

THE IMPACT OF CHEMICAL AND PHYSICAL PROPERTIES OF FUELS ON DIESEL
ENGINE EMISSIONS

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ABSTRACT: Studies considering engine type and mode of operation as the most important factors in the characteristics of diesel emissions may be valid when looking at the gross emission parameters: total particulate matter (TPM), soluble organic fraction (SOF), and solids. Recently, we have concentrated on quantifying specific chemical species, such as polynuclear aromatic hydrocarbons (PAH), which have lead us to believe that chemical composition of the fuel plays a major role in determining the concentration of these species in the emissions.

This paper is a summary of studies where sufficient data have been obtained to allow us to test for relationships between fuel composition and emission parameters. Data obtained from samples collected at Michigan Technological University and the United States Bureau of Mines were analyzed. Four number 2 diesel fuels were investigated which varied in cetane number, sulfur and aromatic content. Specific PAH, TPM, SOF, volatile organics (XOC), sulfates, hydrocarbons (HC) and nitrogen oxides (NOx) data were tested in this study. The results show that fuel composition may have effects on specific pollutant emissions.

INTRODUCTION: Diesel fuels are characterized on the basis of: 1) physical properties (such as density, viscosity, and distillation profile); 2) a performance property (cetane number); and 3) chemical properties (such as sulfur, aromatic and olefin content). Blending of distillates or feedstocks may be used to produce fuels with desired properties to meet the demands of the users and to satisfy the engine emission standards promulgated by government agencies.

In previous studies (1-4), we have proposed that the type of engine and mode of operation are the most important factors in determining emission characteristics. This may be valid when looking at gross characteristics of emissions such as total particulate matter (TPM), soluble organic fraction (SOF), and sulfate. More recently, however, we have concentrated on quantifying specific chemical species, such as certain polynuclear aromatic hydrocarbons (PAH), which may have human health impacts, and proposing that chemical composition of the fuel plays a major role in determining the concentration of these species in emissions.

Studies on fuel effects have been carried out by Baranescu (5), Wall et. al (6) and Ullman et. al (7). Baranescu (5) and Wall et. al (6) investigated the impact of fuel sulfur on emissions and both concluded that sulfur must be removed from diesel fuel for effective particle emission control. Ullman et. al (7), on the other hand, studied the impact of cetane number and aromatic content showing that as cetane number increased there were significant decreases in

both gaseous and particle emissions, while aromatic content reductions produced varied results on the diesel emissions studied. Weaver et. al (8) have reviewed the literature and have concluded that the most important emission-related properties of diesel fuel are sulfur and aromatic content. The emissions of PAH compounds, however, were not considered in these fuel evaluations.

This study is a summary of results of research activities where sufficient data have been obtained to allow us to test for significant relationships between a number of parameters. Data obtained at Michigan Technological University (MTU) and from samples provided by the Twin Cities Research Center of the United States Bureau of Mines (USEM), Minneapolis, MN were primarily used as the basis of the study. Fuel studied consisted of types where cetane number, sulfur content and aromatic content were varied in fuels with the physical properties of a number 2 standard blend. Specific PAH, TPM, SOF, volatile organics (XOC), sulfates, nitrogen oxides (NOx), and hydrocarbons (HC) were measured in most studies.

EXPERIMENTAL: Four fuels were used in gathering the data used for this paper. The data from the MTU engine studies were obtained using Amoco regular sulfur fuel (ARS) and a Chevron low sulfur (CLS) fuel. Data from the USEM engine studies were obtained using a specially prepared low aromatics diesel fuel manufactured by Chevron (CLAD) at its El Segundo refinery, and another Chevron cetane-adjusted diesel (CCAD), a commercially available fuel used in California which had its cetane number adjusted from an initial value of 45 to 53 by the addition of 0.3 weight percent Naltane 5308 cetane improver (to the same level as the CLAD fuel). Properties of these fuels are summarized in Table 1. Fuel analyses were provided by the supplier and analysis methods (where available) are indicated in Table 1.

Emission data analyzed were from engine test runs conducted at MTU and USEM. Engines used were a Cummins 1988 Model L-10 224 kw direct-injection diesel engine at MTU, representative of on-highway, heavy-duty diesel engines, and a 3304 Caterpillar 75 kw, indirect-injection engine at USEM representative of current mining engines. The MTU engine was operated at EPA steady-state modes 9 and 11 (rated speed at 75% and 25% load, respectively) while the USEM engine was operated a light-duty transient cycle representing mining engine operation. The specifics on the engines, dynamometers, and emissions collection systems are described in references 9 and 10. The emissions parameters measured were TPM, sulfate, SOF, semi-volatile organics, collected on XAD-2 resin (XOC), HC, and PAH (fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, and benzo[a]pyrene). All TPM, sulfate, SOF, XOC and PAH analyses were carried out at MTU. NOx and HC were measured at both sites.

Sampling for TPM, SOF and sulfate was done on Teflon-coated Pallflex filters, XOC was collected on XAD-2 resin directly downstream from the Pallflex filter. TPM and SOF were determined gravimetrically from filter masses before and after exposure and by the mass of material extracted, respectively. Sulfates were measured by ion chromatography of the aqueous extract of the Pallflex filter using a conductance detector. HC were measured using a heated flame ionization detector and NOx were analyzed using a chemiluminescence analyzer. PAH were analyzed from a fraction

taken from the methylene chloride extract that was subsequently cleaned-up using column chromatography and analyzed by high performance liquid chromatography (HPLC) with fluorescence detection. The sampling and analysis procedures for these parameters are described in detail in reference 9.

The MTU data for NOx, HC, TPM, SOF, sulfate and XOC were analyzed using a 3-way analysis of variance (ANOVA) to determine if significant differences in test variables (mode, fuel, or aftertreatment device) could be detected within an entire data set (9). Two way ANOVAs for the same parameters were used for the USBM data to test for fuel or aftertreatment device effects (10). All null hypotheses being tested stated that there were no significant differences due to mode, fuel or aftertreatment device for the MTU data or fuel or aftertreatment device for the USBM data. A significance level of 0.05 was used for all statistical comparisons. The statistical treatment of the PAH data sets was further complicated due to the presence of less than minimum detection limit (MDL) data. These data sets were also analyzed using ANOVA techniques, with the less than MDL values replaced by the MDL values divided by two (9). In this paper, only the effects of fuel and mode are considered for the MTU data and only fuel for the USBM data.

RESULTS AND DISCUSSION: The results of the chemical analyses for the engine emissions parameters TPM, SOF, sulfate, XOC, NOx and HC are reported in Table 2. Particle- and vapor phase-associated PAH values are given in Table 3. Each of these tables is separated into two portions with the upper and lower portions, representing the values from the MTU studies and the USBM studies, respectively. Since the data were obtained on two different engines with MTU operating at steady-state conditions and USBM operating under transient mode conditions, the data were analyzed separately. However, comparisons on a relative basis can be made between the studies to assess fuel composition effects on emissions.

Gaseous Emissions -The values for the gaseous emissions from the MTU study are given in Table 2. All emissions values have been converted to mg/std m³ (25°C, 101 KPa). USBM data are given in ppm.

For the MTU NOx data a significant difference was found for both mode and fuel. Both low (CLS) and conventional sulfur (ARS) fuels gave a mode 9 to mode 11 difference in NOx of 68% with the lower value at mode 9 attributed to higher combustion temperatures compared to mode 11. A significant difference is illustrated in the NOx data between fuel types, particularly at mode 9. The USBM data gave a 9% decrease in NOx when the low aromatic fuel was used. Differences in fuel cetane number may also be responsible for this trend in the MTU study, while the USBM study utilized fuels with the same cetane number. Ullman et. al (7) have shown an inverse NOx correlation in their studies of cetane number, as well as a direct relationship between NOx and fuel aromatic content. These observations are consistent with our findings.

The HC emissions from the MTU study were also dependent on both fuel and mode. Mode 9 compared to mode 11 emissions (Table 2) for the CLS and AHS fuels were 20% and 53% lower, respectively. Mode-dependent differences are again explained by the increased temperatures of mode 9 and subsequently, more of the fuel is

oxidized. Fuel-dependent differences in HC may also be related to the cetane number of the fuels. Ullman et. al (7) also showed an inverse relationship between cetane number and HC emissions.

TPM, SOF, SULFATE, and XOC Emissions - The mean values for these emissions from the MTU data and the USBM data are also reported in Table 2 for all fuels studied. The variability of all measurements were within the normal expected ranges for these measured values.

The only significant effect of fuel type on TPM composition was on the sulfate concentrations which were at or below the minimum detection limit (MDL) for all of the MTU low sulfur (CLS) fuel samples and close to the MDL for the USBM low sulfur (CLAD and CCAD) fuel samples. Within the conventional (ARS) fuel data sets, significant differences in sulfate were detected between modes 9 and 11 (50% lower at mode 11). The USBM study did not utilize any conventional high sulfur fuel for comparison. The TPM concentrations were significantly affected by mode but not fuel type (based on the MTU data). This may be attributed in part to the higher aromatics, lower cetane number, and higher 90% volatility temperature of the CLS fuel (Table 1). These fuel properties might tend to cause increased formation of solid particulate matter as a result of the combustion process. The increase in solids due to fuel properties would then balance, to some extent, the sulfate reduction attributed to the low sulfur fuel. The USBM studies emphasized fuels with significant differences in aromatic content and their results gave a significant difference for TPM with a 13% decrease in TPM for the CLAD compared to CCAD.

Significant differences were not detected in SOF concentrations for mode or fuel in the MTU studies. USBM fuels were significantly different in terms of SOF emissions with a reduction of 17% when comparing the low aromatic fuel (CLAD) to the higher aromatics fuel (CCAD).

Despite the higher variability in XOC measurements, some significant relationships were found between fuels and modes in the MTU studies. Use of the conventional sulfur fuel (ARS) resulted in lower (27%) XOC concentrations than with the low sulfur fuel (CLS) at mode 9; mode 11 showed no fuel dependency. This is similar to the situation with the HC measurements where the differences are more likely due to differences in fuel composition other than fuel sulfur levels. Data for USBM fuels show a significantly different amount of XOC (31% higher) with the CLAD fuel as compared to the CCAD fuel.

PAH Measurements - The particle and vapor phase PAH emissions for all fuels studied are presented in Table 3. For the complete statistical treatment of these data the reader is referred to reference 9 which includes a discussion on handling data below minimum detection levels.

There were numerous significant differences in particle-associated PAH emissions (as determined by analysis of SOF samples) in the MTU study where the CLS fuel gave PAH levels higher than the conventional ARS fuel. Benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, pyrene, chrysene, and benzo[a]pyrene emissions for the two fuels were significantly different when comparing like modes. The only significant difference between modes for vapor phase associated PAH (as analyzed in XOC samples) was for

benz[a]anthracene; this difference was significant for both fuels. For both fuels, the only detectable levels of benzo[k]fluoranthene and benzo[a]pyrene were particle-associated.

For the USBM data set, significantly different PAH values were found for chrysene, pyrene, benz[a]anthracene, and benzo[b]fluoranthene with the higher levels found with lower aromatics (CLAD) fuel as compared to the higher aromatics (CCAD) fuel when the SOF and XOC values were summed to determine the total emissions.

CONCLUSION: From these results, we have provided additional evidence to support the proposal that fuel composition has effects on specific pollutant emissions from diesel engines. More detailed analysis of fuels (including quantification of important PAH compounds and potential PAH precursors in fuel) is necessary in order to further define the correlation of fuel parameters and emissions.

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Table 1. Comparison of Properties of Fuels*

Property	ARS	CLS	CLAD	CCAD
API Gravity	38.4	34.5		
Dist. Profile (°C)				
Initial B.P.	162	183	208	
10%	195	224	251	
50%	254	269	284	
90%	307	317	317	
95%	318	331		
Final B.P.	327	352	355	
Composition				
Carbon (wt.%)	85.6		86.1	
Hydrogen (wt.%)	13.3		13.85	
Sulfur (wt.%)	0.317	0.010	0.03	0.04
Oxygen (wt.%)	0.06			
Total N (ppm)	40	26.9	98	
Hydrocarbon Type (vol.%)				
Paraffins/Napthenes	73.0	67.8	88.9	
Olefins	3.5	2.3		
Aromatics				
FIAM Analysis	23.5	29.9	11	20
Mass Spectrometry		23.7		
HPLC			11.2	
Cetane Number	52.8	42.4	53	53

* Analyses provided by fuel suppliers.

ARS = Amoco conventional sulfur fuel, CLS = Chevron low sulfur fuel
 CLAD = Chevron low aromatic content fuel, CCAD = Chevron cetane
 adjusted fuel available in California

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Table 3. Summary of PAH Emissions Data (ng/m³-std)
Particle Associated PAH

Fuel	Mode	n	FLU	PYR	BaA	CHR	BbF	BkF	BaP
ARS	9	2	1300 (56)	31 (91)	140 (89)	120 (9.1)	94 (54)	3.6 (100)	4.4 (92)
	11	2	600 (16)	79 (20)	170 (19)	120 (9.1)	47 (24)	5.5 (8.7)	4.3 (3.5)
CLS	9	4	800 (33)	2300 (12)	1100 (61)	600 (74)	260 (28)	110 (84)	150 (82)
	11	4	1200 (5.6)	2000 (9.0)	730 (18)	180 (24)	240 (2.9)	140 (69)	220 (12)
CLAD	t ^a	6	950 (8.8)	2300 (9.0)	180 (1.7)	730 (22)	1500 (15)	240 (14)	140 (18)
CCAD	t ^a	5	940 (33)	2100 (43)	190 (40)	370 (36)	910 (39)	250 (58)	370 (63)

Vapor Phase Associated PAH (mg/m³-std)

Fuel	Mode	n	FLU	PYR	BaA	CHR	BbF	BkF	BaP
ARS	9	2	1700 (22)	300 (84)	120 (89)	18 ^b	<3 ^b	<3 ^b	<3 ^b
	11	2	2700 (22)	470 (22)	200 (17)	12 ^b	<4 ^b	<5 ^b	<5 ^b
CLS	9	4	2300 (51)	1800 (28)	320 (29)	240 (28)	4.6 ^b (52)	<6 ^b	<9 ^b
	11	4	1200 (14)	910 (14)	250 (7.3)	270 (55)	6.5 (18)	<5 ^b	<7 ^b
CLAD	t ^a	5	1400 (10)	1800 (15)	180 (28)	15 (37)	32 (24)	<2 ^b	<2 ^b
CCAD	t ^a	6	1200 (6.4)	1100 (18)	29 (47)	24 (58)	28 (13)	7.5 (32)	<2 ^b

FLU = fluoanthene, PYR = pyrene, BaA = benz[a]anthracene,
CHR = chrysene, BbF = benzo[b]fluoranthene, BaP = benzo[a]pyrene,
BkF = benzo[k]fluoranthene

^a light-duty transient cycle

^b less than minimum detection limit, no CV reported