

INVESTIGATION OF METHODS FOR AROMATIC STRUCTURAL INFORMATION
IN MIDDLE DISTILLATE FUELS

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ABSTRACT

The combustion characteristics of a fuel are related to its chemical and physical properties. The fuel aromatic content is expected to have significant influence on the production of soot in the combustion process. Detailed structural information on the fuel aromatic component is desirable for prediction of soot formation and isolation of certain molecule, responsible for soot formation. Various structural parameters such as the number of aromatic rings and the extent and type of substitution could be provided by ultraviolet spectroscopy, nuclear magnetic resonance, mass spectroscopy, and supercritical fluid chromatography. Information derived from these analytical techniques for a series of middle distillate fuels will be described and relationships among the number of aromatic rings and soot formation will be discussed.

INTRODUCTION

Energy conservation technologies and energy efficiency programs are no longer new in Western world in the eighties. The global increase in demand for petroleum products and the natural decline of existing conventional crude resources reflect the industry's effort to maximize the product yield from the crude barrel and to explore suitable fossil fuel supply sources. While overall demand for distillate oils is expected to increase (1), the transportation fuels are forecast to increase in demand with the fastest rate compared to other middle distillates(2). This scenario could encourage the refiners to maximize the yield of jet fuels and diesel fuels thereby increasing the heavier components in the heating fuel pool.

In Canada, where energy demand per capita is one of the highest in the world, it is expected that, by 1995 more than half of the total domestic production will be derived from the oil sands bitumens, heavy crudes and heavy oil deposits from western Canada(3). Synthetic distillate oils processed from these nonconventional sources have entered the Canadian market over a decade and the supply is increasing. Compositional analysis of synthetic distillates showed larger proportions of aromatics with fewer proportions of paraffins compared to conventional distillates(2). Current energy conservation trends plus the use of synthetic distillate have encouraged the Canadian refiners to produce oils containing higher aromatic components. The problems associated with the use of highly aromatic fuels are widely documented and have prompted performance evaluations on various combustion equipment. At the Canadian Combustion and Carbonization Research Laboratory, a research program is being carried out to study the influence of fuel quality on burner performance in residential heating appliances.

In the course of the study, it has become apparent that reliable analytical techniques for fuel property determinations are critical for accurate interpretation of combustion performance. Especially for aromatics, a method with better accuracy and versatility than commonly used ASTM D1319(fluorescent indicator adsorption;FIA) is desirable since its detection mechanism suffers poor accuracy and its application is restricted low boiling oils only(4). The search for such a method has led to the development of a new technique utilizing supercritical fluid chromatography (5-7), and the review process of several techniques has provided relevant

information associated with each technique. In addition to total aromatic content, in depth hydrocarbon distribution data of the fuel is desirable in order to establish accurate property-performance correlations. While fuel aromatics are generally considered responsible for excessive particulate emissions, knowledge on how specific aromatic type compounds contribute to the process, could provide the lead to technologies for efficient process quality control in refinery and for reduced combustion emissions.

Initial survey of analytical data from two laboratories indicated considerable variance between a data set provided by the same method and caused concern over the accurate interpretation of results provided by different techniques. Without reliable fuel property data, accurate prediction of combustion performance can not be achieved. This document reports preliminary data from analysis of middle distillate oils, provided by five independent laboratories. Information provided by the techniques of ASTM D1319, nuclear magnetic resonance, mass spectroscopy, supercritical fluid chromatography, ultraviolet spectroscopy and silica-alumina column chromatography are described. More importantly, emphasis is given to the comparison in data supplied by independent laboratories. Correlations between soot production and specific aromatic compound types are also discussed based on the data resulted from two analysis techniques.

EXPERIMENTAL

Ultraviolet spectroscopy (UV)

Ultraviolet spectra of distillate samples were recorded on a UV spectrophotometer within the range of 350 nm to 190 nm after dilution with spectrograde cyclohexane solvent. 1.0., 0.10, and 0.010 cm path sample length cells were utilized with matching reference cells in the analysis depending on the aromatic concentration of the sample. Detailed analytical methodology was described elsewhere (8) and the method is currently under further refinement.

Column chromatography

A modified procedure of the U.S. Bureau of Mines API method (9) as reported by Sawatzky et. al (10) was used to determine saturates, monoaromatics, diaromatics and polyaromatics in distillate samples. In this procedure, the saturates were eluted from the silica/alumina column with n-pentane and the aromatics with different volumetric mixtures of pentane in toluene, followed by careful removal of solvents by air drying. Dried fractions were quantified by a gravimetric method as well as a gas chromatographic method after dilution with suitable solvent.

Supercritical fluid chromatography

The procedure for this new method for the determination of aromatics in diesel fuels and heating fuels was reported in 1987 by Fuhr et. al(5). Saturates and aromatics in distillate fuels are separated on a packed silica column (5 u silica adsorbosphere, 250mm x 2.1 mm) using supercritical carbon dioxide as mobile phase. A Shimadzu model GC-8A equipment with a flame ionization detector was used. A Varian model 8500 syringe pump was utilized to maintain the mobile phase pressure through the chromatographic column.

Nuclear magnetic resonance spectroscopy

The ^1H NMR spectra were obtained on a Varian model EM-390 spectrometer operated at 90 MHz. The samples were prepared by mixing the oil with chloroform- d_1 in a 50/50 volume ratio and a drop of Me_4Si was added as a reference. Total aromatic content of the fuels were calculated from hydrogen intensities by the

method of Muhl et.al (11). Aromatic breakdown compositions such as mono-,di-, poly- were further derived using other physical properties of the fuels(12).

Mass spectrometry

A Finnigan 4500 quadrupole mass spectrometer was used for the determination of paraffin, olefins, naphthenes, aromatics (PONA) as well as the separation of mono-, di-, and poly- aromatic fractions. The samples were separated using a 1.83m column (3% Dexil 300 on acid washed Chromosorb W) heated from 60°C to 300°C. Chemical ionization(methane) mass spectra were acquired continuously during the gas chromatographic separation on a 3 second cycle. The series of peaks characteristic of paraffins, naphthenes and aromatics were summed continuously throughout the run in characterizing the compound type classes. The olefin content was determined by the ¹H NMR method. The detailed PONA method is available in the published literature(13).

Measurement of soot production from combustion process

Soot produced in residential furnaces from the fuels are reported in terms of smoke opacity% per start cycle. It is the maximum peak opacity of the transient soot peak from a cold burner start. It represents the real life soot emission from cold temperature conditions such as in the furnace start-up in the morning after an overnight reduced thermostat setting. Opacity values also indicate general trends of other incomplete combustion products such as carbon monoxide and hydrocarbons. In addition properties of a fuel have the most significant effects on cold start operation of an appliance. The experimental program for measurement of performance characteristics in residential oil combustion has been reported elsewhere(14).

RESULTS AND DISCUSSIONS

Two set of data from two groups of fuels are presented in this paper for discussion. One group of fuels were analyzed by four independent laboratories by NMR, MS, SFC, UV and FIA while the second group was analyzed by two laboratories using MS and column chromatography. Soot production data were available only for the second group.

In Table 1, total aromatic content as determined by four different techniques is presented. Each method determines and describes aromatics in different way. For FIA, volumetric per cent of aromatic compounds are reported whereas in MS-PONA, results are based on the fragmentation pattern and the total number of counts for each compound type. Since the total number of ion counts is proportional to weight of hydrocarbons, it can be considered as pseudo weight per cent or simply a compound type percent. SFC and NMR data are in weight per cent. The table therefore describes the type of information one can obtain from a particular method. Absolute comparison of data were not made for obvious reasons and only the correlation trends between these methods are investigated. Linear regression data are as follows.

Methods	correlation coefficient	slope of the line
SFC(wt.%) vs FIA(vol %)	0.90	0.97
SFC(wt.%) vs NMR(wt.%)	0.96	0.98
SFC(wt.%) vs MS (%)	0.92	0.81

The statistical data indicate generally good agreement between the methods with the strongest correlation between SFC and NMR. The carbon aromaticity data from Laboratory 1, from which the NMR weight per cent data are calculated is

reported in Table 2. These values represent the percentage of aromatic ring carbons present in the total numbers of carbon present in the average fuel molecule. The correlation of NMR aromaticity and SFC weight per cent show a linear relation with a correlation coefficient of 0.89 and a slope of 0.69. The aromatics by SFC are a measure of the amount of molecules having at least one aromatic ring with paraffinic and naphthenic substituents attached. Therefore this SFC-NMR correlation data with a slope of 0.69 indicates that on average, 69% of the carbon atoms in the aromatic molecules of these samples are contained in aromatic rings with the remainder in the substituents.

Table 2 also compares fuel aromaticity data provided by two independent laboratories. The data indicates that Laboratory 2 has consistently lower values than laboratory 1 for all fuels. Laboratory 2 used Brown-Ledner equation (15) whereas Laboratory 1 derived results from detailed rigorous calculations (11,12). This minor difference alone cannot be accounted for the large difference between the two laboratories. Other variables such as instrument calibration and operator manipulation techniques are more likely the cause of such discrepancy.

Table 3 contains the aromatics ring distribution information provided by NMR, UV, SFC, and MS-PONA techniques. NMR-UV pair describes ring carbon weight per cent while SFC reports aromatic breakdown in total weight per cent. Since MS data is closer to total weight per cent, it was paired with SFC data. It should be pointed out that these SFC data are resulted from preliminary experiments and additional work is being carried out currently. Monoaromatic values from each pair indicate acceptable agreement but none of the pairs show comparable values for diaromatics. Diaromatics from the UV method are significantly lower than NMR method while MS diaromatics show lower values than SFC method to a similar degree.

Table 4 reports aromatic ring distribution in other set of middle distillate fuels. Opacity % reading is the maximum soot opacity measured from a cold start transient cycle from combustion of each fuel. Limited data indicate that both monoaromatics and diaromatics from the column chromatographic method are lower than those from MS method and show no particular relation to the opacity. The column chromatographic is normally suitable for fuels having initial boiling points of at least 200°C, since light fuel components can be lost during solvent removal prior to weighing of the fractions. The method was selected for investigation based on its simplicity requiring only common laboratory equipment. The component loss during solvent removal can be eliminated by analyzing the liquid fractions by gas chromatography instead of gravimetric analysis. This would require a more complicated procedure and trained operator which offsets the simplicity of the method.

Data from column chromatographic method, monoaromatics as well as diaromatics, show no apparent trend of interrelation with soot production. Figure 1 illustrates the correlations between mono- and diaromatic fuel components determined by PONA method and opacity of soot emitted. Diaromatic compounds indicate a general relation with cold start soot emissions with the exception of few outliers. Monoaromatics do not exhibit any particular interrelation.

CONCLUSIONS

1. Based on the information provided by participating laboratories, NMR and SFC show the strongest agreement for total fuel aromatics weight per cent. MS data show the lowest value.
2. Fuel aromaticity determination using NMR technique by two independent laboratories resulted in significantly different values. Regardless of the technique used, the analytical results seem to be more laboratory dependent than method dependent. Due to the highly complex nature of the middle distillate, larger

discrepancies between laboratories are observed.

3. For aromatic ring distribution in fuels, no significant trends between the methods were observed. Further studies are being planned.
4. The survey of analytical techniques suggests that MS and NMR are the most powerful tools for the detailed structural information in fuel analysis. These techniques, however, are not entirely suitable to refinery process quality control.
5. It appears that supercritical fluid chromatography could be the best candidate for a new aromatic standard method for the petroleum industry. The method's agreement with NMR indicates good accuracy and it has potential application for aromatic breakdown analysis. It can handle higher boiling samples using instrumentation of moderate sophistication.
6. Preliminary studies indicates that fuel diaromatics show greater influence on soot production than monoaromatics, in residential combustion.
7. The critical requirement of a reliable analytical methods for fuel aromatic structural information still exists in combustion research.

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TABLE 1. Total aromatic content of fuels as determined by different methods.

Fuel	NMR,wt.%	SFC,wt.%	FIA,vol.%	MS,%
1	41.8	40.3	35.0	28.2
2	29.1	30.7	28.9	23.4
3	30.6	34.6	41.8	19.9
4	37.1	37.1	46.7	16.4
5	43.0	42.9	37.0	25.5
6	38.2	39.1	33.3	25.1
7	33.9	30.4	25.0	19.3
8	48.2	46.8	39.1	31.2
9	57.5	55.2	63.9	29.8
10	42.3	46.4	44.7	37.2
11	87.3	80.8	74.2	68.0
12	25.2	23.8	20.6	28.6
13	29.8	28.4	24.1	16.9
14	45.9	50.2	44.9	29.5
15	48.2	49.5	43.7	31.7
16	48.7	51.7	44.2	35.7
17	61.9	69.6	64.0	46.4
18	74.6	79.0	75.0	64.7
19	30.0	37.6	33.3	21.0
20	29.9	37.6	33.0	21.0
21	29.8	37.7	24.9	20.8
22	30.3	25.4	19.6	17.9

TABLE 2. Carbon aromaticity % as determined by two different laboratories.

Fuel	NMR,% (Lab.1)	NMR,% (Lab.2)
1	28.8	20.0
2	19.1	13.0
3	20.9	14.0
4	24.1	21.0
5	29.8	24.0
6	27.2	21.0
7	21.4	14.0
8	33.5	24.0
9	35.1	28.0
10	27.0	18.0
11	59.9	50.0
12	22.4	12.0
13	15.2	12.0
14	34.6	27.0
15	33.1	25.0
16	33.7	29.0
17	47.2	42.0
18	51.9	51.0
19	14.7	16.0
20	14.6	16.0
21	19.3	16.0
22	19.6	11.0

TABLE 3. Aromatics ring distribution in fuels as determined by different methods.

Fuel	Ring carbon wt.% (NMR) vs (UV)			Aromatics wt.%(SFC)			Aromatics %(MS)					
	mono-	di-	poly-	mono-	di-	poly-	mono-	di-	poly-			
1	6.7	18.4		7.8	9.2	1.1	16.9	18.4	4.3	19.9	7.0	1.3
2	7.0	9.6		6.8	4.3	0.3	un	28.8	1.1	14.3	7.5	1.3
3	6.3	11.8		6.5	4.4	1.7	un	33.7	0.5	12.8	5.4	1.4
4	6.8	14.2		4.7	4.3	1.9	un	28.8	8.5	10.3	4.8	1.3
5	7.3	18.7		8.5	10.2	0.9	17.3	21.5	2.8	16.5	8.6	0.4
6	6.2	17.4		6.7	9.7	1.0	14.9	19.8	3.4	17.5	7.6	0.1
7	9.9	8.6		9.1	3.3	0.1	un	28.8	1.0	16.7	2.5	0.1
8	7.1	22.3		9.5	11.9	2.2	19.3	20.5	6.0	18.6	12.6	0.1
9	11.6	19.7		8.9	9.1	3.3	un	47.9	6.0	19.0	9.6	1.2
10	14.3	8.8		13.8	3.6	0.2	un	43.8	1.4	30.0	4.3	2.5
11	7.5	46.7		8.3	38.1	3.1	12.7	58.7	7.9	25.1	40.8	2.1
12	na	na		5.1	2.1	<0.1	un	22.7	na	27.2	0.9	0.5
13	na	na		9.3	2.5	<0.1	un	26.8	0.3	15.6	0.8	0.4
14	na	na		10.4	10.3	1.9	22.1	20.7	6.0	25.2	3.6	0.7
15	na	na		10.1	8.2	2.9	21.3	17.7	9.5	21.0	10.1	0.7
16	na	na		10.0	10.1	2.8	20.1	20.5	9.0	24.8	10.6	0.3
17	10.6	6.7		11.4	17.9	6.0	20.3	28.6	1.5	28.9	17.4	0.2
18	13.0	34.6		11.8	22.3	7.5	21.0	36.3	18.3	39.9	24.6	0.2
19	na	na		10.5	3.8	0.4	un	34.8	2.0	19.0	1.8	0.1
20	na	na		10.5	3.8	0.4	un	34.9	1.7	19.0	1.8	0.1
21	10.6	30.8		8.0	3.5	0.3	un	29.2	1.5	9.2	16.4	4.0
22	9.4	7.4		5.3	2.6	<0.1	un	23.9	un	16.0	1.9	<.1

na is for not available

un is for unsatisfactory separation
value reported under di is for both mono & di

TABLE 4. Fuel aromatic ring types and their correlation to soot production.

Fuel	Aromatics Wt.% by CC			Aromatics Wt.% by MS			Smoke opacity % at cold start combustion
	mono-	di-	poly-	mono-	di-	poly	
C	18.2	16.3	1.3	29.8	11.8	0.60	1.3
D	16.2	7.2	0.2	20.7	11.5	0.83	1.2
E	14.9	7.7	0.7	18.1	6.2	0.57	1.8
F	15.9	13.6	1.9	28.9	11.5	0.99	1.5
G	31.1	31.6	1.0	41.4	38.5	0.09	31.7
L	15.9	13.4	0.3	21.3	13.0	1.03	1.9
M	23.8	23.5	0.6	43.0	19.3	2.51	52.3
N	24.5	6.3	0.4	21.5	8.4	0.31	0.7
O	55.9	22.8	0.8	30.6	43.9	1.10	16.8
P	NA			41.9	30.3	1.87	9.1
Q	13.2	6.9	0.8	41.9	30.3	1.87	1.6
S	17.4	6.6	0.9	31.5	4.2	0.12	NA
V	NA			21.6	1.8	0.27	1.6
W	NA			20.4	4.1	0.69	2.03
X	NA			28.3	15.05	0.58	2.12
Y	NA			23.5	21.65	0.71	10.45

TABLE 4. Fuel aromatic ring types and their correlation to soot production.
(continued)

	Aromatics Wt.% by CC			Aromatics Wt.% by MS			Smoke opacity % at cold start combustion
	mono-	di-	poly-	mono-	di-	poly	
Z	NA			16.4	6.6	0.20	2.37
AA	NA			15.7	5.7	0.50	14.8
BB	NA			22.9	13.0	0.00	3.3
CC	NA			33.0	18.0	0.30	5.0
DD	NA			25.0	34.1	0.7	15.4
EE	NA			25.5	18.5	0.0	20.9
FF	NA			18.8	9.7	0.0	2.3

NA is for not available.

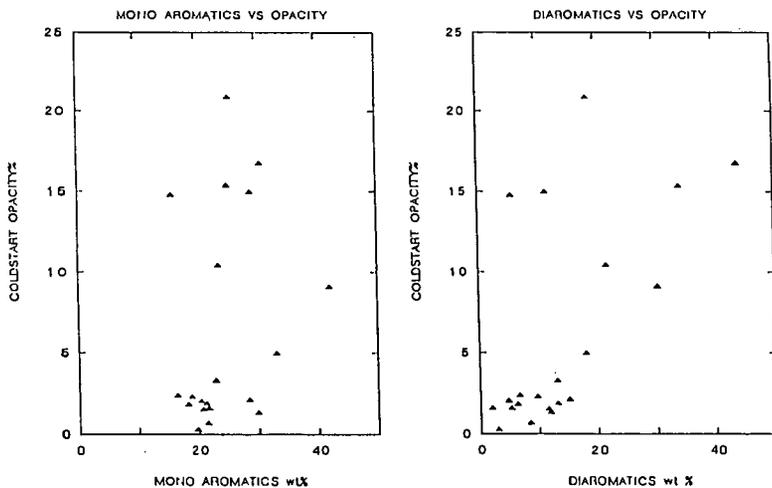


Figure 1. Correlations between fuel monoaromatic and diaromatic components and soot production at cold start combustion.