

PARTICULATE EMISSION FROM A SPARK IGNITION
AND A LIGHT DUTY DIESEL ENGINE

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ABSTRACT

Particulate emission was studied from a spark ignition engine with and without a catalytic converter, and from a light duty passenger type diesel engine.

First particulate and sulfuric acid emissions were studied in the exhaust of a production 1970 Chevrolet 350 CID V-8 engine. Steady state dynamometer tests were run with and without a catalyst in the exhaust system. Both pelleted and monolithic catalysts were examined. Particles were collected at points along a specially constructed exhaust system. The weight and sulfuric acid content of the particulate matter, and the percent of fuel sulfur emitted as H_2SO_4 were determined under different operating conditions. Tests were performed at various constant speeds in the range $35-96 \text{ km h}^{-1}$. The effects of the following parameters were studied during the tests: a) catalyst temperature in the range $573-773 \text{ K}$, b) fuel sulfur content in the range $0.1-0.3\%$, c) fuel consumption, d) exhaust gas flow rate through the catalyst (space velocity), e) amount of secondary air, and f) air-fuel ratio. The results showed that with the sulfur storage-release processes equilibrated the sulfuric acid, particulate emissions and the sulfur conversion depended primarily on the first four of these parameters. Within the temperature range and secondary air range studied the air-fuel ratio and the

amount of secondary air did not seem to affect the results significantly. The weight and sulfuric acid content of the emitted particulate matter were also measured during a simulated 7 Mode Federal Test Procedure using different sulfur content fuels.

Second, tests were performed with a Mercedes Benz type OM 616 diesel engine. Particles were collected at points along the exhaust system. The weight of the particulate matter emitted was measured under different operating conditions. The effect of sampling temperature on particulate emission was evaluated at various constant speeds in the range 35-96 km h⁻¹ and under a simulated 7 Mode Federal Test Procedure. The effect of engine load and speed on particulate and smoke emissions was also studied during the tests. The results showed that the particulate emission was insensitive to sampling temperature (within the 300-550 K temperature range achieved in the exhaust), but both the particulate and smoke emissions were highly dependent on engine speed and load. The particulate matter collected was analyzed for its chemical composition showing that 60 to 75 percent (by weight) of the particulate matter was organic compounds.

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PART I

SULFATE AND PARTICULATE EMISSIONS FROM AN
OXIDATION CATALYST EQUIPPED ENGINE

CHAPTER 1

INTRODUCTION

Gasolines contain a small amount of sulfur which, if the engine is not equipped with a catalyst, is emitted mostly in the form of sulfur dioxide. When the engine is equipped with an oxidizing catalyst some of the sulfur dioxide is converted into sulfur trioxide which, combining rapidly with water vapor in the exhaust, is emitted in the form of sulfuric acid. Thus, while oxidation catalysts reduce gaseous emissions they give rise to the emission of sulfuric acid [1-14]. In addition, the installation of oxidation catalysts in automobile exhaust systems causes an increase in the amount of particulate matter emitted [2-10].

Owing to the possible problems created by the increased sulfuric acid and particulate emissions from catalyst equipped engines, it would be desirable to understand the mechanisms and parameters which control such emissions, and to determine the amounts of sulfuric acid and particulates emitted. In recent years several investigations have been addressed to this problem. Nevertheless, many aspects of the problem remain unresolved. Sulfuric acid and particulate emissions from actual engines operating at steady and cyclic speeds were reported in refs. [2-11]. These studies do not indicate fully the important role of the catalyst temperature because this temperature was either not reported [2,3,4], was varied only over a limited range (793-939 K) [5-8], or data were taken under transient conditions [9,10]. The effect of catalyst history on sulfate emissions was studied by Trayser et al [11]. Sulfate emissions in simulated catalyst-exhaust systems were studied by

Mikkor et al [12], Hammerle and Mikkor [13], and Hammerle and Truex [14]. The storage of sulfates in catalysts was investigated by Hammerle and Mikkor [13].

Results are not yet available to indicate the full effects of engine variables, fuel sulfur content, and catalyst temperature on the sulfuric acid and particulate emissions from an actual spark ignition engine equipped with oxidation catalysts. The overall objective of this investigation was, therefore, to study the influence of these parameters on emissions from a Chevrolet V-8 engine operating on a test stand dynamometer. Specifically, the amount of particulate matter and sulfuric acid emitted and the percent of the fuel sulfur emitted as sulfuric acid (sulfur conversion) were measured as a function of a) catalyst temperature, b) fuel sulfur content, c) exhaust gas mass flow rate through the catalyst (space velocity), d) fuel consumption, e) air fuel ratio, and f) amount of secondary air. The tests were performed with both a pelleted and a monolithic oxidation catalyst.

CHAPTER 2

EXPERIMENTAL APPARATUS

The apparatus employed in this study was essentially the same as the one used by Sampson and Springer [15] and by Ganley and Springer [16]. Therefore, only a brief summary will be given to indicate the changes made and to facilitate the reading of the thesis.

The apparatus consisted of the engine, the simulated exhaust system, and the sampling train. These components are described in the following sections.

2.1 Engine and Fuel

The engine used was a 1970 350 CID 250 HP Chevrolet V-8 production engine. The engine specifications and operating conditions are given in Appendix A.

The engine was mounted on a Midwest Dynamatic eddy current dynamometer test stand located in a test cell in the Automotive Engineering Laboratory at The University of Michigan. The engine and dynamometer were instrumented to monitor and control coolant temperature, oil temperature and pressure, manifold vacuum, exhaust pressure, and engine speed and load. The air flow rate to the engine was measured by a rounded approach air cart manufactured by General Motors Corporation. The fuel flow rate was measured with a burette.

Tests were conducted using Indolene HO 0 (clear) fuel. Di-t-butyl-disulfide was added to adjust the sulfur content of the fuel to the desired value. The physical and chemical properties of the fuel are given in Appendix B.

The engine was lubricated with Valvoline 10 W 40 oil, which is typical of commercially available motor oils. The oil, oil filter, and PCV valve were changed at 40 hour intervals.

2.2 Simulated Exhaust System

Tests were first conducted under cyclic conditions without the catalysts. Then, in turn a pelleted and a monolithic catalytic reactor were installed in the exhaust system and tests were performed with each catalyst under steady and cyclic operating conditions. In the following paragraphs the basic exhaust system without the reactor is first described. The changes made to install the reactors are outlined subsequently.

The exhaust system, connected to the engine, consisted of the standard exhaust manifolds and cross-over pipe, a surge tank, a 4.3 m long 50 mm diameter pipe, and a sharp edged orifice (Fig. 2.1).

The surge tank was a 30 cm diameter 60 cm long steel cylinder, insulated with a wrapping of Kaowool. The surge tank was added to reduce the pressure and flow fluctuations in the exhaust (Sampson and Springer [15]).

The simulated exhaust system consisted of three 60 cm long black pipe sections, a 180° bend followed by 3 additional 60 cm sections of black iron pipe. There were six holes in each of the sections. Three 1/8 NPT holes were located along the top and three 1/4 NPT holes along the sides to allow for the installation of thermocouples and sampling probes, respectively. All holes were fitted with plugs when not in use.

A 22.2 mm sharp edged orifice (Orifice A), made to ASME specifications, was placed at the end of the simulated exhaust system. The pur-

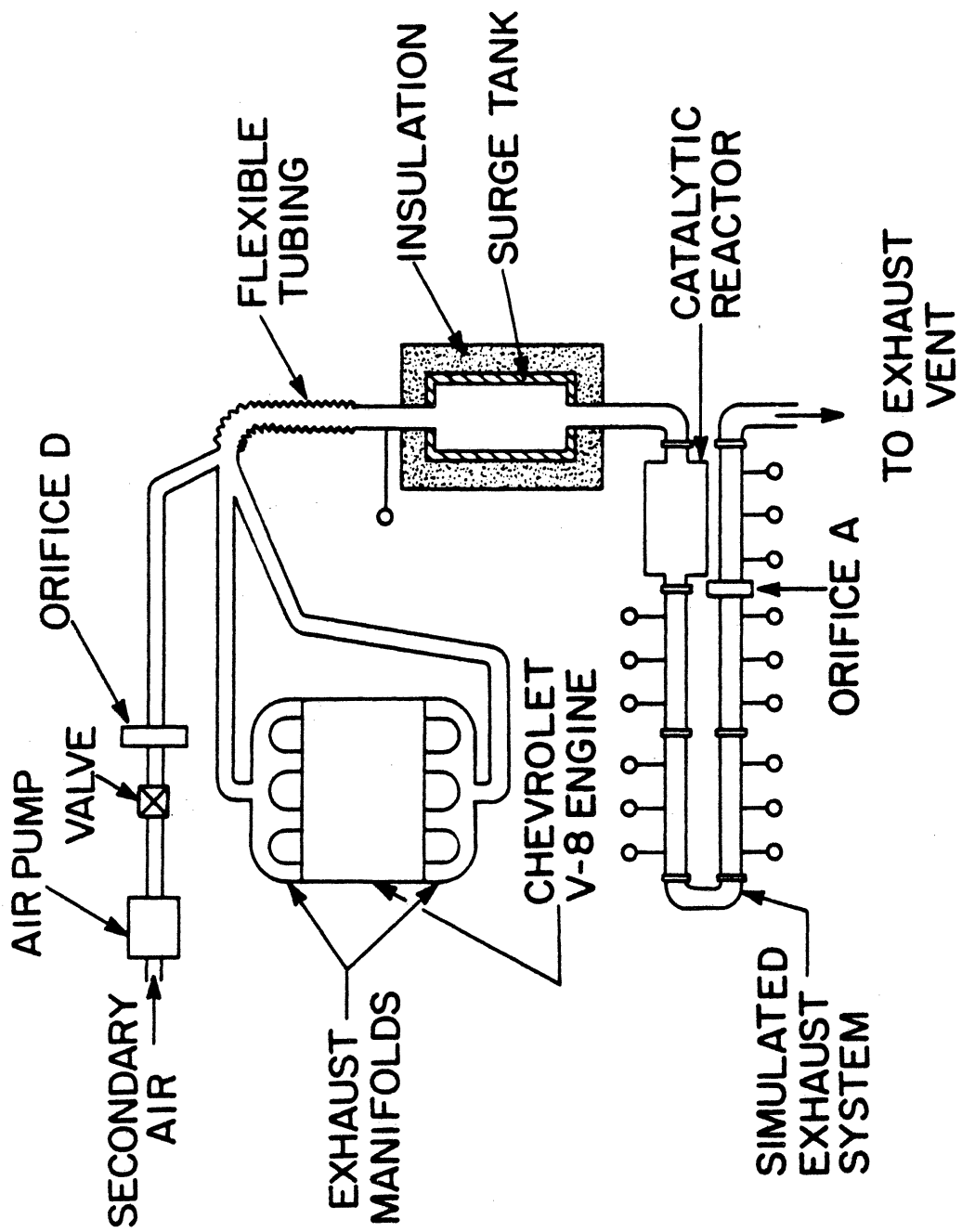


Fig. 2.1 Experimental apparatus. Circles represent thermocouples and sampling locations.

pose of this orifice was to measure the exhaust flow rates during cyclic sampling, as described in the next section.

2.3 Catalysts

Emissions with two catalysts were investigated. One was a pelleted catalyst supplied by General Motors Corporation, the other was a monolithic catalyst supplied by Engelhard Industries (Appendix A).

The catalytic reactors were installed in place of the first segment of the simulated exhaust system. No other modifications of the exhaust system were necessary.

After the tests with the pelleted catalytic reactor were completed the reactor was removed and the monolithic catalytic reactor was installed in its place. The monolithic reactor was designed to process only half the volume of the exhaust gas. Therefore, for the monolithic reactor only four of the eight cylinders (the right bank of cylinders) were connected to the simulated exhaust. The other four cylinders were connected directly to the test cell exhaust vent.

For both catalysts secondary air was injected into the simulated exhaust (before the surge tank) by an air pump driven by a V belt from the crankshaft pulley. The amount of secondary air was controlled by a valve and was measured by an 18 mm sharp edged orifice (Orifice D, Fig. 2.1) made to ASME specifications.

2.4 Sampling Train

The sampling train consisted of a probe, a particle collection unit, a flow control mechanism, and two vacuum pumps (Fig. 2.2). Each of these components is described below.

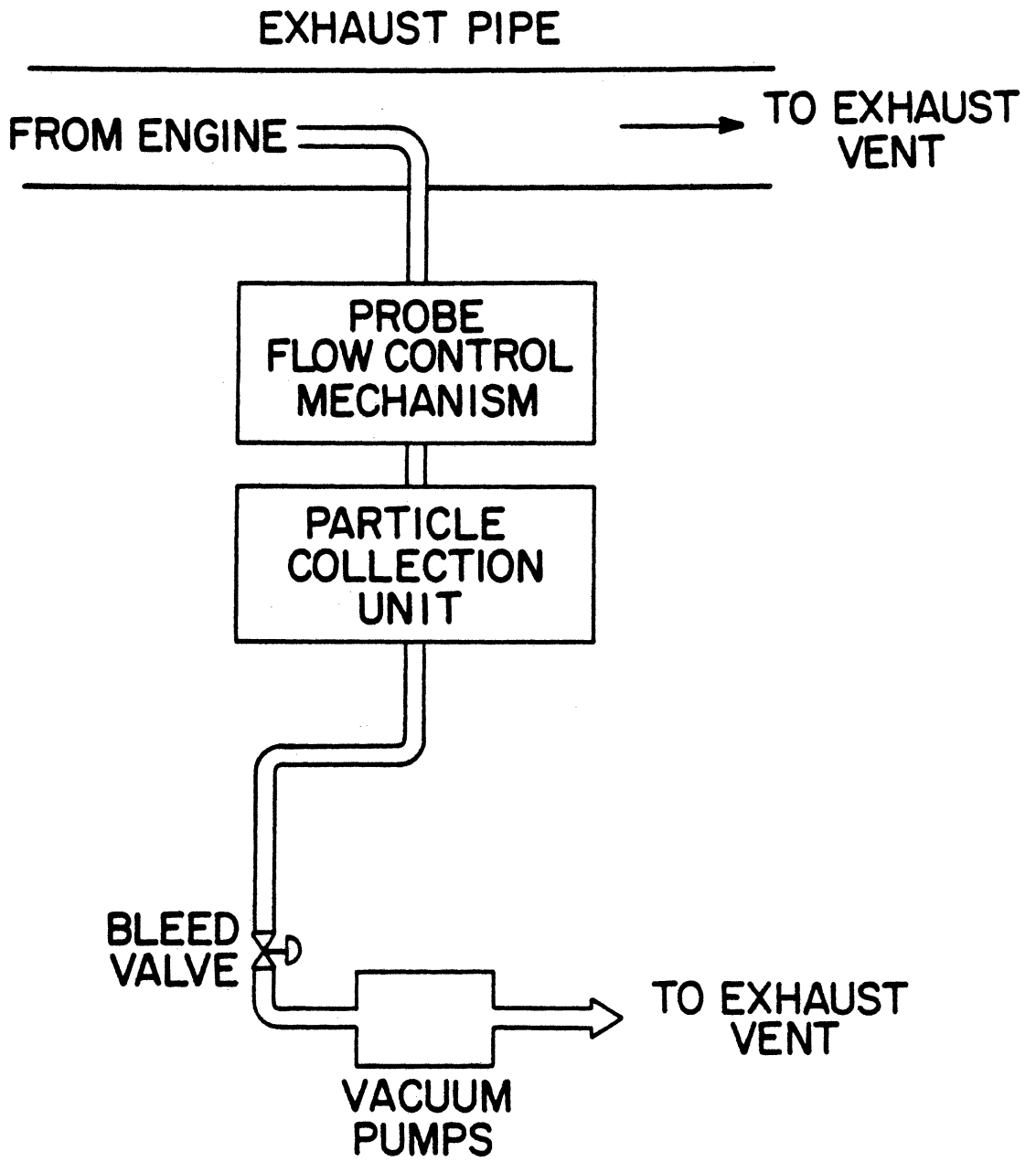


Fig. 2.2 Sampling train

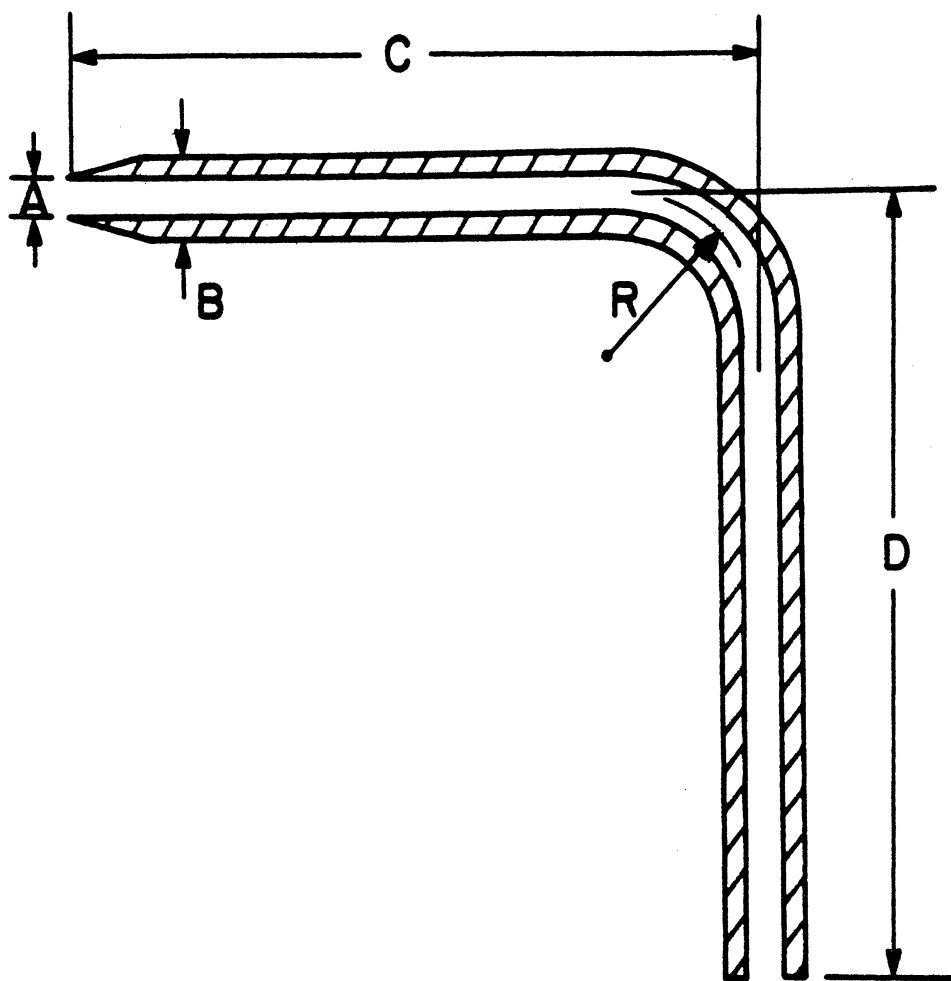
Two different size probes were utilized in the course of this study. They were constructed of 316 stainless steel tubing and had the dimensions given in Fig. 2.3. The larger probes were used during cyclic tests, the smaller ones during steady state tests. The probes were located in the center of the exhaust pipe facing the direction of the flow.

The particle collection unit housed a single filter (Fig. 2.4). The matter collected on the filter was analyzed to determine particulate and H_2SO_4 emission. The filters used were Gelman 47 mm diameter type A glass fiber placed in a modified Gelman 2220 filter holder.

The entire collection unit was surrounded with beaded heaters and enclosed in a 25 mm thick wrapping of Kaowool held in a sheet metal shell. The current to the heaters was controlled by voltage controllers. The temperature of the gas sample was measured with chromel-alumel thermocouples inserted into the gas stream on both sides of the filter holders.

The exhaust gases could be diluted with ambient air. All the data given in the Results (Section 4) were obtained by diluting the sample with air (dilution ratio 8:1), and by keeping the temperature of both the sample gas and the collection unit (including the filter) in the range 305-315 K. The reasons for selecting these sampling conditions are discussed under Experimental Procedures in Section 3.5. The flow rate of the dilution air was controlled by the mechanism described below.

The flow rate through the probe and the amount of dilution air must be carefully regulated through the tests. The flow rate through the probe must be adjusted to the proper value for isokinetic sampling (Ganley and Springer [16]). The dilution air was kept constant at an 8:1



PROBE	A	B	C	D	R
I	3.98	6.35	114.2	160.3	24.6
II	2.66	4.99	51.5	56.1	11.5

All Dimensions in mm

Material: 316 Stainless Steel

Fig. 2.3 Geometry of probes used

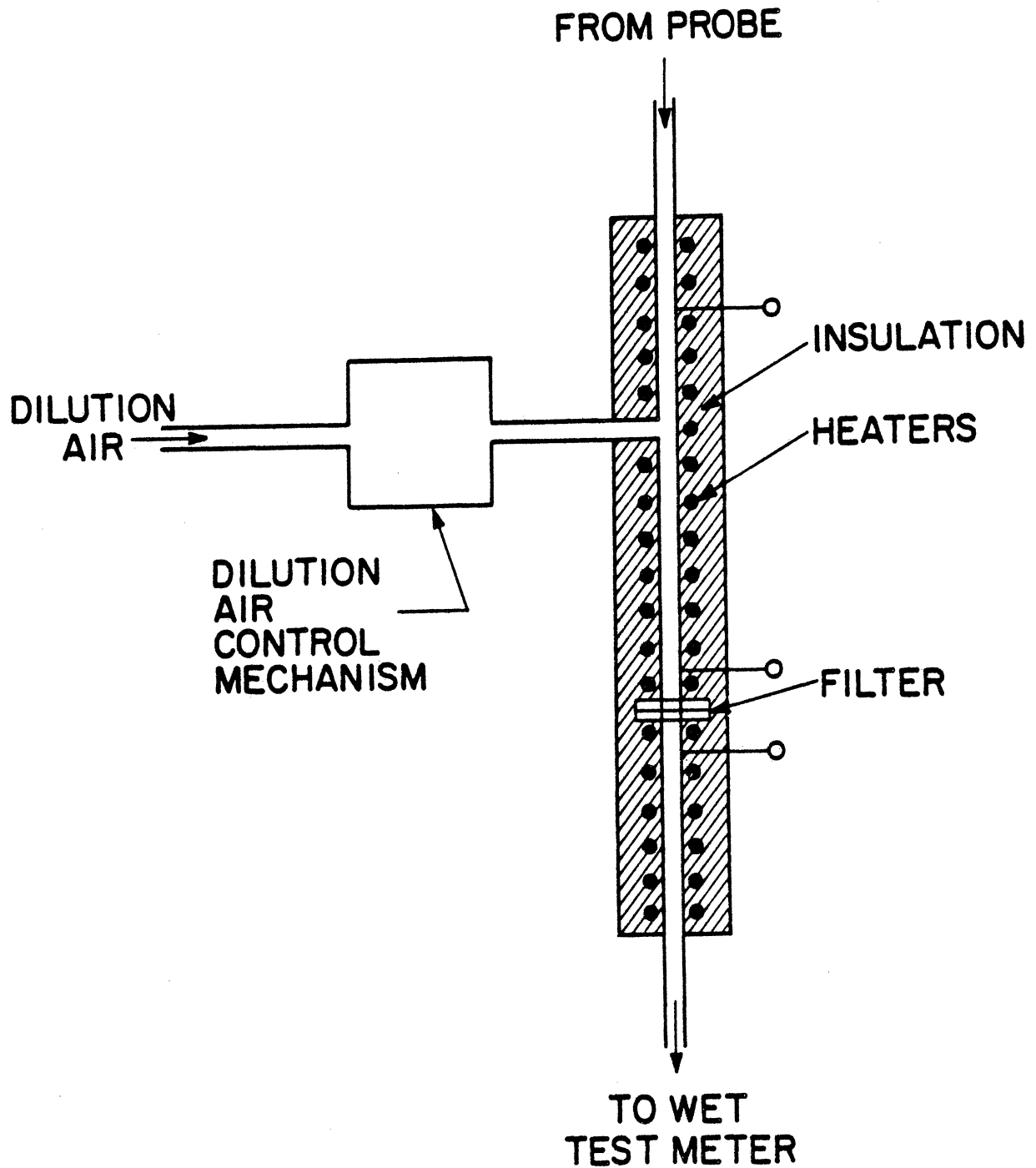


Fig. 2.4 Schematic of the collection unit. Open circles represent thermocouple locations

dilution ratio. At steady operating speeds flow rates of the dilution air and the total sample were measured by wet test meters installed in the system and the flow rates were set appropriately. Under cyclic operating conditions the flow rates through the probe and the dilution system were modified and adjusted continuously. To accomplish this a special flow control system was designed (Fig. 2.5). The flow rate through the probe was regulated as follows. A standard 1.3 mm diameter sharp edged orifice (Orifice B) was installed in the sampling line (Fig. 2.5). The pressure drop across this orifice was measured by a Ptran 0-0.1 psi differential pressure sensitive transistor immersed in a silicon oil bath to minimize temperature fluctuations. The pressure drop across the orifice in the exhaust system (Orifice A) was measured by a Rahm PT (C) 71 potentiometer type differential pressure transducer. The signals from the two transducers were compared on an Analog Devices 118A Operational Amplifier. A schematic of the amplifier circuit is given in Fig. 2.6. The difference in the two signals was amplified by an AST/SERVO Systems Model A-176 DC error signal servoamplifier (Fig. 2.6) and fed to a Kollsman 8090160650, 115 volt, 2 phase, 2 pole motor generator. This motor generator was connected to a stainless steel Whitey IRS4 type valve through a 50:1 ratio link "high-precision" gear box. The flow rate through the probe was regulated by the valve.

The amount of dilution air was controlled by a similar control system (Fig. 2.5). The orifice in the dilution air line was 5.6 mm in diameter. The pressure transducer used was a Bourns Model 503 differential pressure transducer and the valve used to control the flow was a Whitey IRS8 brass valve.

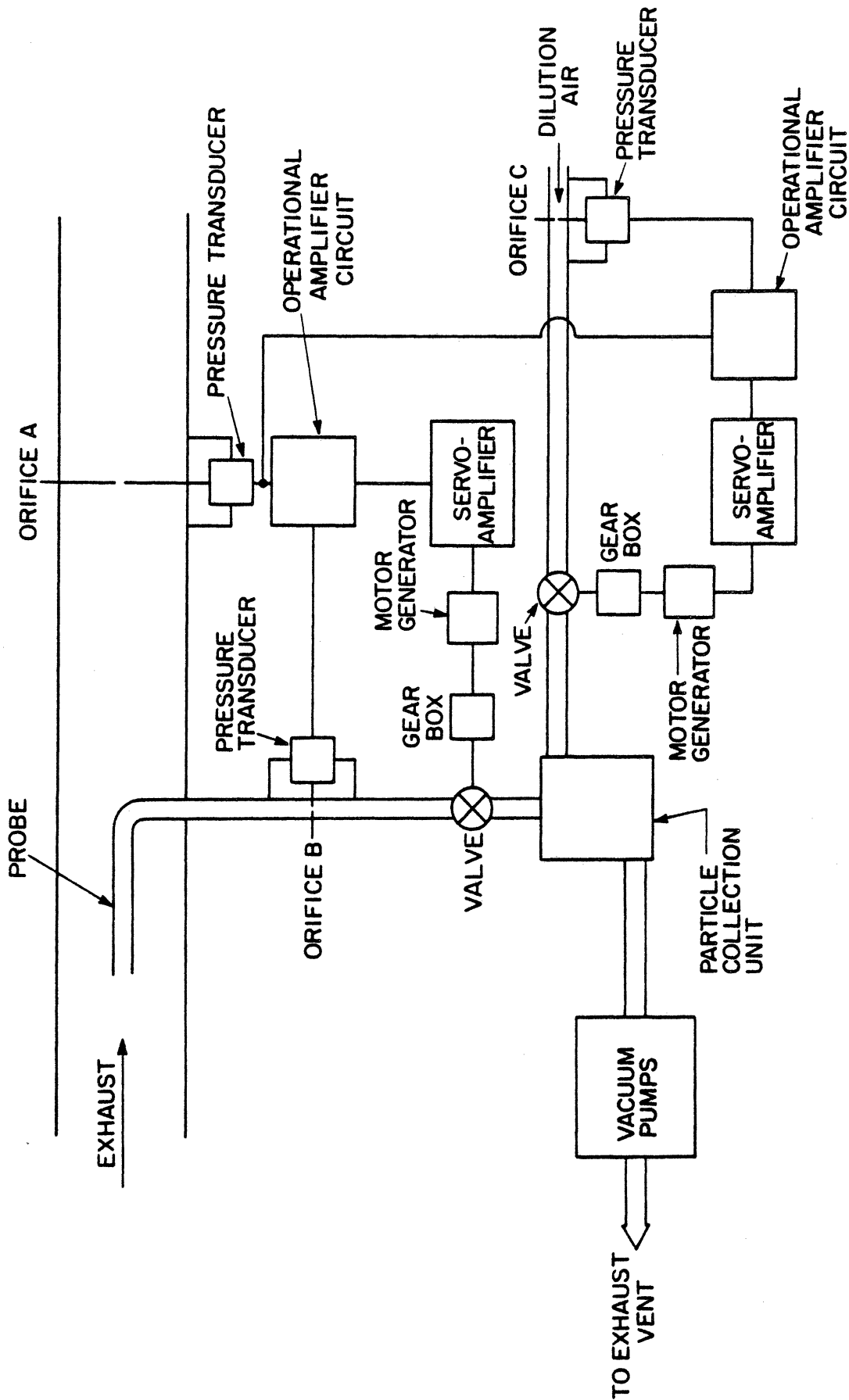


Fig. 2.5 Schematic of the automatic control system

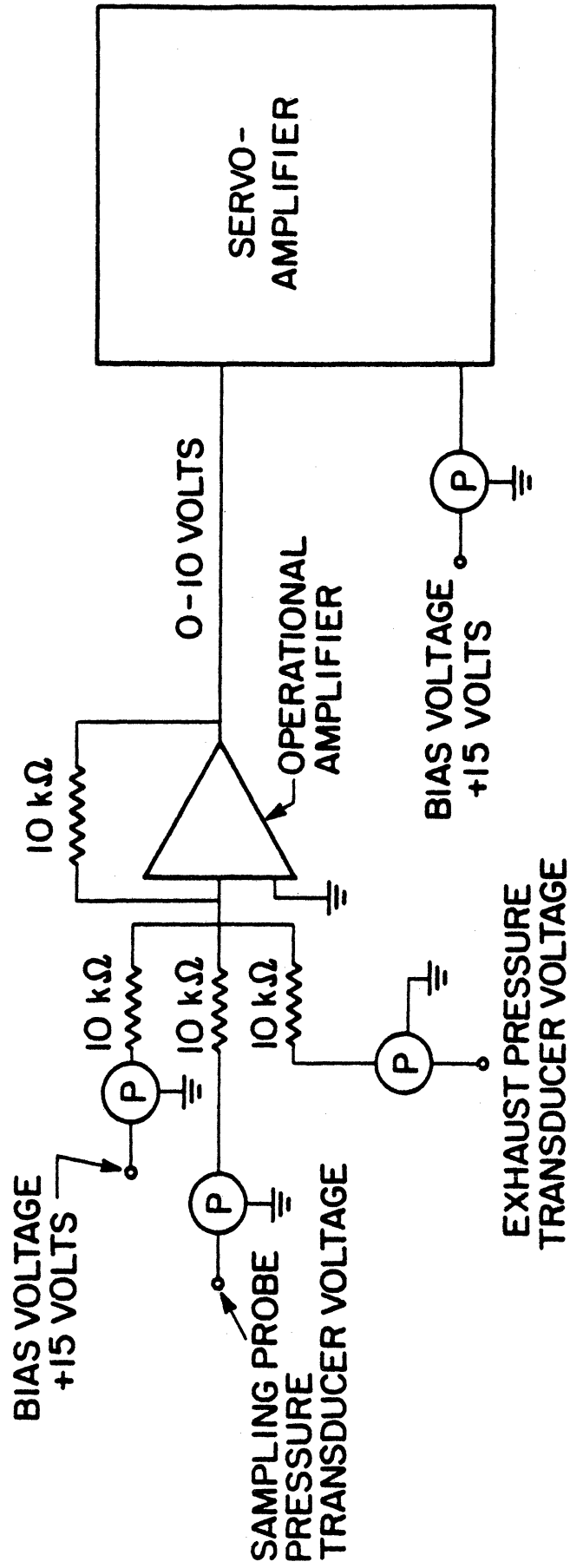


Fig. 2.6 Operational amplifier circuit. Circles with P represent potentiometers

The voltage necessary for the pressure transducers was provided by Kepco Model CK18-3 and Thornton 201D type DC power supplies while the servoamplifier and the motor generator were connected to the 117 volt AC line. The orifices were calibrated under steady state conditions. The orifice in the exhaust system (Orifice A) was calibrated with a rounded approach air cart manufactured by General Motors Corporation. The orifices in the sampling line (Orifice B) and in the dilution air line (Orifice C) were calibrated using the wet test meters.

With the schemes described above the ratios of the pressure drops across Orifices A-B and A-C ($\Delta P_A/\Delta P_B$ and $\Delta P_A/\Delta P_C$) were kept constant during the tests.

Two high vacuum pumps were used to provide the flow through the sampling train.

CHAPTER 3

EXPERIMENTAL PROCEDURES

All tests were performed following the same sequence of steps: a) the engine and exhaust system were conditioned, b) particulate samples were collected, c) the weight of the collected particles was measured, and d) the samples were analyzed for sulfate content.

3.1 Test Conditions

A summary of the test conditions under which the samples were taken is given in Table (3.1).

In test series I and II samples were collected at different positions along the simulated exhaust system. In all other tests the samples were collected at one position 40 cm downstream of the catalytic reactor. Tests III through XX were performed first with the pelleted reactor. The tests were then repeated with the monolithic catalytic reactor.

The last column in the table describes the variables studied during each test.

3.2 Engine and Exhaust Conditioning

Before taking the final data the engine and exhaust system were operated at the test conditions to allow the emissions to stabilize. When the pelleted catalyst was installed the engine was conditioned for a period equivalent to 8000 km at 88 km h^{-1} with fuel containing 0.017% sulfur and then for a period equivalent to 2500 km at 88 km h^{-1} with fuel containing 0.1% sulfur. When the pelleted catalyst was replaced by the monolithic catalyst the engine was operated for a period equivalent to 2500 km at 88 km h^{-1} with 0.1% sulfur content fuel.

Table 3.1 Test Conditions

Test Series	Catalyst	Engine Speed (RPM)	Engine Load BHP	A/F Ratio	Initial Spark Advance	Road Speed Equivalent	Test
I	None	-	-	-	4°	Cyclic(*)	-
II	Pelleted	1800	24.5	14.6	4°	88 km h ⁻¹ Cruise	H ₂ SO ₄ Condensation
III	Pelleted & Monolithic	1800	24.5	15.0	4°	88 km h ⁻¹ Cruise	Secondary Air and Space Velocity
IV	Pelleted & Monolithic	1800	24.5	15.0	4°	88 km h ⁻¹ Cruise	Fuel Sulfur Content
V	Pelleted & Monolithic	1800	24.5	15.0	-8°	88 km h ⁻¹ Cruise	Spark Retard
VI	Pelleted & Monolithic	1800	24.5	13.5	4°	88 km h ⁻¹ Cruise	A/F Ratio
VII	Pelleted & Monolithic	1800	24.5	16.7	4°	88 km h ⁻¹ Cruise	A/F Ratio
VIII	Pelleted & Monolithic	2000	30.0	15.0	4°	96 km h ⁻¹ Cruise	Secondary Air
IX	Pelleted & Monolithic	2000	30.0	15.0	4°	96 km h ⁻¹ Cruise	Fuel Sulfur Content
X	Pelleted & Monolithic	2000	30.0	17.0	4°	96 km h ⁻¹ Cruise	A/F Ratio

(*) The cycle employed in the tests was an approximation adopted in order to simulate on an engine dynamometer the 1967 7 Mode Federal Test Procedure developed for cars. The simulated cycles are described in Appendix A2.

Table 3.1 (continued)

Test Series	Catalyst	Engine Speed (RPM)	Engine Load BHP	A/F Ratio	Initial Spark Advance	Road Speed Equivalent	Test
XI	Pelleted & Monolithic	2000	30.0	15.0	4°	96 km h ⁻¹ Cruise	Space Velocity
XII	Pelleted & Monolithic	1300	11.7	15.0	4°	64 km h ⁻¹ Cruise	Secondary Air
XIII	Pelleted & Monolithic	1300	11.7	15.0	4°	64 km h ⁻¹ Cruise	Fuel Sulfur Content
XIV	Pelleted & Monolithic	1300	11.7	13.7	4°	64 km h ⁻¹ Cruise	A/F Ratio
XV	Pelleted & Monolithic	1300	11.7	16.5	4°	64 km h ⁻¹ Cruise	A/F Ratio
XVI	Pelleted & Monolithic	1300	11.7	15.0	4°	64 km h ⁻¹ Cruise	Space Velocity
XVII	Pelleted & Monolithic	750	3.9	13.0	4°	35 km h ⁻¹ Cruise	Secondary Air
XVIII	Pelleted & Monolithic	750	3.9	13.0	4°	35 km h ⁻¹ Cruise	Fuel Sulfur Content
XIX	Pelleted & Monolithic	750	3.9	13.0	4°	35 km h ⁻¹ Cruise	Space Velocity
XX	Pelleted & Monolithic	-	-	-	-	Cyclic*	Fuel Sulfur Content

When the engine was started it was warmed up for 1 1/2 hours. Then, before each steady engine speed test the engine was operated for three hours at the condition of the test. The sampling was done for a thirty minute period. For cyclic tests the system was warmed up through 10 cycles before sampling. Each test was repeated five times and the average of the five data points are shown in the results presented in the next section. There was a maximum of ± 20 percent spread in the data. Within this spread there were no noticeable changes in any of the parameters measured. This suggests that within the time span of the tests thermal storage did not have an appreciable influence on the results.

3.3 Test Procedure

A typical test was performed in the following manner. The probe was placed in the location under study, the filters were weighed, placed in the collection unit, and the system was warmed up.

After the engine warmed up, the temperature of the collection unit was adjusted to the appropriate value and sampling started. During steady operation (test II through XIX) the temperatures of the sample and the catalyst were recorded every five minutes. During cyclic operation the temperatures were measured at the end of each cycle. It is noted that the catalyst temperature was measured with a thermocouple inserted into the reactor and imbedded among the pellets. For the pelleted catalyst the thermocouple was near the middle of the reactor, for the monolithic one it was near the exit.

In addition to these temperatures the following parameters were recorded throughout each test: a) temperature and pressure of the gas through the wet test meters, b) the engine speed and load, c) fuel flow

rate, d) air flow rate, e) manifold vacuum, f) atmospheric pressure, and g) room temperature.

After each test the filters were placed for 24 hours in an airtight container containing CaCl_2 as desiccant, and were then weighed and prepared for chemical analysis.

3.4 Measurement of Sulfuric Acid Content

The sulfuric acid content of the collected particulate sample was determined by the Barium-Thorin Titrimetric procedure [17,18].

The filter was placed in a covered Pyrex flask containing 50 ml of deionized water. After 12 hours, 25 ml of the liquid were taken from the flask, and placed in a centrifuge for 15 minutes to separate out filter fibers. Following the centrifuging 15 ml of the liquid were passed through a weakly acid, carboxylic (polymethacrylic) cation exchange resin (RCOO-H^+) to remove all positive ion interferences. This liquid was then diluted with deionized water to give a total volume of 25 ml. Ten ml of this solution were mixed with 40 ml of isopropanol. Two drops of thorin indicator solution were added to this liquid. The liquid sample thus prepared was titrated with a 0.001 molar solution of $\text{Ba}(\text{ClO}_4)_2$ diluted in a mixture containing 20% deionized water and 80% isopropanol. The change in color of the liquid was monitored with a Bausch and Lomb Spectronic 20 colorimeter by measuring the change in absorbance of the solution at a wavelength of 520 nm. The amount of titrant added up to the end of the titration was proportional to the H_2SO_4 concentration in the sample.

The titrant solution was calibrated against a solution of H_2SO_4 of "known" concentration. This "known" solution was calibrated by tit-

rating it with a NaHCO_3 solution using a glass electrode pH meter to monitor the titration. Several blank filters were tested and their sulfuric acid contents were found to be negligible (less than 2%) compared to the sulfuric acid content of the sample. The effect of filter material on the SO_2 to H_2SO_4 conversion was checked by making tests without the catalyst in the exhaust. Even at high SO_2 concentrations H_2SO_4 could not be detected on the filters.

3.5 Sampling Temperature and Sample Dilution

Sulfuric acid condenses and collects on the filters only below about 350 K, the exact temperature being dependent upon the test conditions. The exhaust gas is generally above this temperature. Thus, in order to measure the sulfuric acid content the sample had to be cooled. However, at low temperatures water also condenses and collects on the filters. Water condensation may be prevented by diluting the sample with ambient air, and this method was adopted in the present tests. A series of preliminary tests were performed to establish the proper sampling temperature and to determine the effects of dilution on the emission of particulates.

First, particulate emission was measured with the engine operating without the catalyst (unleaded fuel). Above 400 K the particulate emission (g km^{-1}) was determined both with and without dilution (dilution ratio 8:1). When the sample temperature was higher than 400 K, the sample temperature was adjusted to the same value as that of the exhaust gas at the location of the probe. Above 400 K the results were unaffected by the dilution and were insensitive to changes in the sample gas temperature (Fig. 3.1). This can be explained by the fact that

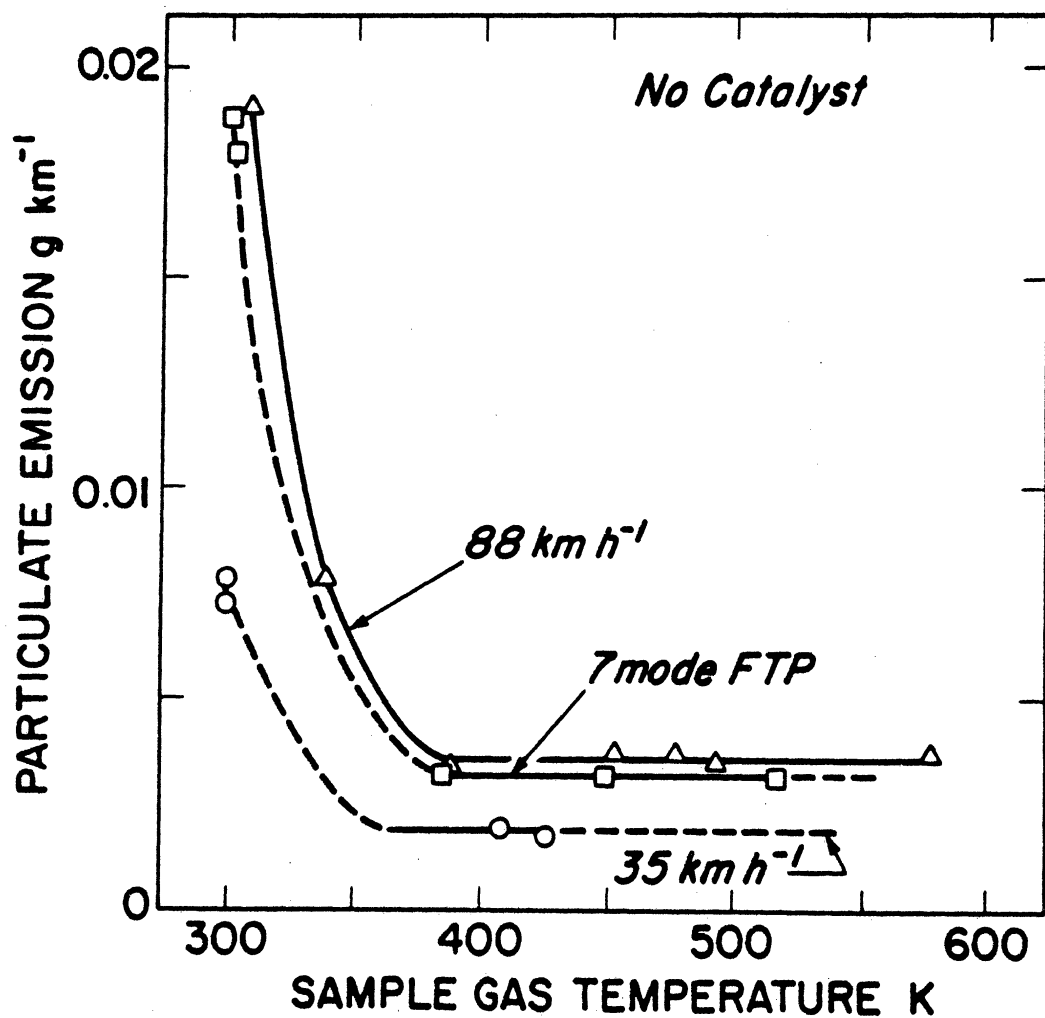


Fig. 3.1 Particulate emission versus sample gas temperature during the simulated 7 Mode Federal Test Procedure, and 35 km h⁻¹ and 88 km h⁻¹ cruise conditions (— ---) fit to data

particulates collected above 400 K are mostly carbon formed in the combustion chamber due to the dehydrogenation of hydrocarbons [16,19].

Below 400 K the sample was diluted with air. These measurements showed that below 390 K there is a large increase in particulate emission, due mostly to condensation of high molecular weight organic compounds present in the exhaust gas [20-23].

It is interesting that during the simulated 7 Mode Federal Test Procedure approximately twice the amount (by weight) of particulates is emitted as at 35 km h⁻¹ steady speed (35 km h⁻¹ corresponds to the average speed of the cycle). A similar trend was observed by Ter Haar et al [24].

Second, particulate emission as a function of sample gas temperature was measured with fuel containing 0.017% sulfur (Fig. 3.2). These tests were performed both with and without the catalysts with the objective of determining the sample gas temperature at which most of the sulfuric acid condensed. Above 400 K neither dilution nor the presence of the catalysts affected the amount of particulate matter emitted suggesting that most particles were carbon emitted directly from the combustion chamber (Ganley and Springer, [16]). Deposition in the catalyst may account for the small difference in the results.

Below 400 K the sample was diluted (dilution ratio 8:1). There is a sharp increase in the amount of particulate matter emitted below 390 K. In the absence of the catalyst this increase is due to condensation of heavy hydrocarbons. For the catalyst equipped engine the increase is most likely due to condensation of sulfuric acid. Below 350 K the amount of particulate matter collected remained nearly constant when using a catalyst, implying that most of the sulfuric acid condensed out

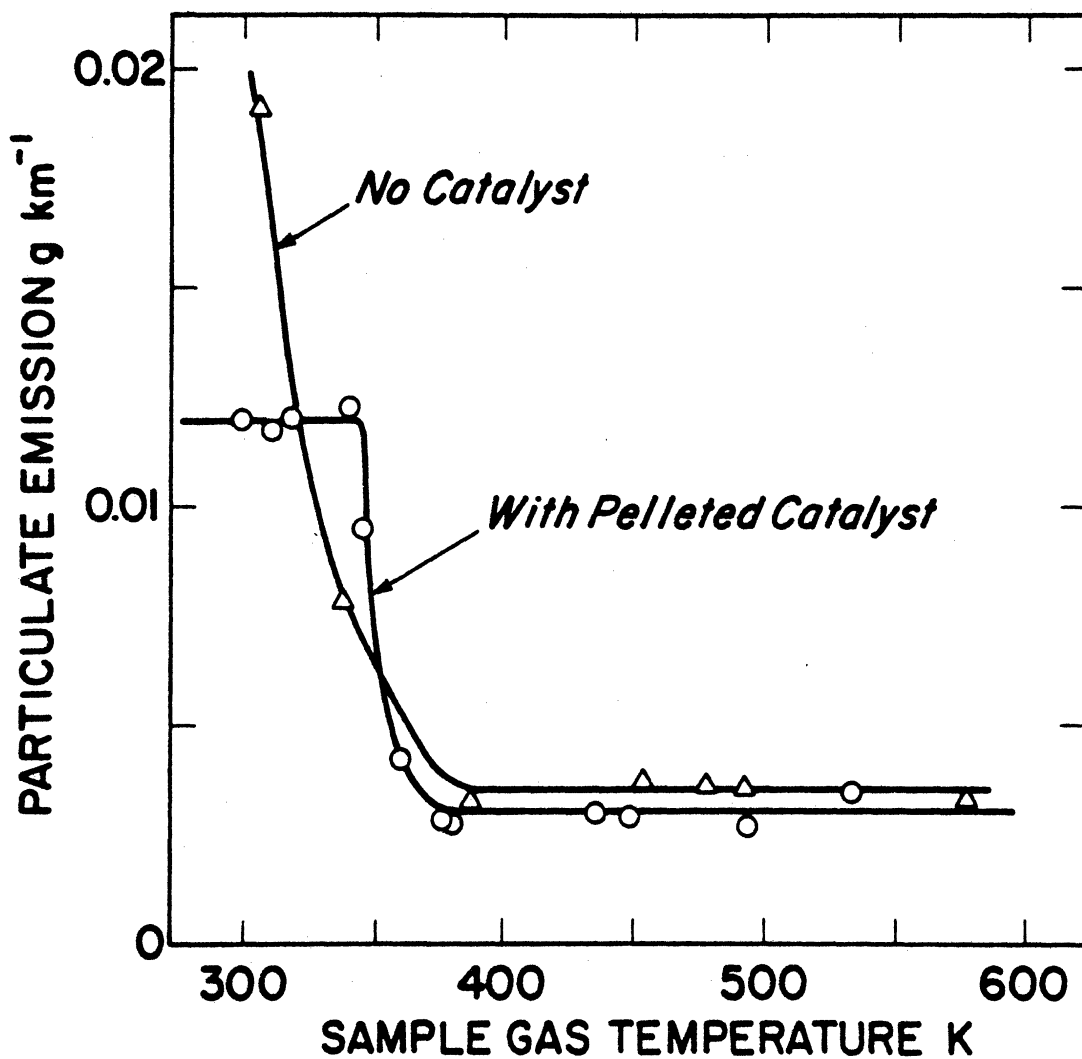


Fig. 3.2 Particulate emission with and without a pelleted catalyst. 88 km h^{-1} cruise condition. Catalyst temperature 755 K . (—) fit to data

of the gas stream. On the basis of these results, in all subsequent tests (i.e. for all the data reported in the next section) the collection unit was kept in the 305-315 K temperature range by diluting the sample with ambient air (dilution ratio 8:1). These temperatures were appropriate also when fuels with higher sulfur content (i.e. sulfur content above 0.017%) were used since in this case the condensation process was completed at even higher temperatures.

CHAPTER 4

RESULTS

The major objective of this investigation was to evaluate the parameters which affect the sulfate and particulate emissions from spark ignition engines equipped either with a monolithic or with a pelleted catalyst. Particular attention was focused on the effects of a) catalyst temperature, b) fuel sulfur content, c) exhaust gas mass flow rate through the catalyst (space velocity), d) fuel consumption, e) air fuel ratio, and f) amount of secondary air on the amount of particulate matter emitted, on the amount of sulfuric acid emitted, and on the sulfur conversion. Tests were performed at engine speeds and loads corresponding to a 1970 full size Chevrolet cruising at 35, 64, 88 and 96 km h⁻¹, and under a simulated 7 Mode Federal Test Procedure.

It is important to note that in the following tests the effects of the various parameters were separated. This was accomplished by varying one parameter at a time. For example the temperatures of the catalysts were regulated by heating tapes and were thus unaffected by the engine speed and load or the secondary air. This must be borne in mind when evaluating the data and when comparing them to the results of other studies where generally several parameters were varied simultaneously.

4.1 Sulfur Conversion

The sulfur conversion (percent weight of sulfur in the fuel converted to sulfuric acid) as a function of space velocity, exhaust gas mass flow rate, speed, fuel sulfur content, and catalyst temperature is shown in Fig. 4.1. The data points are from the measurements. The lines were computed from the expression (see Appendix C),

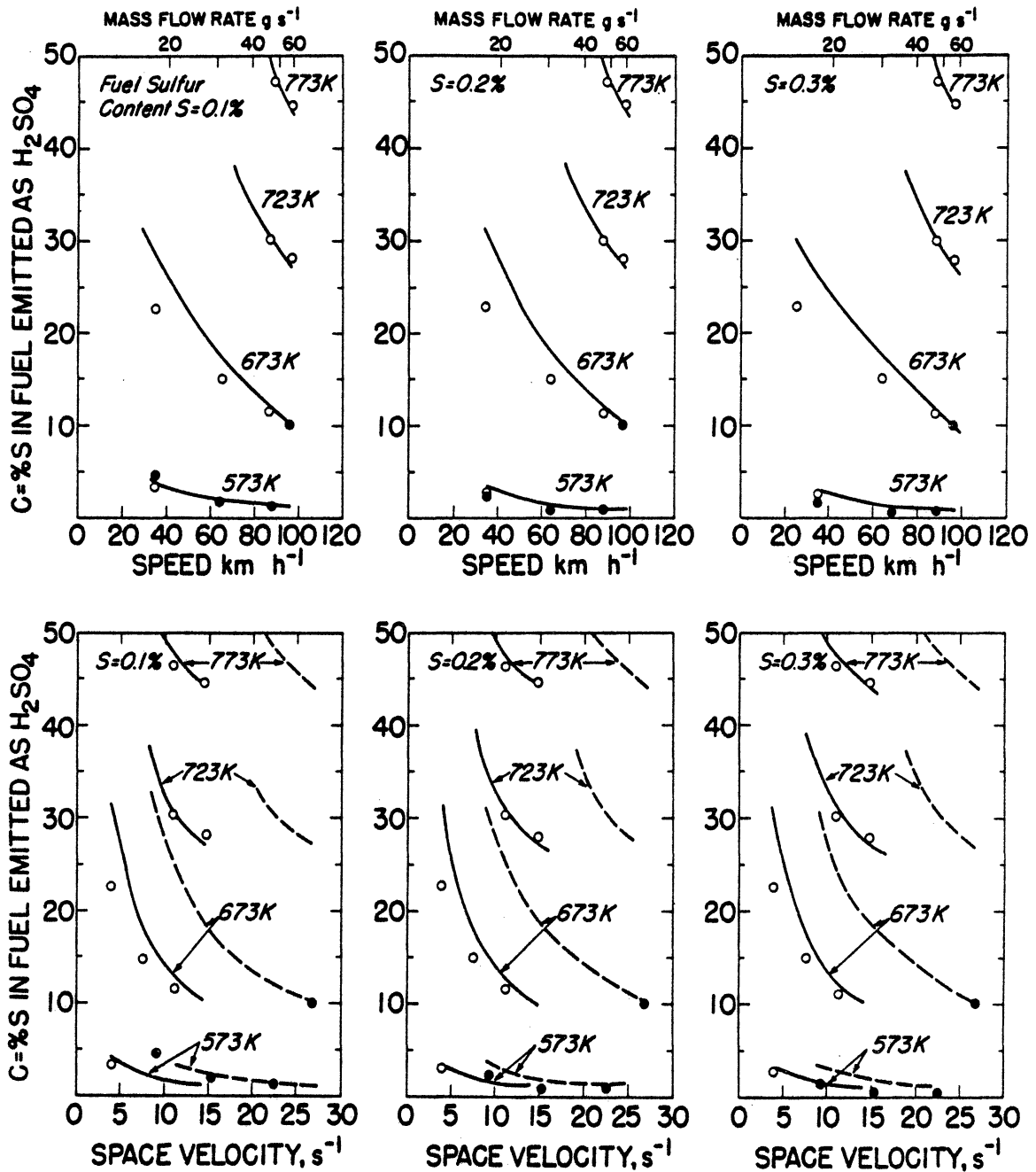


Fig. 4.1 Effects of space velocity (at 273 K and 1 atm), exhaust gas mass flow rate through the catalyst, catalyst temperature, and fuel sulfur content on the sulfur conversion. Indolene HC 0 fuel, A/F = 15.0, excess air = 25% ($\sim 5\% O_2$).
 ○ Pelleted catalyst data. ● Monolithic catalyst data.
 Solid and dashed lines were calculated from eq. (4.1) for the pelleted and monolithic catalysts, respectively.

$$C = (X_{SO_2})_E \left[1 - \exp\left(\frac{-km \frac{m_f}{m_c + m_f} \rho_{exh}}{m_f}\right) \right] \times 100 \quad (4.1)$$

where $(X_{SO_2})_E$ is the fraction of SO_2 converted into SO_3 at equilibrium, k is the rate constant for the conversion of SO_2 to SO_3 inside the catalyst, m is the mass of the catalyst, m_f is the mass of fuel burned in the engine per hour, m_c is the mass of air entering the engine per hour plus the mass of secondary air entering the reactor per hour, and ρ_{exh} is the density of the exhaust gas ($kg\ dm^{-3}$). Values for $(X_{SO_2})_E$ and for the product km are given in Appendix C.

In Fig. 4.2 the results of Fig. 4.1 were crossplotted using temperature as the abscissa and the exhaust gas mass flow rate (and speed) as the variable parameter. The solid lines in Fig. 4.2 were calculated from eq. (4.1) with the values of km given in Appendix C. The left side of the peak corresponds to reactions in the kinetically limited region, the right side corresponds to reactions in the region limited by chemical equilibrium. The data of Creswick et al [6], Trayser et al [7], and Holt et al [8] obtained with pelleted and monolithic catalysts are also included in Fig. 4.2. The data reported by these investigators were shifted 70 K to the right (as suggested by Dr. W.R. Pierson) to allow for the fact that these investigators measured the catalyst temperature at the catalyst exit and not inside the catalyst. The results of Bradow and Moran [2], and Somers et al [3] are not included in Fig. 4.2 because these investigators did not report the catalyst temperature. The data of Begeman et al [9] and Irish and Stefan [10] were not included because these data were taken under transient conditions.

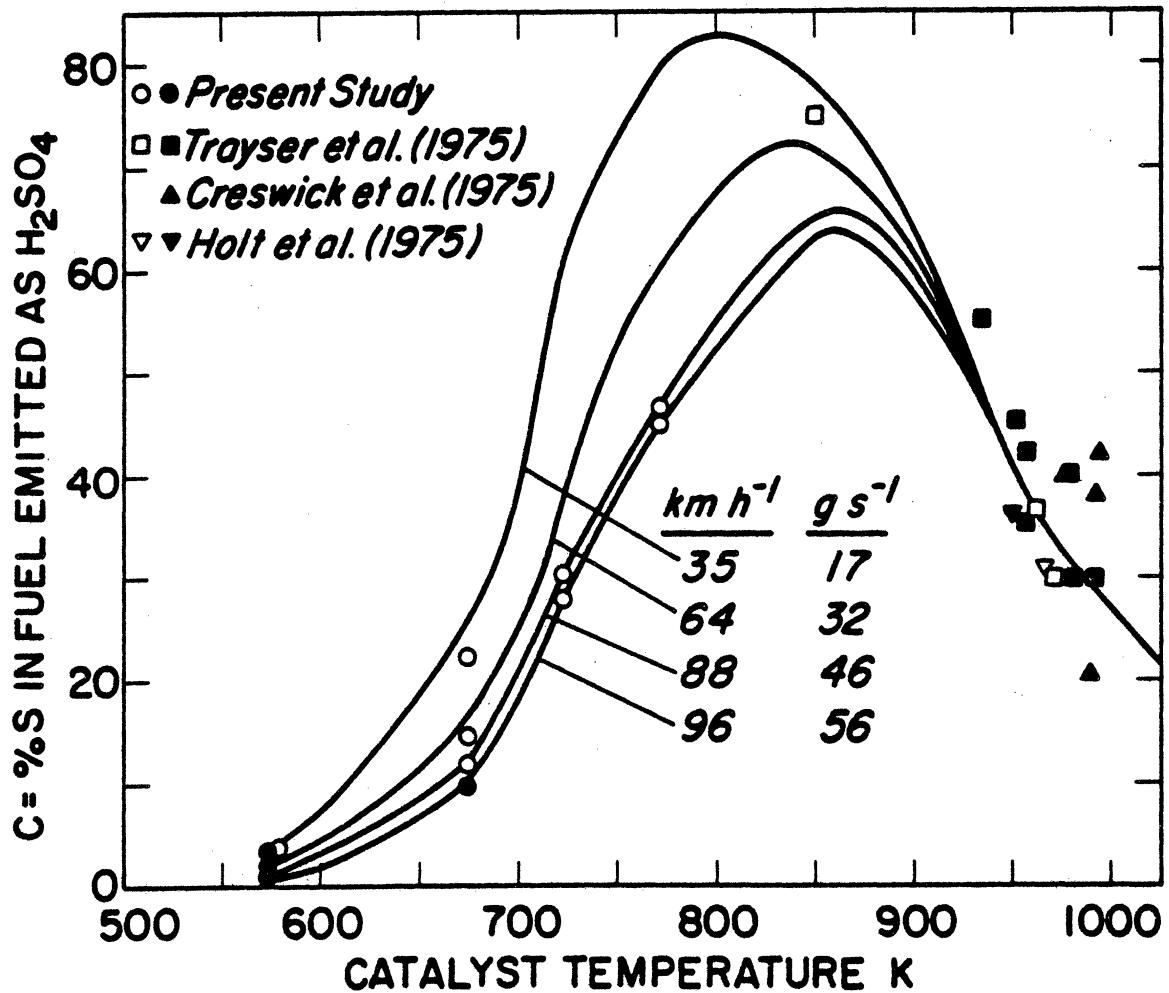


Fig. 4.2 Sulfur conversion as a function of temperature, speed, and exhaust gas mass flow rate through the catalyst. Indolene HO 0 fuel with 0.1% sulfur content. A/F = 15.0, excess air 25% (~5% O₂). Open and closed symbols represent pelleted and monolithic catalyst data, respectively. Solid lines were calculated from eq. (4.1)

Mikkor et al [12], Hammerle and Mikkor [13], and Hammerle and Truex [14] also measured sulfur conversion. Their data are not included here because instead of an engine they used a simulated exhaust system. Nevertheless, their results show a trend similar to the curves in Fig. 4.2.

From Fig. 4.2 it is seen that for all the temperatures used in the present tests (catalyst temperatures less than 800 K) the sulfur conversion increased with temperature. This indicates that the reaction in the catalyst was kinetically limited as opposed to being limited by chemical equilibrium [25]. At catalyst temperatures above ~ 900 K, where most other tests were performed, the reactions were in the chemical equilibrium region.

Figure 4.1 shows that in the temperature range of the present tests (i.e. below ~ 800 K) the sulfur conversion decreased with increasing exhaust gas mass flow rate and increasing space velocity, the latter being defined as the exhaust gas volume flow rate at 273 K and 1 atm divided by the catalyst volume [25]. The reason for this is that at higher flow rates (which corresponds to higher engine speeds and loads) the flow rate through the catalyst increased, decreasing the residence time inside the catalyst. However, the residence time (inverse space velocity) affects the conversion only in the kinetically limited region. At catalyst temperatures above ~ 900 K the reactions are in the chemical equilibrium region and the conversion is not influenced by the flow rate.

At catalyst temperatures below ~ 800 K, at the same space velocity the sulfur conversion is different for the two different types of catalysts. However, for a given exhaust gas mass flow rate (i.e. given

engine speed and load) the sulfur conversion is practically the same for both the pelleted and monolithic catalysts. Thus, under the same conditions, in a given engine both catalysts would result in approximately the same sulfur conversion.

Figure 4.1 also shows the effect of fuel sulfur content on the sulfur conversion. The conversion is insensitive to the fuel sulfur content above ~ 573 K indicating that the catalytic oxidation of SO_2 is limited by adsorption of SO_2 by the catalyst. Using the monolithic catalyst the amount of sulfur emitted as H_2SO_4 and the sulfur conversion were also measured at 530 K. The results in Fig. 4.3 show that for 530 and 573 K the conversion decreases with fuel sulfur content indicating that the limiting mechanism is desorption of SO_3 from the catalyst [25].

4.2 Sulfuric Acid Emission

Once the percent conversion of SO_2 into SO_3 (denoted by the symbol C) is known (see Fig. 4.1) the amount of sulfuric acid emitted can be calculated from the expression

$$\text{H}_2\text{SO}_4 = 3.06 (F) \left(\frac{S}{100}\right) \left(\frac{C}{100}\right) \text{ g km}^{-1} \quad (4.2)$$

where F is the fuel consumption in g km^{-1} (Fig. 4.4), and S is the sulfur content of the fuel (percent sulfur per weight in the fuel). 3.06 is the gravimetric factor between H_2SO_4 and sulfur. Note that the engine speed, space velocity and catalyst temperature do not enter into eq. (4.2) directly. These variables affect the H_2SO_4 emission through their effects on F, S, and C.

The measured H_2SO_4 emission and the values calculated from eq. (4.2) are shown in Fig. 4.5. The sulfuric acid emission has a minimum at about

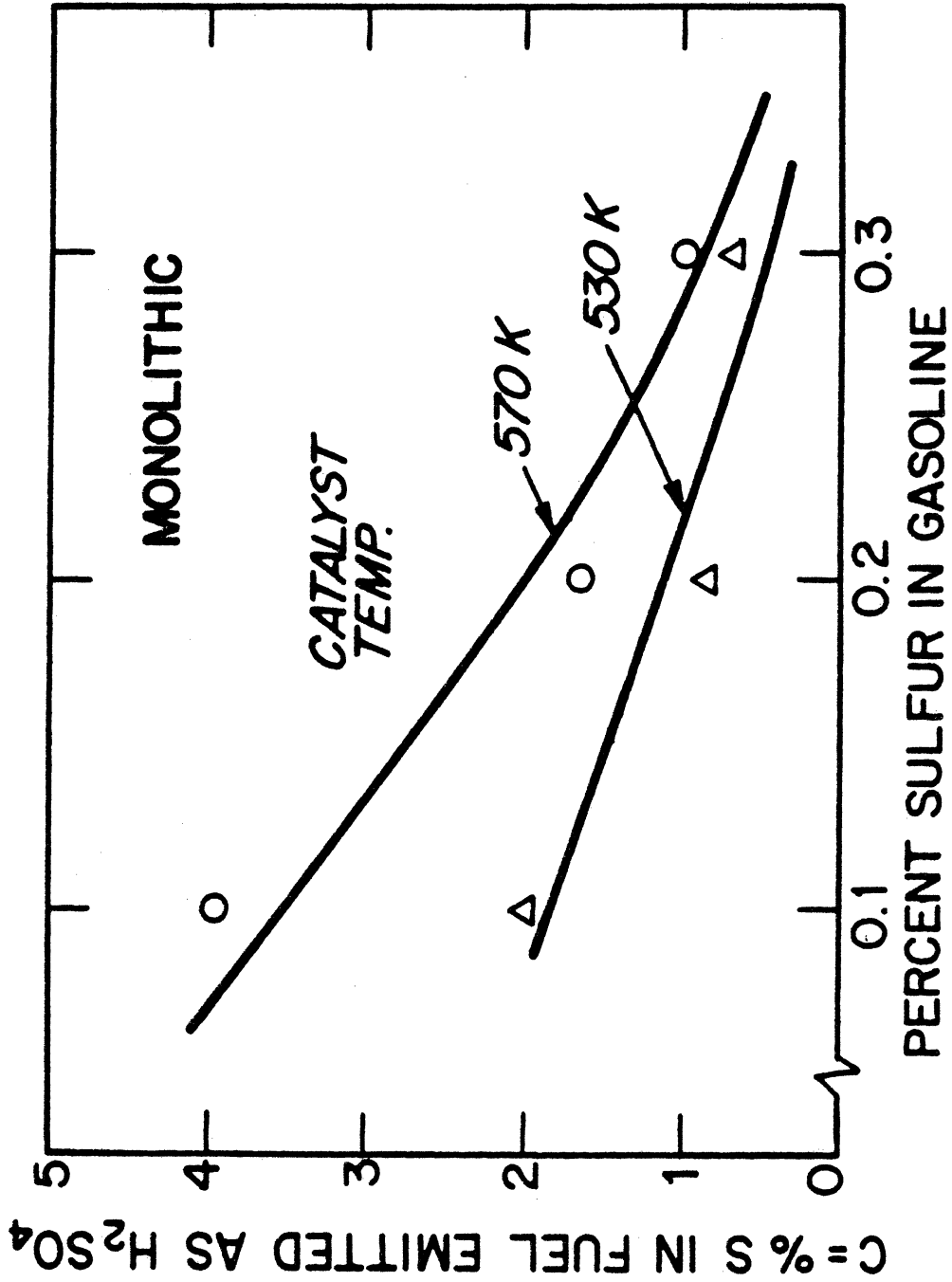


Fig. 4.3 Sulfur conversion versus percent sulfur in fuel for 530 and 570 K. Monolithic catalyst.

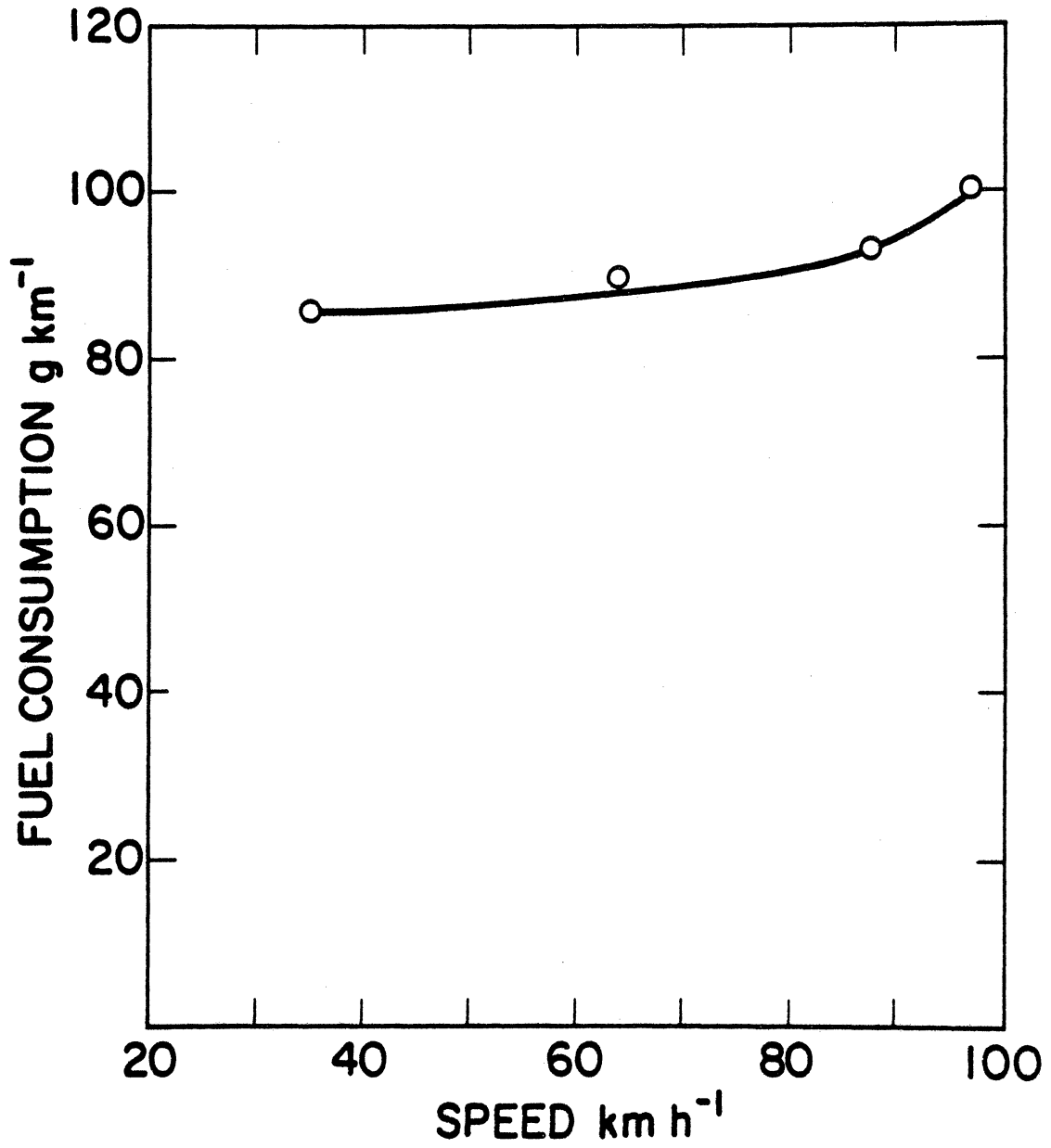


Fig. 4.4 Fuel consumption versus speed (—) fit to data

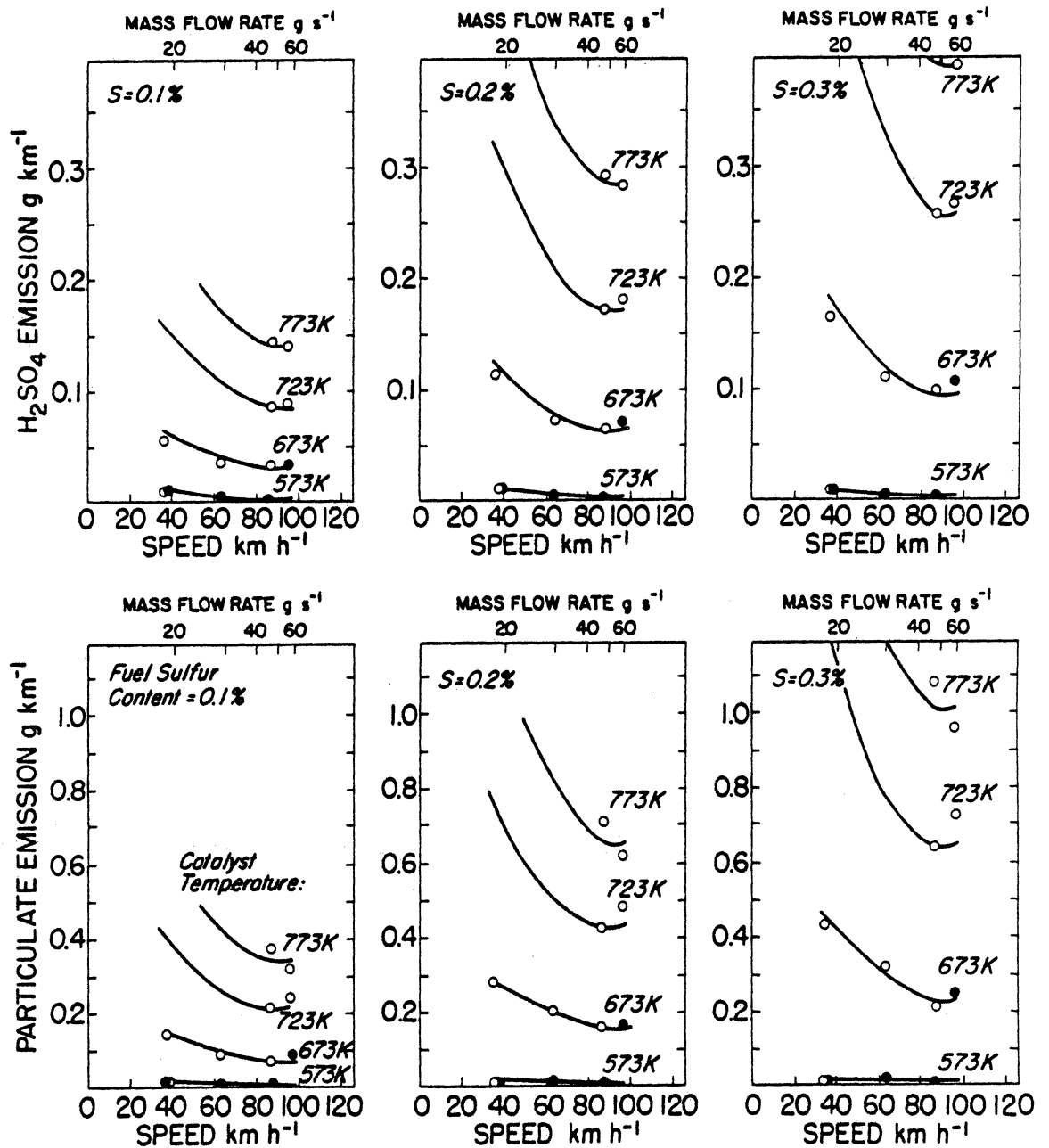


Fig. 4.5 Effects of speed, exhaust gas mass flow rate through the catalyst, catalyst temperature, and fuel sulfur content on H_2SO_4 and particulate emissions. Indolene HC 0 fuel, A/F = 15.0, excess air = 25% ($\sim 5\% O_2$). \circ Pelleted catalyst data. \bullet Monolithic catalyst data. Solid lines were calculated from eqs. (4.2) and (4.4)

90 km h⁻¹. As was shown before, the sulfur conversion decreases continuously with increasing speed. However, the fuel consumption increases with speed giving rise to the minimum in the sulfuric acid emissions.

The sulfuric acid emission for the simulated 7 Mode Federal Test Procedure is shown in Figs. 4.6 and 4.7. In these figures the ranges of sulfuric acid emission at the steady speed corresponding to the average speed of the cycle (35 km h⁻¹) are also shown. For the simulated 7 Mode Federal Test Procedure the amount of sulfuric acid emitted increased linearly with the fuel sulfur content. At 35 km h⁻¹ a similar increase in sulfuric acid with fuel sulfur content was observed with the pelleted catalyst. With the monolithic catalyst at the steady 35 km h⁻¹ speed the sulfuric acid emission seems to be insensitive to the fuel sulfur content. The latter can be explained by noting that the rate of reaction at which the SO₂ to SO₃ conversion occurs depends on the concentration of SO₂ in the exhaust gas at the inlet to the catalyst and on the catalyst temperature [25]. At low SO₂ concentrations and at high temperatures the mechanism limiting the formation of SO₃ is the adsorption of SO₂ by the catalyst. Under these conditions the reaction rate varies nearly linearly with the SO₂ concentration. At high SO₂ concentrations or low temperatures the rate of reaction becomes constant. In this region the reaction is controlled by desorption of SO₃ from the catalyst. In between the adsorption and desorption controlled regions the reaction is governed mostly by chemical reaction. The fact that the amount of sulfuric acid emitted remained constant indicates that the reactions in the catalyst are in the desorption controlled region (high SO₂ concentration, low catalyst temperature) where the SO₂ concentration at the catalyst inlet

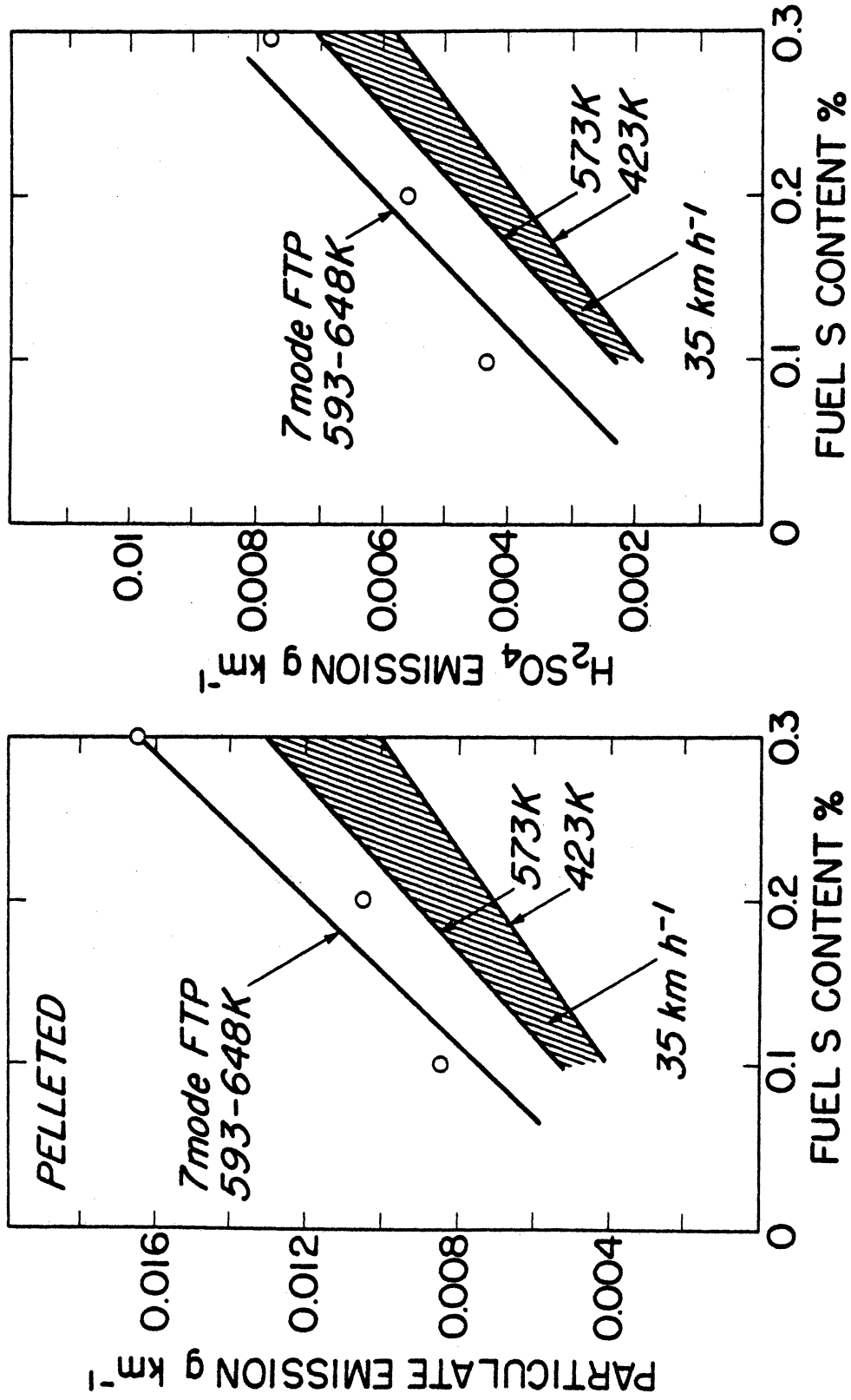


Fig. 4.6 Particulate and H_2SO_4 emissions during simulated 7 Mode Federal Test Procedure and 35 $km\ h^{-1}$ cruise condition. Pelleted catalyst. Temperatures indicated correspond to catalyst temperature. Indolene H0 0 fuel

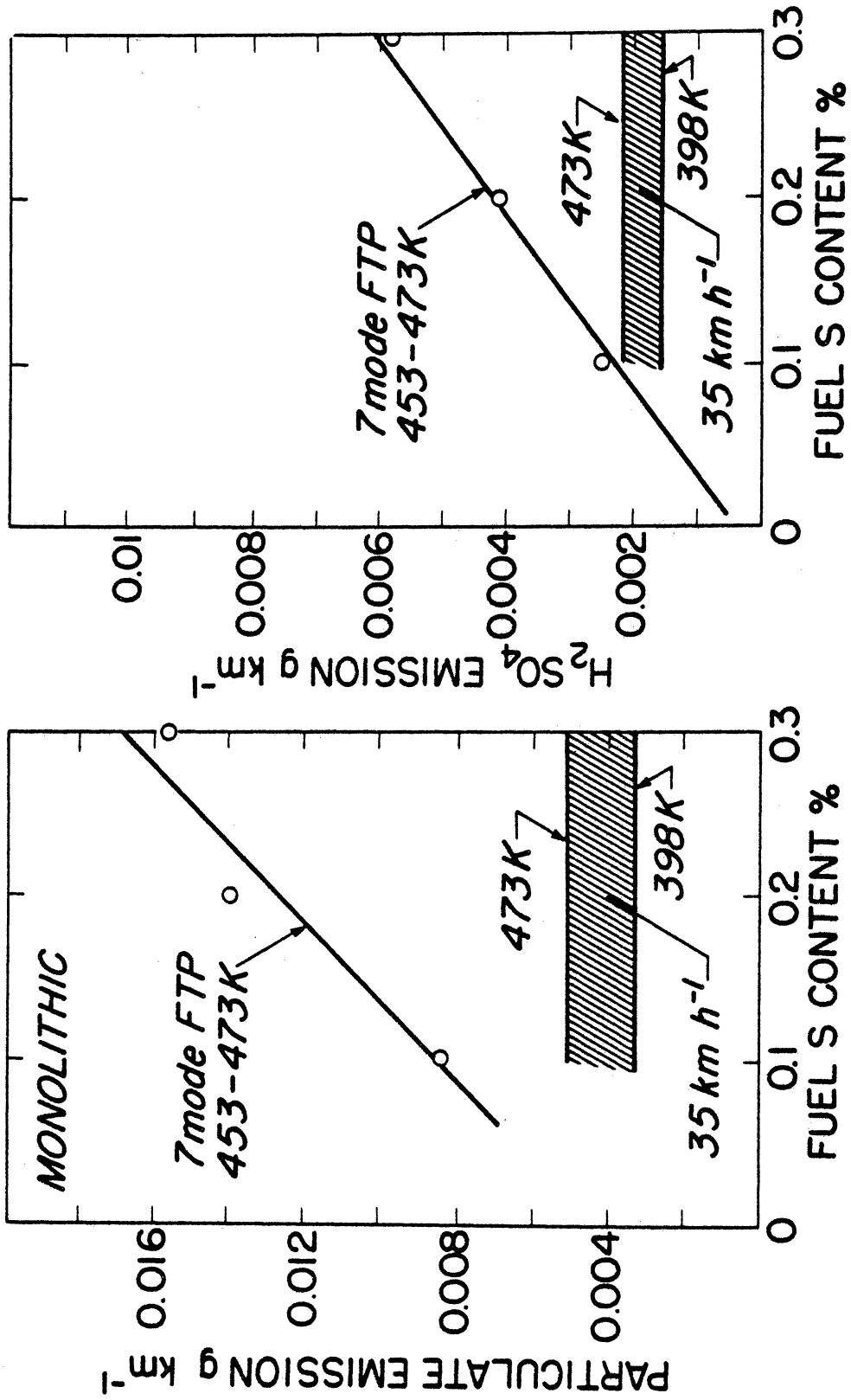


Fig. 4.7 Particulate and H_2SO_4 emissions during simulated 7 Mode Federal Test Procedure and 35 $km\ h^{-1}$ cruise condition. Monolithic catalyst. Temperatures indicated correspond to catalyst temperature. Indolene H0 0 fuel

does not affect the reaction. Since the amount of SO_2 is proportional to the fuel sulfur content, in this region the fuel sulfur content does not influence the results significantly. At higher catalyst temperatures the reactions are not in the desorption region and the amount of sulfuric acid emitted depends on the fuel sulfur content.

4.3 Particulate Emission

There is a distinct similarity between the amounts of sulfuric acid and particulate matter emitted, because the particulates are composed mostly of sulfuric acid and water [4]. Consequently, the amount of emitted particulate matter P is expected to be proportional to the amount of H_2SO_4 emitted, i.e.

$$P = A (\text{H}_2\text{SO}_4 \text{ emitted}) \quad g \text{ km}^{-1} \quad (4.3)$$

where A is a proportionality factor accounting for the presence of the water. Equations (4.2) and (4.3) give

$$P = A (3.06)(F) \left(\frac{C}{100}\right) \left(\frac{S}{100}\right) \quad g \text{ km}^{-1} \quad (4.4)$$

The value of A was obtained by matching eq. (4.4) to data obtained at steady speeds (Fig. 4.5). This procedure yielded A in the range 2.2-2.8. The lines in Fig. 4.5 were computed using the average value of $A = 2.4$.

As in the case of sulfuric acid emission, the engine speed affects the particulate emission only through the parameters F , S , and C .

Particulate emission under cyclic operation (simulated 7 Mode Federal Test Procedure) is shown in Figs. 4.6 and 4.7. As expected, the trend in the results is the same as for the sulfuric acid emission because of the relationship between the amounts of sulfuric acid and particulate matter emitted.

4.4 Space Velocity

Under the same engine operating conditions (speed and load), the effects of space velocity on particulate and sulfuric acid emissions and on the sulfur conversion are shown in Figs. 4.8 and 4.9. A reduction in space velocity and a corresponding increase in residence time results in an increase in sulfuric acid conversion and hence in an increase in the amounts of sulfuric acid and particulate matter emitted.

4.5 Secondary Air and Air Fuel Ratio

The effects of secondary air and air fuel ratio on the particulate emission were investigated at various steady engine speeds. Sulfur conversion, sulfuric acid, and particulate emissions as a function of secondary air injected into the exhaust before the catalyst are given in Figs. 4.10 and 4.11. The amount of secondary air does not seem to affect the results suggesting that there is sufficient oxygen for the reaction to be completed. These results tend to agree with those reported by Mikkor et al [12] and Hammerle and Truex [14]. At smaller amounts of secondary air the secondary air might affect the results but the amounts needed to observe these effects could not be achieved in the present tests.

The air fuel ratio does not seem to influence the results provided the catalyst temperature is kept constant, and sufficient oxygen is supplied (through secondary air injection) to the catalyst to oxidize the unburned hydrocarbons, carbon monoxide, and sulfur dioxide (Fig. 4.12).

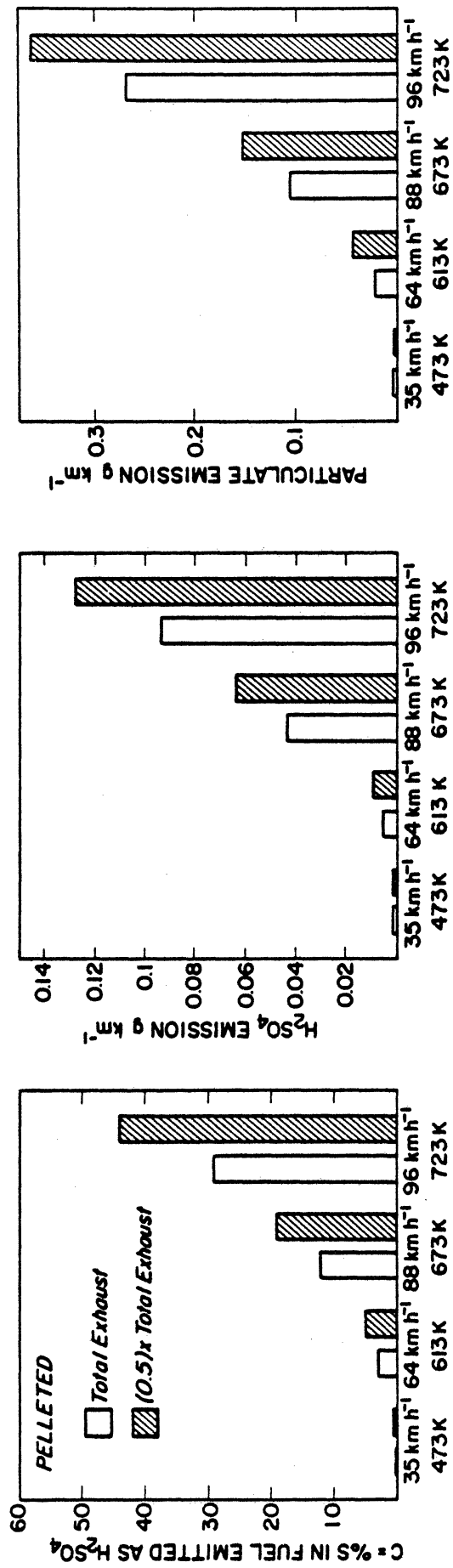


Fig. 4.8 Effects of flow rate through a pelleted catalyst on sulfur conversion, H₂SO₄ emission, and particulate emission. Open symbols are for the entire exhaust passing through the catalyst. Shaded symbols are for reduced flow rates. Indolene HC 0 fuel with 0.1% sulfur content. 25% excess air (~5% O₂). A/F = 15.0. Temperatures given are catalyst temperatures.

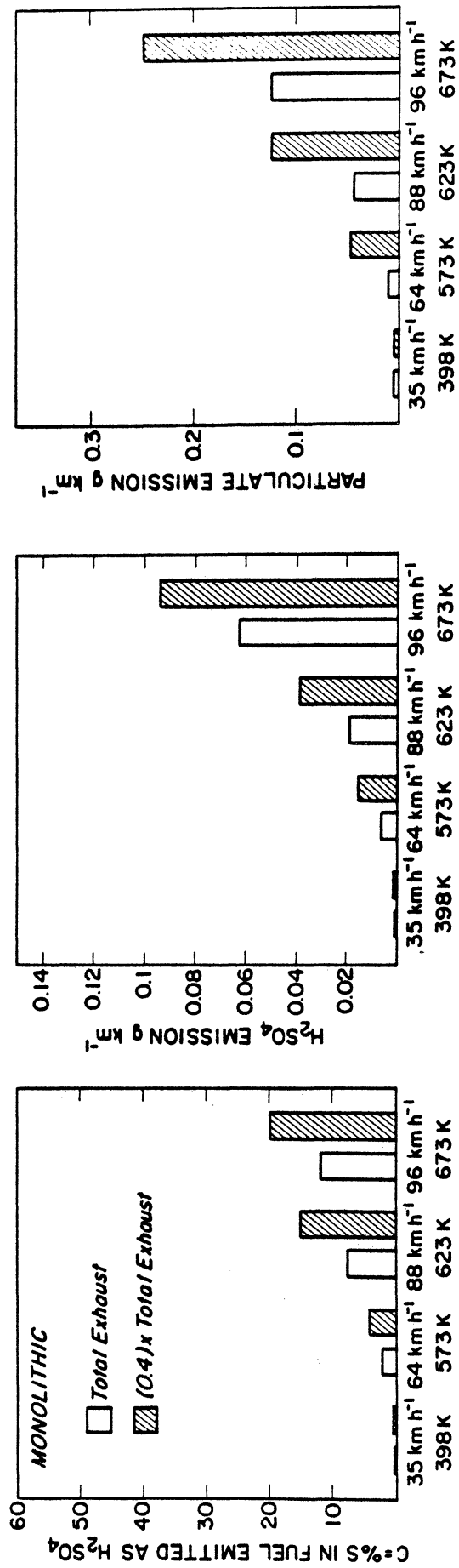


Fig. 4.9 Effects of flow rate through a monolithic catalyst on sulfur conversion, H₂SO₄ emission, and particulate emission. Open symbols are for the entire exhaust passing through the catalyst. Shaded symbols are for reduced flow rates. Indolene H0 0 fuel with 0.1% sulfur content. 25% excess air ($\lambda/F = 15.0$). $\lambda/F = 15.0$. Temperatures given are catalyst temperatures

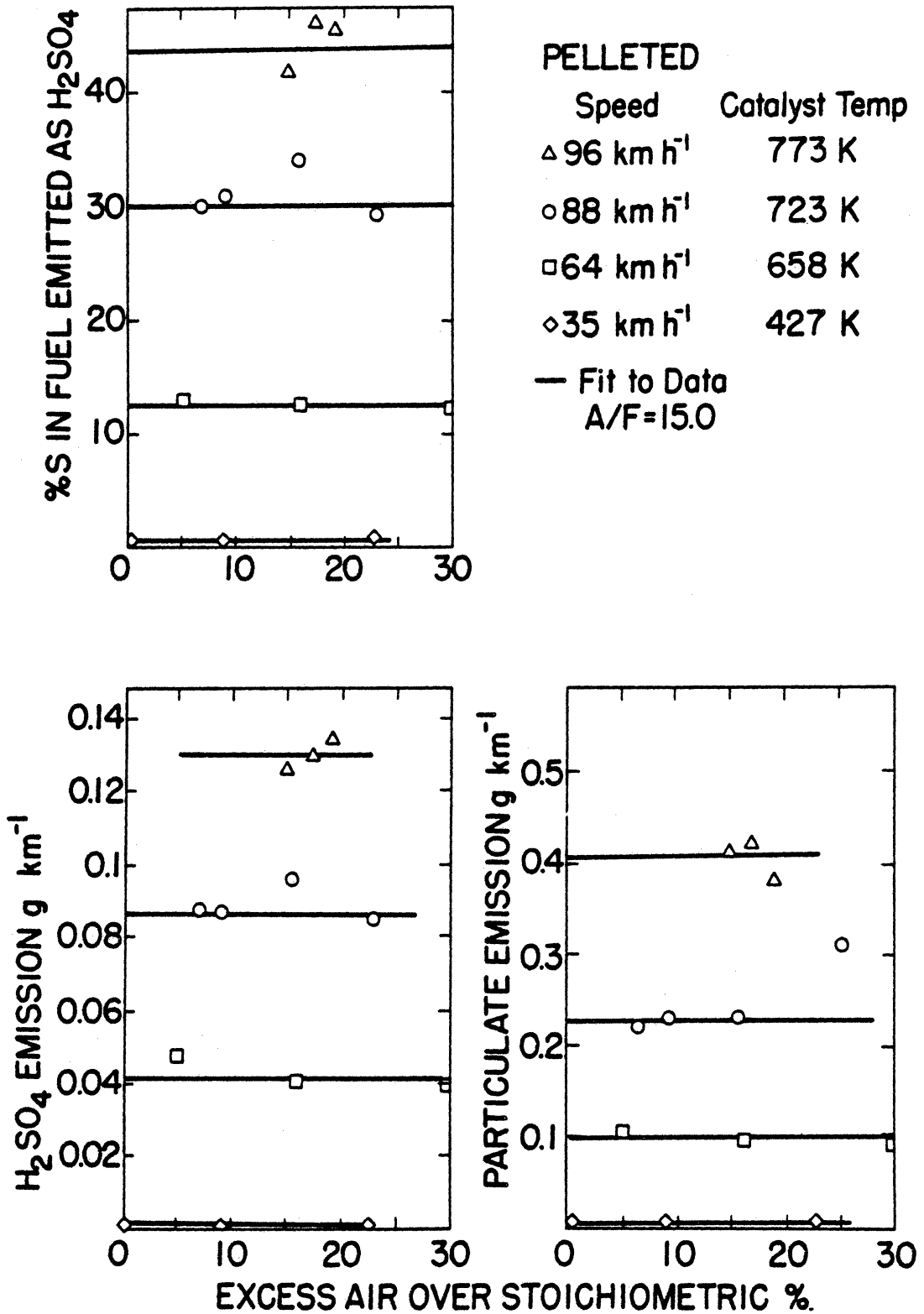


Fig. 4.10 Effects of secondary air on sulfur conversion, H₂SO₄ emission, and particulate emission for a pelleted catalyst. Indolene HO fuel with 0.1% sulfur content

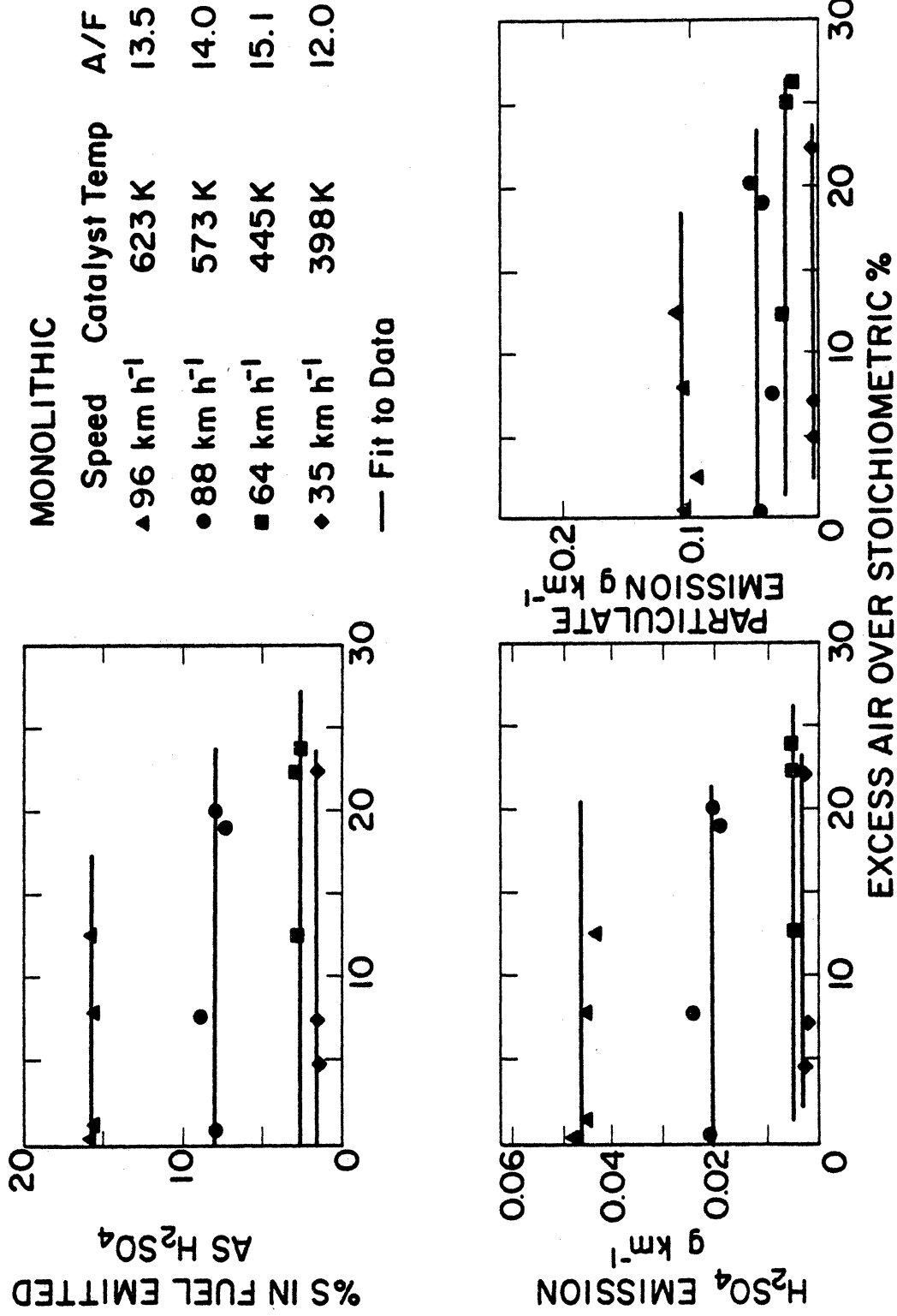


Fig. 4.11 Effects of secondary air on sulfur conversion, H₂SO₄ emission, and particulate emission for a monolithic catalyst. Indolene H0 C fuel with 0.1% sulfur content.

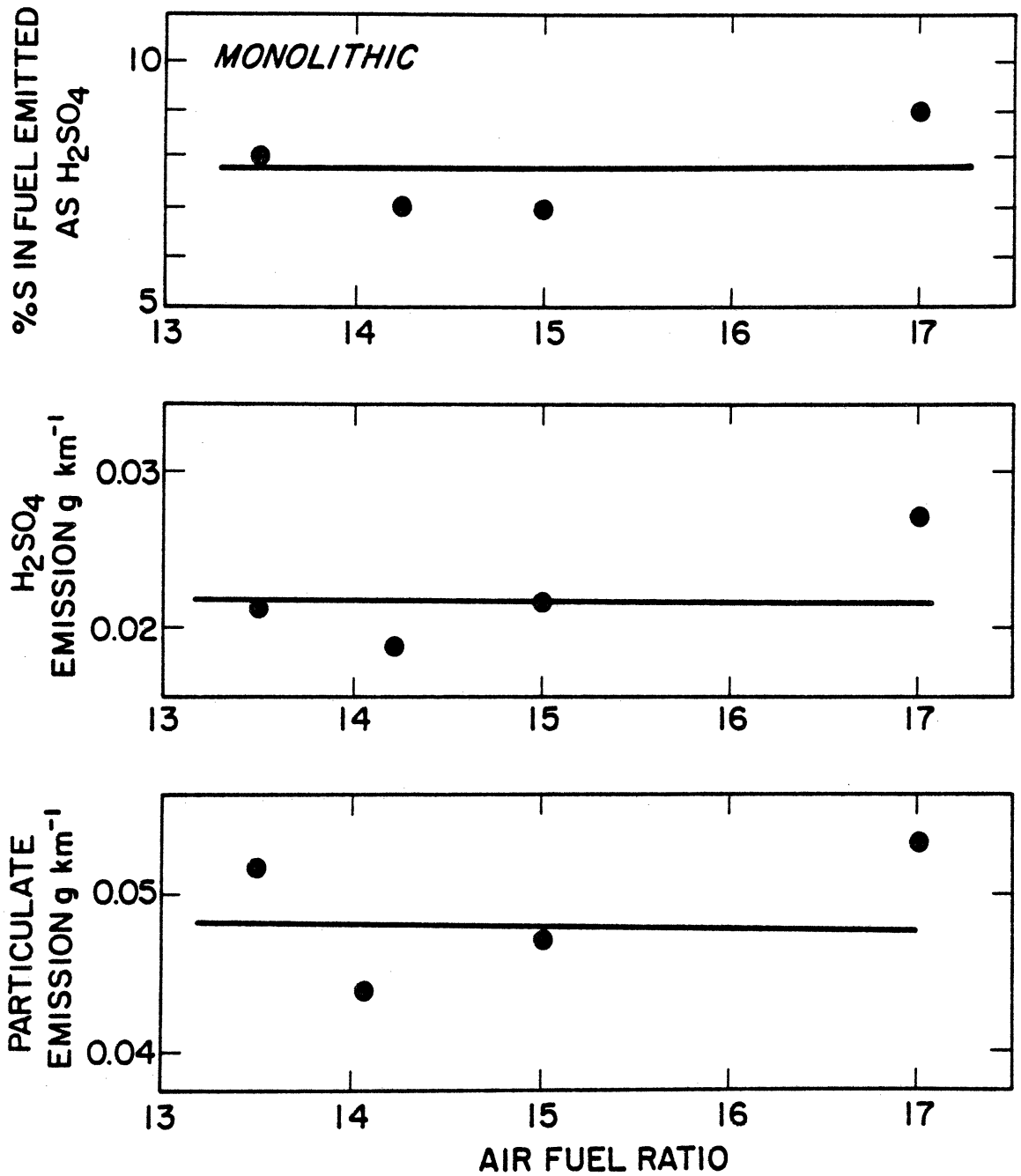


Fig. 4.12 Effects of air fuel ratio on sulfur conversion, H₂SO₄ emission and particulate emission for a monolithic catalyst. 88 km h⁻¹ cruise condition. Excess air 25% (5% O₂) catalyst temperature 623 K, Indolene HC 0 fuel with 0.1% sulfur content. (—) fit to data.

SUMMARY

Sulfate and particulate matter were measured in the exhaust of a 1970 Chevrolet 350 CID V-8 engine. The engine was equipped with either a pelleted or a monolithic catalyst. Samples collected in the exhaust of the engine were analyzed for total particulate weight and for sulfuric acid content. First, tests were performed to assess the appropriate sampling temperature. The results of the tests showed that for a dilution ratio of 8:1 the sulfuric acid condensed out of the gas stream at a temperature of about 350 K. All subsequent tests were performed at sampling temperatures below 315 K.

Measurements with a pelleted and a monolithic catalytic reactor were performed to study the particulate and sulfuric acid emissions at steady speeds (35, 64, 88, and 96 km h⁻¹). The effects of the following variables were studied

- a) catalyst temperature in the range 573-773 K
- b) fuel sulfur content in the range 0.1-0.3%
- c) fuel consumption
- d) exhaust gas flow rate through the catalyst (space velocity)
- e) amount of secondary air in the range 0-30% excess air
- f) air fuel ratio in the range 13.5-17.

The following general conclusions can be made on the basis of the results obtained.

- a) The conversion of SO₂ to SO₃ depends primarily on the catalyst temperature and mass flow rate through the catalyst.
- b) The amount of sulfate emitted depends on the sulfur conversion, fuel sulfur content, and fuel consumption.

c) Particulate emission depends on the sulfur conversion, fuel sulfur content, and fuel consumption.

d) The amount of secondary air did not seem to affect the sulfur conversion, particulate emission and sulfate emission. The amount of secondary air might affect the emissions for very small values (less than 1%) of oxygen available. However, such small values of excess oxygen could not be achieved in this experiment.

e) The fuel air ratio did not affect sulfur conversion, particulate emissions, and sulfate emission.

f) The engine variables (i.e. speed, load, spark timing) did not influence the sulfur conversion, particulate and sulfuric acid emissions. The effects of these parameters are manifested through their influence on the catalyst temperature, mass flow rate through the catalyst, and fuel consumption.

An analytical model of the processes occurring inside the reactor was developed. The model described well the present data in the temperature range 573-773 K. The model extrapolated to 1000 K also showed good agreement with data reported by other investigators.

Particulate and sulfate emissions were also investigated under a simulated 7 Mode Federal Test Procedure. The results showed that the particulate and sulfate emissions increased linearly with the fuel sulfur content.

PART II

PARTICULATE AND SMOKE EMISSIONS FROM A MERCEDES
BENZ LIGHT DUTY DIESEL ENGINE

CHAPTER 5

INTRODUCTION

Diesel engines emit substantial amounts of particulate matter, which may contribute to the problem of air pollution. In order to minimize the particulate emission from diesel engines it is necessary to understand the effects of the various engine and exhaust system parameters on the amount and composition of the emitted particulate matter.

In recent years a considerable amount of work has been directed towards the study of particulate emission in diesel engines. However, most of the previous work dealt with the emission of visible smoke from heavy and medium duty engines. Only a few investigators studied emissions from light duty diesel engines, the main emphasis having been on the measurement of smoke, odor of gaseous emissions [29-32]; particulate emission having only been investigated by Monahan et al [32]. However, Monahan et al [32] did not report the effect of the engine variables upon particulate emission. Thus the objective of this investigation was to study the physical and chemical characteristics of the particles emitted from a light duty diesel engine. A four cylinder in line Mercedes Benz type OM 616 diesel engine was used in the tests. Specifically, the amount of particulate matter emitted was measured as a function of sample temperature at both steady speeds and under a simulated 7 Mode Federal Test Procedure, and engine speed and load. Smoke emission as a function of engine speed and load were also measured. The particulate matter collected was analyzed for its chemical composition.

CHAPTER 6

EXPERIMENTAL APPARATUS

The experimental apparatus employed in these experiments was essentially the same as the one used in Part I. Therefore, the apparatus will be described only briefly with emphasis on the changes made.

6.1 Engine and Fuel

The engine was a four cylinder in-line 1976 Mercedes Benz type OM 616 diesel engine (standard engine in the Mercedes Benz model 240 D car). A complete description of the engine is given in Appendix D. The engine was installed on a test stand dynamometer. The engine speed and load corresponding to an actual car cruising on the road, and the simulated 7 Mode Federal Test Procedure employed in the tests are also given in Appendix D.

The engine was lubricated with valvoline 10 W 40 oil. The oil and oil filter were changed at 70 hour intervals.

American Oil Company number 2 diesel fuel was used throughout the experiments. The chemical composition of the fuel is given in Appendix E. The fuel flow was measured with a burette.

6.2 Exhaust System

The standard exhaust manifold (supplied with the engine) was connected to a surge tank, the latter being the same as the one used with the Chevrolet engine. The surge tank was connected to the exhaust pipe which was also the same as the one used with the Chevrolet engine (Fig. 6.1), but a catalyst was not included in the exhaust. The flow through the exhaust system was controlled by two valves. The exhaust gas flow could either be fed through the exhaust pipe or dumped directly into the

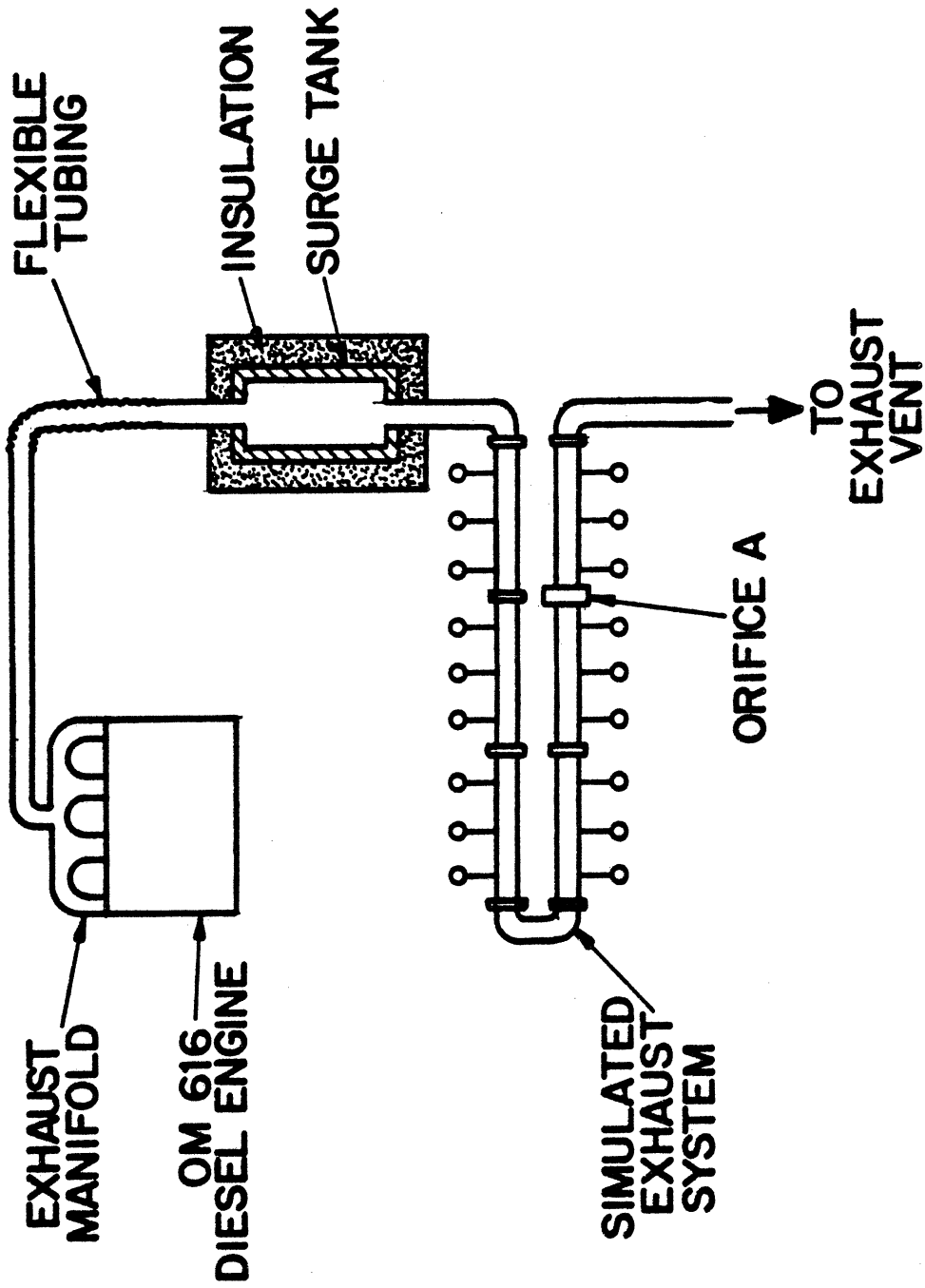


Fig. 6.1 Experimental apparatus. Circles represent thermocouples and sampling locations

tunnel vent of the building. There was a 25 mm diameter sharp edged orifice near the end of the exhaust system (Orifice A, Fig. 6.1).

6.3 Sampling System

The sampling system was the same as the one used with the Chevrolet engine (see Section 2.4). With the diesel engine probe number 2 (see Fig. 2.3) was used in every test.

CHAPTER 7
EXPERIMENTAL PROCEDURES

7.1 Test Conditions

A summary of the test conditions is given in Table 7.1.

In tests I through V the sampling was performed at different positions along the exhaust system. The objective of this series of tests was to evaluate the effect of sampling temperature on particulate emission.

Tests VI through XI were performed by placing the sampling probe near the end of the exhaust system (~ 3 m downstream from the surge tank). During this series of tests the effects of engine load and speed on particulate and smoke emissions were studied.

7.2 Test Procedures

Before taking data the engine was operated at 1800 rpm and 18 hp for 30 hours in order to break in the engine and to condition the exhaust system. Before each new series of tests the engine was operated for four hours at the conditions of the tests.

Before each cyclic test the engine was run 10 complete cycles. With these procedures, during the actual tests changes were not observed in any of the measured parameters, at least within the scatter of the data.

Before each test the engine and exhaust system were warmed up for one hour. The sample was collected on a glass fiber filter as explained in Section 3.3. The filter was then weighed and the collected particulate matter was analyzed for its chemical composition. The weighing was done according to the procedure described in 3.3. The sulfate con-

Table 7.1 Test Conditions

Test Series	Engine Speed (RPM)	Engine Load BHP	Equivalent Road Speed	Parameters Changed
I	1150	3	35 km h ⁻¹ Cruise	Sample Temperature
II	2150	9	64 km h ⁻¹ Cruise	Sample Temperature
III	2900	17	88 km h ⁻¹ Cruise	Sample Temperature
IV	3100	23	96 km h ⁻¹ Cruise	Sample Temperature
V	-	-	Cyclic *	Sample Temperature
VI	800	-	-	Load
VII	1150	-	-	Load
VIII	1500	-	-	Load
IX	2150	-	-	Load
X	2900	-	-	Load
XI	3100	-	-	Load

* The cycle used was an approximation of the 1967 Federal Test Procedure developed for cars. (See Table D.2)

tent of the particulates was examined by the Barium-Thorin Titrimetric procedure (Section 3.4). It is noted that blank filters (i.e. before particulates were collected on them) were tested for sulfate content. The results did not show any sulfate.

In addition, the particulate matter collected was analyzed for organic solubles by extracting (for three hours) the organic solubles from the particulate sample by the soxhlet technique (benzene was used as a solvent). The solvent (benzene) was then evaporated and the remnant weighed, giving the weight of the organic solubles. After weighing the extracted organic solubles all the samples were combined. The samples were then analyzed by infra-red absorption to determine the most common types of molecular groups present in the exhausted organic matter.

The total particulate matter collected on the filters was subjected to electron microprobe analysis to determine the metals present in the sample. The intensity of the emitted smoke was measured with a Bosch smoke meter.

CHAPTER 8

RESULTS

The results presented in this section show the effects of sample temperature, engine speed and load on particulate and smoke emissions.

In order to study the possible formation of particulate matter in the exhaust system, samples were collected along the entire length of the exhaust system at steady engine speeds and loads corresponding to a 1976 240 D Mercedes Benz diesel car cruising at 35,64,88, and 96 km h⁻¹, and under a simulated 7 Mode Federal Test Procedure. The results are presented in Fig. 8.1. The horizontal axis in this figure is the sample temperature. The data in Fig. 8.1 suggests that no significant amounts of particulates form in the exhaust within the temperature ranges achieved in these tests (300 - 550 K). This implies that most particulate matter forms either in the combustion chamber or in the exhaust manifold. Particulate formation due to condensation in the exhaust pipe was insignificant.

Data obtained between 300 and 350 K were taken both by diluting the sample with ambient air (dilution ratio 8:1) and without dilution. The results were the same with and without dilution. Since sample temperature and dilution did not affect the results all subsequent data were taken without dilution at a point where the sample temperature was about 300 K.

It is noted that dilution was unnecessary even at sample temperatures as low as 300 K because water condensation on the filter was not a problem. Water condensation did not occur because the air fuel ratio

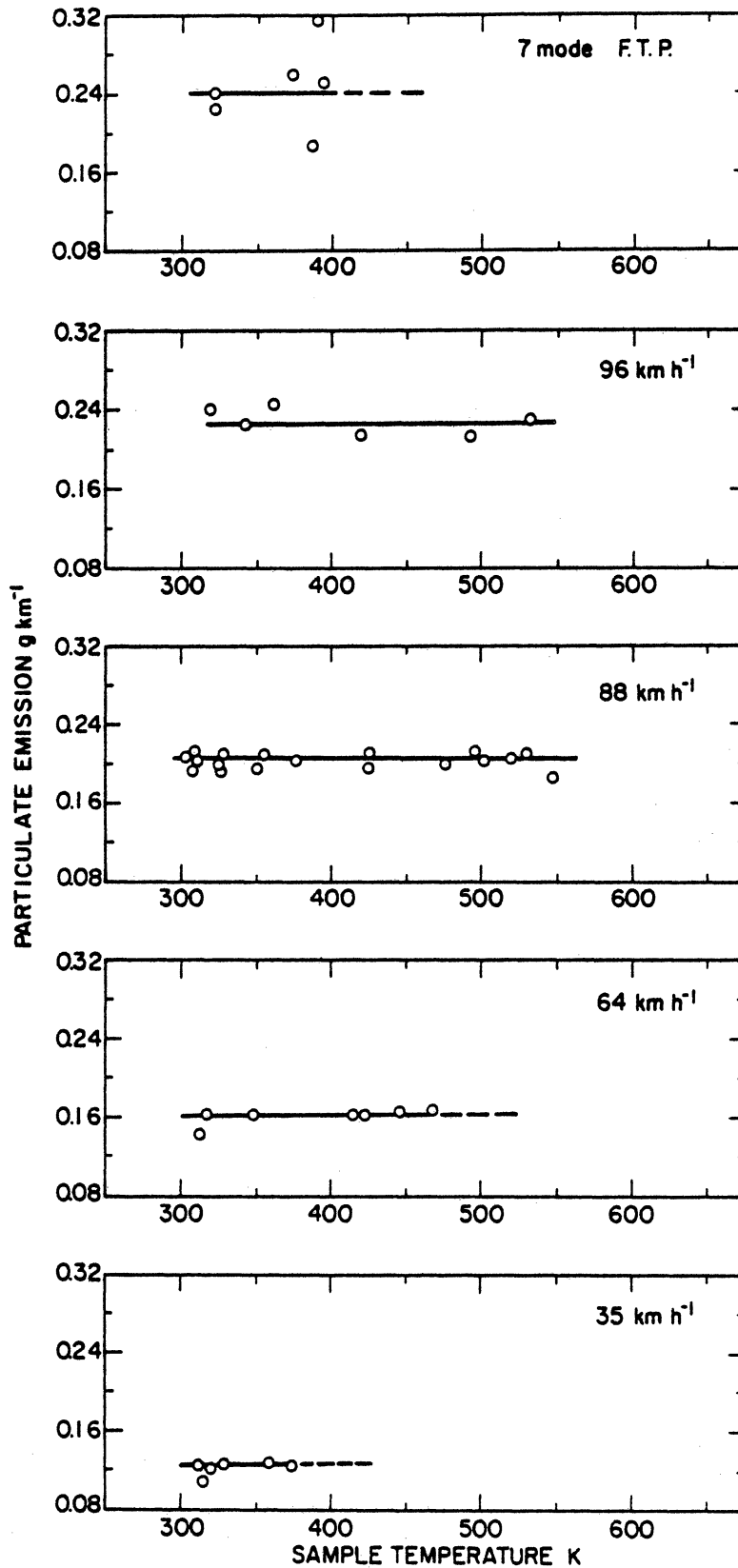


Fig. 8.1 Particulate emission versus sample gas temperature during the simulated 7 Mode Federal Test Procedure, and 35 km h⁻¹, 64 km h⁻¹, 88 km h⁻¹, and 96 km h⁻¹ cruise conditions (— — — —) fit to data

in the diesel engine was high (ranging from 25:1 to 40:1). This is in contrast with the operation of the spark ignition engine (see Part I) where the air fuel ratios were much lower ($\sim 15:1$) resulting in water condensation on the filter at temperatures below ~ 300 K.

The results presented in Fig. 8.1 are cross plotted in Fig. 8.2 to evaluate the dependence of the particulate emission on speed. Figure 8.2 indicates the mass of particulate matter emitted at various steady engine speeds corresponding to road load conditions. As can be seen, the emission increases significantly with speed. It is interesting to observe that at corresponding speeds, the mass of particulate matter emitted by the diesel engine is about 10 times higher than the mass emitted from the 350 CID Chevrolet engine operating on unleaded fuel (Fig. 3.1) and about five times higher than the mass emitted by the same Chevrolet engine operating on leaded fuel [16].

The change in particulate concentration in the exhaust with load and engine speed (rpm) is shown in Fig. 8.3. The amount of particulate matter emitted is governed by the combustion chamber geometry, the position and geometry of the fuel jet spray, the combustion chamber temperature, the time available for combustion, and the amount of fuel injected per stroke [33]. In this work changes in the geometries of the combustion chamber and of the fuel jet spray were not considered since they were fixed for the engine. Thus the amount of particulate matter emitted was mostly governed by the combustion chamber temperature, the combustion time and the mixture composition. Accordingly, the results of Fig. 8.3 may be explained, at least qualitatively, as follows. High combustion chamber temperature, long combustion time (i.e. low rpm) and lean mixtures result in lower particulate emission, while lower combustion chamber

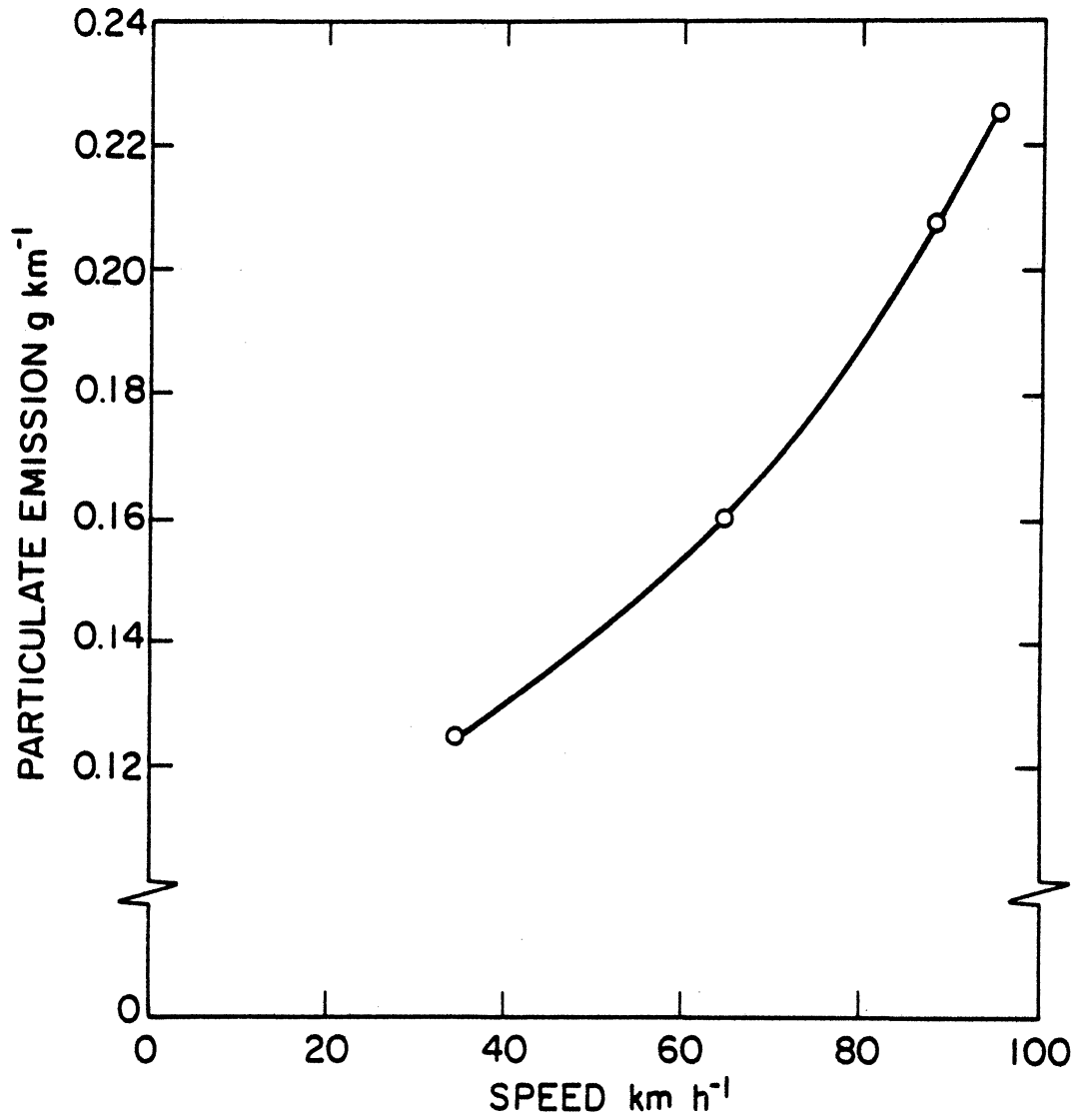


Fig. 8.2 Particulate emission versus speed

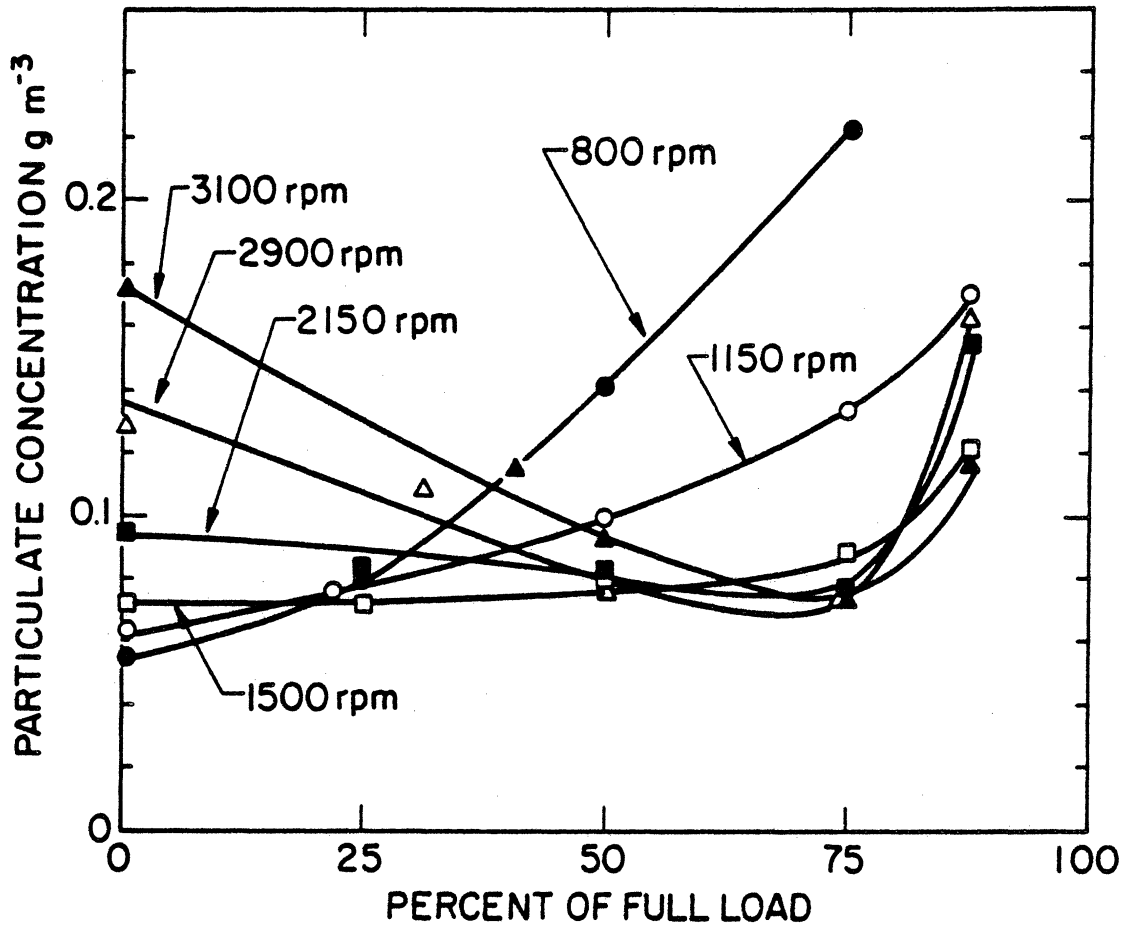


Fig. 8.3 Exhaust particulate concentration as a function of engine load and speed, engine speed as parameter

temperatures, shorter combustion times, and richer mixtures lead to higher emissions. The combination of these factors may explain the behavior of the particulate emission presented in Fig. 8.3. Above 1500 rpm the particulate concentration decreases with load up to about 75% of full load. Above 75% of full load the particulate concentration increases with load. At a fixed rpm the time available for combustion remains constant. However, an increase in load results in higher combustion chamber temperatures and richer mixtures. Up to 75% of full load the combustion temperature is sufficiently high to assure efficient combustion and relatively low emission rates. Above 75% of full load the mixture becomes too rich to achieve complete combustion at the prevailing combustion chamber temperature. Hence, above 75% of full load the amount of unburned combustion products and, correspondingly, the particulate emission increases.

As the engine speed decreases the time available for combustion increases while the combustion chamber temperature decreases. At lower speeds (below about 1500 rpm), the increase in combustion temperature due to the increase in load is insufficient to compensate for the larger amounts of fuel necessary to produce the higher loads. Hence an increase in particulate emission with load.

At constant load (Fig. 8.4) the particulate emission initially decreases with speed, reaches a minimum between 2000 and 3000 rpm and then increases. In the lower rpm ranges the combustion chamber temperature increase is sufficient to compensate for the smaller time available for combustion (higher rpm) resulting in improved combustion and decreased particulate emission. At higher speeds (about \sim 2000 rpm) the

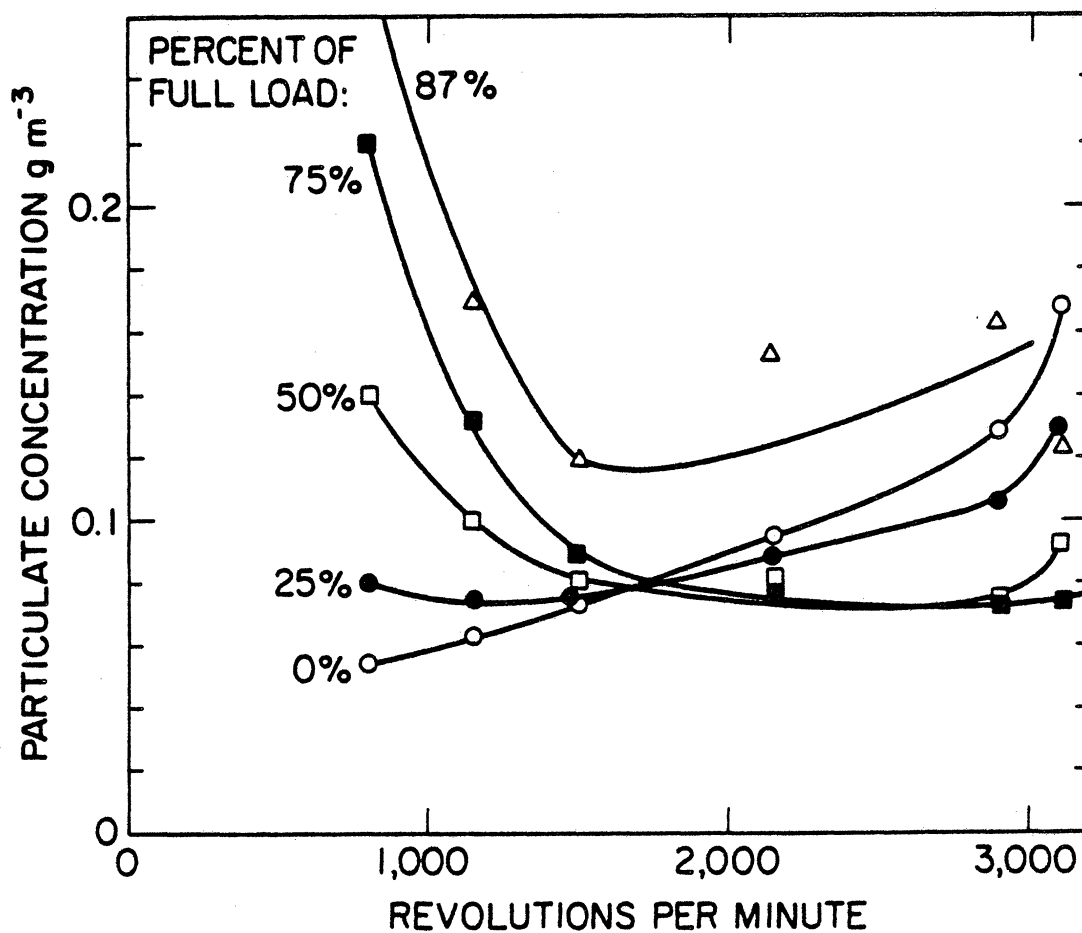


Fig. 8.4 Exhaust particulate concentration as a function of engine speed and load, engine load as parameter

opposite happens, i.e. the increase in temperature is insufficient to compensate for the decrease in combustion time yielding increased emissions. At very low loads (near zero load) the temperature may be very low in the combustion chamber causing the particulate emission to increase with speed at all speeds.

The mass of particulates emitted per unit mass of fuel burned as a function of speed and load is shown in Figs. 8.5 and 8.6. These results show a trend similar to those in Figs. 8.3 and 8.4. The slight difference in the trend of the data is due to the fact that the fuel consumption is not a constant but varies both with speed and load (Fig. 8.7).

The amount of smoke emitted (expressed in Bosch units) as a function of load and speed is shown in Figs. 8.8 and 8.9. As expected, the smoke varies with speed and load in the same manner as the mass of emitted particulate matter.

The results of the chemical analysis of the particulate matter emitted at steady speeds are shown in Table 8.1. Neither sulfates nor metals could be observed in the particulate samples. This implies that the emitted particulate matter contained less than 1% (by weight) of sulfates and metals.

The major portion of the particulate matter was organic solubles. The mass percent of organic solubles varied from 75% at 35 km h⁻¹ to 60% at 96 km h⁻¹. An attempt was made to identify by infrared spectra the structure of the organic solubles. Since benzene was used as solvent it was possible to detect the presence of Alkyl groups only. The presence of aromatics and other groups could not be detected because their absorption peaks were blocked by the absorption peaks of the solvent.

SUMMARY

Particulate and smoke emissions from a light duty Mercedes Benz OM 616 diesel engine were investigated. Samples were collected at different points along the exhaust system and were analyzed for total particulate weight, chemical composition of the particles, and smoke intensity.

Measurements were performed at various steady engine speeds (800, 1150, 1500, 2150, 2900 and 3100 rpm) and at various loads (0, 25, 75, and 87 percent of fuel load). The results obtained showed that

a) both the particulate and smoke emissions depend on engine load and speed, but are independent on sampling temperature in the range 300-550 K.

b) The particulate matter is composed mostly of heavy hydrocarbons (60-75% by weight) and carbon. The amounts of sulfates and metals were found to be negligible.

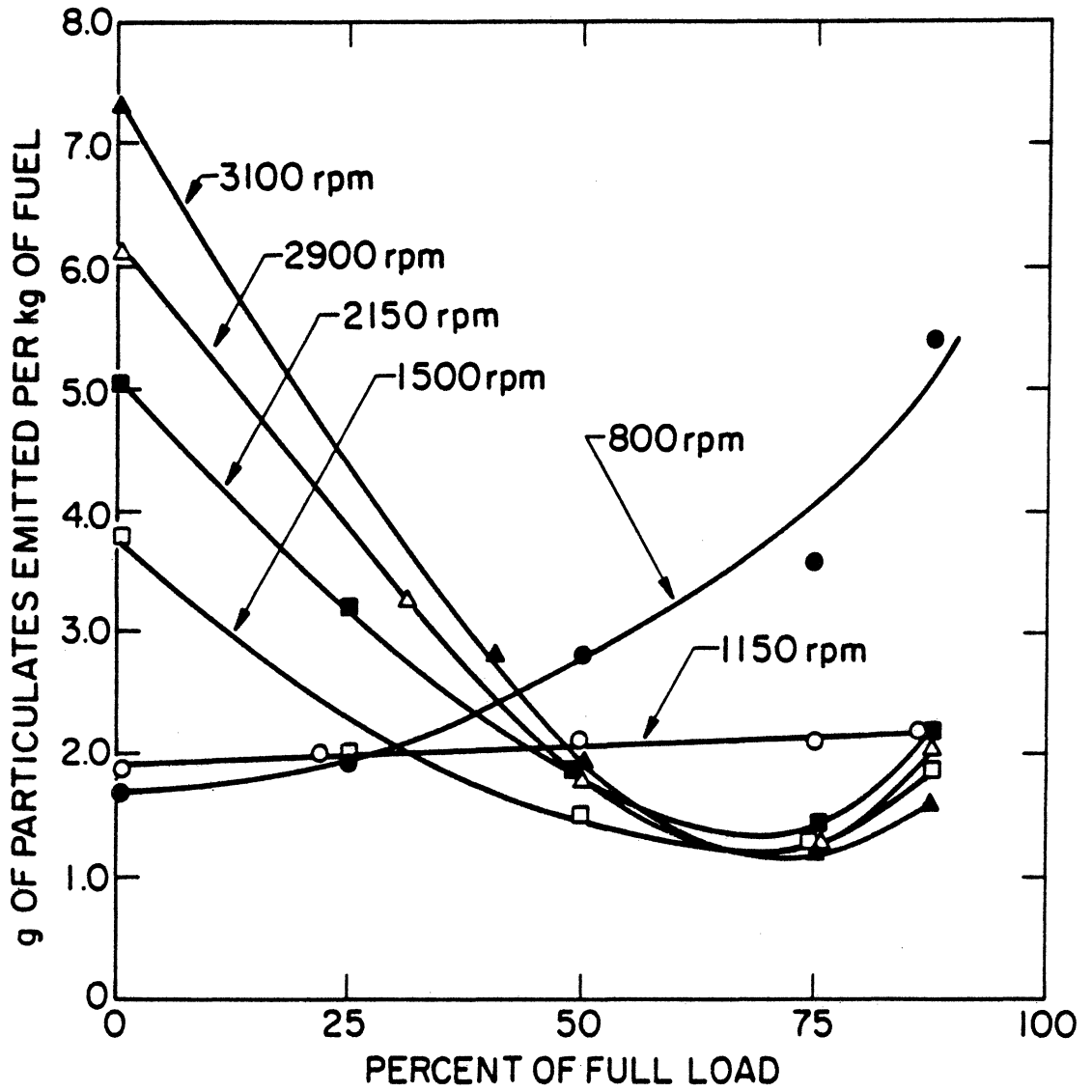


Fig. 8.5 Particulate emission per unit mass of fuel consumed as a function of engine load and speed, engine speed as parameter

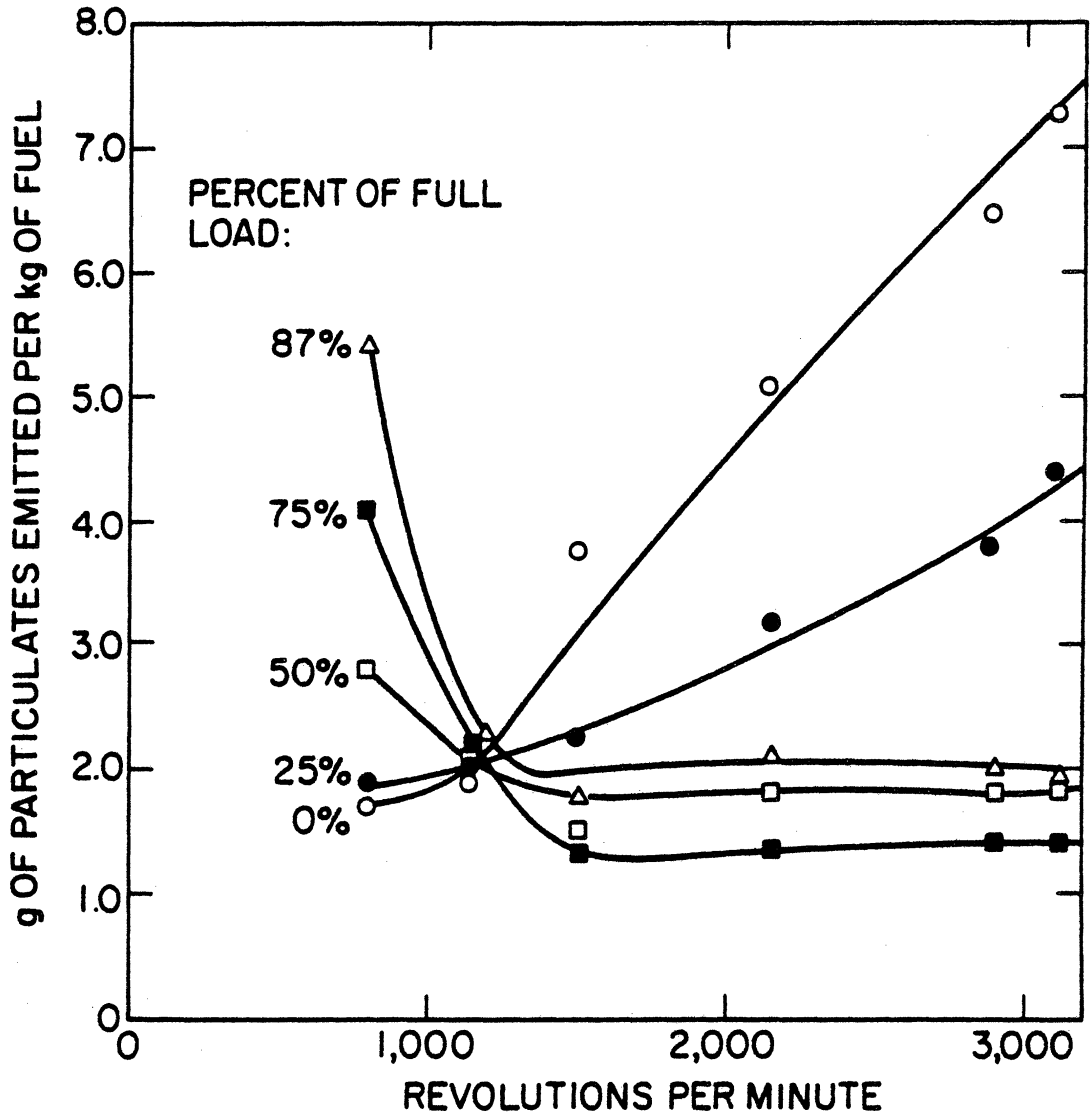


Fig. 8.6 Particulate emission per unit mass of fuel used as a function of engine speed and load, engine load as parameter

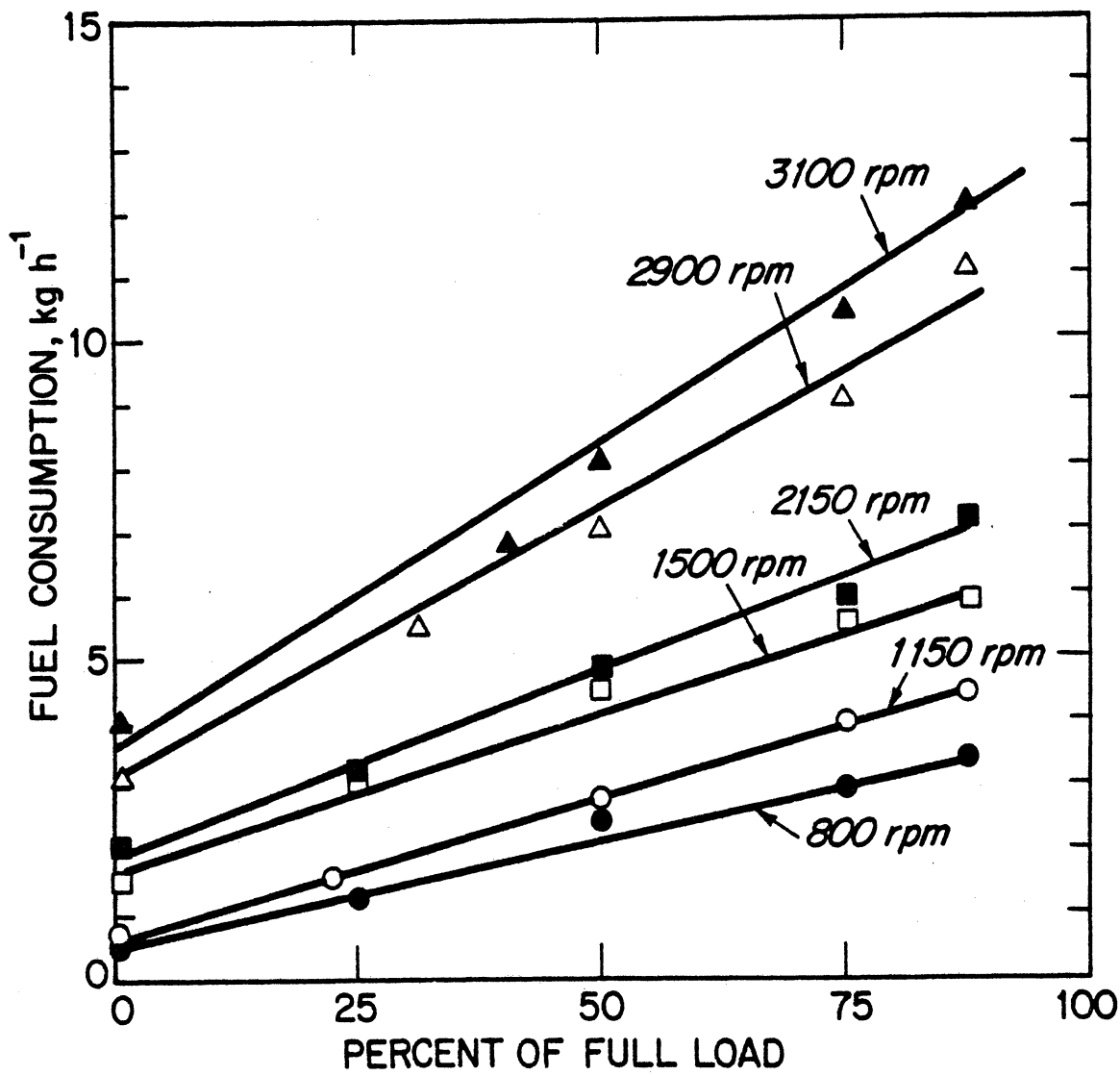


Fig. 8.7 Fuel consumption as a function of engine speed and load, engine speed as parameter

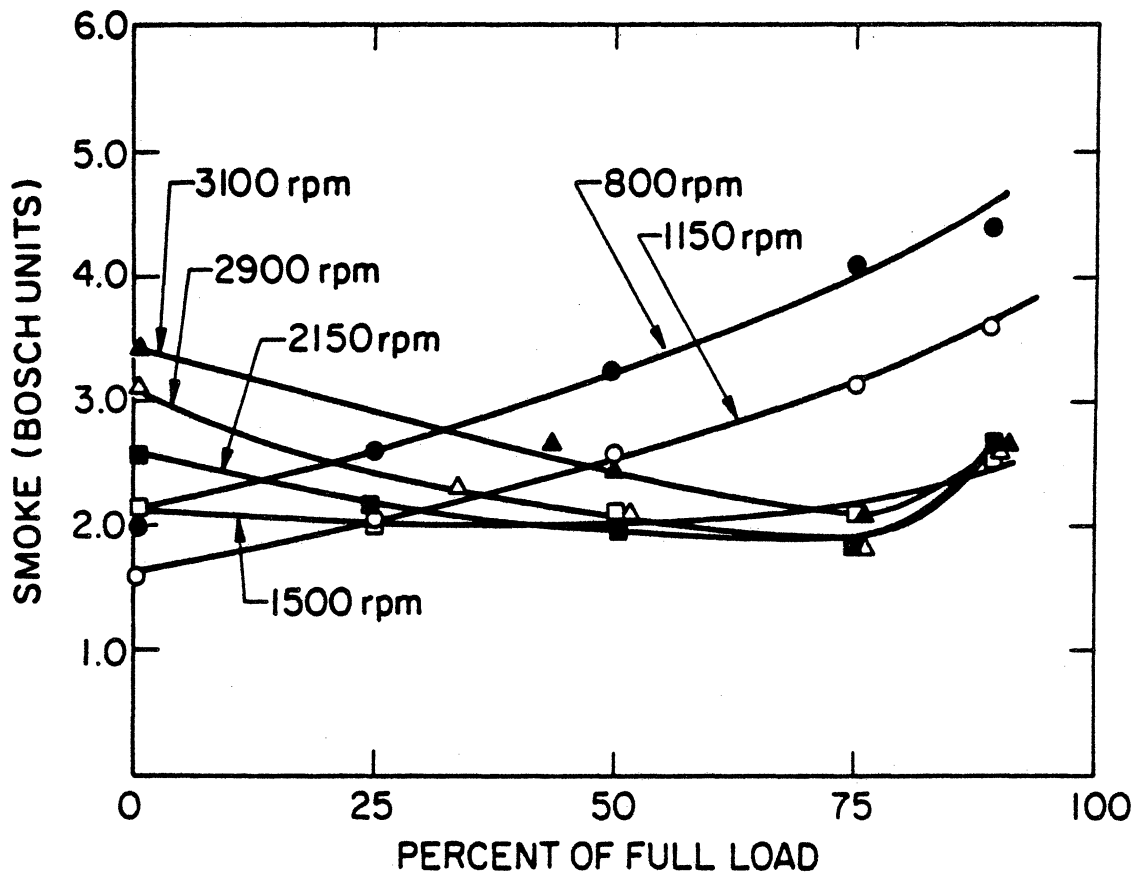


Fig. 8.8 Smoke emission as a function of engine load and speed, engine speed as parameter

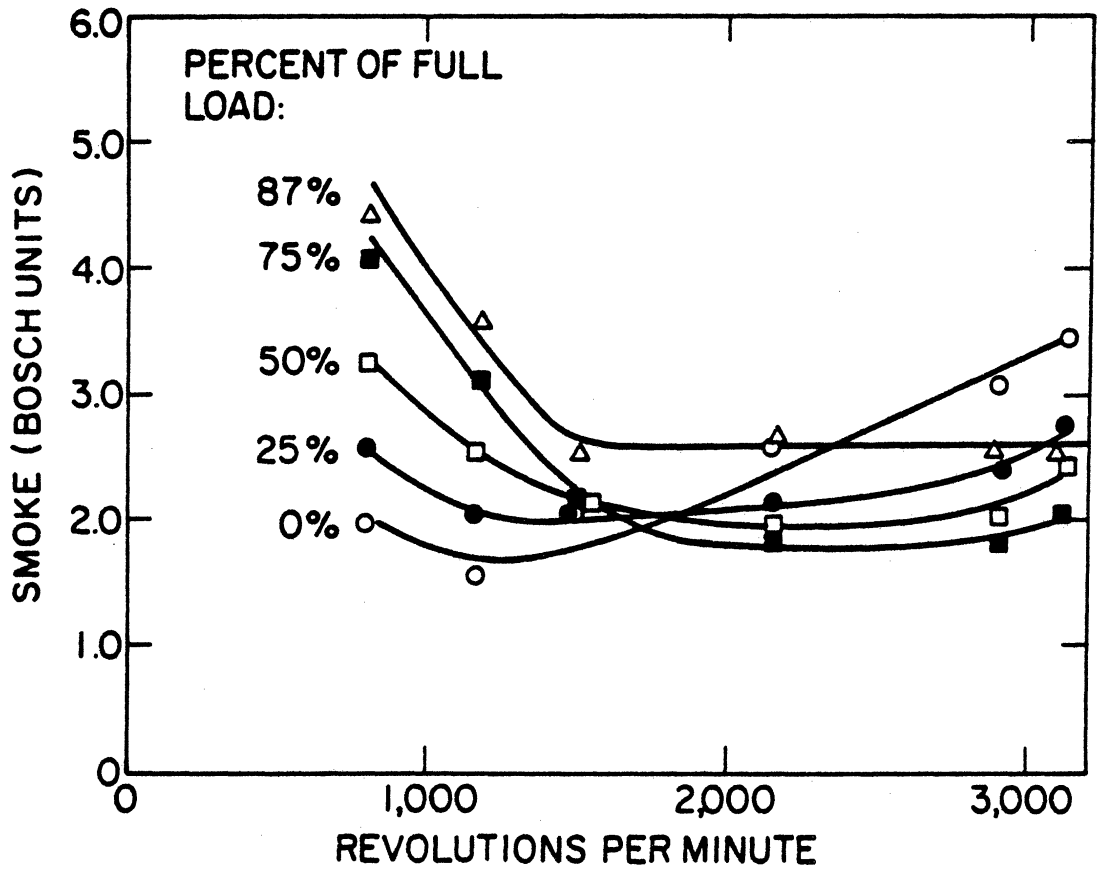


Fig. 8.9 Smoke emission as a function of engine speed and load, engine load as parameter

Table 8.1 Chemical Analysis

Equivalent Road Load	Percent by Weight Organic Solubles ^a	Sulfate Content ^b	Metal Content ^c
35 km h ⁻¹	75	Not Observed	Not Observed
64 km h ⁻¹	65	Not Observed	Not Observed
88 km h ⁻¹	70	Not Observed	Not Observed
96 km h ⁻¹	60	Not Observed	Not Observed

a) Soxhlet extraction

b) Barium-Thorin Titrimetric procedure. Lowest sulfate weight observable was $\sim 10 \mu\text{g}$. This is less than 1% of the total sample weight.

c) Electron microprobe. Weight of metal content was less than 1% of the total sample weight.

APPENDIX A

ENGINE SPECIFICATIONS AND OPERATING CONDITIONS

A.1 Engine Specifications

Engine	1970 Chevrolet V-8
Displacement	350 cubic inches
Horsepower (adv.)	250 at 4800 RPM
Carburetor	2 barrel Rochester
Compression ratio	9.0:1
Bore	4.00 inches
Stroke	3.48 inches
Spark plugs	AC R455
Point dwell	30 degrees

A.2 Steady Speeds

All tests at steady speeds were performed at conditions corresponding to a full sized 1970 Chevrolet cruising under road load conditions.

The engine speed n was calculated from

$$n = \frac{S^* R}{2 \pi r} \quad (\text{A.1})$$

where S^* is the car speed, R is the rear axle ratio, and r is the radius of the rear tires. For a standard Chevrolet R is 3.07 and r is 351 mm [26]. The load on the engine was calculated from

$$BHP = \frac{V}{600} (0.0027 W + 0.0053 A V^2) \quad (\text{A.2})$$

where V is the vehicle speed (km h^{-1}), W is the total weight of the car (17796.8 N) and A is the projected area of the automobile (2.88 m^2) [26].

A.3 Cyclic Operating Conditions

The cycle under which the engine was run was an approximation to the 7 mode Federal Test Procedure, Table A.1 [27,28]. The cycle used in the tests is given in Table A.2.

A.4 Catalysts Specifications

Pelleted Catalyst:

The pelleted catalyst was a General Motors extrudate catalyst with a 5 to 2 platinum-palladium ratio and a nominal loading of 0.35 g l^{-1} .

Monolithic Catalyst:

The monolithic catalyst was an Engelhard PTX, type IIB catalyst.

Table A.1 Actual 7 Mode Federal Test Procedure [27,28]

Mode	Speed km h ⁻¹	Time, s	Cumulative time, s
	0 (idling)	20	20
I	0-48	14	34
II	48-48	15	49
III	48-24	11	60
IV	24-24	15	75
V	24-80	29	104
VI	80-15	25	129
VII	10-0 (idling)	8	137

Table A.2 Approximation to the 7 Mode Federal Test Procedure

(For every new mode the torque was set to the value necessary to produce 14 HP at the maximum rpm).

Mode	rpm	Time, s	Cumulative time, s
	700 (idling)	20	20
I	700-1150	14	34
II	1150-1150	15	49
III	1150-900	11	60
IV	900-900	15	75
V	900-1800	29	104
VI	1800....	25	129
VII700	8	137

APPENDIX B

PHYSICAL AND CHEMICAL PROPERTIES OF INDOLENE HO 0
 FUEL SUPPLIED BY AMOCO OIL COMPANY

Test	ASTM Method	Specification Control Limit	Test Values
API Gravity	D287	58.0-61.0	59.6-61.9
Distillation % F	D86		
Initial Boiling Point	D86	75-95	86-93
10% Evap.	D86	120-135	129-135
50% Evap.	D86	200-230	220-221
90% Evap.	D86	300-325	315-318
Maximum	D86	NMT 415	398-406
10% Slope	D86	NMT 3.2	2.9-3.9
Reid Vapor Pressure	D323	8.7-9.2	8.9-9.0
Oxidation Stability Minutes	D525	NMT 600	600+
Gum, mg/100 ml (after Heptane wash)	D381	NMT 4.0	0.2-3.0
TMEL grm. lead/gal.	D526	NMT 0.05	0.0-0.01
Sulfur-Weight, %	D1266	NMT 0.10	0.01-0.017
Olefin, %	D1319	NMT 10	3.9-7.4
Aromatic, %	D1319	NMT 35	26.1-29.5
Saturates, %	D1319	Remainder	63.1-71.1
Octane Research (Clear)	D2699	95.0-98.5	96.6-97.4
Octane Research (3cc TEL/gal)	D2699	NLT 103.0	105.0-106.2
Phosphorus, gms./gal.	D3231	NMT 0.005	0.000-0.003
Sensitivity (Clear)		7.0-10.5	8.3-9.4
Sensitivity (3cc TEL/gal)		NMT 9.0	7.1-8.5

APPENDIX C

CALCULATION OF THE CONVERSION OF SO₂ TO SO₃

SO₃ is produced by the reaction



For this reaction the overall rate constant inside the reactor (dm³/(h) x (catalyst mass in kg)) may be approximated by [25]

$$k = \frac{-r_{SO_2}}{C_{SO_2} - (C_{SO_2})_E} \quad (C.2)$$

where $(-r_{SO_2})$ is the rate of disappearance of SO₂ (moles of SO₂ reacted/catalyst mass kg x h), C_{SO_2} is the concentration of SO₂ (moles/dm³) at a given position inside the catalyst, $(C_{SO_2})_E$ is the chemical equilibrium concentration of SO₂ (mole/dm³). r_{SO_2} and C_{SO_2} are not known directly but must be determined from the information available which are the amount of SO₂ entering the catalyst (reactor) and the amount of SO₃ leaving the catalyst. In order to utilize the available information we assume that the reaction takes place in a plug flow type reactor shown in Fig. C.1. For a differential element containing a dm mass of the catalyst an SO₂ mass balance gives [25]

$$(F_{SO_2})_{in} dX_{SO_2} = -r_{SO_2} dm \quad (C.3)$$

Upon integration eq. (C.3) becomes

$$\frac{m}{(F_{SO_2})_{in}} = - \int_{(X_{SO_2})_{in}}^{(X_{SO_2})_{out}} \frac{dX_{SO_2}}{r_{SO_2}} \quad (C.4)$$

m is the mass of the catalyst in the reactor, (F_{SO_2}) is the molar flow

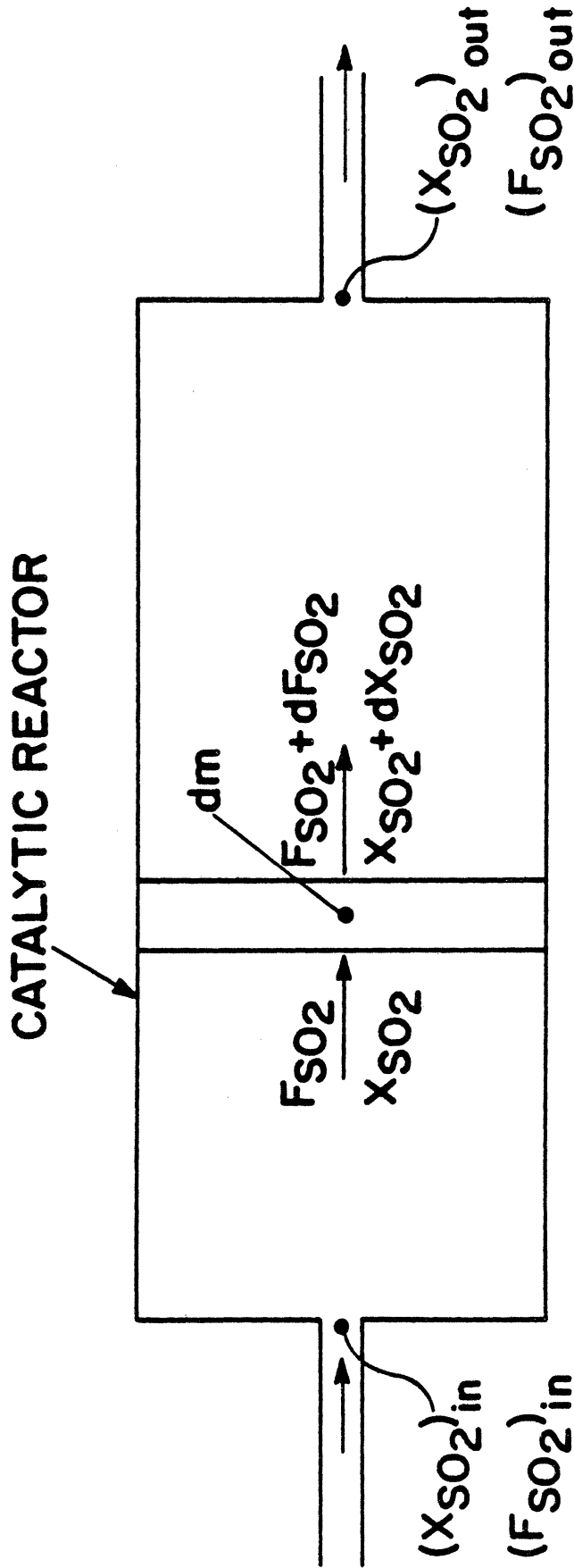


Fig. C.1 Plug flow reactor for calculating S_{O_2} conversion. X_{SO_2} denotes the fraction of S_{O_2} transformed to S_{O_3} . F_{SO_2} denotes the molar flow rate of S_{O_2} (mole h^{-1}). The subscripts in and out represent the conditions at the inlet and outlet of the catalytic reactor.

of SO_2 , (X_{SO_2}) is the fraction of SO_2 converted into SO_3 . The subscripts in and out represent the conditions at the inlet and outlet of the reactor, respectively,

$$(X_{SO_2})_{out} = \frac{(C_{SO_3})_{out}}{(C_{SO_2})_{out} + (C_{SO_3})_{out}} \quad (C.5)$$

By assuming that $(X_{SO_2})_{in} = 0$, and substituting eq. (C.2) into (C.4) we obtain

$$\frac{m}{(F_{SO_2})_{in}} = \int_0^{(X_{SO_2})_{out}} \frac{dX_{SO_2}}{k(C_{SO_2} - (C_{SO_2})_E)} \quad (C.6)$$

With the definitions

$$X_{SO_2} = \frac{C_{SO_3}}{C_{SO_2} + C_{SO_3}} = \frac{(C_{SO_2})_{in} - C_{SO_2}}{(C_{SO_2})_{in}} \quad (C.7a)$$

$$(X_{SO_2})_E = \frac{(C_{SO_3})_E}{(C_{SO_2})_E + (C_{SO_3})_E} = \frac{(C_{SO_2})_{in} - (C_{SO_2})_E}{(C_{SO_2})_{in}} \quad (C.7b)$$

eq. (C.6) yields

$$\frac{km}{(F_{SO_2})_{in}} (C_{SO_2})_{in} = \int_0^{(X_{SO_2})_{out}} \frac{dX_{SO_2}}{(X_{SO_2})_E - X_{SO_2}} \quad (C.8)$$

The subscript E denotes chemical equilibrium. Integration of eq. (C.8)

gives

$$km = \frac{\ln \left[\frac{(X_{SO_2})_E}{(X_{SO_2})_E - (X_{SO_2})_{out}} \right]}{\frac{(C_{SO_2})_{in}}{(F_{SO_2})_{in}}} \quad (C.9)$$

$(X_{SO_2})_E$ as a function of temperature was calculated by Hammerle and Mikkor [13] and their result is reproduced here in Fig. C.2. $(X_{SO_2})_{out}$ (which is the same as C/100) was measured in the present experiments (Fig. 4.1).

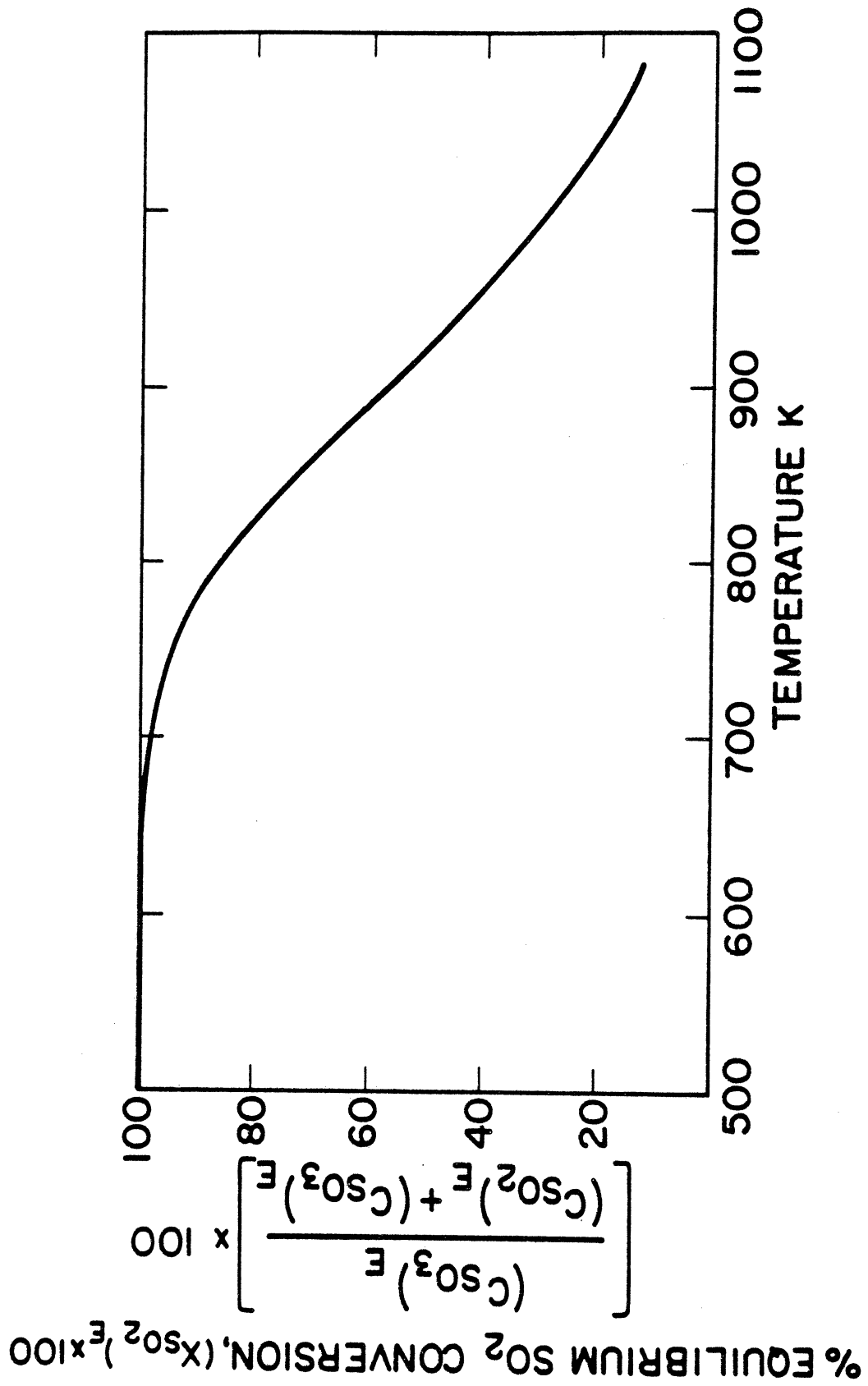


Fig. C.2 Conversion of SO₂ to SO₃ at chemical equilibrium [13]

$(C_{SO_2})_{in}$ was determined as follows. The catalyst was operated with 25 percent excess over stoichiometric. This corresponds to an "air fuel ratio" of 19:1 through the catalyst. The "air fuel ratio" through the catalyst is defined as

$$\left(\frac{A}{F}\right)_{cat} = \frac{m_c}{m_f} = 19 \quad (C.10)$$

The amount of sulfur (kg) per kg of exhaust gas is

$$m_S^* = \frac{m_f}{m_c + m_f} \cdot \frac{S}{100} \quad (C.11)$$

where S is the percent sulfur in the fuel by weight. The number of moles of SO_2 per kg of exhaust gas is

$$(C_{SO_2})_{in} = \frac{m_S^*}{32} \quad \frac{\text{kg mole}}{\text{kg exhaust}} \quad (C.12)$$

since one mole of S in the fuel gives rise to one mole of SO_2 . Equations (C.10), (C.11) and (C.12) give

$$(C_{SO_2})_{in} = \frac{1000}{(20)(32)(100)} S \quad \frac{\text{g mole}}{\text{kg exhaust}} \quad (C.13)$$

or

$$(C_{SO_2})_{in} = \frac{1000}{(20)(32)(100)} S \rho_{exh} \quad \frac{\text{g mole}}{\text{dm}^3 \text{ exhaust}} \quad (C.14)$$

where ρ_{exh} is the density of the exhaust gas (kg dm^{-3}). This density was calculated by assuming that the density of the exhaust gas is the same as the density of air at the temperature and pressure of the exhaust.

In eq. (C.9) $(FSO_2)_{in}$ is the number of moles of SO_2 entering the catalyst per hour

$$(F_{SO_2})_{in} = m_f \cdot 1000 \left(\frac{S}{100} \right) \left(\frac{1}{32} \right) \frac{\text{g moles}}{\text{hour}} \quad (C.15)$$

In order to obtain the product km the right hand side of eq. (C.9) was plotted for various temperatures (Fig. C.3). The slope of the lines gives km , given as a function of inverse temperature in Fig. C.4. Equations (C.9)-(C.15) yield eq. (4.1) in the main text.

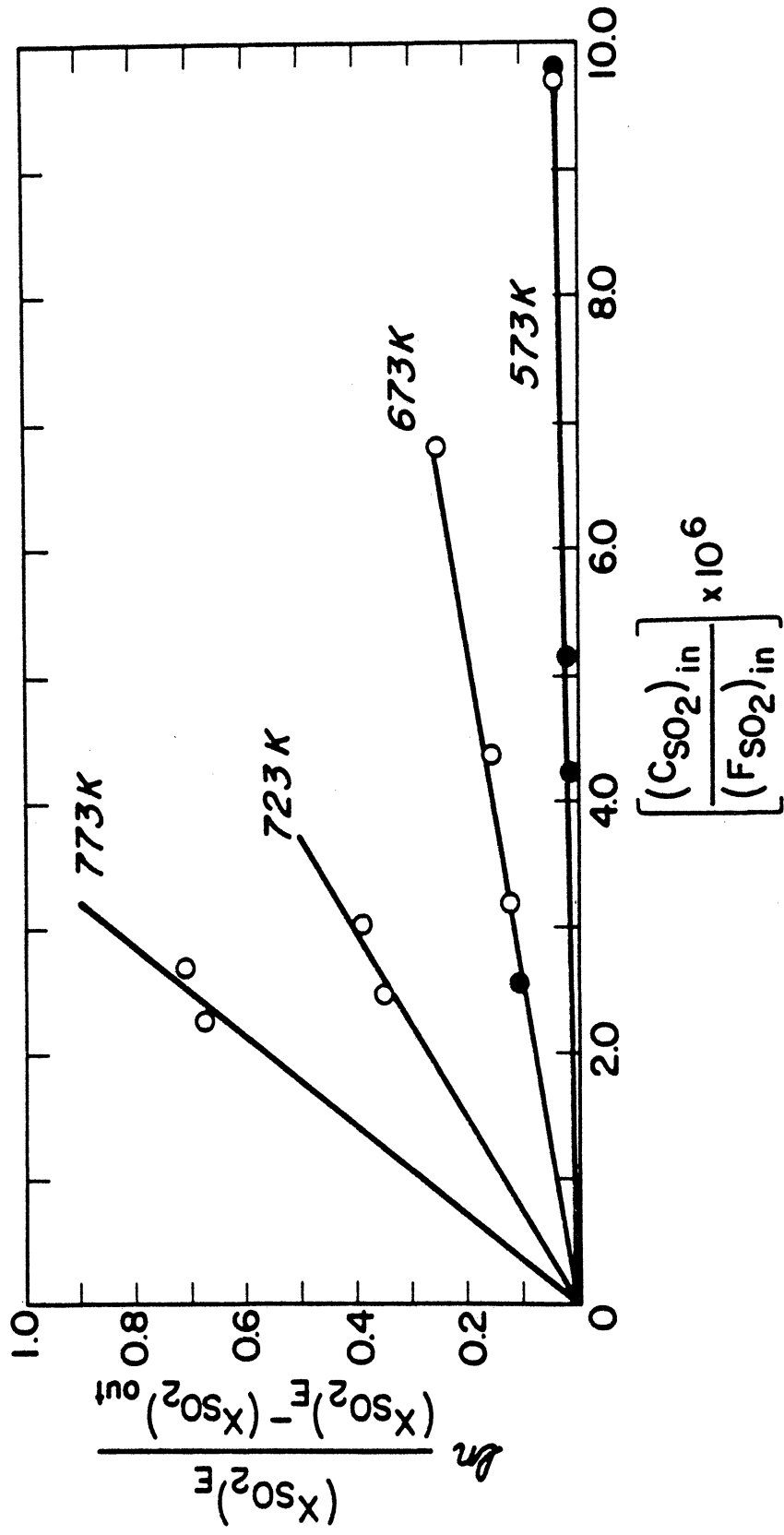


Fig. C.3 Relationship between fractions of SO₂ converted to SO₃ and the SO₂ concentrations as a function of temperature. $(F_{SO_2})_{in}$ represents the molar flow rate of SO₂ (mole h⁻¹). The subscripts in and out denote the conditions of the inlet and outlet of the catalytic reactors

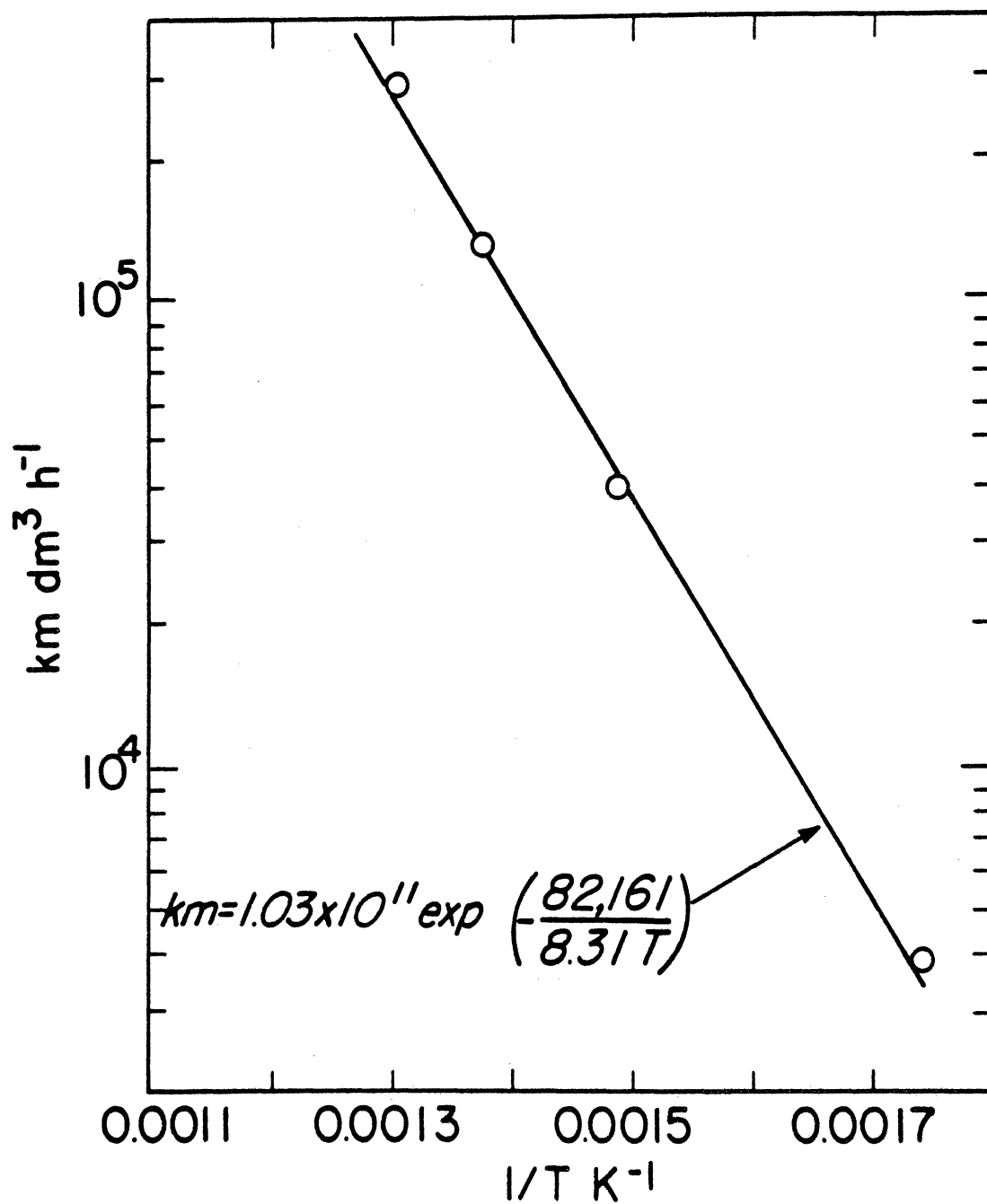


Fig. C.4 k_m as a function of temperature

APPENDIX D

ENGINE SPECIFICATIONS AND OPERATING CONDITIONS

D.1 Engine Specifications

Engine	Mercedes Benz type OM 616
Work cycle	Diesel four stroke
Number of cylinders	4
Bore	91 mm
Stroke	92.4 mm
Total piston displacement	2,404 cm ³
Compression ratio	21:1
Maximum engine speed	4,350 rpm
Start of delivery	24° BTDC

D.2 Steady Speeds

All tests at steady speeds were performed at conditions corresponding to a Mercedes Benz 240 D car cruising under road load conditions. The engine speed was calculated from

$$n = S^* \frac{R}{z \pi r} \quad (D.1)$$

where S^* is the car speed, R is the rear axle ratio and r is the radius of the rear tires. The value of 52.45 was used for the ratio $(R/2\pi r)$ as suggested by EPA.

The load of the engine was calculated from

$$\text{BHP} = \frac{V}{600} \left(0.0027 W + 0.0053 A V^2 \right) \quad (D.2)$$

where V is the vehicle speed (km h^{-1}), w is the total weight of the car (14,847 N) and A is the projected area of the automobile (2.22 m^2).

D.3 Cyclic Operating Conditions

The cycle under which the engine was run was an approximation to the 7 mode Federal Test Procedure (see Appendix A, Table A.1).

The cycle used in the tests is given in Table D.1.

Table D.1 Approximation to the 7 Mode Federal Test Procedure

(For every new mode the torque was set to the value necessary to produce 14 HP at the maximum rpm)

Mode	rpm	Time, s	Cumulative
	800 (idling)	20	20
I	800-1700	14	34
II	1700-1700	15	49
III	1700-1300	11	60
IV	1300-1300	15	75
V	1300-2600	29	104
VI	2600	25	129
VII700	8	137

The actual cycle developed for cars is given in Appendix A.

APPENDIX E

PHYSICAL AND CHEMICAL PROPERTIES OF NUMBER 2

DIESEL FUEL SUPPLIED BY AMOCO OIL COMPANY

Appearance	Pass
Carbon Residue, Ramsbottom, 10% Bottoms, %	0.11
Caustic, Free Phenolphthalein Test	Pass
Cetane	45.5
Cloud Point, °F.	-10
Color, ASTM	0.5
Corrosion, D 130, 3 Hours @ 212 °F.	1 a
Distillation, D 86, °F.	
10% Recovery	393
90% Recovery	581
95% Recovery	599
End Point	631
Filterability Index	1.4
Flash, TCC, °F.	157
Gravity, °API	35.0
Pour Point, °F.	-35
Stability:	
Acid Flocc Gum, mg/100 ml	2.3
Sediment, mg/100 ml	0.2
Sulfur, Weight, %	0.35
Viscosity, cs @ 100 °F.	2.31
Water & Sediment, Volume, %	0.00
BTUs per Gallon (Gross Heating Value)	138,000

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