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Mutagenic Potential of Particulate Matter Emissions from a Diesel Engine Operating on Diesel No. 2 and Fischer-Tropsch Fuel: Effect of PM Size and Engine Operating Conditions

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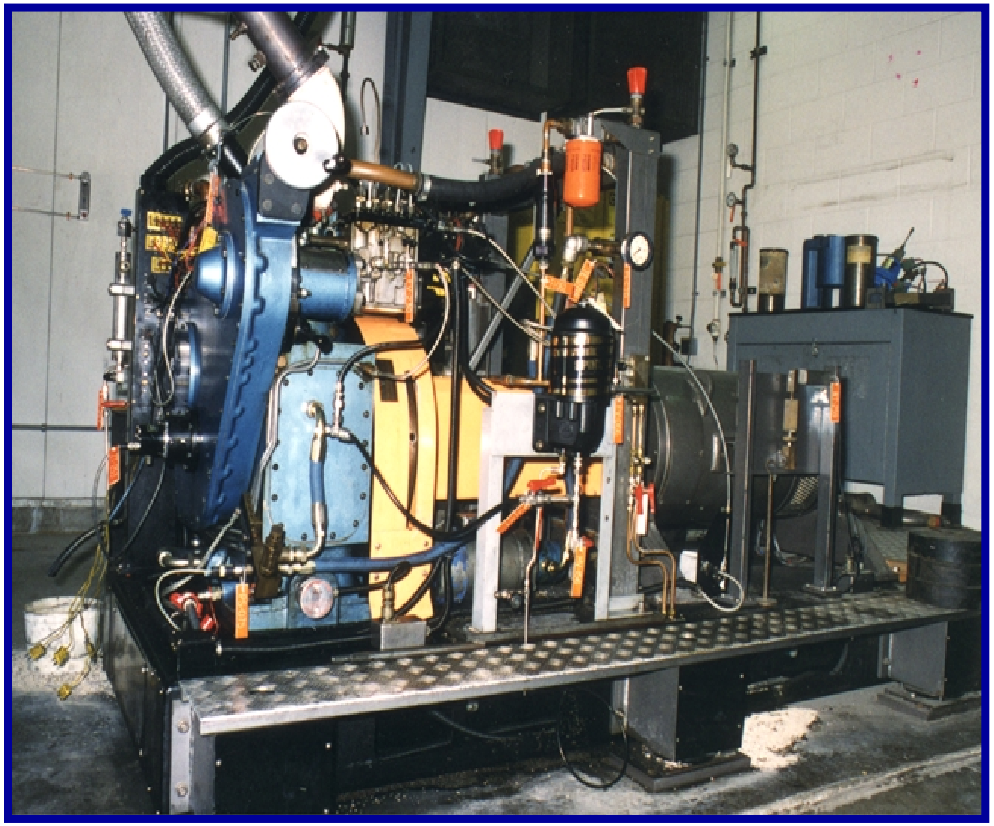
Objectives

- Determine mutagenicity of natural gas derived Fischer-Tropsch (FT) fuel at seven steady-state engine operating conditions and compare to low sulfur Federal Diesel No. 2.

- Determine mutagenicity as a function of particle size.

- Compare particulate matter concentration and size distributions and determine the origin of PM emissions.

NETL Engine Test Bed



Ricardo Proteous Single-
Cylinder 2-liter, direct-injected
Diesel Engine

Bore: 130 mm (5.1 in.)

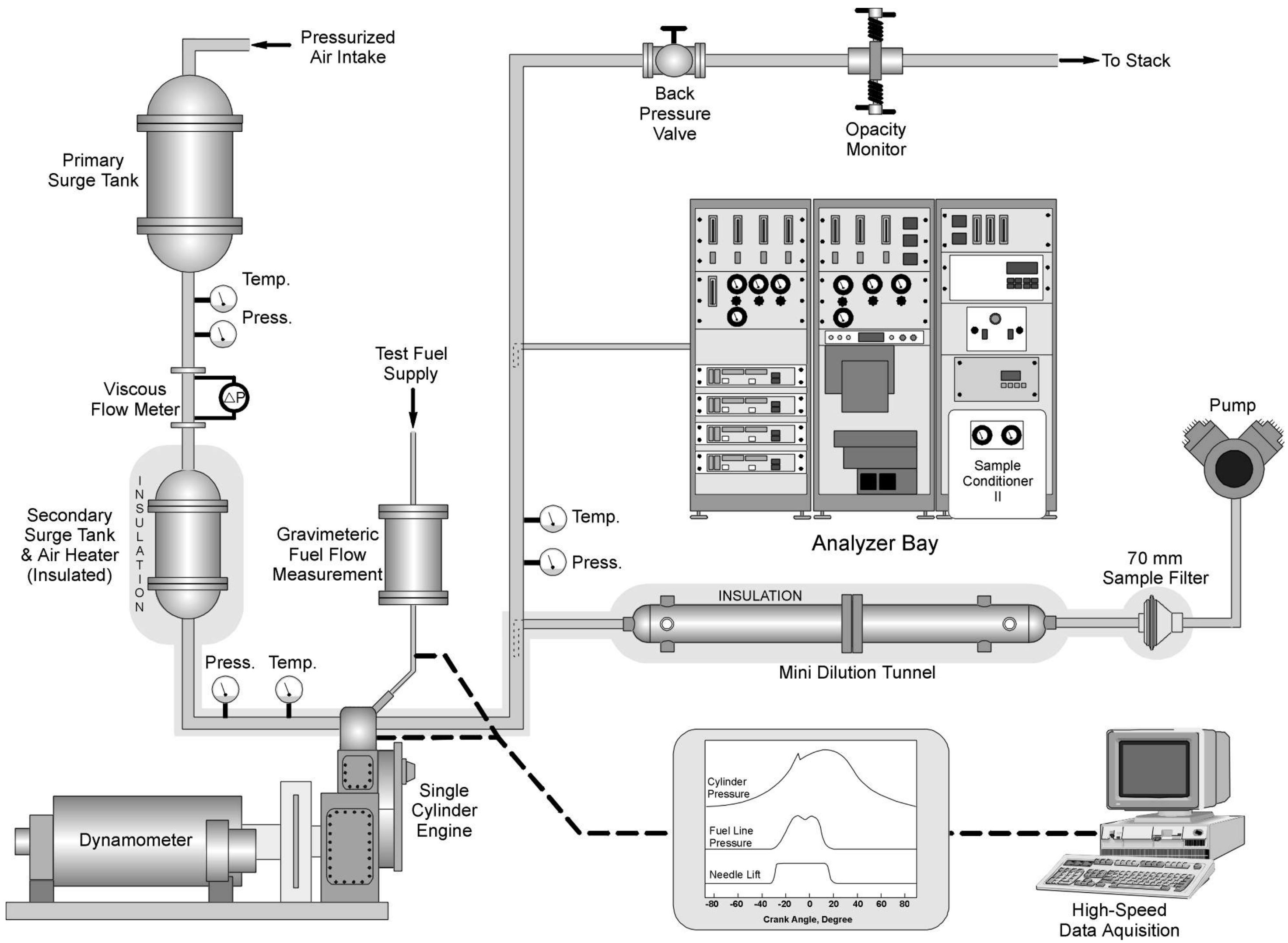
Stroke:150 mm (6.0 in.)

CR: 13.3:1

Output: 55KW (74 hp) @ 2200 rpm

FIE: Bosch A700 PLN, 3850 psi NOP

NETL Engine Test-bed Schematic



How do we determine *Mutagenicity*?

- **Soluble organic fraction of the diesel particulate matter (DPM) is analyzed using the Ames method (Maron and Ames, 1983; and Wantanabe, 1990)**
  - **TPM filters**
  - **Micro-orifice Uniform Deposition Impactor (MOUDI)**
    - **Size dependent Ames bioassay analysis at two key operating states**
    - **Key State 2 and 4 (representing low speed-low load and intermediate speed-high load conditions respectively) for each fuel are collected**

- **Concentration (dosage) ranges are from very low dosages to, in some cases, levels at which toxicity effects are apparent.**

- **Experiments use four replicates, and dose-adjustment confirmation tests.**

- **Known mutagens and the solvent dichloromethane (DCM) are used as positive controls and the dispersants, dimethyl sulfoxide (DMSO) and Tween 80, are used as a negative controls.**

Ames Method

- **YG1024 and YG1029 bacterial tester strains in the presence and absence of 10% concentration of S9, a preparation made from the livers of laboratory rats**
  - **Strains accounts for both frameshift and basepair substitution types of mutation.**
  - **S9 demonstrates whether the mutagens cause genetic damage directly or whether they require activation by metabolic enzymes produced in mammalian livers.**

- **In the Ames test, the relationship between revertant count (bacteria lack ability to metabolize histidine) and dosage is used to develop a measure of mutagenicity.**
  - **For small dosages, the mean revertant count is typically assumed to be a linear function of the dose of a mutagenic substance and the slope of the line relating revertant count to dose is a measure of the mutagenicity of the substance.**
  - **At large doses, Salmonella death begins to dominate due to PM sample extract toxicity. This effectively reduces the revertant count and reduces the slope of the revertant-vs-dose curveand the data will be biased downward.**

- **Toxicity effects are removed using the statistical method of Bernstein et al; 1982 in which a full data set of dose response slopes are compared with successively reduced data sets with the largest remaining dose removed. This process is repeated until no toxicity effects are indicated or until there are only three remaining doses. Then:**
  - **Test for mutagenic effect**
  - **Test for remaining toxicity effects**

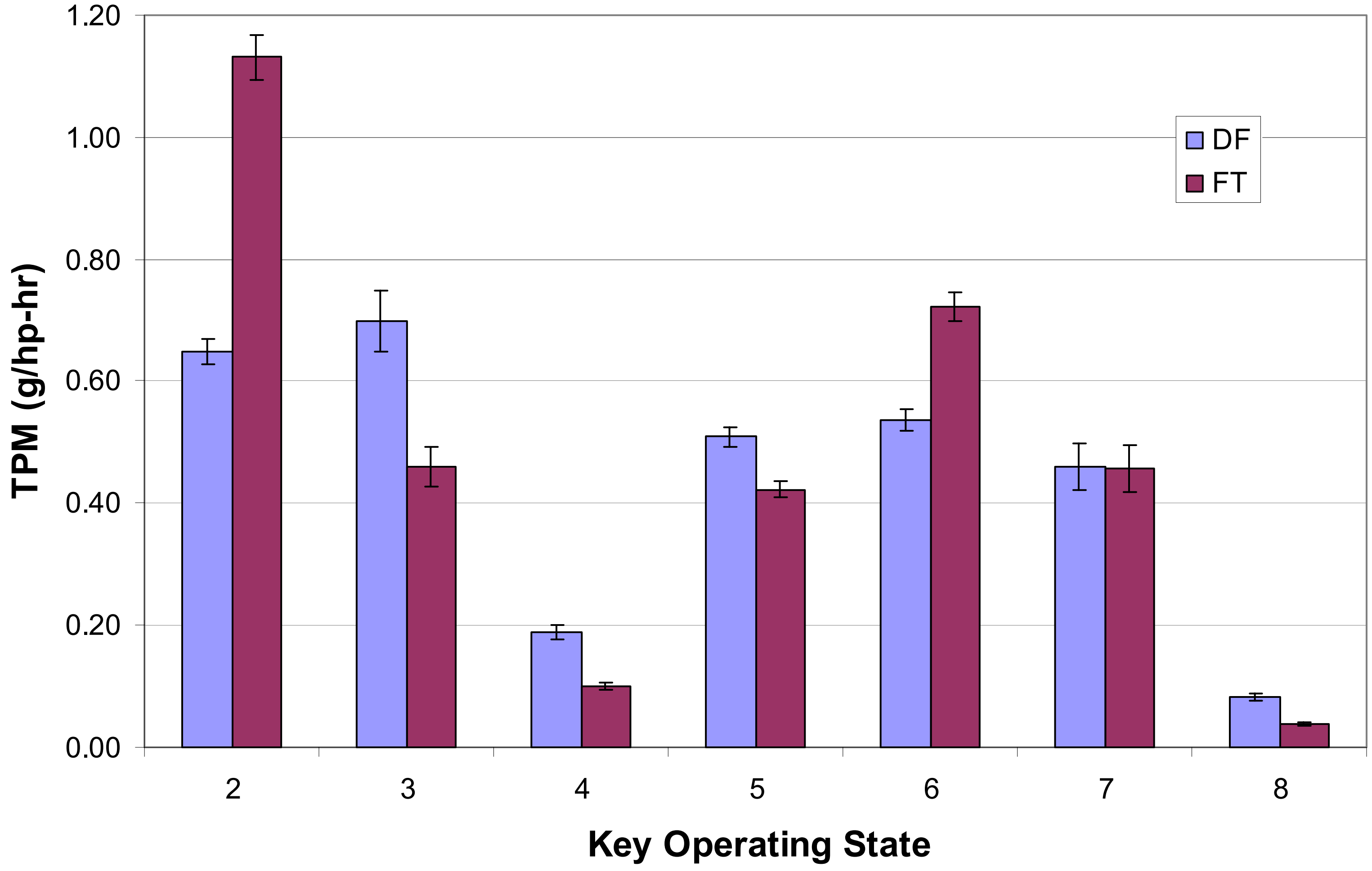
Steady State Operating Conditions (Key States)

Table 2. Steady-State Engine Operating Conditions

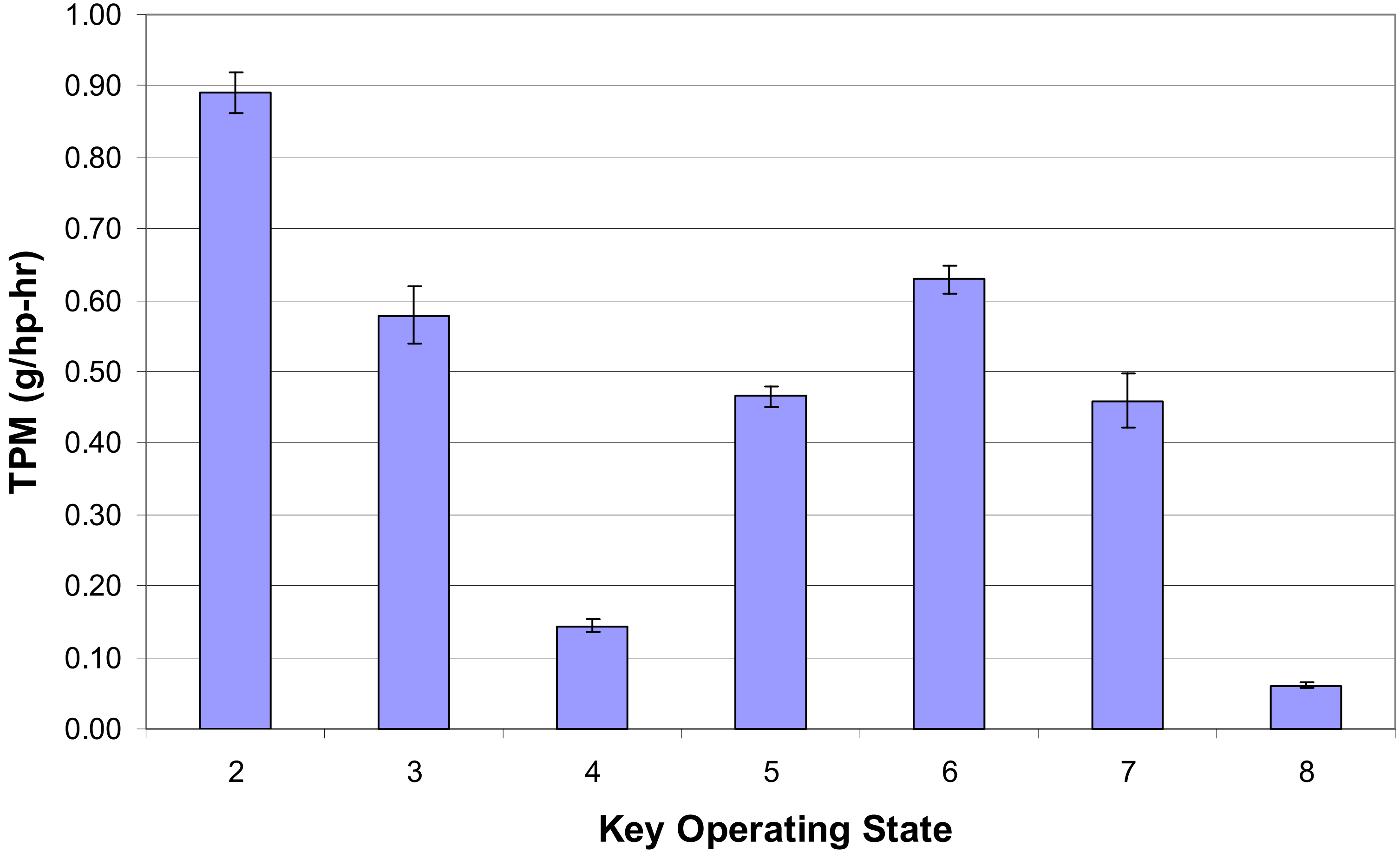
Key State	Engine Speed (Hz)	Engine BMEP (bar)	Torque (Nm)	Boost (KpaG)	Inlet Air (C)	Static Timing @	Exhaust (KpaG)
2	16	2	31.8	0	40	11	0
3	16	10	158.9	30	40	13	10
4	24	16	254.3	125	40	17	42
5	24	2	31.8	0	40	10	0
6	32	2	31.8	15	40	16	5
7	32	12	190	160	40	22	53.5
8	24	10	158.9	70	40	15	23.5

@ The same static timing was used for each fuel.

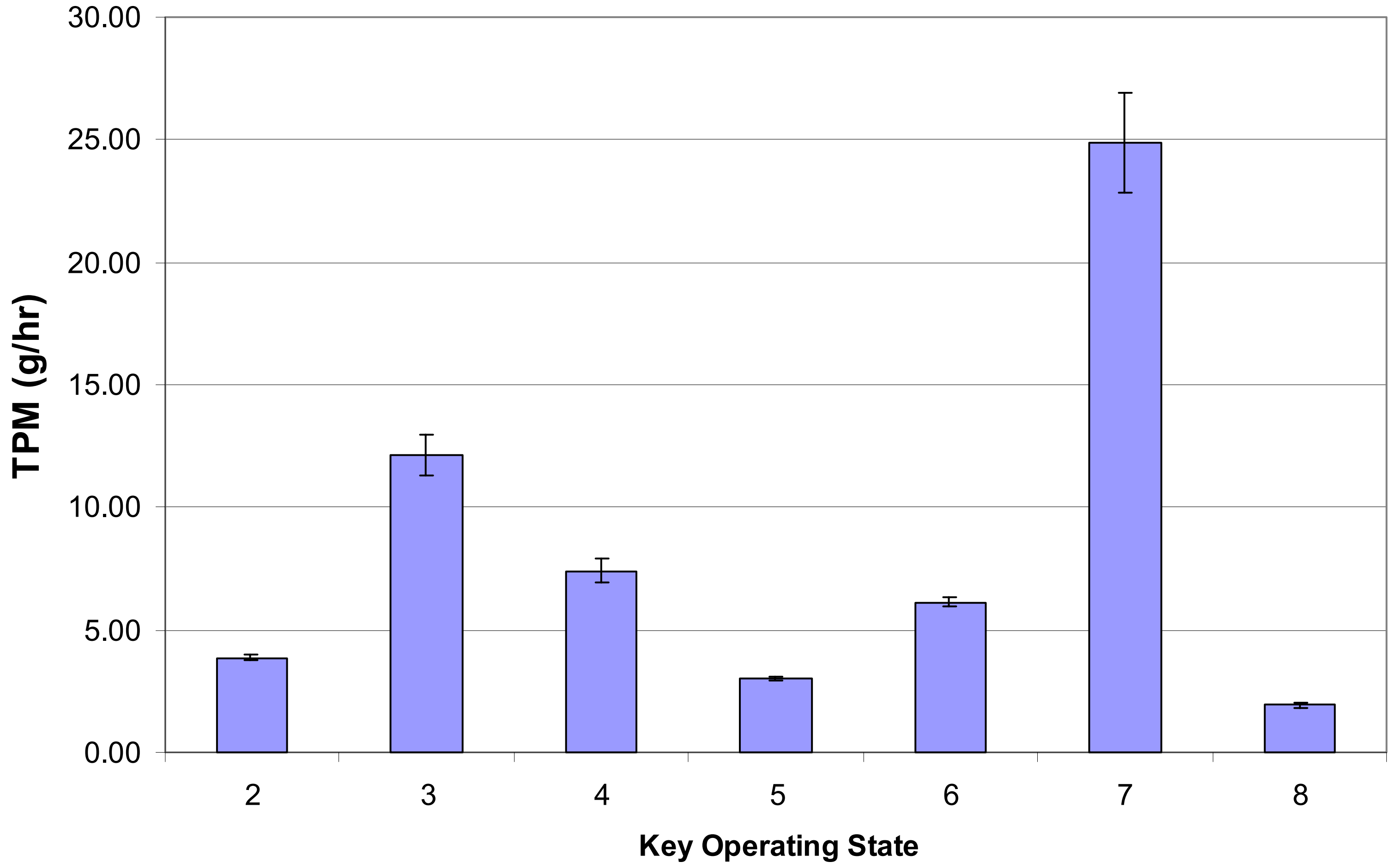
TPM by Fuel Type and Key State



TPM
(Average by Key-state)

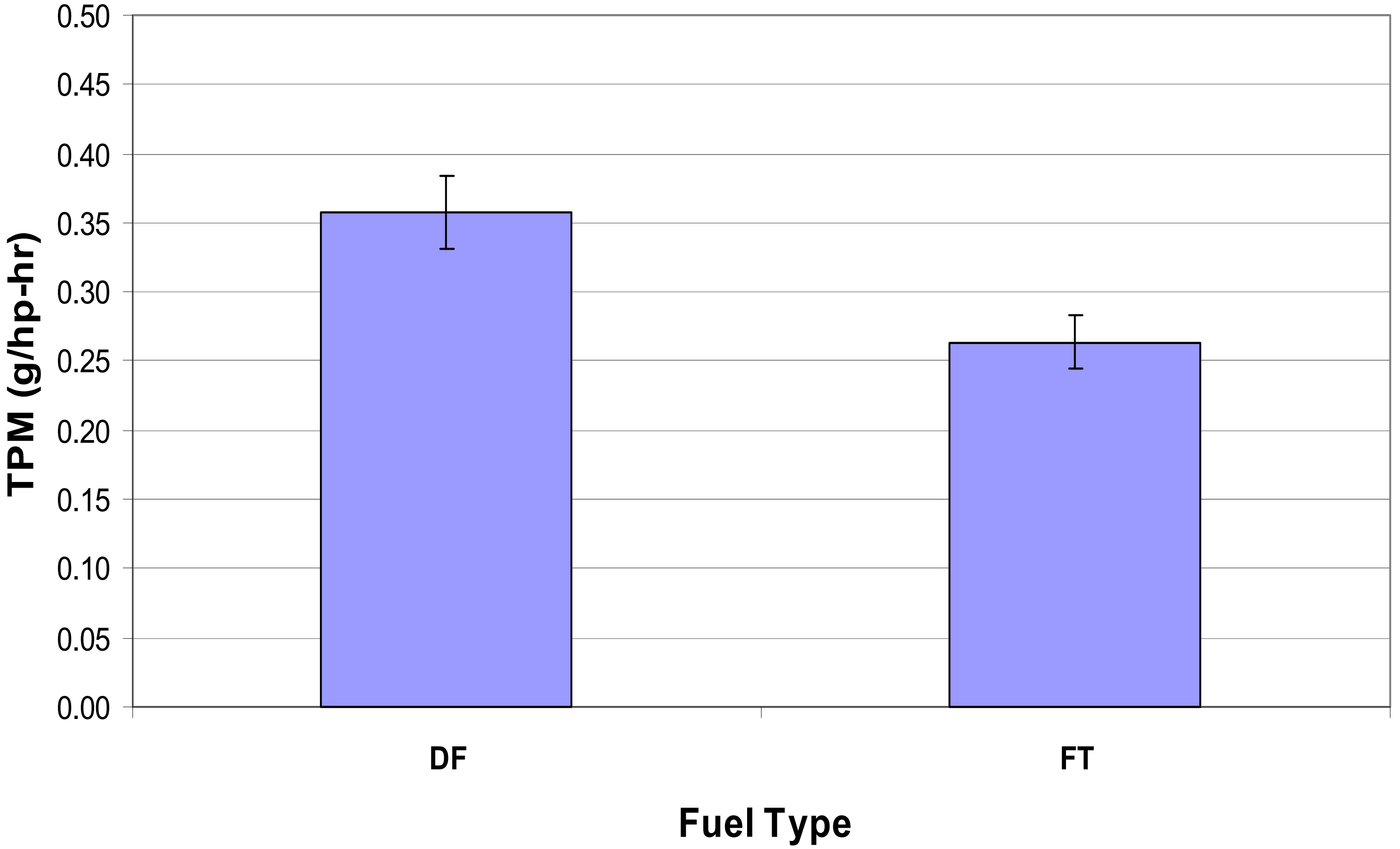


TPM (g/hr)



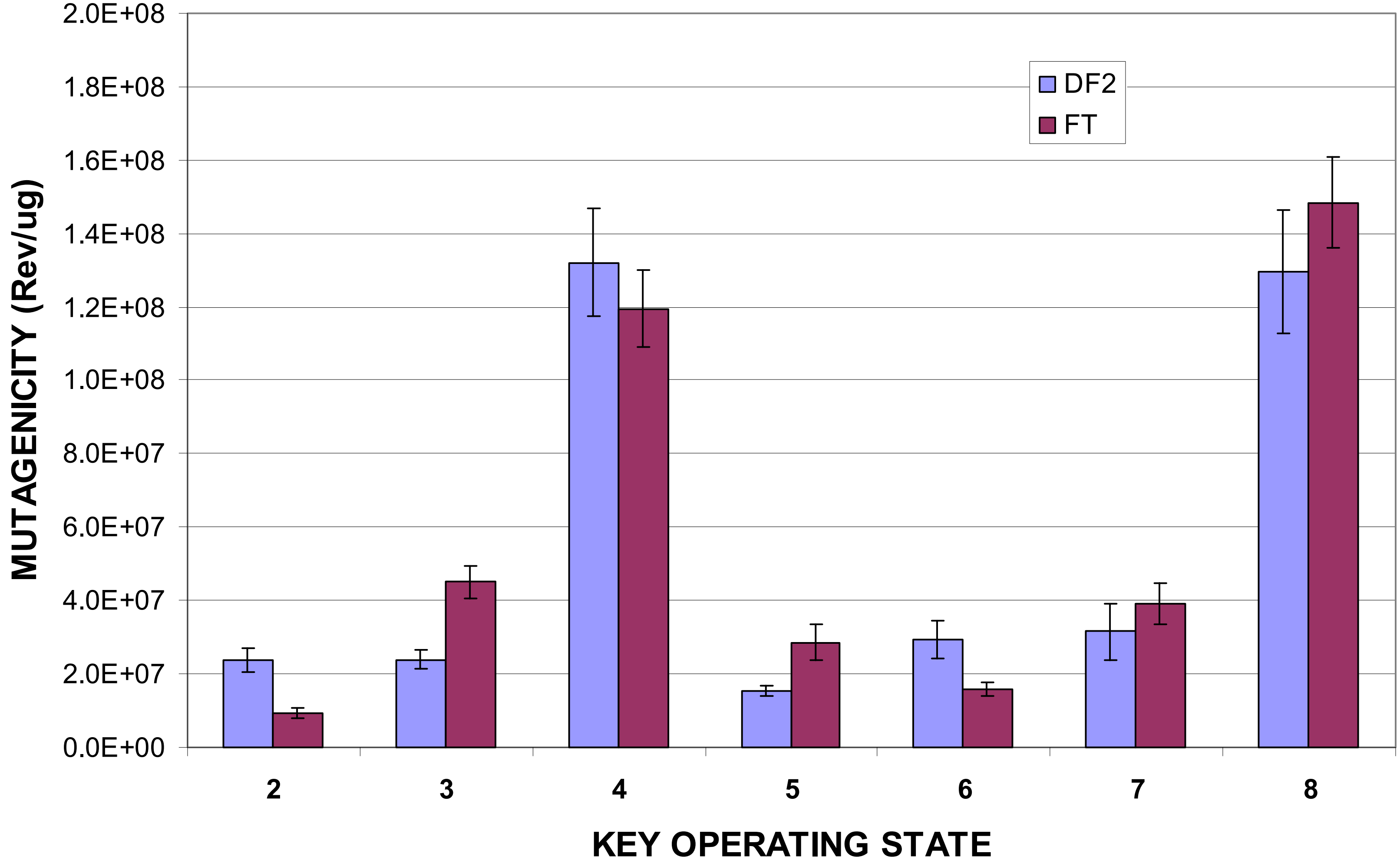
30.00
25.00
20.00
15.00
10.00
5.00
0.00
TPM (g/hr)
2
3
4
5
6
7
8
Key Operating State

Average (Med & High Load) TPM (g/hp-hr)

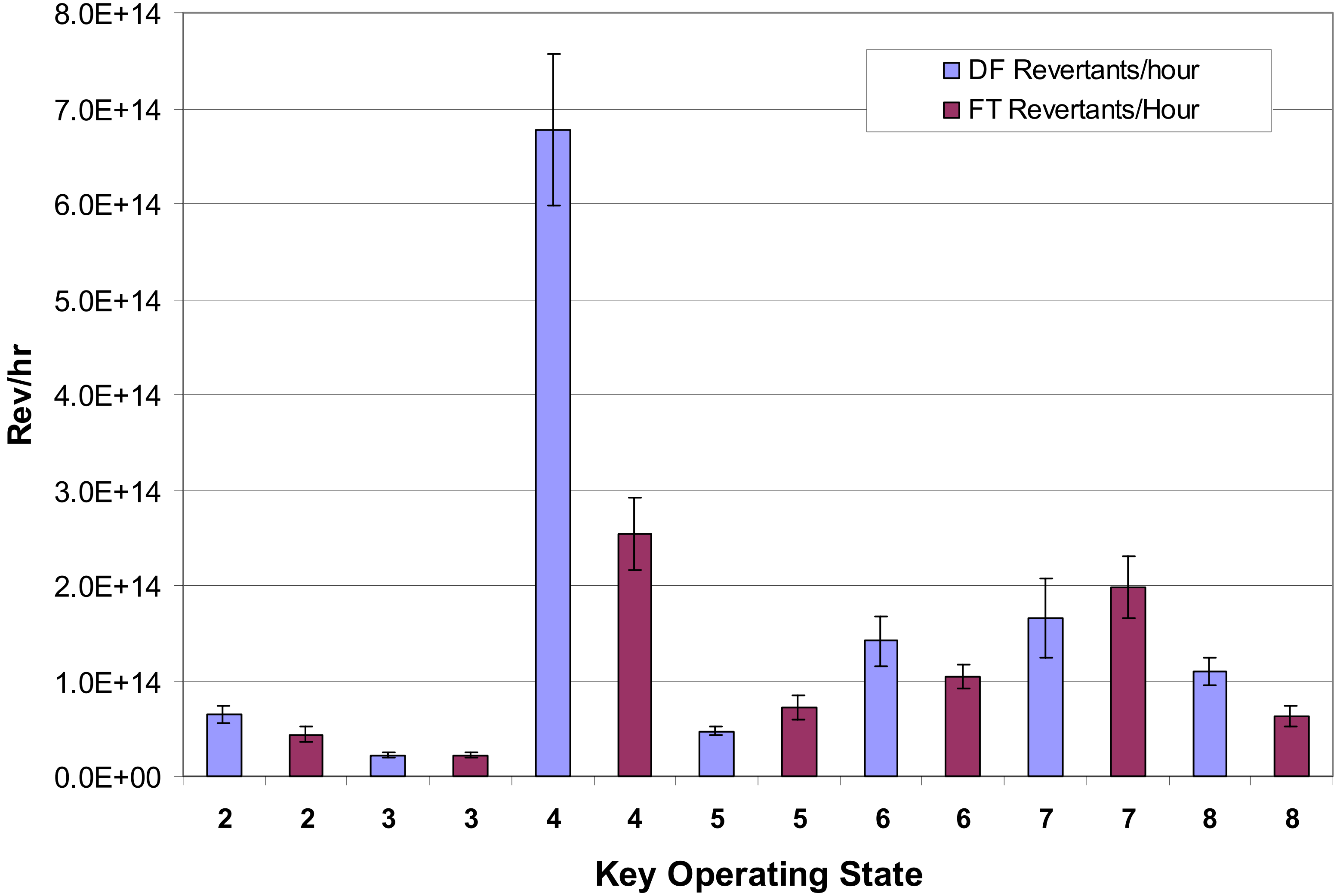


Medkum: Modes 3 & 4
High: Modes 7 & 8

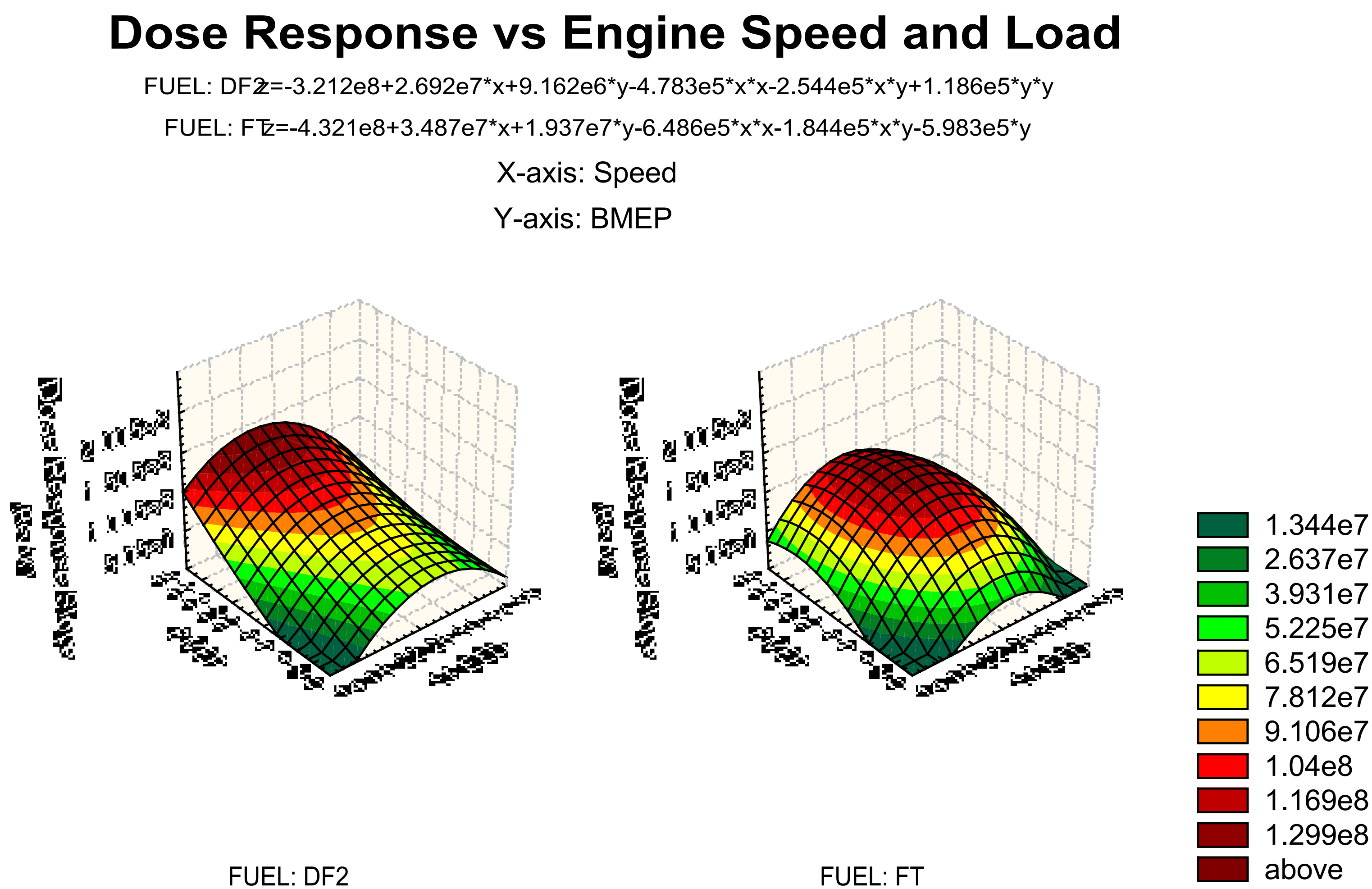
Average Mutagenicity (Rev/µg)
(Key-state and Fuel Type)



Mutagenicity (Rev/hr)



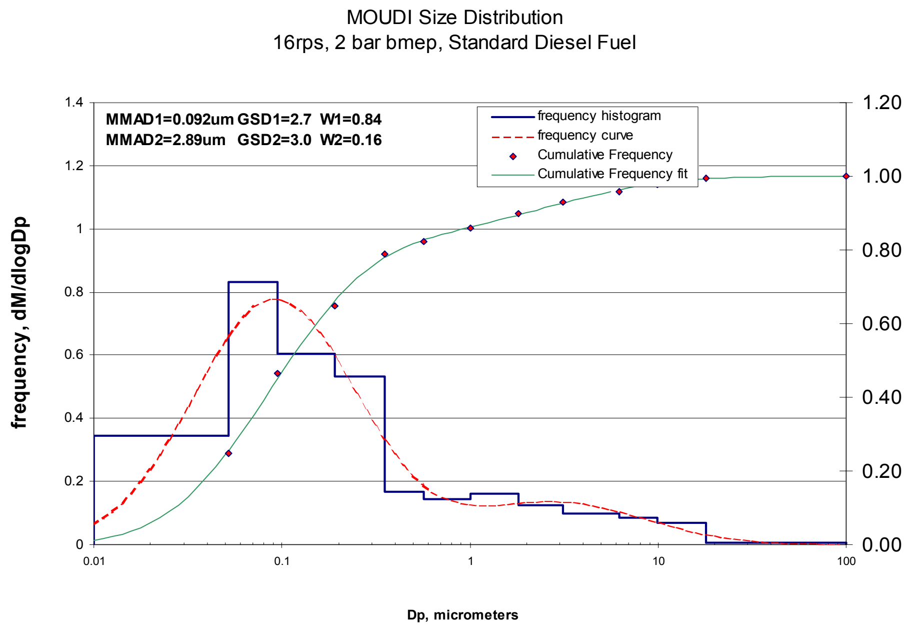
Quadratic Response Surface of Mutagenicity as Function of Engine Speed and Load

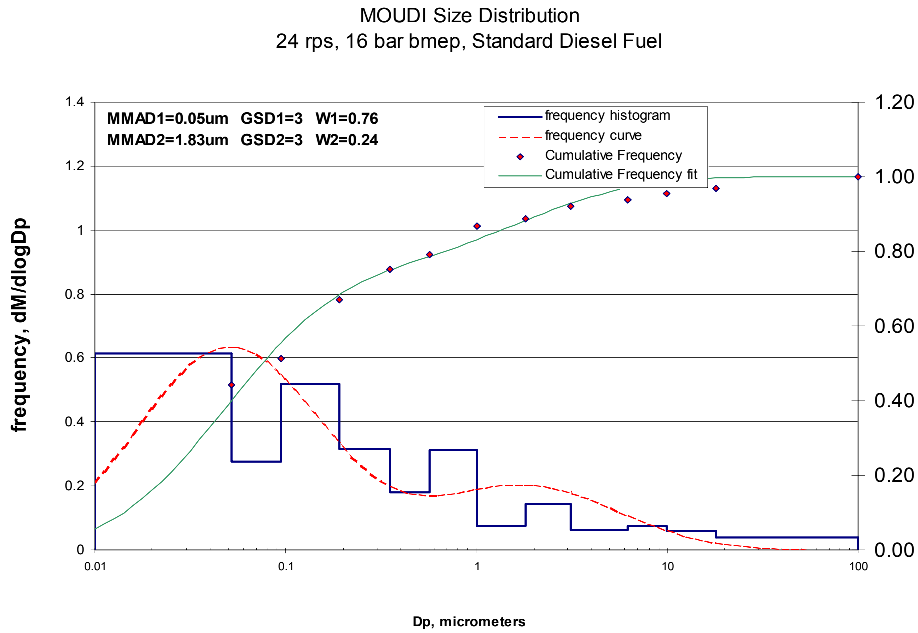


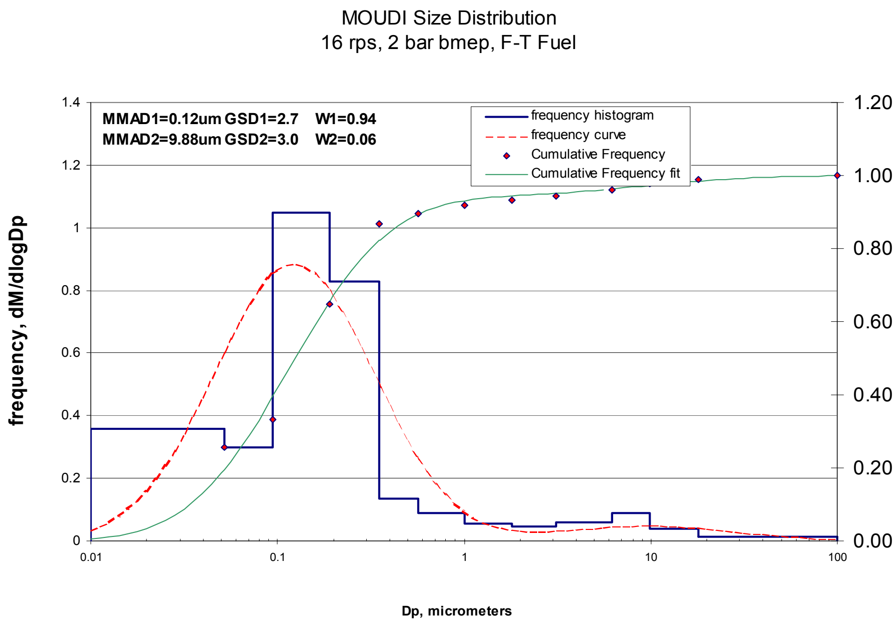
Operating Conditions for MOUDI Sampling

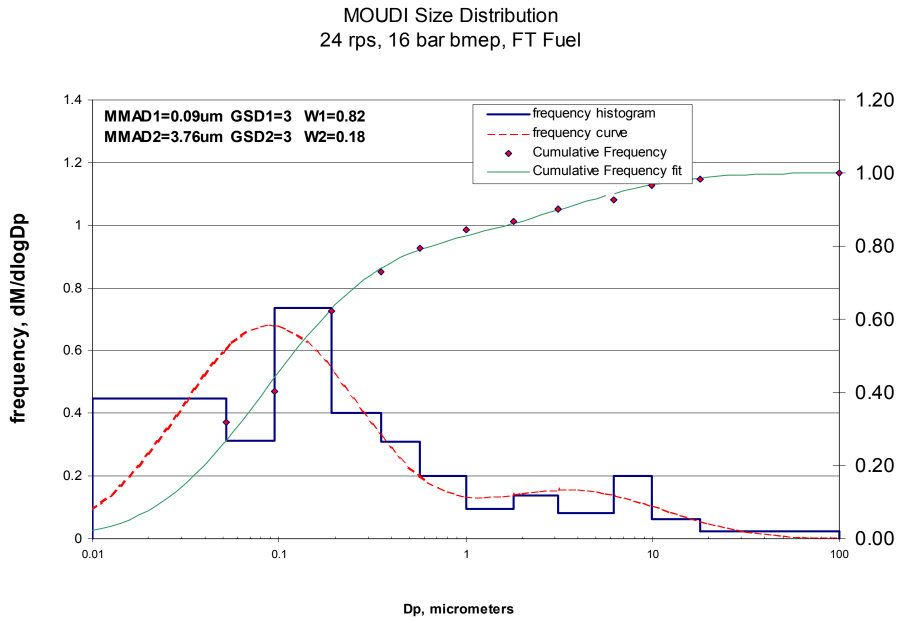
Table 3. Steady-State Operating conditions for MOUDI Sampling

Key State	Engine Speed (Hz)	Engine BMEP (bar)	Torque (Nm)	Boost (KpaG)	Inlet Air (C)	Static Timing (used for each fuel) °CA	Exhaust (KpaG)
2	16	2	32	0	40	11	0
4	24	16	254	125	40	17	42

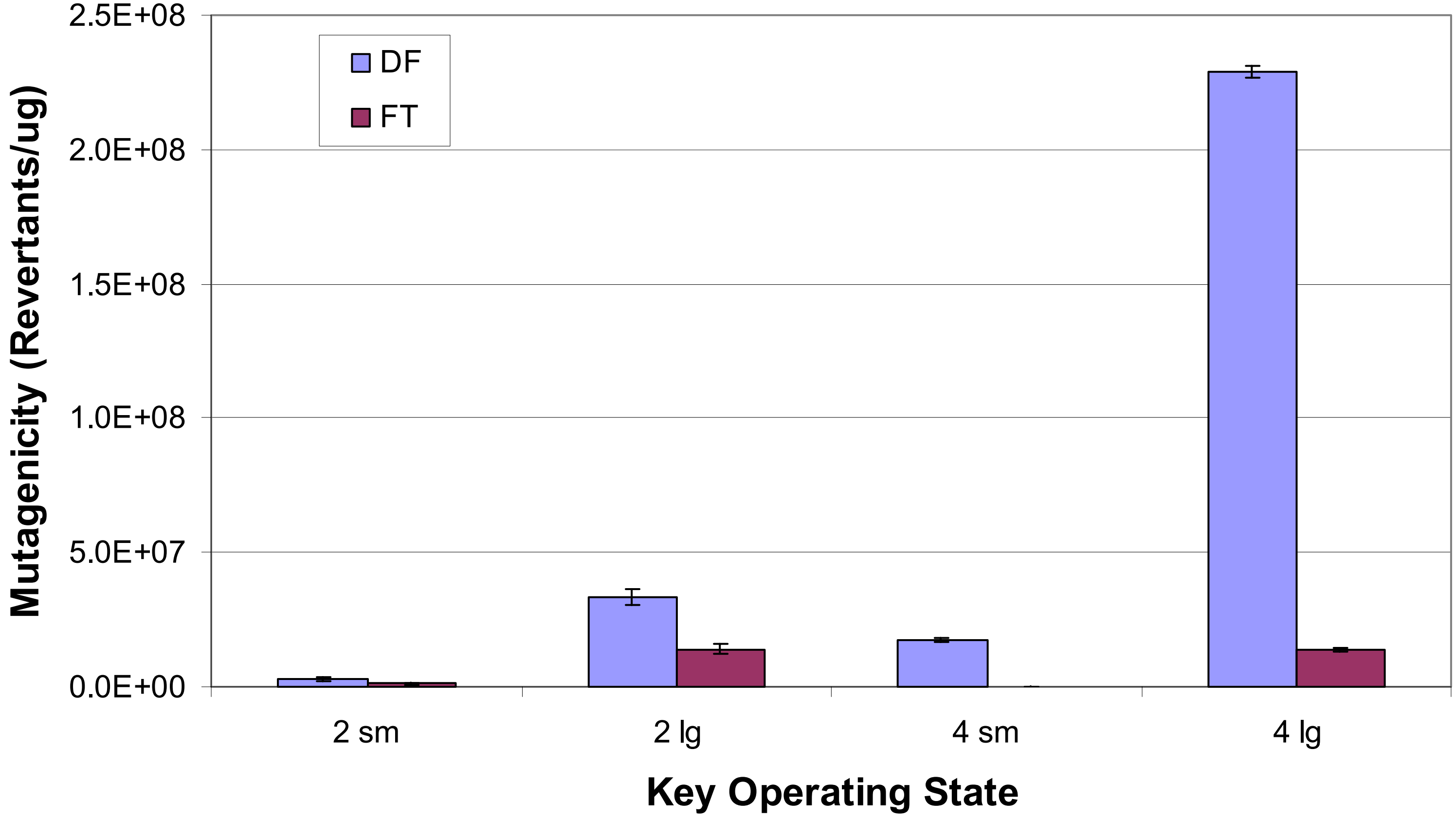

MOUDI Size Distribution
16rps, 2 bar bmep, Standard Diesel Fuel
MMAD1=0.092um GSD1=2.7 W1=0.84
MMAD2=2.89um GSD2=3.0 W2=0.16
frequency histogram
frequency curve
Cumulative Frequency
Cumulative Frequency fit
frequency, dM/dlogDp
Dp, micrometers


MOUDI Size Distribution
24 rps, 16 bar bmep, Standard Diesel Fuel
MMAD1=0.05um GSD1=3 W1=0.76
MMAD2=1.83um GSD2=3 W2=0.24
frequency histogram
frequency curve
Cumulative Frequency
Cumulative Frequency fit
frequency, dM/dlogDp
Dp, micrometers

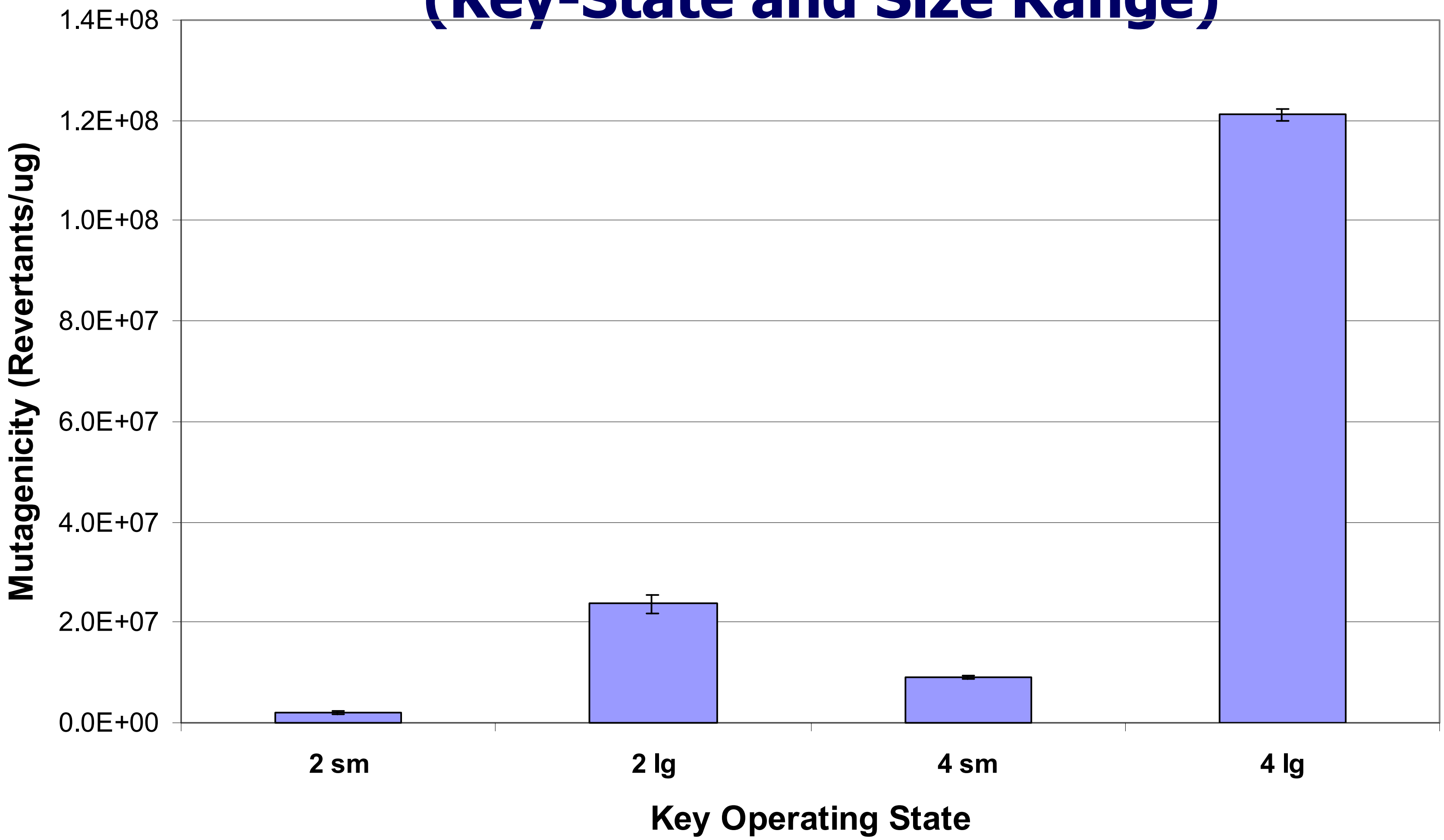

MOUDI Size Distribution
16 rps, 2 bar bmep, F-T Fuel
MMAD1=0.12um GSD1=2.7 W1=0.94
MMAD2=9.88um GSD2=3.0 W2=0.06
frequency histogram
frequency curve
Cumulative Frequency
Cumulative Frequency fit
frequency, dM/dlogDp
Dp, micrometers

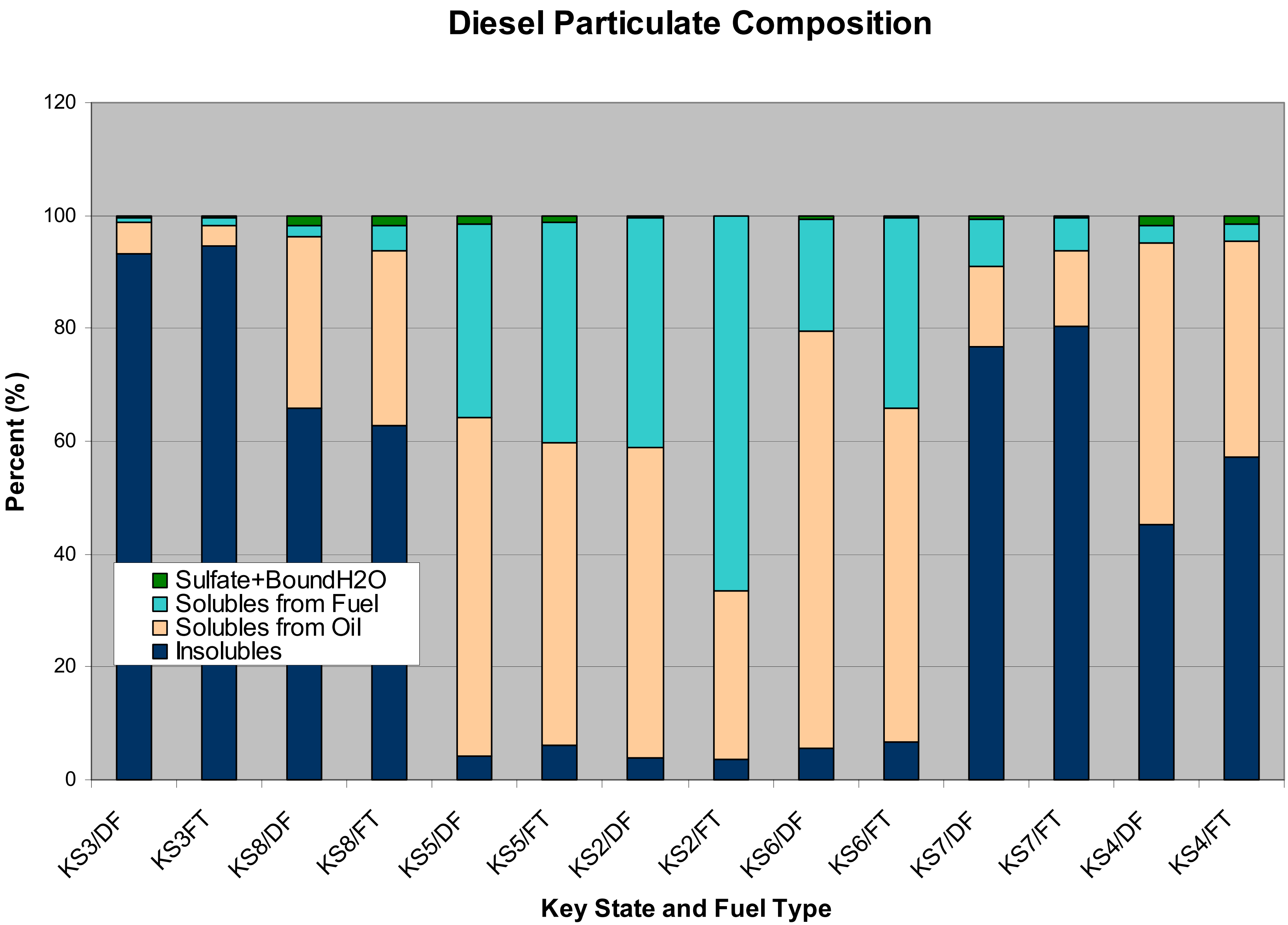

MOUDI Size Distribution
24 rps, 16 bar bmep, FT Fuel
MMAD1=0.09um GSD1=3 W1=0.82
MMAD2=3.76um GSD2=3 W2=0.18
frequency histogram
frequency curve
Cumulative Frequency
Cumulative Frequency fit
frequency, dM/dlogDp
Dp, micrometers

Mutagenicity
(Fuel Type, Key-State and Size Range)



Mutagenicity
(Key-State and Size Range)





Diesel Particulate Composition
Percent (%)
120
100
80
60
40
20
0
Sulfate+BoundH2O
Solubles from Fuel
Solubles from Oil
Insolubles
KS3/DF
KS3FT
KS8/DF
KS8/FT
KS5/DF
KS5/FT
KS2/DF
KS2/FT
KS6/DF
KS6/FT
KS7/DF
KS7/FT
KS4/DF
KS4/FT
Key State and Fuel Type

Conclusions

- **When considering cases other than low-load conditions the relative reduction in brake-specific TPM emissions from FT fuel was 26% over the DF fuel.**

- **When coupled with TPM production rate (rev/hr), the FT fuel provided a 45% reduction in revertant rate (rev/hr) over the DF fuel averaged over intermediate and high-load operating conditions and 38% over all operating conditions (key states).**

- **<u>Significant differences</u> between fuel type and key state as well as strain and activation type was indicated.**

Conclusions cont.

- **The measured mass weighted size distributions obtained on the MOUDI substrates, expressed in a log-normal form dM/d(log D) and fitted to a bimodal distribution gave:**
  - **FT fuel mass distributions that were larger than DF in the smaller sized mode (120 nm vs. 92 nm for DF for low-speed, low-load operation.**
  - **Overall larger FT MMAD for the ultrafine (smaller size) mode with less material in the larger mode than the Federal diesel No. 2 fuel.**
- **Significant differences in mutagenicity between fuel type, key state and particle size was indicated as were second order interactions between fuel, key state and particle size.**
- **Larger particles (>100 nm) tend to exhibit a significantly greater mutagenic response than smaller (ultrafine) size particles (<100 nm).**
- **The mutagenicity was not as sensitive to fuel or particle size low-speed low-load as it was medium-speed high-load where it was very responsive to fuel type and size fraction.**