

DETERMINATION OF FUEL AROMATIC CONTENT AND ITS EFFECT ON
RESIDENTIAL OIL COMBUSTION

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ABSTRACT

The increasing use of distillate fuel oils processed from synthetic crudes has caused concern for deteriorated performance due to increased levels of aromatic compounds and increased viscosity of these fuels. The performance characteristics of middle distillate fuels of varying physical and chemical properties, derived from both conventional and synthetic crudes, are being determined on residential combustion systems at the Canadian Combustion Research Laboratory.

The aromatic properties of the fuels are determined using a range of techniques: the fluorescent indicator absorption method (FIA) for total aromatics; the proton nuclear magnetic resonance method (PNMR) for aromaticity and hydrogen distribution; the gas chromatographic/mass spectrometric (GC/MS) method and column chromatographic method for aromatic compound types; the mass spectrometric (MS) method for paraffins, olefins, naphthenes and aromatics (PONA); theoretical calculations based on physical properties for total aromatics; and aniline point measurements.

In this study 22 fuels were examined, and observations correlating the fuel aromatic properties with transient particulate emissions are presented.

INTRODUCTION

An increased awareness of dependency on the oil exporting nations and the volatility of the world oil price market has changed the outlook of the oil industry. Ever since the energy crisis of the 1970's, industry and consumers have come to realize the potential savings of implementing energy conservation measures. The North American petroleum industry has reduced energy consumption significantly in recent years and according to a 1985 survey (1) an additional 14% reduction is technically feasible. One approach, taken by refiners, is to reduce the manufacturing cost by maximizing the use of lower cost components. At the present time, this approach

is highly attractive since good quality conventional resources are being depleted rapidly all over the world, while the global demand for middle distillates is expected to increase (2). The combined effects of energy conservation measures and the natural decline of good quality conventional feedstocks have created new concerns for refiners over fuel oil quality.

Due to cold climate and immense distances, Canada is one of the largest per capita users of oil in the world (3). As a result of these "hardships", Canadian industry and consumers face greater energy conservation challenges than almost anywhere else in the world. In addition to an overall reduction in energy consumption by the population, innovative solutions have to be considered to extend the life of the conventional resources. Such efforts include replacement of oil with alternate energy sources and development of alternate oil supplies such as those from frontier reserves, heavy oils and tar sands from western Canada. Middle distillates processed from synthetic crudes derived from the heavy oils and tar sands of Alberta and Saskatchewan are already on the Canadian market and their production is increasing. By 1990, Canadian tar sands development is expected to increase production capacity from the current 12% to 23% of Canadian crude oil demand with a future increase to 39% in the year 2005 (4). Regardless of fluctuating world oil prices, which depend on numerous unpredictable events and circumstances, it is in the industry's best interest to have at hand the technology which will best utilize the available indigenous resources.

Middle distillates processed from tar sand crudes contain higher proportions of aromatic and naphthenic compounds which can degrade combustion quality (5). The problems associated with the use of highly aromatic fuels are well known and widely documented (6 - 11). A better understanding of the relations between oil properties and their performance could help refiners to better handle such problems and allow more blending flexibility. In the case of heating oils, possible use of lower grade fractions will reduce manufacturing costs and allow diversion of more quality components into diesel fuel and gasoline. With these objectives in mind, an experimental program to study the effects of oil quality on residential oil combustion characteristics is being carried out at the Canadian Combustion Research Laboratory.

In the course of this study, it has become apparent that accurate and reliable analytical techniques for fuel property determinations are critical in order to achieve accurate correlation with performance characteristics. The suitability of the various techniques for use in petroleum refineries is also an important consideration. For example, in the determination of aromatics there are numerous methods available, but limitations associated with each technique restrict its use to certain areas. This paper describes the approaches taken to determine the aromatic content of middle distillate fuels, and presents the correlations observed between fuel aromatics and particulate emissions.

EXPERIMENTAL

Experimental facility.

Detailed descriptions of the experimental equipment and procedures developed for the fuel quality evaluation program have been reported elsewhere (12). Figure 1 is a schematic diagram of the equipment used in the combustion experiments. The experimental rig includes a commercial warm air furnace, a chilled air distribution system, fuel conditioning unit, continuous emission analyzers, and data acquisition and processing equipment. Special emphasis was given to the design of the test rig so that experimental conditions would simulate those of a "real life" residential environment.

Fuel variety.

The middle distillate oils selected for this study were obtained from six major Canadian oil companies and from the National Research Council of Canada. The oils include commercial No. 2 fuels, No. 2 fuels processed from synthetic crudes, light gas oils, light cycle oils, jet fuels, diesel fuels from conventional crudes, laboratory-blend synthetic diesels and oil blends prepared for specific properties.

Experimental procedure.

A typical experimental run required 40-60 minutes of preparation to set the control conditions in the test rig and to calibrate the analyzers. The actual test procedure started with an initial burner start-up (cold start), followed by a continuous one hour run, off for 10 minutes, followed by five 10 minute on/10 minute off cycles operations. A complete experimental run lasted a total of 170 minutes. The control conditions selected for evaluation of all the test fuels included the following: fuel temperature of 7°C and 15°C, oil pump pressure of 689 K pascal (100 psi), furnace exit draft of 0.1 cm (0.04 in) water column, cold air return temperature of 15°C and fuel firing rate of 2.6 litres per hour (0.65 U.S. GPH). The oil nozzle used was of the hollow type (NS) with 80° spray angle. The combustion air supply was set independently for each fuel to obtain a steady-state smoke number of 2 when tested with a Bacharach smoke test instrument prior to the run.

Gaseous emissions of O₂, CO₂, CO, NO_x, and hydrocarbons, along with selected temperatures were continuously monitored during the entire run. Data acquisition was carefully planned at selected intervals so that the critical start-up and shut-down transient emissions were recorded. Particulate emissions were measured during the start-up transient period using calibrated diesel exhaust smoke opacity meter (Celesco model 107, Berkeley Instruments) which had been previously modified for these tests.

Fuel characterization methods.

The analytical techniques used to characterize the fuels include ASTM standard methods for density, viscosity, distillation, flash point, pour point, aniline point and aromatic components. Additional techniques used for the determination of aromatics are proton nuclear magnetic resonance (PNMR) for aromaticity and gas chromatography/mass spectrometry (GC/MS) for hydrocarbon compound types.

Proton nuclear magnetic resonance spectroscopy.

Two laboratories were utilized for this analysis. Laboratory 1 used a Varian CFT-20. Laboratory 2 applied a 90 MHz Varian EM-390 spectrometer. Sample to solvent concentration ratios of 50/50 were used to record the spectra. Chloroform -d₁ (99.9%) with ME₄Si was used as solvent.

Mass spectroscopy.

A Finnigan 4500 quadropole mass spectrometer was used for MS and GC/MS determinations of PONA and mono-, di-, and poly-aromatic fractions. The samples were separated using a 1.83 m column (3% Dexil 300 on acid washed Chromosorb W) heated from 60°C to 300°C at a programmed rate of 8°C/min. Chemical ionization (methane) mass spectra were acquired continuously during the gas chromatographic separation on a 3 second cycle. The series of peaks characteristic of each given class of compounds - paraffin, naphthenes, and aromatics - were summed continuously throughout the run in characterizing the compound type classes. The olefin content was determined using the PNMR method and any interfering peaks in the mass spectra were corrected. The detailed PONA method is available in the published literature(13).

RESULTS AND DISCUSSIONS

Determination of aromatic components in test fuels.

While it is well known that aromatic hydrocarbons increase particulate emissions and cause related problems in combustion, the method for determining aromatics is not straightforward. The FIA (fluorescent indicator absorption) method is the most widely used standard method (ASTM D 1319) in the oil industry, although it is known to have poor accuracy. Its application is also limited to light distillate oils. GC/MS and NMR methods provide better accuracy and precision but are labour and cost intensive. The industry has

not completely accepted these sophisticated instrumental techniques since they require specially trained operators and temperature controlled environments. High performance liquid chromatography (HPLC), with its efficient chromatographic column, is known to provide good separation of hydrocarbons but its detection technique is somewhat limited. The two most common detection systems, ultraviolet (UV) and refractive index (IR), are very compound specific to hydrocarbon compound types and require extensive calibration for all compounds present in oils. Therefore, this method is not practical for refinery applications although the instrumentation is less costly and less sophisticated than for GC/MS and NMR. Two detectors considered to be preferable to the UV and IR are the flame ionization detector (FID) and the dielectric constant (DC) detector. As part of the research program described herein, further work is being carried out to develop a nonconventional simple method for determining the aromatics in oils by HPLC with FID detection.

Due to the above discussed variations and limitations involved in aromatic analysis, it was decided to apply several different techniques to determine the aromatic components of the test fuels evaluated in this study. Table 1 shows the aromatic data of 22 test fuels as determined by different techniques. Since it is critical to have accurate fuel property data in establishing the fuel quality/performance characteristics, attempts were made to have duplicate analyses done by independent laboratories whenever possible. Aromatic content is gathered from PONA data using the GC/MS technique. It is defined as the percent of aromatic type hydrocarbons determined on a molecular basis. Aromaticity as described herein represents the percent carbon in aromatic rings or the ratio of aromatic carbons to the total number of carbons (14). It can be determined by proton NMR or carbon 13 NMR methods. Aromaticity data were chosen for duplicate independent analysis since NMR is less dependent on the instrument, operator, and method than GC/MS. Aniline point measurements were made using the ASTM D 611 standard method.

The correlation between different analysis methods can be seen in Figures 2 and 3. The aromatic content and aromaticity data are in good agreement and have a linear correlation coefficient of 0.958. The aniline point data show greater spread (Figure 2) which could be due to the fact that aniline point is not an absolute parameter but only provides a measure of aromatics. As well, aniline point is known to give poor accuracy in the analysis of heavy fuels. The correlation coefficient for the aniline point data is 0.928.

Figure 3 is the regression plot of the FIA and aromatic content data. It shows a positive linear correlation with a correlation coefficient of 0.963. However, the method cannot provide data for some heavy fuels due to incomplete separation in column chromatography.

Figure 4 compares the aromaticity data from two independent laboratories. The slight variation is due to the difference in data manipulation methods used by the two laboratories. Laboratory 1 used

the Brown and Ladner method which assumes that the paraffinic hydrogen to carbon ratio is exactly 2.0 (15). Laboratory 2 took the assumption that the hydrogen to carbon ratio is larger than 2.0 and also incorporated corrections associated with other physical properties such as density and refractive index (16). The combined data show good agreement with a correlation coefficient of 0.971.

The physical and chemical properties of all the test fuels are reported in Table 2. The correlation between physical properties, e.g. fuel density, and aromatic properties was also studied as illustrated in Figure 5. Aromaticity and density exhibit a good linear relation with a correlation coefficient of 0.942. Aniline point data show wide variation which can be attributed to the reasons previously discussed.

Significant improvement can be seen in aniline point data correlation when it is related to the K factor of the fuels. K factor, also known as the Watson characterization factor, is defined as

$$K = \frac{(T_{b,R})^{1/3}}{s}$$

where $T_{b,R}$ = molal average boiling point, °R
 s = specific gravity at 60/60 F (17).

K factor is the most widely used index of composition in the characterization of petroleum crude oils.

From Figure 6, the improved correlations are 0.979 and 0.963 for aromaticity-K factor and aniline point-K factor respectively. The improvement is due to the incorporation of boiling points rather than considering only one parameter: density (specific gravity). K factor is the most promising parameter for refinery use since it can be easily calculated from the boiling points and specific gravity data, which are readily available from fact sheets. As part of this research study, correlations are being developed to use K factor in place of fuel aromaticity to predict fuel performance.

Effect of fuel aromatics on soot production.

The effects of fuel aromatic compounds on combustion processes have been widely studied and are well documented in the literature. The impact of aromatics on residential oil combustion, especially on the increased generation of incomplete combustion products (e.g. particulates, carbon monoxide and hydrocarbons) have been examined under the research program described herein. Discussion in this paper is limited to soot production.

In the literature on solid particle emissions from combustion processes measurements for parameters such as smoke, particulates,

opacity and soot are reported based on the specific methods and instrumentation used. Particulates, which are generally defined for regulatory purpose as "any material with the exception of water that collects on a filter operated in an air-diluted exhaust stream" require multi-step, time consuming and expensive operations. Soot or carbon is defined as the nonvolatile portion of particulates and can be measured by thermogravimetric analysis or by the removal of condensed hydrocarbons from the particulates. Commercial smoke meters provide smoke opacity or transmittance readings and smoke testers such as Bosch and Bacharach (ASTM smoke number) offer smoke numbers. Although these methods all measure some sort of "unburnt combustion solids", conversion between the various methods is difficult if not impossible. Attempts at this have been made by Homan(17) who reports conversion factors among 11 smoke measurements; Alkidas(18) reported on the relationship between smoke measurements and particulates.

In this study, solid particles from furnace exhaust are measured with a Celesco smoke opacity meter and a Bacharach smoke number tester. The calibration of the smoke meter, and correlation with particulate mass concentration, has been carried out and reported elsewhere (20). Analytical data are reported in terms of percent opacity for ease of discussion; each reading represents opacity per transient phase or per cycle. For cyclic operations, data reported is the mean of a 5 cycle test.

The analytical precision of the data from opacity measurements of all test fuels has been discussed in a previous publication(12). Each value represents the mean of data from a minimum of 3 runs, with precision expressed as the coefficient of variation. For regular commercial No 2 fuels, transient emissions show variation of less than 7%. Heavy and highly aromatic fuels which usually experience combustion problems, show poor precision with errors usually higher than 20%. The error increases with decreasing oil quality. The regression plots in this paper show data from both a wide range of fuels. The errors associated with the lower grade fuels (usually on the right hand of the graph) are much larger than for the better quality oils (data on the left hand side).

The precision of the data is also affected by the run type. Transient opacity readings from cyclic operations show better precision than for cold start trials. This is a direct reflection of the effect of oil temperature on combustion. Cold start operations are subject to cold fuel and environment, whereas the subsequent cyclic starts experience more favourable conditions. For example, even though for all the experiments reported herein the fuel tank temperature was maintained at 15°C, the oil temperature at the nozzle adapter at the beginning of a cold start averaged 17 - 20 °C as compared to 40 - 75 °C for cyclic runs.

Opacity readings from cold start and cyclic transient phases from combustion tests of 22 fuels are reported in Table 4. Figure 7 graphically compares cold start and cyclic data. Aromaticity, being the most reliable among 4 different parameters, is used as the measure of fuel aromatic components. The current data indicate an

exponential increase in smoke opacity at cold start ignition for an increase in aromatic components. The breakaway point at 45% aromaticity suggests the upper limit which the fuels can tolerate without excessive emission levels. Opacity readings normally observed from domestic furnaces firing with commercial No. 2 fuels are 1.5% to 2.5% at the cold start transient phase. Cyclic operations generate much lower smoke due to a more favourable combustion environment. The effect of aromatics during normal furnace on/off operation is less pronounced even when oils with considerably high aromatic content are used. The average opacity per cyclic start for commercial furnace fuels is between 0.3% to 0.7%. The worst case observed (1.8% opacity) is for fuel with aromaticity of 59%.

From these observations, it appears that aromaticity is the prime factor causing soot production from residential burners. In reality, the observed combustion characteristics including gaseous and particulate emissions and burner ignition behaviour are caused by several physical and chemical properties, interrelated in a complex manner. For example, the breakaway point at 45% aromaticity, as seen in Figure 7, coincides with the following breakaway points in the applicable plots: 60% aromatic content, 4 c St fuel viscosity and cetane index of 25. Results describing the overall effects of aromatics, viscosity, and other physical and chemical properties on soot production have been reported elsewhere (18). It should be noted that in the opacity - aromaticity regression plots data from fuels with viscosity higher than 3.5 c St are omitted in order to try and isolate viscosity effects. It is impossible to totally isolate the effect of any one parameter on combustion performance, however a general indication of its importance may be drawn.

The research program described in this paper is continuing with the objective of incorporating all of the significant fuel oil properties into a mathematical model which predict combustion performance based on oil properties.

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Table 1. Aromatic Properties of Fuels.

Fuel	FIA %			MS %				Aromaticity %		Aniline point °C
	A	O	S	P	O	N	A	Laboratory1	Laboratory2	
C	45	3	53	24	0	34	42	31	31	45
D	na	na	na	29	0	38	33	24	22	60
E	23	11	66	32	0	43	25	21	19	61
F	na	na	na	21	0	26	42	42	44	31
L	38	1	61	29	0	36	35	21	27	55
M	71	1	28	15	0	20	65	40	48	26
N	29	1	70	33	0	37	30	16	22	57
O	78	2	21	10	0	14	76	51	59	5
P	78	1	22	13	0	13	74	48	54	7
Q	28	1	71	32	0	41	27	15	19	61
R	20	0	82	37	0	40	23	9	16	56
V	32	1	31	31	0	46	28	14	17	46
W	30	1	70	33	0	42	30	15	22	50
X	42	1	57	27	2	28	48	32	42	29
Y	55	2	44	23	1	30	50	34	43	36
Z	34	1	66	31	0	46	27	18	21	57
AA	33	1	67	28	0	51	26	18	23	56
BB	45	4	52	31	0	35	39	28	38	41
CC	59	1	39	25	0	27	54	36	44	30
DD	69	3	28	19	0	21	64	46	53	14
EE	62	2	36	14	0	17	68	45	49	25
FF	31	2	67	35	1	35	29	20	25	56

A, O, S denotes aromatics, olefins, saturates
P,O, N,A denotes paraffins, olefins, naphthenes, aromatics
na denotes not available

Table 2. Physical and Chemical Properties of Fuels.

Fuel	Density kg/l 15°C	Viscosity c St @ 40°C	Heat of combustion MJ/Kg	Simulated distillation °C 5% °C 95%		Flash point °C	Pour point °C	Refractive index
C	0.88	2.91	44.8	160	387	62	-39	1.50
D	0.86	3.04	46.2	188	357	64	-29	1.48
E	0.86	3.26	46.8	211	351	88	-26	1.48
F	0.92	3.42	44.6	189	421	67	-52	1.49
L	0.86	2.68	44.0	190	404	62	-18	1.49
M	0.93	3.60	42.9	221	359	114	-13	1.53
N	0.85	2.09	44.3	196	357	62	-30	1.47
O	0.95	2.82	42.4	179	309	87	-24	1.55
P	0.94	2.82	43.2	184	316	101	-27	1.54
Q	0.85	2.59	45.5	172	363	63	-29	1.47
R	0.80	1.28	46.2	121	220	48	-51	1.45
V	0.84	1.74	45.3	94	414	11	-60	1.47
W	0.84	1.88	45.3	134	356	21	-36	1.47
X	0.86	1.35	44.2	127	376	10	-60	1.51
Y	0.91	3.26	43.7	207	380	70	-33	1.52
Z	0.87	4.09	44.8	204	378	72	-33	1.49
AA	0.88	5.12	44.7	211	386	74	-42	1.49
BB	0.88	2.65	44.5	206	332	73	-24	1.50
CC	0.90	2.70	43.9	213	329	78	-36	1.51
DD	0.94	2.77	42.7	224	330	83	-27	1.54
EE	0.92	2.90	43.2	185	380	65	-51	1.53
FF	0.86	2.52	45.1	200	325	70	-30	na

* na denotes not available

Table 3. Correlation of Fuel Properties and Particulate Emissions.

Fuel	Aroma- ticity%	Aromatic content%	Analine point°C	Diaromatics %(GC/MS)	K factor	Opacity%		Smoke #	
						(cs)	(cy)	(cs)	(cy)
C	31	42	45	12	11.29	1.3	0.7	6	6
D	22	33	60	12	11.56	1.6	0.5	8	6
E	19	25	61	6	11.64	1.8	0.6	7	6
F	44	42	31	12	11.01	1.5	2.2	9	7
L	27	35	55	13	11.45	1.9	1.3	7	7
M	* 48	65	26	19	10.81	* 52.3	1.8	>9	7
N	22	30	57	8	11.55	0.7	0.2	6	6
O	59	76	5	44	10.46	16.8	1.9	>9	7
P	54	74	7	30	10.62	9.1	2.1	8	7
Q	19	27	61	5	11.68	1.6	0.4	7	6
R	16	23	56	3	11.79	0.3	0.1	6	4
V	17	28	46	2	11.54	1.6	1.2	8	7
W	22	30	50	5	11.58	2.0	0.6	7	6
X	42	48	29	18	11.21	2.1	1.8	7	6
Y	43	50	36	22	11.03	10.4	1.2	>9	7
Z	* 21	27	57	7	11.52	* 2.4	1.0	>9	6
AA	* 23	26	56	6	11.43	*14.8	0.6	9	5
BB	38	39	41	13	11.22	3.0	1.2	8	6
CC	44	54	30	19	11.01	5.0	2.3	8	7
DD	53	64	14	34	10.61	15.4	1.8	>9	7
EE	49	68	25	na	10.81	20.9	2.9	>9	7
FF	25	29	57	10	11.57	2.3	0.6	5	4

cs denotes cold start
cy denotes cyclic start

- data not used in regression plots as fuel viscosity was higher than 3.6 c St.

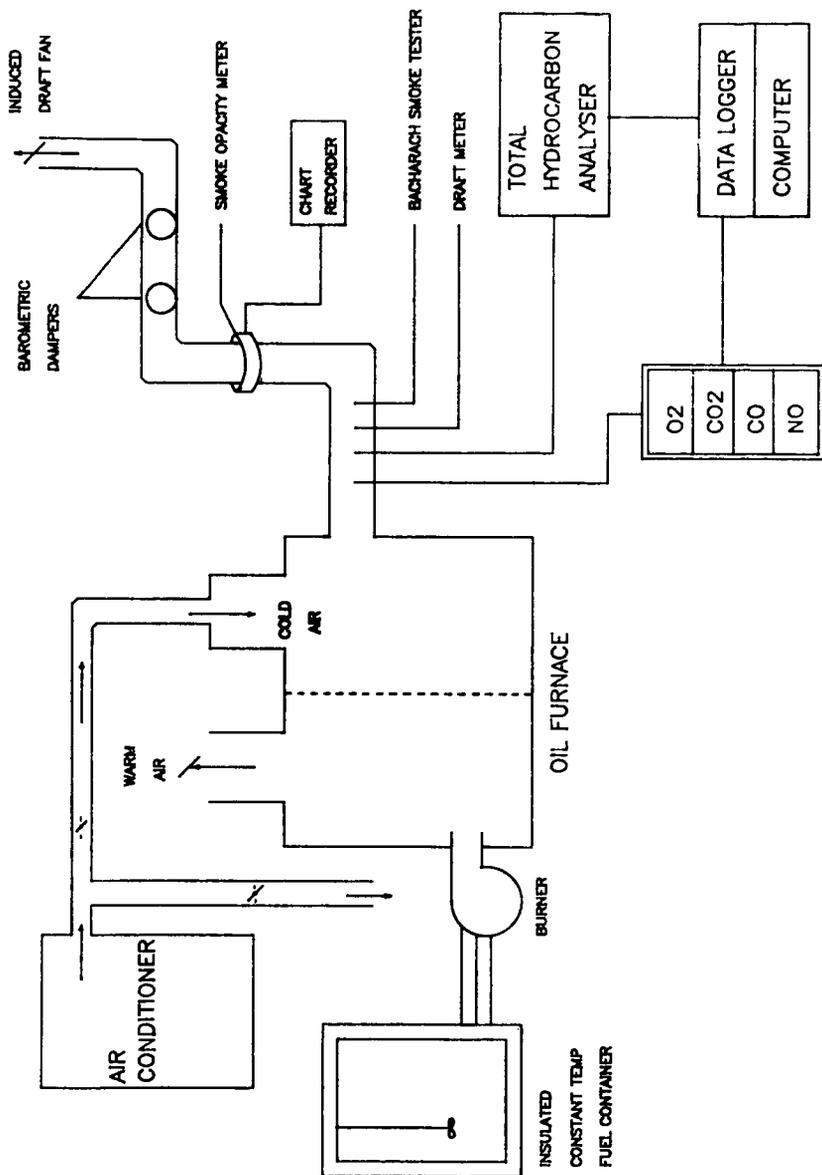


Figure 1. Schematic of the laboratory equipment facility used in the fuel quality evaluation experimental program.

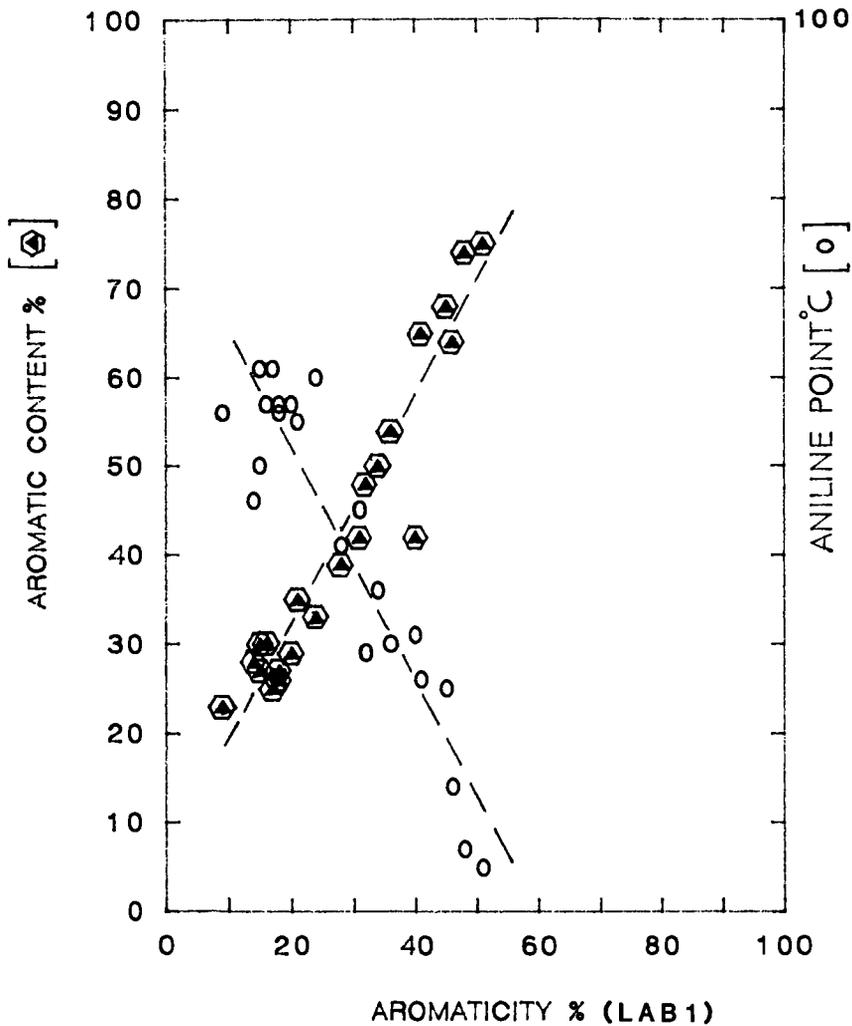


Figure 2. Comparison of fuel aromatic data as determined by three different analytical techniques.

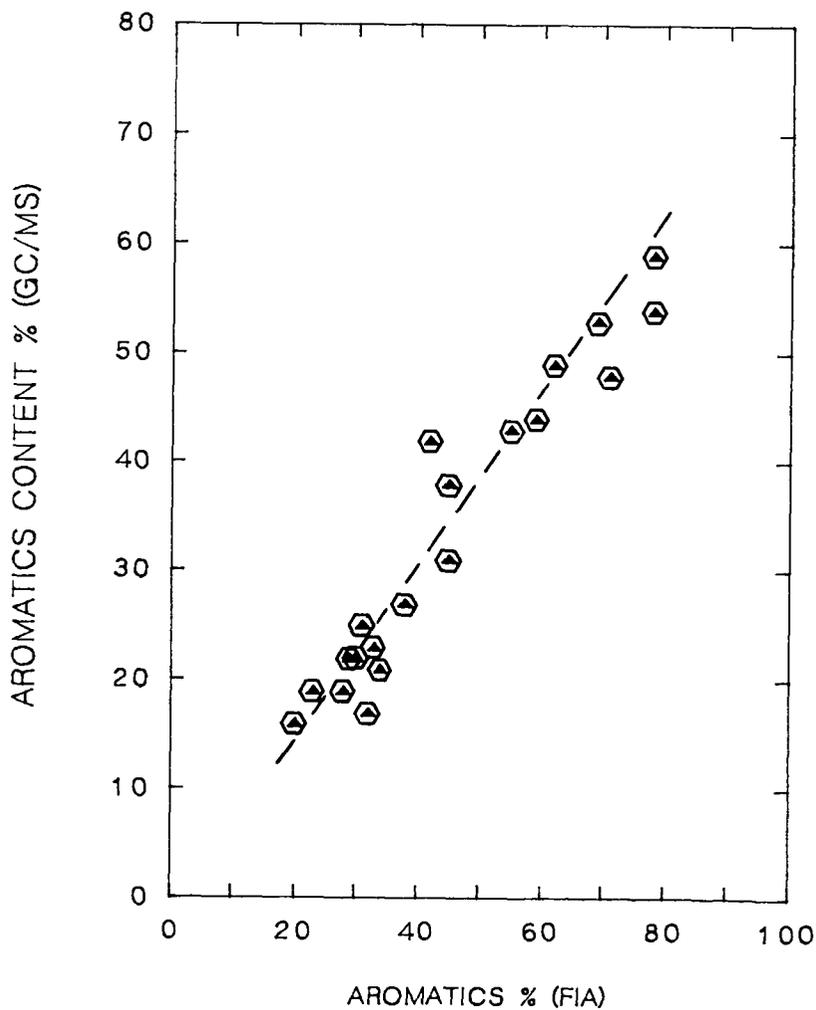


Figure 3. Correlation between fuel aromatic data as determined by GC/MS method and FIA method.

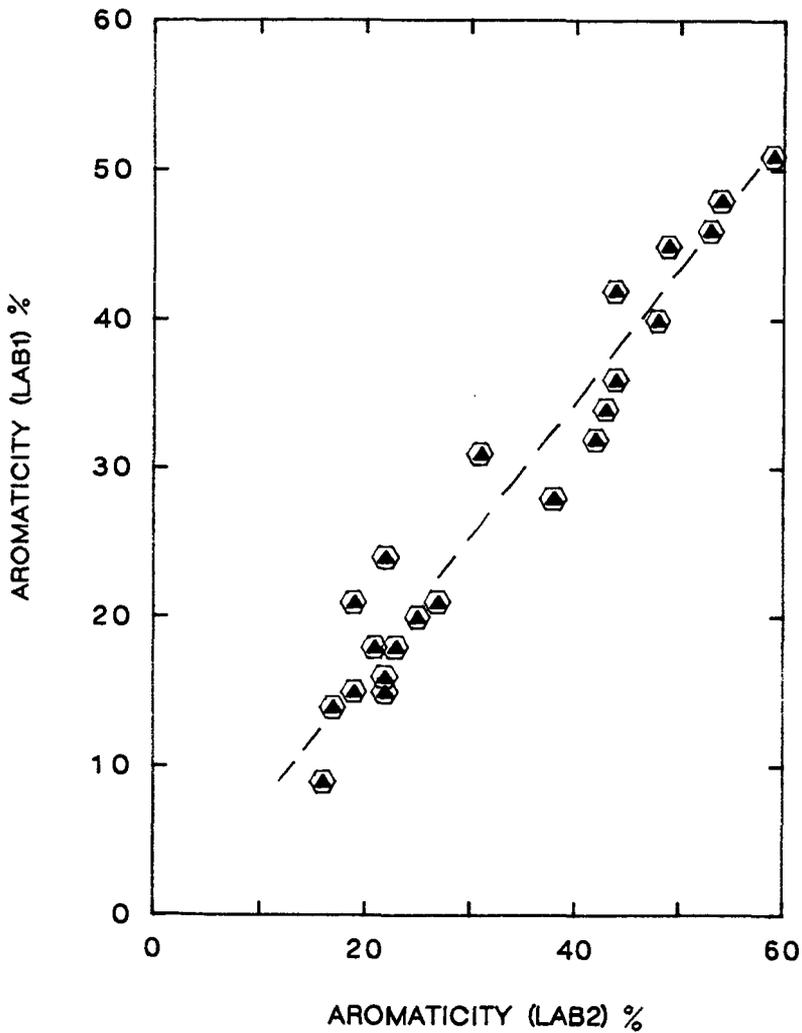


Figure 4. Comparison of fuel aromatic data as determined by two independent laboratories using PNMR technique.

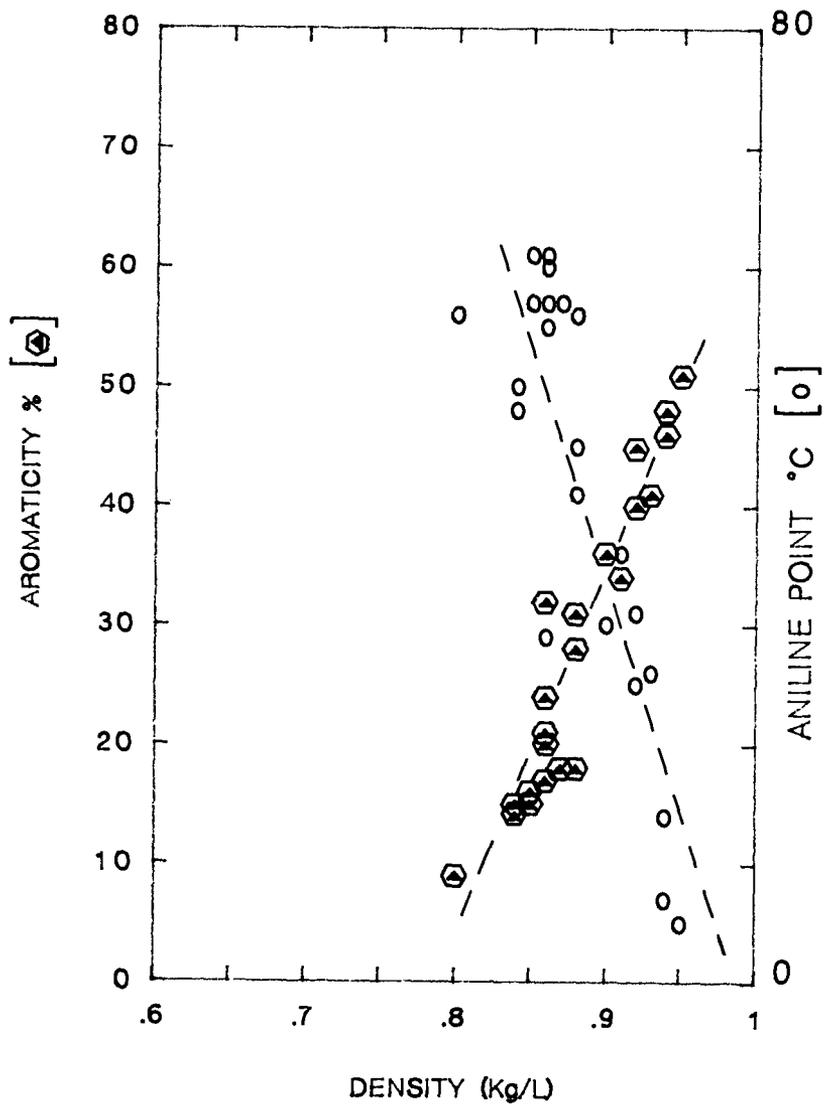


Figure 5. Correlations between fuel density and fuel aromatic data as determined by PMR and aniline point determination techniques.

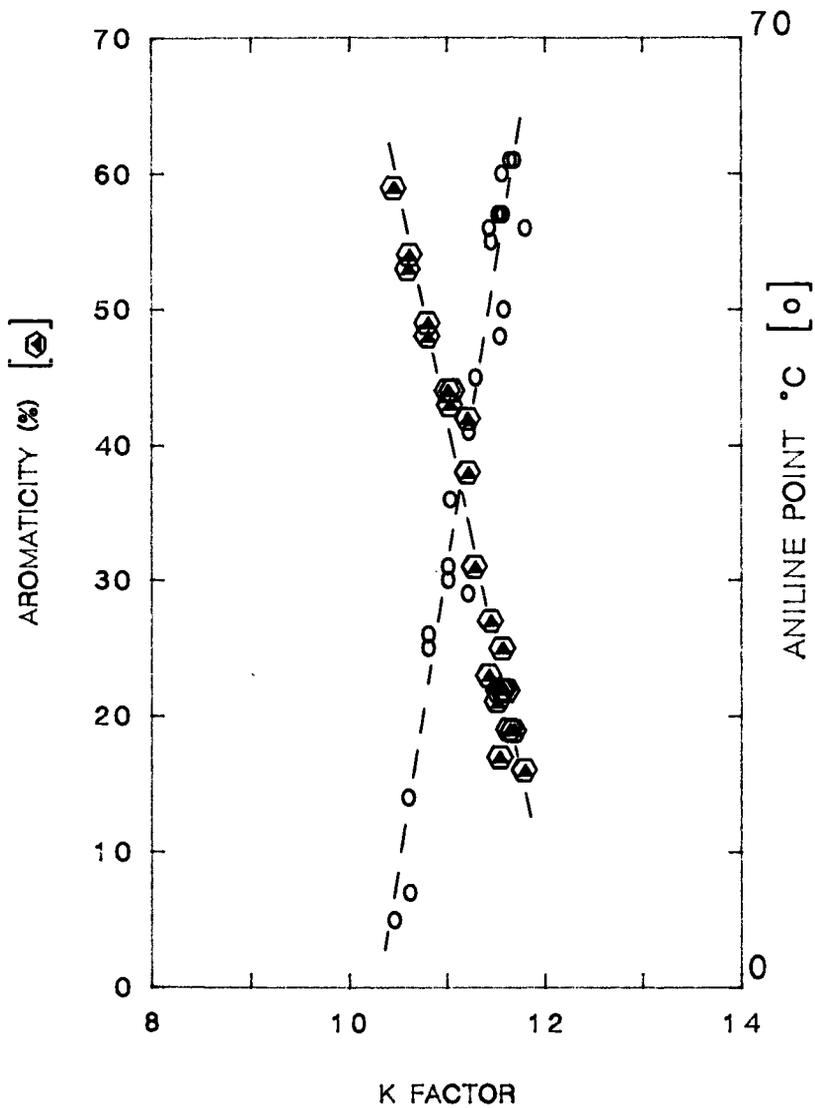


Figure 6. Correlations between Watson K factor and fuel aromatic data as determined by PNMR and aniline point determination techniques.

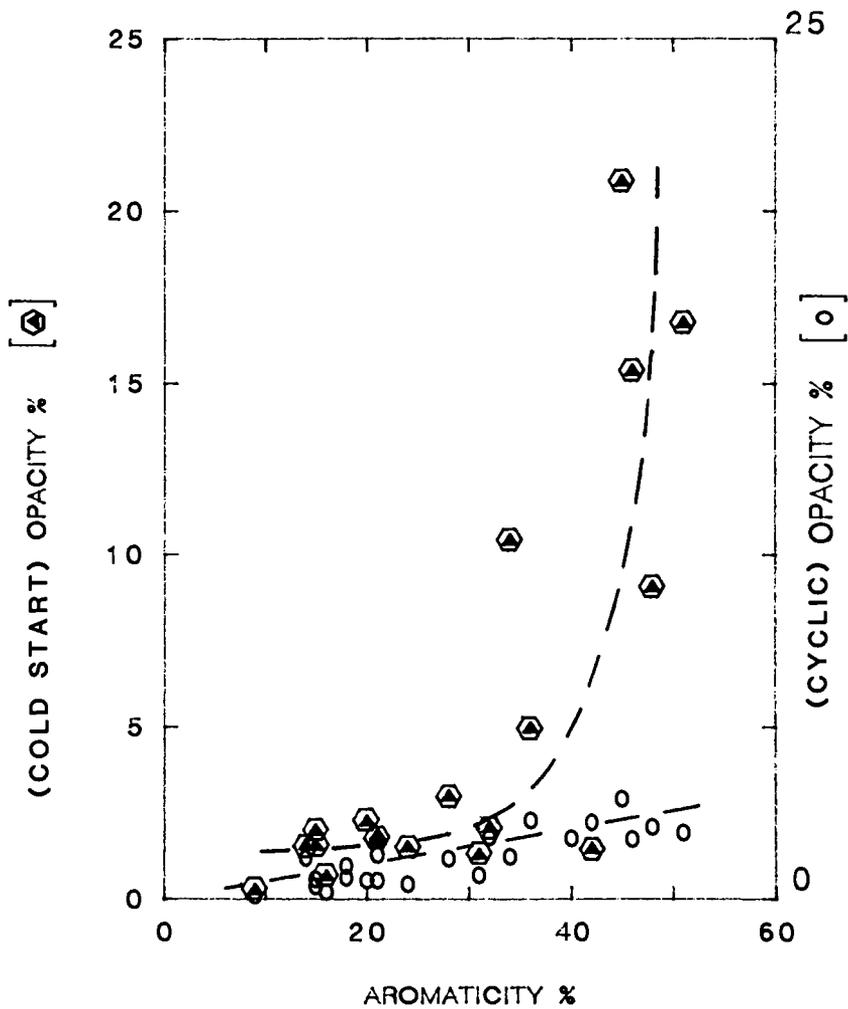


Figure 7. Correlations between fuel aromaticity and transient smoke opacity from cold start and cyclic operations.