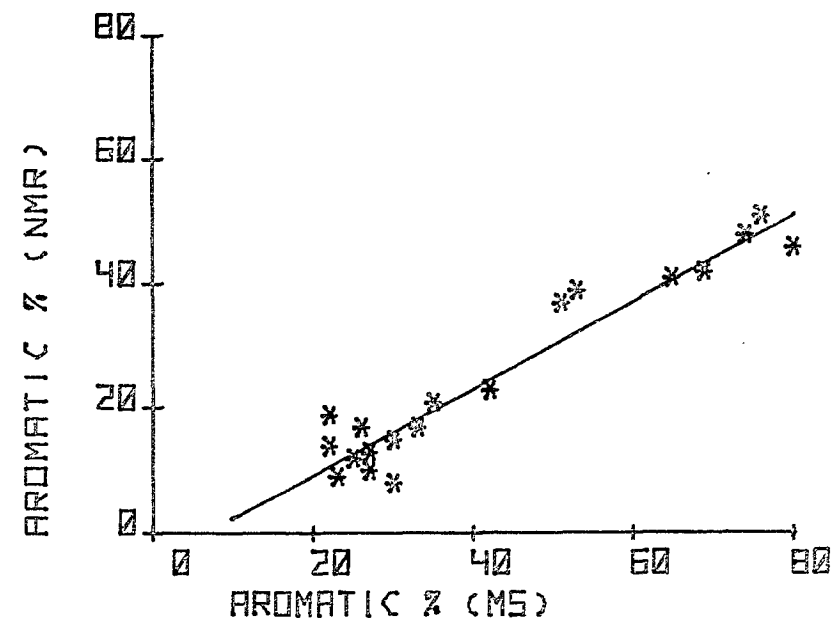
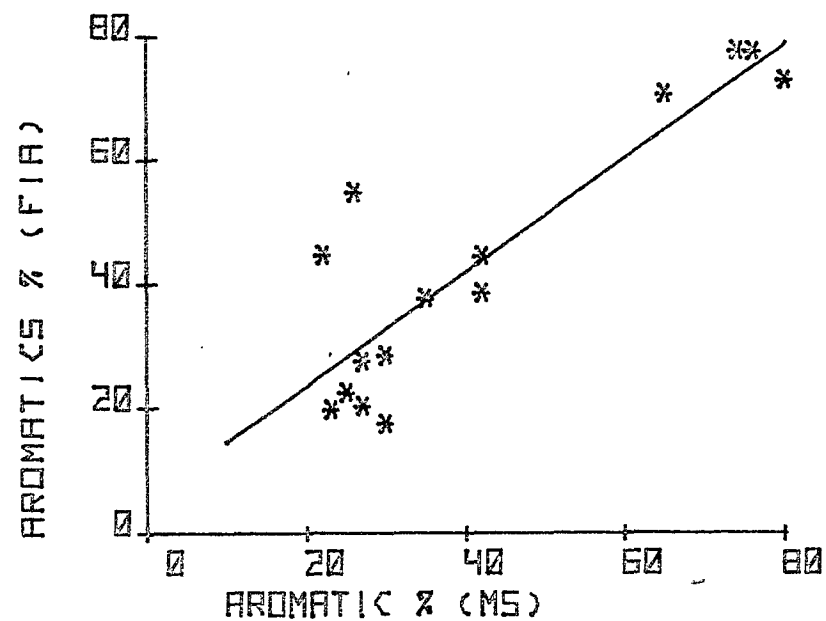
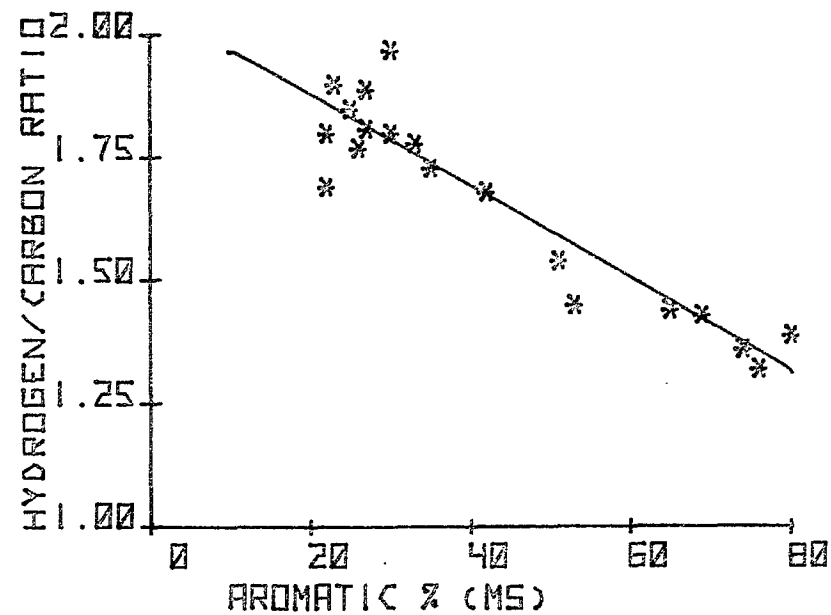
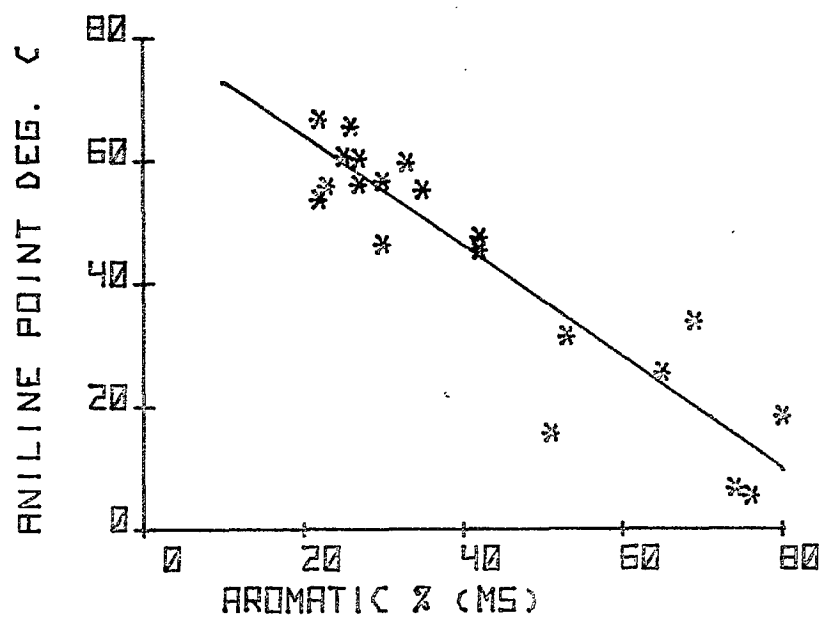


FIGURE 5