THE EFFECT OF SULPHUR IN FUEL ON THE PERFORMANCE OF AUTOMOTIVE CATALYSTS

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I, J J (Hans) Siemelink submit this half-thesis in fulfilment of the requirements for the degree of Master of Science in Applied Science.

I claim that this is my original work and that it has not been submitted in this or in a similar form for a degree at any University.

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ABSTRACT

Catalysts have been used on cars since 1974 to reduce tailpipe emission levels of carbon monoxide, hydrocarbons and oxides of nitrogen. Initially, oxidation catalysts were used that operated under very lean air/fuel conditions and gave rise to increased sulphate particulate emissions. These sulphate emissions could fortunately be reduced by better air/fuel control.

However, the introduction of more active catalyst compositions, in particular the use of cerium oxide components on the wash coat, led to bad odour complaints from motorists. In the report it is shown that under fuel-lean conditions, sulphur, originating from the fuel, is stored as aluminium and cerium sulphates onto the washcoat. Upon a rapid change to fuel-rich engine operation the stored sulphates are released as hydrogen sulphide and is the cause for the smell observed. The sulphur storage/release process results in hydrogen sulphide emissions many times higher than is possible from steady-state conversion from the fuel sulphur level.

By using a catalyst/engine combination on a testbed the experiments have shown that the hydrogen sulphide release is a kinetically limited reaction and, apart from the air/fuel control, depends mainly on the catalyst temperature.

The deposits of sulphur also meant that catalysts could deteriorate (poison) when high sulphur fuels were used. It is shown that the use of high sulphur fuels will lead to deterioration of the catalyst efficiency. The deterioration, or poisoning, was found to be immediate but could be reversed upon the use of low sulphur fuels.

The experiments indicate a maximum limit for the sulphur levels in fuels below which no noticeable poisoning, and only marginal hydrogen sulphide emissions, occur. Fuels with sulphur content below this limit did not give better catalyst performance. Stringent tailpipe emissions regulations do not allow any deterioration of the catalyst conversion efficiencies and therefore this threshold might give guidance in setting the maximum sulphur level in reformulated fuels.

It has been shown that the effect of sulphur on the catalyst behaviour is determined by the catalyst composition, the engine air/fuel control, and the sulphur level of the fuel used. By optimising these three variables, the sulphur effects can be brought down to negligible levels.

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NOMENCLATURE

SYMBOLS

Al	Aluminium
C	Carbon
Ce	Cerium
Co	Cobalt
Cu	Copper
Fe	Iron
Ge	Germanium
H	Hydrogen
Ir	Iridium
La	Lanthanum
Nd	Neodymium
Mn	Manganese
N	Nitrogen
Ni	Nickel
O	Oxygen
Pb	Lead
Pd	Palladium
Pr	Praseodymium
Pt	Platinum
Rh	Rhodium
S	Sulphur
Zn	Zinc

ABBREVIATIONS

A/F	Air/fuel ratio
EGR	Exhaust gas circulation
EHC	Electrically heated catalyst
IBP	Initial boiling point
FBP	Final boiling point
MTBE	Methyl tertiary butyl ether
ppb	Parts per billion
PGM	Platinum group metal
ppm	parts per million
RVP	Reid vapour pressure
TWC	Three-way catalyst

GLOSSARY

Closed-loop control	An oxygen or lambda sensor in the exhaust provides feedback to the electronic control unit on combustion efficiency
Conversion efficiency	The ratio of the rate of mass flow removal of a particular constituent in the catalyst to the rate of mass flow of that constituent into the catalyst.
Equivalence ratio	The actual fuel/air ratio used compared to that for chemically correct combustion.
Fuel-lean condition	See: Reducing condition
Fuel-rich condition	See: Oxidising condition
Lambda value	The inverse of the equivalence ratio. The actual air/fuel ratio used compared to that for chemically correct combustion
Light-off temperature	The temperature at which a catalyst becomes 50 per cent effective
Open-loop control	The oxygen or lambda sensor is disconnected from the electronic feedback loop
Oxidising condition	There is more air present than needed for chemically correct combustion
Reducing condition	There is more fuel present than needed for chemically correct combustion.
Space velocity	The exhaust volume flow rate divided by the catalyst volume
Stoichiometric condition	The chemically correct ratio of air and fuel for optimum combustion
Three-way catalyst	The simultaneous removal of carbon monoxide, hydrocarbons and nitrogen oxide from the exhaust stream

CHAPTER ONE
INTRODUCTION

1.1 BACKGROUND AND OBJECTIVES

The problems of photochemical smog in Los Angeles and Tokyo in the late 1960s resulted in the introduction of Clean Air acts in both USA and Tokyo. This required emission standards of a severity that could not be achieved by the traditional means of ignition retardation, fuel management, exhaust gas recirculation (EGR) or manifold injection. Catalytic systems were identified as the only means possible of achieving the required 90 per cent control of exhaust emissions of carbon monoxide, hydrocarbons and the nitrogen oxides. In order that the catalyst should not be poisoned or coated by lead compounds, thus limiting its effectiveness, unleaded petrol was introduced from mid 1974 for use with cars fitted with catalysts from 1975 onwards. Most cars in the USA, Europe and Japan are now fitted with effective 3-way catalytic converters; that is one which catalytically controls emissions of carbon monoxide, hydrocarbons and nitrogen oxides.

In 1975, however, the first generation of catalysts, called oxidation catalysts, was introduced and exhaust emissions of carbon monoxide and hydrocarbons were converted into carbon dioxide and water. Following some complaints on their function, it was found that the particulate emissions from converter-equipped cars were higher than those of non-catalyst cars by a factor of two to five (1,2,3). Conventional elemental analysis for trace metals, carbon and hydrogen failed to reveal the nature of this particulate material. Further investigations, however, showed that sulphate was the principle component and contributed about half the particulate mass. It was postulated, and later confirmed, that the sulphur present in the fuel, oxidised to SO_2 by the combustion process in the engine, is partly converted to SO_3 and actually emitted as sulphuric acid vapour or mist (4), resulting in increased particulate emissions.

Another problem became apparent when sulphur-induced deterioration or poisoning was noticed on the oxidation catalysts. The SO_3 formed by the catalyst attacked the materials and was stored on the catalyst as a sulphate, thereby reducing the efficiency in conversion of carbon monoxide and hydrocarbons to water vapour and carbon dioxide (CO_2). It was possible to release this stored sulphur at high temperatures and by adjustments on the engine but this again had a negative effect on the durability of the catalyst and on the drivability of the car. Different catalysts,

most of them using base metals only, varied in susceptibility to sulphur poisoning and the level of sulphate emissions (2). The negative effects were enhanced when noble metals were introduced to promote the catalyst conversion reactions for the main automotive pollutants.
Catalyst formulations were modified to counteract the sulphate problem and this, together with recommended changes in the engine settings, reduced the catalyst induced sulphate emissions to negligible levels (3). However, the deterioration of the catalyst activity by the sulphur in the fuel remained.

More recent tighter emission legislation called for the control of nitrogen oxide emissions and three-way catalysts (TWCs) were introduced. TWCs simultaneously reduce the three main pollutants in toxicity but can be the cause of another problem. With the advanced engine control systems and with the significantly more active catalyst formulations in use, in particular the use of cerium components such as cerium oxide (CeO_2) for enhanced oxygen storage within the catalyst, the formation of high levels of hydrogen sulphide (H_2S) became noticeable. These high levels of H_2S were first observed not by the deterioration in conversion efficiency of the catalyst but by the production of extremely bad odour (rotten eggs) under certain driving conditions. The reason for the formation of H_2S was discovered as the ability of modern three-way catalysts to store significant quantities of sulphur. This happened during <u>lean</u> (excess air) or slightly lean engine operation, and was in the form of sulphate in the ceramic coating of the catalyst. The stored sulphur is released rapidly not as sulphates, but as H_2S as a result of the reaction with hydrogen during subsequent <u>rich</u> (excess fuel) operation. The concentration of the H_2S released is much higher than can be expected from steady-state conversion of the sulphur in the fuel and lasts for a relatively short time. But it is observable as a bad odour. The odour problem is most apparent during transient states from lean-to-rich driving conditions, as is typical for stop/go driving in town.

Development work conducted to find a cure for the H_2S release problem focussed on either reformulating the catalysts to reduce sulphur retention or finding a suitable H_2S scavenger.

The objective of the thesis is to quantify the problems experienced with sulphur in petrol. Experiments are described using a Volkswagen Digifant engine on a test bed with a commercially available closed-loop controlled three-way catalyst to investigate the effects of the sulphur in the fuel on exhaust emissions. The engine was equipped with a sophisticated state-of-the-art, electronic engine management system for air/fuel ratio control, ignition and fuel injection. Catalyst activity degradation was determined for fuels doped with various sulphur levels. The storage/release mechanisms leading to peak H_2S were investigated. Since the sulphur problems decrease with lower levels of sulphur in the fuel, recommendations on the maximum acceptable sulphur content with this catalyst/engine combination can be given.

1.2 THESIS OUTLINE

The second chapter of this thesis contains a description of the development and composition of the automotive catalyst since 1974. This knowledge is relevant in order to understand the interaction between engine and catalyst and what factors contribute to a catalyst's susceptibility to sulphur in fuel. Chapter three discusses the effects of sulphur on the early oxidation catalysts under very lean engine operating conditions and the resultant increased particulate emissions.

An integral approach in oxidation catalyst design and engine control seemed to reduce the problems caused by sulphur in the fuel. However, emission legislation again called for lower emissions levels and this time particularly for nitrogen oxides reductions. This resulted in the development of three-way catalysts that are operated near stoichiometric air/fuel ratio's for optimum functioning. Chapter four gives a review into the cause and possible solution to the emission of hydrogen sulphide by these three-way catalysts.

Chapter five gives an evaluation of the effect of sulphur on the tailpipe emissions. Sulphur not only poisons the catalyst but also affects the regulated and non-regulated emissions.

Several approaches to investigate the effects of sulphur on the catalyst are possible and the route taken in this thesis is discussed in chapter six. This chapter also gives a description of the engine, fuels and emission test system used and presents the scope of the experimental work undertaken.

Chapter seven gives the results and subsequent discussion of the tests and at the end provides a general discussion of the findings of the experiments. An indication is given whether this particular engine and catalyst combination is likely to experience sulphur problems in the market place with South African fuels.

Finally, a summary of the findings and the main conclusions from the experimental work conducted for this thesis are presented in chapter eight.

CHAPTER TWO
CATALYST DEVELOPMENTS

2.1 AIR/FUEL RATIO CONTROL

In a spark-ignition engine the mixture formation of air and fuel begins with the supply of intake air for the fuel. For gasoline, the average ratio for complete combustion of the fuel (stoichiometric ratio) is 14.7:1, i.e. roughly 14.7 kg of air is required to completely combust 1 kg of fuel. Given this optimum air/fuel ratio, normally called the stoichiometric air/fuel ratio, the excess factor lambda is defined as:

$$\text{lambda} = \frac{\text{quantity of air supplied}}{\text{theoretical requirement}} = \frac{(A/F)_{actual}}{(A/F)_{stoich}}$$

The inverse of lambda is called the equivalence ratio.

A fuel-lean mixture contains more air (lamba > 1), while a fuel-rich mixture (lambda < 1) contains less air. With excess air, power is reduced and the engine and exhaust temperatures are higher due to a slower rate of combustion. With excess fuel the power of the engine is improved but the fuel economy is worse. Careful control around a lambda value equal to unity is thus required for most driving conditions.

Though this condition of stoichiometric can be obtained using ordinary carburettors, the ability to control transient conditions is not very good and frequently, the air/fuel ratio is either very lean or very rich. With the introduction of automotive catalysts the need for more accurate control led to the use of electronic fuel injection. Normally the air/fuel ratio is maintained close to stoichiometric through the use of a sensor in the exhaust system, which provides a voltage signal dependent on the oxygen concentration in the exhaust gas stream. This signal is the input to a feedback system which controls the fuel feed to the intake at various speeds and loads. The sensor is called an oxygen sensor or lambda sensor. Holding the air/fuel ratio precisely on the chosen stoichiometric value is not a practical expectation of any feedback system, and lambda oscillates around the stoichiometric point within a small window.

The air/fuel mixture must be extremely fuel-rich for an engine to start, since a certain amount of fuel will condense on cold walls of intake manifold and cylinders. A lean mixture with a lambda value of 1.1 is desirable in the middle of a part-load range (normal driving) for optimum fuel economy. The lowest carbon monoxide (CO) and hydrocarbon (HC) emissions are also achieved at this setting while the emissions of oxides of nitrogen (NO_X) reaches their maximum at this point. A comparatively rich mixture (lambda = 0.9) is required at full load, during acceleration and at idle as well as in the lower part of the part-load range.

A precise mixture adjustment under all conditions is achieved by fuel injection systems with electronic engine management. Control of the air/fuel ratio depends primarily on the engine design, in particularly the valve timing, manifold design, air filter design, etc. and will be different for each model car.

The composition of exhaust gases in the spark-ignition engine can be controlled by several means. Engine design, after-treatment, and to a lesser effect, fuel composition are all effective although after-treatment devices, or catalytic converters, are the most economical option. In order to keep the active coating on these catalysts from becoming ineffective due to lead poisoning, unleaded petrol must only be used.

2.2 THE AUTOMOTIVE CATALYTIC CONVERTER

Catalysts work by providing 'active sites', where the gas molecules which are required to react together can be adsorbed in close proximity. The process of adsorption weakens chemical bonds within the molecules and thereby assists in their interaction. The degree to which molecules are adsorbed depends on their polarity. Highly polar molecules are more readily adsorbed and less polar substances are more readily desorbed. For an automotive catalyst to operate effectively, it should chemisorb the gas molecules in the desired exhaust gas temperature range and in such a fashion that any conversion reaction occurs readily. Then, the converted gas molecules, having achieved a lower energy state, must desorb at the same temperature and free the active sites for further reaction. The catalyst must not be susceptible to "poisons" which adsorb strongly but do not desorb and thus physically block active sites.

There are four important parts of a catalyst (5):

1 The base of the catalyst is the substrate or support. Initially, pellets were used but there were problems of differential thermal expansion between catalyst support and container. Also, powdering occurred due to any rubbing between the pellets under vibration. As an alternative, monolithic ceramic honeycombs were developed as supports which were lighter, stronger and provided a low back pressure. Frequently, cordierite (a magnesium aluminium silicate made from natural china clay, talc and alumina) is used for the honeycomb substrate. It has a low thermal expansion and improved shock resistance. Metal alloy catalyst support systems were introduced because of their larger surface area, thermal properties and strength. They did not achieved much popularity because of their more complex manufacturing process, higher cost and unproven reliability. Again, demand on decreased engine emission levels required a more rapid light-off of catalysts. Therefore metal catalysts are now more frequently placed as close as is possible to the engine exhaust manifold (close-coupled catalysts).

2 A washcoat of alumina is coated on to the substrate to produce a high surface area. Its purpose is to provide a suitable medium for doping with platinum or any other Platinum Group Metal (PGM). Frequently a promoter, such as ceria, is added to the washcoat. Ceria promotes the participation of water vapour in the conversion reactions, the oxygen storage capacity of the catalyst and reduces the light-off temperature of the catalyst. The light-off temperature is the temperature at which 50 per cent conversion of the pollutants occurs. The substrate is then fired, giving the washcoat a surface area equivalent to two or three football fields.

3 The actual chemical catalyst (platinum, palladium, or rhodium) is added using sophisticated doping techniques after which the substrate is fired again to increase the surface area even more. A typical Three-Way Catalyst (TWC) contains 1.75 g of platinum and rhodium.

4 A stainless steel canister, designed by the car manufacturer, is used to accommodate the finished autocatalyst. The final system is then described as a catalytic converter. It is installed in the exhaust system under the floor of the car and ahead of the silencer. The position of the converter is critical; the closer to the exhaust manifold, the higher its operating temperature and conversion efficiency will be but an increased chance of thermal degradation.

The objectionable components in automotive exhaust are carbon monoxide (CO), hydrocarbons (HC), and oxides of nitrogen (NO_x). In a three-way catalyst they can be changed to water vapour (H_2O), carbon dioxide (CO_2) and nitrogen (N_2), as follows:

Oxidation (under fuel-lean condition)

$$2\,CO + O_2 \longrightarrow 2\,CO_2 \qquad (1)$$

$$4\,HC + 5\,O_2 \longrightarrow 4\,CO_2 + 2\,H_2O \qquad (2)$$

Reduction (under fuel-rich condition)

$$2\,CO + 2\,NO \longrightarrow 2\,CO_2 + N_2 \qquad (3)$$

$$4\,HC + 10\,NO \longrightarrow 4\,CO_2 + 2\,H_2O + 5\,N_2 \qquad (4)$$

The hydrocarbons in equations (2) and (4), and in the rest in this report, are represented by the symbol HC. This is done for simplicity and has no effect on any of the following discussions.

The above reactions are speeded up and happen at lower temperatures, under the influence of a catalyst. Base metal catalysts using iron or copper as catalyst agent have a limited (30-50 per cent) conversion efficiency and deteriorate rapidly with age. Therefore, all present-day catalysts make use of one or more metals from the platinum group for increased efficiency and durability.

In 1991, 34 per cent of the platinum demand, 83 per cent of the rhodium demand and 8 per cent of the palladium demand in the Western world was for use in autocatalyst and this market is still growing. A problem free operation under all conditions is essential.

2.3 TYPE OF CATALYSTS

There are three catalytic converter systems for different exhaust designs and applications. Oxidations catalysts were first introduced and later replaced by two-stage catalysts. With the advancements of engine control systems and fuel injection, three-way catalysts have become the most effective. They reduce CO, HC and NO_x emissions simultaneously at stoichiometric conditions.

2.3.1 Oxidation catalysts

The oxidation catalyst functions under very fuel-lean (excess air) conditions and transforms hydrocarbons and carbon monoxide into water vapour and carbon dioxide through oxidation. It is often used together with an air pump that supplies additional air equal to 25 per cent of the exhaust flow to provide sufficient oxygen in the exhaust from engines that run slightly rich for improved drivability.

The NO_x is controlled by Exhaust Gas Recirculation (EGR) resulting in reductions in levels up to 60 per cent. The theory behind EGR is that some of the CO_2 and water returned to the combustion chamber are dissociated and absorb heat. This reduces the peak combustion temperature to below 1650 °C, a temperature at which nitrogen oxides are formed. However, exhaust gas recirculation has a negative effect on the fuel economy and deposits from the exhaust frequently lead to restrictions in valves and lines.

Oxidation catalysts were used in 1975 for the then current United States of America exhaust regulations. Platinum (Pt) or platinum/palladium (Pt/Pd) mixtures were most common catalyst materials and oxidation catalysts were fitted to over 80 per cent of all new cars. However, tighter emissions legislation, particularly for NO_x, has practically stopped the use of these catalysts, except maybe in some cars with lean-burn engine technology. Oxidation catalysts and exhaust gas recirculation are increasingly being used with diesel engines.

2.3.2 Two-stage catalysts

Two-stage or dual-bed catalysts were then developed to eliminate the need for exhaust gas recirculation. The catalytic converter actually consists of two catalysts in series. The first stage operates under reducing (fuel-rich) conditions to remove the nitrogen oxides (NO_X), and a second stage, following air injection, operates under oxidising conditions to remove carbon monoxide (CO) and hydrocarbons (HCs). It was found that platinum/rhodium catalysts could reduce the NO_X to nitrogen and water without producing much ammonia (NH_3) (which could again be converted to nitrogen oxides in the second catalyst) as was the problem with some earlier catalysts. Cheaper platinum/palladium catalysts were tested in some countries but considered less effective in converting the NO_X.

With the above systems it was possible to meet tight emission standards without reducing engine performance or losing too much fuel economy since the engines could be run close to stoichiometric conditions, at 14.7:1 air/fuel ratio, but on the rich side. Exact and frequent engine tuning was essential to maintain optimum operating conditions for the catalysts.

Using two catalysts in series meant that a sufficient amount of space was needed underneath a car and, because of the injection of cool air, the oxidation catalyst ran at fairly low temperatures. Attempts were made to fit both the reducing and the oxidation catalyst in one housing. The use of advanced catalyst compositions and fuel injection technology resulted in the possibility of using three-way catalyst systems.

2.3.3 Three-way catalysts

The advent of electronic engine management systems, coupled with oxygen (lambda) sensors in the exhaust and the use of fuel injection control, has meant that engines can now be operated under conditions very close to the stoichiometric air/fuel ratio at all operating conditions. This has led to the effective use of three-way catalysts (TWCs) which can treat CO, HC and NO_X simultaneously. Such systems eliminate the need for other equipment such as exhaust gas recirculation or air pumps and preserve fuel economy. Most of the current TWCs use a platinum/rhodium mixture in a 5:1 ratio although the cheaper palladium is increasingly being used. Platinum (Pt) particularly promotes the oxidation of CO and HC under lean conditions while rhodium is exceptionally effective in the conversion of NO_X under fuel-rich condition. Rhodium is also thought to be responsible for stimulating the participation of water vapour in conversion reactions for CO removal under rich conditions.

The three-way catalyst (TWC), combined with a lambda feed-back (closed-loop) system, has become the most effective pollutant-reduction system available to date. TWCs can be used without closed-loop control engine management systems (in so-called open-loop mode) and an approximately 50 per cent (6) reduction in pollutant levels is still achievable. Emissions from cars with TWCs in open-loop mode are dependent on the air/fuel settings of the engine.

For modern catalysts the light-off temperature, the temperature at which 50 per cent conversion of all three pollutants occur, is very important. This temperature is typically at 280-320°C and reached within a minute after a cold start (7).

Tighter emission standards can be met with improved engine control systems, with increased amounts of platinum group metals on the catalyst, with more efficient catalysts and by positioning the catalyst nearer to the engine for quicker light-off operation. The latter objective can also be achieved by the use of an electrically heated catalyst (EHC) which can precede a normal catalyst in the exhaust. Electrically heated catalysts heat up faster and remove up to 50 per cent of the hydrocarbons and NO_X compared with conventional catalysts. EHCs also virtually eliminate formaldehyde emissions from methanol-fuelled cars. However, current problems with this type of catalyst include the amount of battery power and the length of time required for the catalyst to warm-up, the durability and the cost (8). Fitting a small metal catalyst near the exhaust manifold before the main TWC has also been considered a feasible option.

The removal of methane by catalytic means remains a problem as methane is virtually non-polar and is not readily adsorbed onto the surface of the catalyst. Methane emissions are not considered important as they are not very reactive photochemically but increased concern is being shown because of their influence on the greenhouse effect.

Some advanced engine management systems make use of two lambda sensors, one before and one after the catalyst, so that even better air/fuel control can take place at stoichiometric conditions. In addition, it appears possible to determine the catalyst degradation and a warning signal might inform the driver his catalyst is ineffective (9).

CHAPTER THREE
SULPHATE EMISSIONS BY OXIDATION CATALYSTS

3.1 CATALYST REACTIVITY

Prior to 1950 it was generally thought that sulphur in gasoline is oxidised to SO_3 during combustion in the engine and is emitted as H_2SO_4 (10). It was demonstrated in that year, however, that the sulphuric acid found by previous investigators was a sampling artifact and that the sulphur is actually emitted as SO_2 (11).

$$\text{Gasoline sulphur} + O_2 \text{-->} SO_2 \qquad (5)$$

The emission levels were, however, relatively low and did not cause any problems.

The next significant development occurred in 1972 when deterioration was studied in oxidation catalysts with excess air supplied by air-pumps. The loss in activity was thought to be due to the presence of sulphur in the fuel (1). The SO_2 from the combustion in the engine was oxidised in the catalyst:

$$SO_{2(g)} + \tfrac{1}{2}O_2 \text{-->} SO_{3(g)} \qquad (6)$$

The oxidation of SO_2 to form SO_3 occurs by means of a Langmuir-Hinshelwood mechanism (12). The SO_3 reacts to form stable sulphates with the alumina washcoat and any common base metal catalyst material (often copper) available:

$$CuO + SO_{3(g)} \text{-->} CuSO_4 \qquad (7)$$

$$Al_2O_3 + 3\ SO_{3(g)} \text{-->} Al_2(SO_4)_3 \qquad (8)$$

The forming of sulphates on the oxidation catalyst resulted in decreased activity for CO conversion while the HC conversion remained virtually unchanged (1). The catalyst activity recovered after exposure to high (>700 °C) temperatures, most likely by the reversal of the above reactions. However, such high temperatures were not reached under normal driving conditions and the storage of sulphur was permanent.

Limited sulphur storage was also found in catalysts under **reducing** (fuel-rich) conditions, resulting in decreased conversion of NO to N_2 (1).

From equation (6) the amount of conversion under thermodynamic equilibrium conditions can be expressed [13] as follows:

$$K_{eq} = \frac{((SO_3)_{out})}{((SO_2)_{out}(O_2)_{out}^{1/2})_{equil.}} \tag{9}$$

where K_{eq} is a function of temperature. If an equilibrium in the catalytic conversion is not reached, the quotient is less then K_{eq}. At temperatures 700 °C and higher, a decline in the oxidation was observed. It was concluded that the reaction is kinetically limited and that at low catalyst temperatures the reaction and residence time are sufficient [14]. Too low a temperature makes the catalyst ineffective and experiments proved that maximum sulphur oxidation therefore occurred at 500-550°C [13], and this is also the average operating temperature for most catalysts.

Release of stored sulphur under high temperature conditions is not the reverse of reactions 7 and 8 but occurs in SO_3/SO_2 equilibrium conditions [14]:

$$Al_2(SO_4)_3 \text{ ---> } Al_2O_3 + (SO_3,SO_2,O_2) \tag{10}$$

$$CuSO_4 \text{ --> } CuO + (SO_3,SO_2,O_2) \tag{11}$$

Equations (7) and (8) imply that the chemical composition and reactivity of the catalyst alters. Also, a catalyst will indirectly be a source for sulphuric acid [4,15] as downstream of the catalyst, any SO_3 released combines extremely rapidly with water vapour below 450 °C to form sulphuric acid (H_2SO_4) [2,3,4]:

$$SO_{3(g)} + H_2O_{(g)} \text{ --> } H_2SO_{4(g)} \tag{12}$$

At the dewpoint, calculated to be approximately 140 °C for the concentrations typical in automotive exhaust [16], liquid H_2SO_4 droplets begin to form:

$$H_2SO_{4(g)} \text{ ----> } H_2SO_{4(liq)} \quad (<140°C) \tag{13}$$

Since the exit temperature of an exhaust gas is normally above 140 °C, the H_2SO_4 formation occurs upon leaving the tailpipe. Localised health hazards in high-density traffic situations can exists when high sulphur fuels are used [4].

SO_3 and H_2SO_4 can also react with a variety of other components, including ammonia (NH_3) and the metal in the walls of the exhaust system. Fortunately, under (fuel-lean) conditions which favour SO_3 formation, NH_3 is not a component in the exhaust gas (17). Actually, SO_2 in the exhaust suppresses NH_3 formation (18,19,20). It prevents platinum from promoting the NH_3 reaction across the Air/Fuel ratio commonly used for three-way control. Rhodium, which is quite resistant to SO_2 poisoning, forms NH_3 in significant quantities only under strong reducing conditions (18,21). Thus, under actual closed-loop control, it is expected that any NH_3 formation will be small.

While reaction of sulphur with the metal surface of the exhaust system is possible it is not normally a major sink for SO_3 (4,11). The H_2SO_4 emission rates are many times the emission rates of all metallic cations combined, indicating that H_2SO_4 is the major form in which $SO_4^{=}$ or sulphate is emitted (22).

In raw exhaust, less than one per cent of the sulphur in fuel is emitted as sulphate (4,19) but with the use of monolith and pellet oxidation catalysts up to 40 per cent sulphate emissions can be produced (4,14), the rest being SO_2. Cascade impactor data indicated that over 90 per cent of the H_2SO_4 is found in particles smaller than 0.3 μm, confirming that the acid with associated water is emitted as a very fine mist (2,19,24).

3.2 FACTORS AFFECTING SULPHATE EMISSIONS

3.2.1 Storage/Release

Initially, with a catalyst that is new, the SO_3 generated is quantitatively stored as a metal sulphate (16,23). As the stored amounts builds up and some of the newly stored sulphate is released, the storage rate declines until, after many hours, an equilibrium is reached where the storage and release rates are equal (11). The length of time required to reach this steady state is more or less independent of engine conditions (20) but the amount stored is dependent on temperature and on gas stream composition. If, for example, the temperature is lowered, further storage occurs until a new equilibrium, appropriate to this new temperature, is reached. If the SO_2 in the catalyst feed is turned off or lowered, release occurs until again equilibrium is established. Even small amounts of sulphur present in the fuel will result in stored sulphates on the catalyst and therefore reduction in the activity of the catalyst. As long as sulphur is present in fuel, some degradation of catalyst activity must be accepted.

Research into catalyst storage and release of sulphur was initially seriously hampered by not having accurate analysis techniques available to detect the SO_2 emissions and to determine mass balances (3). The method most favoured was using a dilution tunnel and a particulate sampling system in which, after a 10:1 dilution of the exhaust gas, a size distribution was done on the sulphate condensate (3,15,24). A controlled condensation hydrogen peroxide bubbler method was adopted for SO_2/H_2SO_4 sampling of the exhaust system and found to produce reasonably accurate data (4). However, many of the experiments did not give reproducible data because not sufficient time was taken to allow equilibrium storage and release conditions on the catalyst. However, they did show that a significant fraction of the sulphur was stored (13,14,19,25) and that a rapid increase in temperature gave higher SO_2/SO_3 tailpipe emissions than could possibly be produced by the fuel burned.

Reading through the literature, it appeared that catalyst testing was more orientated towards a quantitative analysis of the sulphate problem then to finding any solutions. A severe lack of useful reference data such as catalyst temperature profile, catalyst composition and history, air/fuel ratio during test conditions, the appropriate space velocity, etc, in the reporting of results made a scientific approach just about impossible for any researcher at the time. Omissions of SO_2 levels measured and the lack of sulphur-balances in some studies added to the difficulty. No uniformity existed in the emission test cycles used, making comparisons between reported data impossible.

Laboratory bench scale reactors and synthetic gas compositions were eventually introduced to simulate the effect of vehicle operating conditions on the conversion of SO_2 to SO_3. In these artificial tests a sample of an automotive catalyst monolith was placed inside a quartz reactor in a temperature controlled furnace and emissions were measured for various simulated exhaust gas compositions. Using these techniques it was not surprisingly shown (14,19) that the SO_3 and sulphate emissions dropped rapidly as the exhaust tail pipe O_2 concentrations were reduced. Interestingly, the CO and HC conversions were unaffected by the excess oxygen reduction. This indicated that the oxidation of SO_2 to SO_3 happens at a much slower rate than the oxidation of CO or HC (25).

The above results gave an added incentive for the development of three-way catalysts with close-loop control where the excess oxygen levels can be carefully controlled. With the air/fuel ratio set only slightly lean sulphate emissions could approached those of a non-catalyst equipped car (23).

3.2.2 Catalyst composition

The catalyst reactivity towards sulphur conversions depends on the noble metal choice and the selected loading; Platinum catalysts show higher $SO_4^{=}$ emissions tendencies than do Platinum/rhodium or Platinum/Palladium catalysts. Platinum/rhodium catalysts produce the lowest sulphate levels (3,14,19). This was confirmed by Krause (15) who found in order of increasing sulphate emissions:

Pt-Rh monolith < Pt-Pd pellets < Pt-Pd monoliths < Pt monolith.

The most active metals for NO_x conversions have been found to be rhodium and iridium (26,27,28). However, rhodium, palladium and platinum rapidly lose their ability to convert NO_x if the air/fuel ratio is set to more fuel-lean. Iridium exhibits superior ability to convert NO_x under oxidising condition (26,28). Most current catalyst formulations use Pt/Rh in a 5:1 ratio.

3.2.3 Temperature

Typical catalyst operational temperatures are 450 °C for idle and low speed cruising and up to 750 °C for high speed cruising. Most driving cycles have an average operating temperature of 500-600 °C. In this range the sulphate emissions were found not to depend much on temperature (19). Higher temperatures will lead to decreased storage of sulphur on to the catalyst (1,13,15,20,25) and to recovery of catalyst conversion activity. At low temperatures the sulphur storage may have a more pronounced effect on the reactivity.

Reducing the sulphate problem by placing the catalyst closer to the engine was not considered feasible as frequently sintering occurred of the catalyst washcoat at temperatures higher than 800°C (24) and this would damage the catalyst permanently.

3.2.4 Space velocity

Increasing the space velocities by using smaller catalyst beds, and thus reducing the gas residence times, predictably reduced the SO_2 conversion rates in laboratory studies (14) but not always during actual field tests with pelletised catalysts (19). Increased space velocities also resulted in a less desirable reduction in catalyst conversion efficiency (14). Therefore, sulphate emission control by increasing the space velocity was abandoned as an option.

3.2.5 Poisoning

SO_2 deactivates the NO_x removal on a platinum catalyst (26) and inhibits the reaction of NO to NH_3 when platinum, palladium or nickel catalysts are used (26,29). In Pt/Rh catalysts the bulk of the NH_3 that is formed under strongly reducing conditions is due to rhodium and not to platinum (26). Other researchers (13,23) did find that platinum can stimulate NH_3 formation but their tests were done under sulphur-free synthetic feedstreams.

Fisher (21,26) studied the effect of SO_2 on a variety of reactions by using single crystals of platinum . He found that the adsorption and desorption of CO, the NO-CO interaction, and the dissociation and desorption of NO are all inhibited to various degrees by SO_2 in the exhaust gas (13,28). This was confirmed by Hunter (24) who observed a clear decrease in activity of HC, CO and NO_x conversion with increased fuel sulphur content. The decrease was most significant for CO conversion activity.

Fisher found (26) that an important feature of sulphur as a catalyst poison is the fact that it is very strongly bonded to the platinum surface (13). In a synthetic reactor it formed a stable, non-desorbing, platinum/sulphur composition at temperatures considerably higher (23) than common for most catalysed chemical processes. This would suggest permanent platinum poisoning.

Fortunately, others (27,29,30,31) found that the sulphur poisoning is reversible, even for platinum catalysts; the catalyst activity that is lost by increasing the fuel sulphur concentration, can be recovered with lower sulphur fuels and not only with increasing temperatures. This finding created a significant interest and catalyst manufacturers were quick to point this effect out to fuel suppliers. They, however, replied that reduction in the fuel sulphur content (desulphurisation) in petrol could indeed be done but would lead to a significant fuel price increase.

3.2.6 Aging

Artificial aging of the oxidation catalyst was considered an alternative to reduce the sulphate emissions (15,19). This option of controlled aging was possible since catalyst activity for SO_2 conversion is lower than for CO and HC oxidation. Therefore any decrease in activity gives a larger decrease of $SO_4^{=}$ emissions than increase in CO and

HC emissions. Sulphate emissions from aged catalysts were often found to be less than 50 per cent than those from fresh catalysts, without any change in CO and HC emissions (19).

Hunter (15) found in his tests that the sulphate emissions of new oxidation catalysts first increased but dropped after 6400 km of vehicle mileage. They eventually stabilised at a steady level. His explanation was that fresh catalysts have a considerable storage capacity for $SO_4^{=}$ and retain a large fraction of any sulphates formed. Indeed, this would mean that initially the sulphate emissions are low, then increase with time as the catalyst becomes saturated with stored sulphur while the conversion activity for SO_2 is still high, and then decrease as the catalyst ages and conversion activity deteriorates. Eventually, an equilibrium level is found for the sulphate emissions. Kraus (15) had confirmed the existence of an stabilised level many years before.

3.2.7 Fuel sulphur

Barnes (25) found a linear relationship between the sulphur content of the fuel and the equilibrium sulphate emissions. However, the sulphate emissions were found more dependent on the composition of the catalyst than on the sulphur content of the fuel. The catalysts suppliers challenged this finding. In subsequent laboratory studies (18), increasing the sulphur content of the fuel from 0 to 0.03 %(m/m) resulted in increased emissions of HC, CO and NO. But a further increase of fuel sulphur content from 0.03 to 0.09 %(m/m) had a negligible effect on emission levels as no more sulphates could be stored on the catalyst.

Although acknowledging the fact that the sulphur in fuel deteriorated the catalyst activity, no legislation was forthcoming to reduce the sulphur levels in fuels. The 1983 legislative emission limits could be obtained even with catalysts poisoned by the sulphur in the fuel. Removing sulphur from the fuel was considered too costly and would thus be an unpopular move.

3.3 SULPHATE EMISSION CONTROL

In addition to modification of the catalyst materials, type and fine-tuning of the engine operating condition, another possible method for the control of sulphate emissions was under investigation. This is by the use of a sulphate trap, containing sorbent particles capable of removing $SO_4^{=}$ from the exhaust gas , downstream of the oxidation catalyst. A study sponsored by the Environmental Protection Agency (EPA) in 1974 (23) identified alkaline calcium based compositions as the most promising sorbent materials. Holt (19) described a test where a calcium oxide (CaO) pellet trap operated satisfactory for a total distance of 42,000 km and where the $SO_4^{=}$ removal was maintained above 95 per cent. However, he did comment that the pressure drop across the trap had increased due to a 13 per cent increase in pellet volume by the sulphation from CaO to $CaSO_4$. In addition. some powdering of the pellets occurred by the pulsating exhaust gas stream. This increase in pressure drop over the trap was considered too large for any practical vehicle operation. Research continued to find a more suitable trap material but was eventually abandoned.

3.4 EVALUATION

By a combination of all the above factors, the sulphate emissions, occurring only under very lean conditions, could be eliminated. By selecting the right platinum group metal, by operating the catalyst at an air/fuel ratio only slightly fuel-lean and operating the catalyst at higher temperatures, the sulphate emissions were reduced to negligible levels. Degradation of the catalyst activity by the sulphur still occurred and therefore demands were made by car and catalyst manufacturers to fuel suppliers to reduce the fuel sulphur levels, in order to meet tighter emission legislation levels.

More legislation demanded lower emission levels and resulted in more active catalyst compositions and better air/fuel control technology. This led, however, to a new sulphur problem. Excessive levels of hydrogen sulphide (H_2S), many times higher than could possibly originate from the sulphur in the fuel burned, were noticed under certain driving conditions. Motorists using these catalysts complained about the production of bad odour. Research by catalyst suppliers failed to assess the size of the problem and very little attention was given to it initially.

CHAPTER FOUR
HYDROGEN SULPHIDE EMISSIONS

4.1 HEALTH EFFECTS

Hydrogen sulphide is both an irritant and an asphyxiant at low concentrations causing eye irritation and, at slightly higher concentrations, irritation of the upper respiratory tract (32). The odour detection thresholds are considerably less than the health effects threshold and are as follows (32):

Bio-characteristics of H_2S	
Offensive odour	150-300 ppb
Exposure limit (10 min.)	15 ppm maximum
Eye irritation	50 ppm
Unconsciousness	$>$200 ppm

Hydrogen sulphide is rarely emitted directly from engines even though thermodynamic studies show this is possible (33). Under the influence of a catalyst, the chemical reaction of sulphur oxide to hydrogen sulphide is promoted. One of the early complaints encountered on the first oxidation catalysts was therefore the smell of 'rotten eggs'. This happened mostly at start-up or at idle, when fuels with high sulphur contents were used. It is thus not a question of a defective reaction owing to the catalyst or an engine fault, but of an undesirable conversion reaction.

During the 1980s, improved catalyst technology had produced considerably more active and durable catalysts than the first generation of oxidation catalysts. Part of this improvement was achieved by increasing the oxygen storage capacity on the catalyst by making use of cerium oxides. This resulted in an increase in the extent of the H_2S odour problem; more stored sulphur could be released. Several mechanisms were suggested to describe the generation of H_2S emission peaks and research was directed to solving a real field problem rather than just satisfying academic curiosity.

4.2 CATALYST REACTIVITY

As early as 1975 it was realised that hydrogen sulphide (H_2S) is the preferred sulphur-containing species under fuel-rich or reducing conditions (25) although COS (carbonyl sulphide) can also be formed during rich operation via a reaction of CO with the sulphur stored on the catalyst. COS is formed under extreme (>700°C) temperature conditions (21,33) and might react with atmospheric moisture to form H_2S:.

$$COS + H_2O \dashrightarrow H_2S + CO_2 \qquad (14)$$

The production of H_2S became especially apparent when dual bed catalysts were introduced to reduce the NO_x emissions. However, any H_2S formed in the first catalyst under excess fuel conditions was oxidised in the second catalyst to SO_2.

Laboratory studies showed (26), using a platinum/rhodium catalyst in a synthetic gas stream, that after the addition of SO_2 to the inlet, the SO_2 content of the catalyst outlet gradually rose with time until it settled at a stabilised value. Subsequent analysis of the catalyst showed that sulphur was stored onto the wash coat. The SO_2 level stabilised down stream was found lower than the inlet SO_2 level and this was thought to be due to direct conversion of SO_2 to H_2S and to COS under net equilibrium conditions. (26). Later catalyst formulation using washcoat including aluminium and cerium oxides gave 100 per cent SO_2 to H_2S conversion under fuel-rich conditions (34). Indeed, H_2S was found to be the dominant species at the catalyst outlet at temperatures in the range 250-900°C (35). At higher temperatures the H_2S emissions decreased and more SO_2 was emitted.
Three main factors were identified for H_2S emissions (36)

1) Fuel-rich operating conditions are required to produce sufficient H_2 for H_2S formation.

2) A period of lean (excess oxygen) operation is required prior to the H_2S production.

3) A catalyst temperature in excess of 500 °C increases the likelihood of H_2S emissions but at temperatures above 700 °C the conversion of sulphur to H_2S is thermodynamically limited and SO_2 levels rise with increased temperature.

Two mechanisms were suggested (37,38) by which H_2S may be formed over a three-way catalyst. The first one is a steady state conversion of SO_2 to H_2S over the noble metals under rich conditions with the H_2S concentration not exceeding the inlet SO_2 concentrations. This conversion was relatively well understood and expected.

The second mechanism, however, involves the storage on and release of sulphur by the catalyst. This results in extremely high peak levels of H_2S emissions for short duration under certain transient conditions.

Deterioration of the catalyst reactivity due to sulphur present in the fuel had been noticed since the early introduction of catalysts (1,2,4,13,15) and sulphur was thought to react with the noble metals leading to poisoning of the catalyst surface (39).

4.2.1 Steady-state emissions

Under steady-state engine conditions and fuel-rich conditions, the inlet sulphur dioxide is converted to hydrogen sulphide in the catalyst, according to the following reaction:

$$SO_2 + 3\,H_2 \rightarrow H_2S + 2\,H_2O \qquad (15)$$

This reaction might involve the formation of chemisorbed sulphur, denoted as $S_{(a)}$, as an intermediate species (33). This is based on the observation that in the absence of O_2, SO_2 dissociates on platinum, palladium and rhodium surfaces in the temperature range 300-800 °C (40,41,42).

$$SO_{2(g)} = SO_{2(a)} = S_{(a)} + 2\,O_{(a)} \qquad (16)$$

Hydrogen then desorbs dissociatively on the surface and reacts with $S_{(a)}$ and $O_{(a)}$, forming H_2S and H_2O, respectively.

The steady state H_2S emissions increase with temperatures above 550°C and are independent of excess H_2. Near the stoichiometric point practically no H_2S is produced (25). Truex et al (34) confirmed the finding by Henk et al (43) that the removal of water from feed gas reduced the H_2S formation by approximately 50 per cent.

Steady-state H_2S emissions are not greatly affected by the presence of either alumina or ceria in the washcoat (44) and are caused by the dissociation and subsequent reactions on the noble metal surface. Others (34) came to the same conclusion with synthetic reactors.

The steady state emissions are, with most fuels, low enough not to cause any problems.

4.2.2 Peak emissions

The second and undesired mechanism is a rapid release of previously stored sulphur with H_2S emissions that exceed the inlet SO_2 concentrations for short durations.

Sulphur is stored under oxidising conditions as sulphates on the washcoat surface and is rapidly released after an air/fuel ratio change to fuel-rich (reducing) conditions:
Oxidising sulphur storage (under fuel-lean condition)

$$SO_2 + \tfrac{1}{2} O_2 \text{ ---> } SO_3 \qquad (17)$$

$$Al_2O_3 + 3\,SO_3 \text{ -> } Al_2(SO_4)_3 \qquad (18)$$

$$2\,SO_3 + CeO_2 \text{ --> } Ce(SO_4)_2 \qquad (19)$$

Reaction (18) occurs above 500°C [45] and is promoted by the presence of platinum [26,29,39]. At temperatures over 700 °C the reaction is reversed. Reaction (19) occurs at temperatures below 195°C (during the warming-up period of a catalyst) but the product decomposes above this temperature [44,45]. In an alternative process, $Ce_2(SO_4)_3$ is formed via the reduction of CeO_2 by SO_2:

$$SO_2 + O_2 \quad \text{---lean exhaust,Pt,Rh,Pd--->} \quad SO_3 \qquad (20)$$
$$3\,SO_3 + 6\,CeO_2 \text{ --> } Ce_2(SO_4)_3 + 2\,Ce_2O_3. \qquad (21)$$

The products (in equation 21) have been reported to form readily at 550°C, and the reaction is reversed above 900°C. Increased catalyst activity can be achieved by higher loadings of cerium oxide and but this might result in significantly higher levels of sulphur storage on the catalyst.

It is unlikely that bulk sulphates are formed with either alumina or ceria and the reaction of these oxides with SO_3 is generally thought to be a surface phenomenon. For instance, the storage of sulphur on alumina is directly related to the surface area of the alumina [43].

Generally speaking, the more sulphur the catalyst is exposed to during storage, the greater the H_2S release during rich operation. The release of stored sulphates under rich conditions happens as follows:

Reductive sulphur release (under fuel-rich conditions)

$Al_2(SO_4)_3 \rightarrow Al_2O_3 + 3\,SO_2 + 1\tfrac{1}{2}O_2$ (22)

$SO_2 + H_2 \rightarrow H_2S + H_2O$ (23)

and

$Ce_2(SO_4)_3 \rightarrow 2\,CeO_2 + 3\,SO_2 + O_2$ (24)

$SO_2 + 2\,H_2 \rightarrow H_2S + 2\,H_2O$ (25)

The reactions with alumina and cerium, equations (22) and (24) above, happen under fuel-rich exhaust conditions and produce H_2S under influence of a platinum group metal. H_2S is rapidly released from the alumina washcoat but more significantly from the rare earth coating (33,43,45). No storage occurs under rich conditions (34).

After a change from fuel-lean to fuel-rich condition, very high emissions of H_2S have been noticed (typically within the first 5 minutes), exceeding the inlet SO_2 levels by a factor of 3-9 (43), followed by a rapid decrease within a few minutes. After 5 or 6 minutes exposure to a rich exhaust, the amount of H_2S leaving the catalyst is approximately that which can be expected for direct conversion of SO_2 from fuel sulphur levels. The observation confirmed that a sulphur storage/ release mechanism was involved and that is was likely due to the presence of rare earth oxides, particularly CeO_2. Indeed, increasing the level of CeO_2 loading in the catalyst gave higher peak H_2S release (46). The nature of the sulphur storage site on the catalyst was also found to have an effect (34,44).

Cerium oxides are added to catalyst formulations since they have the ability to release oxygen atoms (45) and improve catalyst conversion efficiency under fuel rich conditions:

$2\,CeO_{2(s)} \leftrightarrow Ce_2O_{3(s)} + \tfrac{1}{2}O_{2(g)}$ (26)

The free oxygen produced by cerium oxides enables the oxidation of CO and CO emissions for lambda values smaller than 1.0 .
Truex et al found (34), using a synthetic reactor, that the release rates are approximately an order of magnitude greater than the sulphur storage rates with 90 per cent of the H_2S being released in less than one minute.

The rapid peak H_2S release is associated with transient vehicle operation of acceleration, deceleration and low-speed conditions, typical of stop-go driving in heavy traffic (31,34). Little or no H_2S is formed during steady-state cruising since most electronic injection systems operate on the lean side under these conditions (34). For effective emission control of CO, HC and NO_x, lambda oscillates at a frequency of 0.5 Hz in the range $0,96 < \text{lambda} < 1,04$.

Lox et al (30) suggested that the observed H_2S peak might be a composition of two release mechanisms and that the second release comes from storage of sulphur onto the noble metals surface. This would mean that increased catalyst loading with noble metals would give higher peaks, a fact observed by none of the researchers. In addition, thermodynamic studies have indicated that platinum and rhodium sulphates are unstable under the normal operating temperatures of a TWC (400-800 °C). It is more than likely that the peak release originates from two sources; a sharp peak formed by sulphur release from the cerium and the slower release, forming the decay part of the peak, from the alumina.

Near stoichiometric conditions the level of storage and release of sulphur is strongly dependent on exact air/fuel ratio (47) and the lambda value oscillates between values of 0.96 and 1.04 at roughly 0.5 Hz for effective control of CO, HC and NO_x.

Truex et al (34) found that the water-gas shift reaction did not contribute any hydrogen to the release; the water-gas shift reaction is kinetically too slow to participate.

4.3 FACTORS AFFECTING EMISSIONS

4.3.1 Air/fuel control

H_2S emissions are directly dependant on the air/fuel ratio during storage and release conditions and are lowest if this ratio can be kept as close as possible to stoichiometric under all driving conditions (29,30,38,39,43,45). However, this might affect drivability and fuel economy of a car and therefore the air/fuel ratio is on the fuel-lean side during cruising conditions and on the fuel-rich side under acceleration and idle conditions.

Ernest (27) and Von Carlowitz et al (47) both found that the H_2S release levels emissions decreased as the air/fuel ratio was increased from very rich to less rich and approaching stoichiometric conditions. This is likely due to the amount of H_2 available in the exhaust to react with the stored sulphur as the water-gas shift reaction is too slow to contribute. The reverse is also true, the richer the air/fuel ratio, the more rapid the release of H_2S (43,47).

Von Carlowitz et al (47) found that storage near stoichiometric condition, but on the lean side, produced less H_2S emissions during subsequent rich conditions than storage during very lean conditions. They did, however, comment that some drifting to rich air/fuel ratio's may have occurred and might be the cause of the lower emission. The same may have happened with the tests conducted by Henk at al (43) who concluded that storage at a slightly lean air/fuel ratio of 1.016 resulted in higher H_2S release than when storage was done at the stoichiometric point. Lox et al (30) found that peak H_2S emissions are only slightly dependent upon the storage air/fuel ratio and that they did not increase much for storage conditions with lambda values higher than 1.005 .

Using empirical models, a best fit function for peak H_2S emissions was established by Ernest (27):

$$P=K_1[O_2] + K_2[O_2]/[CO] + K_3[O_2]^2/[CO] \qquad (27)$$

The peak emissions depend on the sulphur storage conditions as indicated by the CO and O_2 variables. The model shows how the H_2S emissions reach a maximum when the storage treatment is carried out just lean of stoichiometric conditions. These results may explain why some vehicles emit higher levels of H_2S than others; the magnitude of H_2S emissions depends directly on the air/fuel control of the engine (27).

By minimising the drift of air/fuel ratio's into lean or rich regions the emission levels can be kept to a low level. Sophisticated engine management systems with fuel cut-off have created the possibility of reducing the numbers of extreme fuel rich occurrences (48,49,50).

Extreme fuel-lean conditions have been found to reduce the peak H_2S emissions (27). It might be that during very lean exposure, in addition to higher levels of sulphur storage, greater replenishment of oxygen into the oxygen deficient cerium oxide structure may occur. During subsequent periods of rich exposure, hydrogen may be used for stripping of lattice oxygen from the cerium oxide promoter rather than reacting with any stored sulphates. Sulphates created under these conditions appear to be more tightly bound and more difficult to remove.

An important part of the total emission system is the evaporative carbon canister when fitted to cars. The canister collects evaporative fumes from the fuel tank instead of their being released to the atmosphere. Fumes loaded in the canister are purged back to the engine through the inlet manifold. This might create brief fuel-rich conditions. Indeed, canister purge was found to be one of the main causes for H_2S emissions (30,50). The purge is the greatest at low inlet manifold pressure (low engine loads) when the engine has little ability to burn the purged fumes.

4.3.2 Catalyst composition - wash coat

A large amount of research was focussed on the emissions formed by rare earth metal catalysts alone. Ernest (27) investigated four catalysts using La_2O, CeO_2, Nd_2O_3 and Pr_4O_{11} doped onto a spherical alumina substrate. He found that only CeO_2 in the absence of noble metals exhibited the ability to oxidise sulphur and promote storage and subsequent release of H_2S. However, once impregnated with noble metals all four catalysts produced H_2S emissions, the lanthanum oxide (La_2O) showing the highest levels and plain alumina the lowest. This result is not surprising since lanthanum oxide has a strong basicity and greater affinity for the capture of sulphate. It might explain why some of the advanced catalyst systems (which frequently contain high levels of both lanthanum and cerium oxides) are typically high H_2S emitters. For a short while Lanthanum was used as a washcoat stabiliser (46) but this practise was discontinued after the above findings.

Near stoichiometric conditions and at slightly lean conditions with lambda values of 1.02, cerium (III) sulphate and aluminium sulphates were found to form at temperatures up to 500 °C and 400°C respectively (33). A consideration of the relative stabilities of aluminium and cerium sulphates indicated that $Ce_2(SO_4)_3$ (eq.19) is formed faster than $Al_2(SO_4)_3$ (eq.18), with sustained exposure to suitable sulphur-containing exhaust gas. Decomposition of $Al_2(SO_4)_3$ followed by $Ce_2(SO_4)_3$ then releases a SO_2/SO_3 which may, in the presence of a catalyst, be reduced to H_2S.

At room temperature, exhaust SO_2 can chemisorbs onto the cerium (IV) oxide surface to form sulphite species. Exposure of CeO_2 to SO_2 at the typical operating temperature of a catalyst (550 °C), however, leads to (33):

$$6\,CeO_2 + 3SO_2 \dashrightarrow Ce_2(SO_4)_3 + 2\,\text{"}Ce_2O_3\text{"} \tag{21}$$

where "Ce_2O_3" represents reduced cerium sites in the host CeO_2 structure. Heating this product to 900°C reverses the reaction.

The formation of cerium sulphate compounds involves a surface phenomenon and detailed analysis (45) showed that approximately 10 per cent of the cerium is involved. Most of the cerium sulphates are released during peak emission but Beck et al (45) proved in their tests that a third of the original sulphur stored as cerium sulphates had remained on the catalyst (27). Al_2O_3-only catalysts have a similar behaviour and release only small quantities of H_2S, most of it being permanently stored. Combined CeO_2/Al_2O_3 supported catalyst have a significantly higher release rate and values over 70 per cent have been reported in literature (34,43).

Increased use of rare earth oxides (51) led to increased peak H_2S emissions by providing more sites for sulphur storage on the catalyst. As an example, Rieck at al (46) found that a 17.7 g/l of rare earth loading gave peak H_2S emissions levels of 106 ppm, doubling the rare earth loading increased the peak to 159 ppm.

The initial rate of sulphur removal by H_2 is more rapid with a monolith catalyst than with a pelleted catalyst (27,45). The reason can be partly attributed to a difference in the dynamic behaviour as alumina beads have a typical coating thickness of 1.6 mm compared to 0.01-0.1 mm for a monolith. The monolith can also store more sulphur, partly because of its greater amount of cerium oxide per unit weight present.

Truex at al (34) found a modest storage of SO_2 onto a CeO_2/Al_2O_3 support-only catalyst and a much higher storage level over a $Pt/Rh/CoO_2/Al_2O_3$ catalyst. This confirms the thought that SO_2 conversion to SO_3 results in extensive chemisorption of SO_3 to form stable alumina and ceria wash coat sulphates.

4.3.3 Catalyst composition - noble metals

It is expected, and indeed confirmed by field experience, that H_2S emissions will decrease with use as a result of the catalyst's exposure to high temperatures. Thermal deactivation results in loss of effective surface area in the support material, sintering of the noble metals, as well as a suspected incidence of noble metals-support interactions. The latter is said to happen under fuel rich conditions and high temperatures, as under full throttle enrichment. The phenomena is called **Strong Metal Support Interaction (SMSI)**. Kunomore (52) suggested the formation of a superficial alloy between platinum and aluminium:

$$Pt + Al_2O_3 \text{--->} PtAl_{2/3} * 2/3(Al_2O_3) \qquad (28)$$

Most of the catalyst activity is restored under subsequent mild oxidation conditions. The amount of sulphur in the alumina wash coat can play a role in the above reaction and might promote any partial reduction of the surface alumina even at normal catalyst operating temperatures. This is called a **sulphur-aided SMSI**.

The effect of sulphur on SMSI behaviour at lower temperatures has also been explained as follows (52):

$$Pt + (SO_4^{-2})_{support} \dashrightarrow Pt * S + (O^{2-})_{support} \qquad (29)$$

(under condition of excess H_2,and at 500°C. The reverse reaction occurs under excess O_2 at 450°C.

Current designs strive to optimise the effects of SMSI interactions, and research the fundamental causes of different reactivity patterns and the nature of the specific catalytic sites on different oxide systems. The reactivity patterns and sites can be then designed into future catalytic systems with much higher reaction rates (53,54,55).

The reaction indicated by (eq. 29) might explain (34,43,45) why not all sulphates stored onto the wash coat are released during fuel rich conditions.

Thermodynamic calculations using a free energy minimisation computer programme (33) have indeed suggested that sulphur may react to form sulphides with platinum and rhodium but at lower temperatures (300°C and 500°C respectively).

4.3.4 Temperature

Peak H_2S release rates and steady state emission are greatly temperature dependent (34,43). Truex et al (34) found for $Pt/Rh/Al_2O_3$ catalysts that higher temperatures increased the release rate. Similar experiments with $Pt/Rh/CeO_2/Al_2O_3$ catalysts gave a faster release at 750 °C than at 550 °C.

The total quantity of H_2S released increases rapidly with temperature and is at a maximum at approximately 550 °C (33,34,43). The sulphur storage capacity of most commercial catalysts was found to be at a maximum at this temperature (37).

Equilibrium sulphur storage levels under lean conditions is greatly affected by the catalyst temperature and higher temperatures give faster storage equilibrium conditions.

4.3.5 Space velocity

The space velocity in a catalyst is defined as the volume flow rate of exhaust gas divided by the convertor volume. Von Carlowitz (47) and others (56,57) found that increased space velocities decrease the H_2S emissions. This is not surprising if one considers that the release of stored sulphates from the wash coat is kinetically a slow process and a minimum residence time is required to form H_2S. The finding supports the assumption that first SO_2 is released from the wash coat and then SO_2 is converted to H_2S. At the temperature for maximum emissions (around 550 °C) enough time is available for the reaction of SO_2 with H_2 to take place in the catalyst. Increasing the space velocity (or increasing the temperature) will therefore decrease H_2S emissions.

As a rule of thumb, the ceramic honeycomb volume required for efficient conversion of all exhaust pollutants is about half the displaced engine volume. This gives a space velocity through the convertor over the normal engine operating range of 5 to 30 per second (55).

4.3.6 Poisoning

Many authors (3,19,23,25,29,33,48) observed that sulphur storage and release levels are decreased with poisoning. This poisoning affects both the warm-up and steady-state performance of the catalyst. When poisoning occurs, catalytic activity is impeded through prolonged contact with interfering elements that either physically block the active sites or interact chemically with the active material. The lead in fuel and the phosphorus in oil additives are the most important poisons (12,13).
Platinum is poisoned by exposure to SO_2 alone and to exposure to SO_2 in the presence of H_2 (fuel-rich conditions), but not by exposure to SO_2 in the presence of O_2 (45).
Platinum poisoning is reversible under oxidation conditions at temperatures over 700 °C.

In the presence of excess oxygen SO_2 does not dissociate on the noble metals, but instead reacts to form SO_3 which reacts with the rare earth metals on the wash coat.

Although adsorbed oxygen can also poison a catalyst as adsorbed oxygen atoms (12) according to:

$$SO_{4(a)} \dashrightarrow SO_{2(g)} + 2\ O_{(a)} \qquad T > 300\ °C \qquad (30)$$

they are normally easily removed by reaction with CO or H_2. Sulphur might physically, and also electronically, block some catalytically active noble metal sites and prevent this oxygen removal (26,33,45). It was shown that a typical maximum sulphur coverage is of the order of 0.14 monolayer. This relative low sulphur coverage might suggest that sulphur not only blocks the platinum surface, but also donates some electron density to the metal and therefore electronically affect some adjacent unblocked sites. This electronic effect was confirmed by others (58).

Some study has been done on the direct effect of SO_2 to noble metals (40) but in principle the platinum group metals could store sulphur from this source (12,59). There are at least four bindings states (α_1, α_2,α_3, and α_4) of SO_2 on a clean platinum surface, three different binding states on an oxidised platinum surface, and at least two different binding states for SO_3 (12). The desorption of O_2 (via eq.30) is known to be a second order process.

Poisoned catalysts produced (33) a much smaller "spike" of H_2S than conventional, fresh, catalysts due to their inability to adsorb sufficient SO_2 as sulphates onto the wash coat. A phosphorus-treated catalyst (18) adsorbs sulphur only by interaction between sulphur and excess cerium and aluminium oxides (46). The stable phosphate species, deposited on the catalyst surface, prevent the forming of Ce-S-O components.

Poisoning was considered by several as a means to reduce, or even eliminate, peak H_2S emissions. Both Harkonen et al (35) and Rieck et al (46) doped the surface area of catalysts washcoats with iron (Fe) additives in order to reduce the H_2S release. Thermodynamically, iron does not form any stable sulphides under fuel rich conditions so no chemical reactions could possibly interfere. Although they were partly successful one should wonder whether poisoning is the correct method for reducing H_2S since the same objective can be reached by reducing the cerium loading. In addition, Dettling et al (44) found that doping with some base metals (CaO,BaO, K_2O) actually increased the H_2S levels.

4.3.7 Aging

Demanding a catalyst with excellent activity and lasting durability together with a desire for low H_2S emissions are often conflicting objectives. They might be partly met by aging of the catalyst, either artificially before installation or by normal use.

It was noticed earlier on that aged catalysts showed a reduction in H_2S emissions and artificial aging was investigated by many (25,21) as a possible solution to the peak H_2S emission problem.

As an example, Henk et al (43) found in an aging experiment that by exposing their catalyst to a 760 °C catalyst inlet temperature and with a stoichiometric synthetic exhaust gas composition the peak H_2S emission production was reduced to half the emission level of the fresh catalyst. After an additional four hours of aging the H_2S release was roughly the level expected for steady-state conversion of fuel sulphur to H_2S. Unfortunately they did not check the overall conversion activity of the catalyst but it is more than likely that this was somewhat deteriorated. Longer exposure to high temperatures will lead to more rapid aging.

Thermal aging reduces the ability to generate H_2S emissions because of the migration and agglomeration of sites, thus decreasing their active surface area (27), This results in a reduced storage capacity for sulphur and reduced peak emissions (46). There are conflicting reports on the results of sintering and there are suggestions that it does slow the warm-up time of the catalyst but has a minimal effect on the steady state conversion efficiency (27,30).

Exposing a catalyst to higher temperatures results in more rapid aging (43) and at temperatures above 1000°C the catalyst may be damaged.

One problem with most aging experiments discussed in the literature is that they are conducted on synthetic reactors. Laboratory aging of catalysts is likely to be less severe than aging under real driving conditions where traces of sulphur and lead from the fuel, and phosphorus and zinc from the oil might poison the catalyst (30).
Pulsator aging was thought to be more severe and a closer simulation of aging under real-life driving. Rieck et al (46) injected components like sulphur, lead, phosphorus and

zinc into artificial gas streams while varying the gas temperatures. They concluded that approximately 80 000 km of vehicle operation could be simulated with 90 hours of pulsator aging. Not surprisingly, he did find a reduction in H_2S peak emissions but also in three-way catalyst conversion efficiency.

Though some research workers might have considered artificial aging as a possibility to reduce H_2S emission, more recent American emission limits for CO, HC and NO_x have practically eliminated this option. Any degradation of catalyst activity is unacceptable.

4.4 H_2S CONTROL

4.4.1 Using scavengers

The use of sulphur "scavengers", that prevent the sulphur from being released under fuel-rich conditions, was considered. An extensive study was undertaken by Smith et al (60) and thermodynamic calculations of the stabilities of sulphates and sulphides of metals were done. The solution to the H_2S release was thought to be in the addition of a compound which, under H_2S release, prefers to exists as a sulphide. Such an agent could be referred to as an H_2S "scavenger" or sulphur "getter". The gettering effect is based on the principle of material characteristics analogous to those having unique surface sulphur-oxygen interactions.

One of the H_2S scavengers that received considerable investigation was nickel (Ni) (6,27,58). The early catalysts contained some nickel for oxygen storage (61) and its sulphur holding abilities were well known:

$$H_2S + NiO \rightarrow NiS + H_2O \qquad (33)$$

Golunski et al (58) suggested another mechanism where lowering the partial pressure of H_2, NiO controlled H_2S emissions.
Results showed (44,58) that the H_2S emissions could be suppressed by more than 95 per cent this way without any loss in performance and durability of the catalyst (43). Some European countries, in particular Germany, protested against using nickel in

catalysts as nickel carbonyl, a highly toxic compound, might be formed in the exhaust gas. The America Environmental Protection Agency (EPA), finding no proof of this, permitted the use of nickel. Other scavengers were needed for European markets. However, it has been suggested that the EPA might change their mind in the near future (62).

The use of washcoats with impregnated ferrites such as $CoFe_2O_4$, $CuFe_2O_4$ showed (46) promise in reducing H_2S emissions to the same level as that due to nickel. It was found that a metal ferrite had the same capacity for sulphide adsorption as a pure metal sulphide but could regenerate more readily in oxidising environments.

Metal oxides like CuO, GeO_2, MnO, MoO_3 and V_2O_5 were also considered (35,63). Using CuO gave some activity loss in tests conducted by Harkonen et al (35) but Yammada et al (62) found that MnO performs better and is only slightly less of a sulphur scavenger than NiO. Good results were also obtained with GeO_2.

Apart from its ability as a H_2S scavenger, the melting point of a metal additive has to be considered as catalyst peak temperatures higher than 1000°C can occur during an engine malfunctioning. NiO has a melting point reported as 1984°C (63), CuO could be used but has a low melting point of 1026°C compared to MnO with a melting point of 1650°C. Any melted oxides will react with the precious metals or block them and potentially increase the light-off temperature.

Some aluminates of the form $M^{+2}Al_2O_4$ have also been found to be effective in peak H_2S emission reductions but not as $NiAl_2O_4$ and $CoAl_2O_4$ additives (46).

4.4.2 Using non-scavengers

Considerable attention has been given by catalyst manufacturers to develop low H_2S emission catalysts (64). Usually it involves the use of proprietary impregnation procedures (43) and little is published. Lox et al (30) showed that increasing the CeO_2 crystal diameter and/or chemically modifying the surface hydroxyl-groups reduces the H_2S emissions without affecting the activity of the catalyst.

4.4.3 Temperature

As reported earlier, maximum peak H_2S emission occur in the temperature range 550 - 700 °C which is also the average operating temperature range of a catalyst. Raising the operating temperature of a catalyst (by placing it closer to the exhaust manifold) will result in decreased emissions of H_2S and also in faster light-off times. However, catalyst durability deteriorates rapidly at temperatures above 900 °C due to sintering of the washcoat and noble metal elements and the overall catalyst activity might be decreased.

4.4.4 Vehicle calibration

Modifications to vehicle calibration which limit rich/lean transitions will reduce or eliminate both steady-state and reductive released H_2s emissions (31). On closed-loop systems the adjustment of the fuel injection system should be oscillating in a very narrow range near to the lambda equals one value. There is a general decrease in H_2S release concentrations as the lambda during storage moves closer to the stoichiometric value (47). Holding the lambda close to 1.00 will control the available H_2 and thus significantly reduce the amount of H_2S released.

If the lambda sensor is unplugged an advanced engine control unit will switch to a pre-programmed mode of air/fuel control (65). This control is less accurate and likely will produce lambda values in fuel-lean and fuel-rich regions and might give cause for some H_2S emissions.

Vehicle strategies for air/fuel ratio control, general emission control and catalyst temperatures vary between different makes of cars and sometimes even between different models (66). Under full load conditions and open throttle enrichment the engine is sometimes set to run more rich than necessary, this to keep the exhaust gas temperatures below the functional limit of the catalyst (±950 °C). Some engine management systems provide a fuel shut-off to help limit the extremely rich conditions for excessive HC emissions and peak H_2S emissions under overrun conditions

.

Small swings from stoichiometric conditions to transient richness will be reflected in low levels of H_2S production. Catalyst temperatures which are constantly above 500 °C will promote H_2S formation and are determined by the physical position of catalyst underneath a car and by leanliness of the air/fuel mixture.

It can be expected that more sophisticated A/F ratio control systems will reduce the H_2S problem. An interaction between catalyst supplier and car manufacturer is required since a catalyst can, in principle, emit negligible levels of H_2S with careful air/fuel control (67).

4.4.5 Fuel sulphur

Reduction in fuel sulphur level will reduce both steady-state emissions and peak emissions but also the poisoning effect. The sulphur in the gasoline comes essentially from cracked components, especially catalytic-cracked, and the gasoline sulphur content depends on the refinery configurations (68) . Unfortunately, the removal of sulphur from the fuel (hydro-desulphurisation of cat-cracked components) is not an attractive alternative as it saturates olefinic hydrocarbons and degrades their octane quality (69). It is also an extremely expensive process to use as it reduces the yield of a barrel of oil.

Steady state SO_2 emissions are approximately equal to what can be expected from the sulphur level in the fuel (34), a 1000 ppm sulphur in the fuel produces approximately 60 ppm SO_2 in the exhaust. Von Carlowitz (47) found that the peak emissions were essentially independent of the inlet SO_2 concentrations and the fuel sulphur content above certain values.

Henk et al (43) did not find this effect and found similar peak emissions for fuels with 120 and 350 ppm sulphur content with equal storage times and temperatures. However, the higher sulphur fuel gave a higher H_2S level in its decay curve and indicated that more sulphur had been stored. The similar peak levels indicate that the maximum rate of release of H_2S at a given temperature, exhaust flow and air/fuel ratio is kinetically limited, as had been proven by Barnes and Summers (25).

Mogan (50) did an extensive study with European fuel-injected cars on a chassis dynamometer to establish the extend of the H_2S emissions. After developing a special hydrogen sulphide emission cycle containing moderate-to-severe accelerations and decelerations and using fuels with various sulphur contents he found that the bad sulphur odour is avoided at fuel sulphur levels lower than 100 ppm. In addition, he found extreme car-to-car variation of the H_2S problem.

A reduction in fuel sulphur content, and thus in engine SO_2 emissions, does not necessary lead to a reduction of H_2S peak emissions concentration but only prolongs the time which leads to a complete loading of the catalyst. No emission of H_2S are possible from a sulphur-free fuel (31).

CHAPTER FIVE
CATALYST EFFICIENCIES AND FUEL SULPHUR CONTENT

5.1 THE EFFECT ON LIGHT-OFF TEMPERATURE

The light-off temperature of a catalyst is defined as the exhaust gas temperature at the catalyst inlet which coincides with 50 per cent conversion efficiency being achieved. The light-off temperature, typically around 250 °C for a new catalyst, deteriorates with aging and therefore depends on the catalyst history. Hannington (57) found that the light-off temperature can increase by up to 50 °C with time but eventually settles at a certain value.

The light-off temperature is reduced whenever noble metals are included in the catalysts composition. Therefore, poisoning of the noble metals by sulphur deposits will raise the light-off temperature.

Many of the existing catalysts contain platinum and rhodium in the ratio 5:1 but new technology based on palladium/rhodium at a ratio of 10:1 is being introduced, and palladium only catalysts are being considered. The benefits of palladium are lower cost and faster light-of at lower temperatures. However, palladium based catalysts are known to be more sensitive to lead and sulphur poisoning and can thus only be introduced if low sulphur fuels are made commercially available.

Rhodium is also considered to be more sulphur resistant than Platinum in maintaining its light-off temperature (7).

5.2 THE EFFECT ON REGULATED EMISSIONS

In previous chapters it has been shown that sulphur poisons the noble metals under fuel rich conditions and is stored as sulphate onto the wash coat under fuel lean conditions. The sulphur physically blocks excess of exhaust gas molecules to the catalyst surface and the conversion efficiency is decreased. The poisoning effects is most serious if very stringent emission standards are in place for regulated emissions and where any loss of catalyst performance can spell the difference between success and failure.

Sulphur poisoning of three-way catalysts is a greater concern than for the older oxidation catalyst systems. Under strong oxidising conditions, oxidation catalysts were essentially unaffected by the sulphur in the fuel.

The effect of sulphur poisoning on the three-way activity was investigated by many (12,48,50,69,70,71). They found that there was a direct relationship between tailpipe emissions of HC, CO and NO_X and fuel sulphur levels below 500 ppm. This effect was immediate, almost linear, and reversible. Above 500 ppm sulphur in fuel, the performance of catalysts was essentially steady and did not decrease much.

Sulphur poisoning of noble metal-containing catalysts is primarily associated with the deactivation of platinum or palladium (48). Little effect has been found over rhodium, especially for NO conversion. Several studies with reactors and synthetic exhaust streams have shown that even then SO_2 is a temporary poison for Pt/Rh catalysts (17,18,29). The introduction of SO_2 into the exhaust instantaneously results in a reduction of emission performance, which is rapidly restored upon removal from the exhaust feedstream. For example, this happens with gross HC, CO and NO conversions. While platinum and rhodium appear to recover their activity rapidly upon the removal of SO_2 from the exhaust, there is some concern that the activity of palladium-containing catalysts may not be fully restored (71).

As part of the US Auto/Oil Air Quality Improvement Research Programme (70) the effect of fuel sulphur levels on mass exhaust emissions was investigated for fuels containing Methyl Tertiary Butyl Ether (MTBE). They found that exhaust total- hydrocarbon, non-methane hydrocarbon, CO and NO_X emissions were reduced by 18, 17, 19 and 8 per cent, respectively, when fuel sulphur levels were reduced from 450 to 50 ppm. The study confirmed that the poisoning effect is essential linear, immediate, and reversible. In addition, sulphur appears to affect the performance of a fully warmed-up catalyst to a greater extent than one operating at the lower temperatures during start-up operation.

Mogan (66) found, using European cars on a chassis dynamometer, that the magnitude of sulphur poisoning on HC, CO and NO_X conversion efficiency shows car- and test cycle-dependence. He confirmed that the largest deterioration is seen for CO, followed by HC, but no apparent effect on NO_x could be seen. By reformulating the fuels he found a larger decrease in regulated emission than by reducing the fuel sulphur levels from 100 to 50 ppm. Hence, he concluded that it is important to take a balanced view of the sulphur effect on catalysts and regulated tailpipe emissions and whether costly reductions of sulphur levels in petrol is really required.

5.3 THE EFFECT ON NON-REGULATED EMISSIONS

Summers et al (39) using two-way catalysts found that SO_2 in the engine exhaust significantly inhibits the formation of NH_3 over Pt catalysts. NH_3 emissions can be high under highly reducing conditions but its formation is strongly inhibited by SO_2 and conversion of NO to N_2 is preferred. Under closed-loop control at stoichiometric point, the NH_3 formation is quite small and not a problem. Rhodium in the catalyst suppresses NH_3 formation (5).

The removal of methane, a greenhouse gas, from the exhaust gas by catalytic means remains a problem as methane is virtually non-polar and not readily absorbed onto the surface of the catalyst.

The Auto/Oil AQIR study (70) found that reducing the fuel sulphur content reduced benzene and acetaldehyde exhaust emissions, had no effect on 1,3 butadiene levels, but increased the formaldehyde emissions. It might be that increasing the sulphur level in fuel inhibits a formaldehyde-forming reaction that occurs before the catalyst is fully warmed up. The fact that the fuel contained MTBE could be significant but no interactions between MTBE and sulphur are known. The study also calculated the ozone-forming potential, expressed as ozone formed per mile driven, and found this was reduced by 9-14 per cent as the sulphur level in the fuel was reduced from 450 to 50 ppm. This reduction in ozone-forming potential is partly due to the reduction in hydrocarbon mass emissions.

CHAPTER SIX
EXPERIMENTAL DESIGN

6.1 INTRODUCTION

To investigate any effects of sulphur in fuel on the performance of automotive catalysts, a step-wise approach is the most effective. Engine tests have the disadvantage, although they are close to "real-life" conditions, that not all variables can be controlled at the same time. Therefore, early researchers made use of a reactor with inserted parts of a catalyst substrate. Synthetic gases are used to simulate exhaust gas and their composition carefully controlled. The reactor itself is usually made of quartz to assure inertness against the gas. SO_2 can be introduced from a gas cylinder under reducing or oxidising conditions. By changing one variable at the time a good assessment can be made of the dynamics involved in catalyst poisoning, sulphate emission and hydrogen sulphide emissions using variable compositions of catalyst.

However, any conclusions drawn from synthetic experiments need to be confirmed with an engine and an automotive catalyst. Because the sulphur problem with catalysts is very closely associated with the air/fuel control system installed on a car, it can be expected that some catalyst equipped cars will have more problems than others. Catalysts aging, which suppresses H_2S emissions and reduces catalyst conversion efficiency, also occurs faster and is more severe on the road than can be simulated with a synthetic reactor.

With emission legislation being closely associated with certain driving cycles, rolling road tests are the only scientific way of evaluating any sulphur influences on the exhaust emissions from a particular car model.

To conduct the experiments for this thesis, an engine with catalyst system was placed on a dynamometer in a test cell. Of necessity, the tests had to be of limited scope and fit into a short time frame. It was therefore decided from the beginning to evaluate the engine/catalyst combination for sulphur effects qualitatively, rather than quantitatively. Accurate values for emissions can only be obtained by repeating a test several times and, since the catalyst would age over the duration of the tests and therefore would change its effectiveness, are difficult to get.

In section 6.2 details are given of the engine, catalyst, emission analysis system and fuels used. Section 6.3 discusses the objectives of the tests envisaged and indicates the likely limitations of the test procedure. Presentation of the results and any discussion is given in Chapter 7.

6.2 EQUIPMENT AND FUELS

6.2.1 Catalyst and engine

The engine test cell is fitted with a 224 kW Heenan and Froude eddy current dynamometer and was operated in the speed control mode for the duration of all tests.

A cooling water circuit provides coolant for the engine dynamometer and any additional requirements e.g. oil cooler. The engine operates with a closed coolant circuit, the engine's pump doing the duty of circulating coolant through a wall mounted shell and tube heat exchanger. Water from the heat exchanger is gravity fed to a sump from which a scavenger pump returns the water to a 800 kW evaporative cooling tower. A high pressure centrifugal pump delivers the water to a general manifold from which this, and other tests cells, are fed.

The test cell is provided with a back-pressure controlled exhaust system for general use. The engine under test, however, was installed with its standard exhaust system components.

Fuel flow to the engine could be measured accurately and thermocouples were inserted to measure oil, water, air inlet, catalyst inlet and catalyst outlet temperatures.

The details of the engine, made available by VW Germany in 1991, used for the tests in this report, are as follows:

ENGINE DETAILS

Engine model:	VW Digifant 2E
Displaced volume:	1968 cm^3
Maximum power output:	85 kW at 5400 rpm
Maximum torque:	166 NM at 3200 rpm
Compression ratio:	10.4:1
Engine management system:	Digifant

The engine was supplied with an advanced engine management system with accurate air/fuel control and fuel cut/off during over-run conditions. Fuel injection was provided to each inlet port. Feedback on combustion effectiveness was provided to the digital electronics control unit by a lambda sensor located at the exhaust inlet of an automotive three-way catalyst. The catalyst was supplied by Johnson & Matthey (PtY) Ltd in Johannesburg. Volkswagen (VW) worldwide use catalysts supplied by Degussa and therefore the catalyst under study deviates from those that can be found on catalyst equipped VW cars. VW have a policy of not using the controversial nickel in their catalyst formulations worldwide and rely on improvements in engine management technology to control any H_2S emissions (72).

No analysis of the catalyst material was attempted but it is likely that platinum and rhodium were used in the common 5:1 ratio.

The catalyst had aged for approximately 30 hours at the beginning of the emission tests.

6.2.2 Emissions analysis system and measurement

Exhaust gas is sampled at the entrance and exit of the catalyst housing, approximately 20 mm upstream and downstream of the monolith face by perforated tubes extending the full width of the monolith. Shielded type-k thermocouples are placed in close proximity to the sampling probes.

The exhaust emissions were routinely analysed for hydrocarbons (HCs), carbon monoxide (CO), carbon dioxide (CO_2), oxygen content (O_2), nitric oxide (NO) and for nitrogen oxide (NO_x). A switching manifold was used to sample exhaust gas directly before or after the automotive catalyst. Exhaust gas extraction lines from the catalyst to the analyser system were kept above condensation temperature using heating tape . Sampled gas was led through a heater and cooler system and a dried sample stream could be tested for HC, CO, CO_2, NO, NO_2 and O_2. A wet (uncondensed) sample was analysed for HC using a Flame Ionisation Detector (FID). More details on the emission analysis system can be found in figure 1. The emission system was calibrated twice daily for the duration of the tests.

The readings for HC, NO_x, CO, CO_2 and O_2 were used for calculation of the equivalence ratio and the lambda value using standard equations, as given by Heywood (73).

It was planned to measure both SO_2 and H_2S emissions using a non-dispersive infra-red (NDIR) URAS 3G SO_2 gas analyser. H_2S was to be converted to SO_2 under high temperature conditions and near stoichiometric conditions using a Thermo-Electron converter. A dried exhaust gas sample would be led through a SO_2 selective collection trap before being passed to the converter and subsequent SO_2 analyser. The system had proved effective in some trials done earlier. At the beginning of the tests for this thesis, however, the SO_2 analyser proved cross-sensitive to CO_2 in the exhaust gas and could not be used. This effect was surprising as filters were in place to eliminate this cross-sensitivity but was likely caused by the replacement of a faulty detector some days before. As it worked out, the oven on the H_2S converter burned out within minutes after the start of the tests anyway and an alternative way of measuring H_2S and SO_2 had to be found.

Fortunately, Draeger tubes had been bought some months before as back-up for the tests. Draeger tubes are scale tubes, i.e. tubes in which an indicator layer is discoloured in zones as function of the gas concentration. The length of discolouration is a measure of the gas concentration sampled and the measured value is read-off on a printed tube scale. Gas is sampled using a hand-operated bellows pump and a Draeger tube is inserted into the aperture in the pump head for air inlet. Each gas detector tube requires a fixed number of strokes, each stroke lasting 7-10 seconds depending on the tube. According to the supplier, H_2S detector tubes have marginal sensitivity to high levels of SO_2 and SO_2 detector tube readings can be affected as much as 50 per cent by the simultaneous presence of H_2S. Therefore their readings had to be regarded with suspicion if both gases were present. As a matter of routine all readings were corrected for barometric pressure fluctuations. Using various calibration gases it was found that the accuracy of the tubes was well within 10 per cent.

The H_2S Draeger tubes can be used in two ways; they can be used for either 10 strokes and give the average concentration over this time period, or for a single stroke and give the average concentration over the duration of this stroke. The multi-stroke measurement was used for the determination of the steady state emissions. The shape of any peak release could be determined by using Draeger tubes in a rapid succession and monitoring the time. In this way, a measurement could be taken every 12 seconds, and was the average of approximately 7 seconds. As an alternative to the faulty electronic SO_2 analyser, the Draeger tubes proved acceptable.

6.2.3 Fuels preparation

Two unleaded fuels were made available for the tests, of which the properties are as follows:

PROPERTIES OF TEST FUELS

	Fuel A	Fuel B
Research octane number:	93	93
Motor octane number:	83	83
Sulphur level:	386 ppm (m/m)	0 ppm (m/m)
Volatility:		
IBP	33 °C	33.5 °C
50% Recovery	108 °C	112 °C
90% Recovery	161 °C	173 °C
FBP	194 °C	212 °C
Reid Vapour Pressure	69 kPa	61 kPa

Exact octane numbers and volatility characteristics are irrelevant for the results of the tests undertaken but are given for identification of the fuels.

The sulphur content for fuel A is typical for that what can be expected from a South African crude oil refinery. Fuel B was manufactured from natural gas via a Fischer-Tropsch process.

Fuel A was selected for initial evaluation of the behaviour of the catalyst/engine system. Fuel B was used for a more accurate assessment of fuel sulphur levels on emissions and was doped with thiophene at various levels (figure 2). Thiophene had been used by various researchers before and there is conclusive evidence that the exact format of the sulphur in the fuel is irrelevant for these tests. Fuel B was used as base fuel and doped with various concentrations. The following fuels were prepared and analysed:

Fuel	**B1**	**B2**	**B3**	**B4**	**B5**
Sulphur level:	0 ppm	112 ppm	398 ppm	979 ppm	3461 ppm

6.3 EXPERIMENTAL OBJECTIVES

Based on the discussions in the previous sections it was attempted to evaluate the automotive catalyst system with engine for the following:

1 To evaluate H_2S and SO_2 emissions for various catalyst temperatures.

2 To evaluate H_2S and SO_2 emissions for various air/fuel ratio's.

3 To evaluate H_2S release for various storage and release durations.

4 To evaluate the H_2S and SO_2 emissions for fuels with different sulphur contents.

5 To evaluate the effect of sulphur on the catalyst conversion efficiency for CO, NO, NO_2 and HCs and whether these effects were permanent or could be restored.

and finally:

6 To investigate whether the combination of catalyst and engine was likely to lead to H_2S emissions problems in the market place.

CHAPTER SEVEN
RESULTS AND DISCUSSION

7.1 AGING OF THE CATALYST

It was suggested by the supplier to age the catalyst using a so-called DL-2 aging cycle of which the details are as follows:

DL-2 AGING CYCLE (VW)

Point	Time (min)	Speed (rpm)	Torque (Nm)*	Power (kW)
1	2	1400	26	3.6
2	30	5400	W.O.T.	85
3	4	2800	53	14.7
4	10	3200	W.O.T.	55
5	410	5400	0	0
6	10	6100	W.O.T.	82

* WOT = Wide Open Throttle

In later discussion with Johnson Matthey (62) a simpler cycle was suggested since only comparative tests would be undertaken. It was decided to combine the two suggestions and a cycle was produced which would give a variety of temperatures and gas velocities at the three-way catalyst.

Aging cycle for VW 2.0 litre Digifant engine catalyst

Point	Time (min)	Speed (rpm)	Torque (Nm)	Power (kW)	Temp$_{cat\text{-}in}$ °C	Temp$_{cat\text{-}out}$ °C
1	2	1400	26	3.6	430	440
2	30	5400	W.O.T.	85	860	830
3	4	280	53	14.7	640	650
4	10	3200	W.O.T.	55	740	700
5	4	5400	40	23	790	790
6	10	4000	W.O.T.	63	800	780

The above cycle was run for 24 hours, after which the catalyst was considered to be adequately aged.

7.1.1 Discussion

The reading taken at point 2 were monitored for the effectiveness of the aging. However, the findings were that:

1 the HC readings were erratic and fluctuated between 30 and 60 per cent conversion removal.

2 the CO readings were on the low end of the analyser scale and the instrument, equipped with a percentage scale, was not really suitable for accurate determination of CO levels. No deductions could be drawn from the CO conversion rates.

3 levelling-off of the NO_x conversion efficiency after 20 hours did seem to indicate that aging had taken place and that conversion efficiency had reduced from 96 per cent to 88 per cent.

An accurate assessment could therefore not be done for all three gases but the impression was that aging had taken place.

7.2 ESTABLISHING A STORAGE/RELEASE MODE

The aim of this first session was to evaluate the "willingness" of the engine/catalyst system to emit H_2S emissions under particular operating conditions and to establish a standard release mode for any future tests. The release mode had to give reproducible results within the measurement range of the H_2S detection tubes. Engine conditions would, hopefully, be created that would allowed storage of the fuel sulphur under fuel-lean conditions and removal of the sulphur under fuel-rich conditions.

The catalyst system and the engine in closed-loop operation were warmed up for 30 minutes under idle condition to allow thermal equilibrium to take place. Then, using fuel A, several engine speeds and loads were evaluated for emissions. To simulate sulphur storage conditions the engine was kept at high speed, low load conditions for 20 minutes with equal catalyst inlet and exhaust temperatures at 550 °C. This condition was followed by a rapid deceleration over 10 seconds into the idle mode, usually a slightly rich engine condition and expected to promote release of sulphur from the catalyst. However no H_2S release was noticed. Storage conditions were repeated for longer duration and at several temperatures, the release conditions were changed between idle or wide open throttle condition, but no H_2S emissions were observed.

It was decided to test the engine under open-loop conditions as a large amount of (small) vehicles fitted with catalysts still function under open loop condition or non-feedback controlled management in Europe (74).

It was expected that more fluctuation could be obtained between fuel-lean and fuel-rich engine conditions and the lambda sensor was therefore unplugged.

Indeed, under 20 minutes at high speed and part load conditions and followed by rapid deceleration to idle condition, H_2S (peak) emissions were detected. Repeats of this test condition gave consistent H_2S release and the condition was taken as "the standard H_2S production mode" for many of the further tests. The storage/release mode was thought to be comparable with the situation where a motorist is most likely to pick up the characteristic smell of H_2S, namely under start/stop driving in town (75).

Two-step H_2S production mode (open-loop control)

1	Storage		
	Engine speed:		2700 rpm
	Load:		40 Nm (part Throttle)
	Catalyst temperature		
		Inlet:	555 ±5 °C
		Outlet:	550 ±5 °C
	Duration:		5-20 minutes (Depending on test)
2	Release		
	Deceleration		10 seconds
	Idle		
	Speed:		800 rpm
	Load:		6 Nm
Duration:			5-10 minutes (depending on results)

In closed loop control, the above two-step mode did not lead to any noticeable H_2S emission. The production mode was used for many of the later experiments.

Under fuel lean conditions (lambda > 1) the catalyst has high hydrocarbon conversion efficiencies between 90 and 98 per cent (figure 5). Some conversion also takes place under fuel rich (lambda < 1) but the scatter in results seems to indicate the conversion is erratic and might depend on factors other than just air/fuel ratio.

The conversion to CO_2 and H_2O of CO is extremely effective at a 100 per cent value under fuel lean conditions (figure 6). Fuel-rich conditions produce lower efficiencies (below 40 per cent).

The conversions of the regulated emissions under various values for lambda show the effectiveness of the catalyst. Simultaneous reduction in emission levels takes place at stoichiometric conditions. The results are as expected for this type of catalyst and show that the engine-catalyst system operates satisfactory under open-loop control.

7.4 H_2S RELEASE FOR VARIOUS STORAGE DURATIONS

Using the two-step H_2S production mode presented in section 7.2, the H_2S release emission levels were observed after 5, 10, 15, 20 and 30 minutes of storage under fuel-lean conditions, see table 3 and figure 7.

7.4.1 Results and discussion

Figure 7 shows the estimated H_2S peak concentrations after storage for various durations. The catalyst temperatures were kept at the reported optimum temperature of 550°C and fuel A was used for the tests. Results are quite erratic and this possibly is a result of the initial measurement methodology with the H_2S detection tubes. The figure indicates no relationship between storage duration and the level of peak emission. Some relationship was expected as it was reported (43) that exposure to more sulphur would result in more storage and higher levels of H_2S release. It is also possible that the release of H_2S is a reaction that is kinetically limited. More sulphur storages would in that case not result in higher peak emissions but in longer emissions. This was confirmed in tests. A 5 minute storage duration give no noticeable emission 20 seconds after the occurrence of the peak. A 30 minutes storage condition at the same temperature (560°C) gave H_2S emissions for longer than 2 minutes, see figure 8. This finding agrees with that found by others (45,47,71).

H_2S concentrations were found to exceed 690 after 5 minutes of storage and using 386 ppm sulphur content fuel. Using a typical (37) tailpipe dilution of 100:1, this would give a 7 ppm emission level at the rear of a car and is about 45 times over the lower odour detection limit. The emissions also confirm that no scavenger-like technology had been used in the formulation of the catalyst. The peak emissions are higher than those reported in the literature. However, the maximum values are an indication of the kind of air/fuel control used for an engine and can indeed be very high with bad control (50).

7.5 H_2S RELEASE FOR VARIOUS CATALYST STORAGE TEMPERATURES

Variations in engine conditions, based on the two-step mode, were used to determine the optimum sulphur storage temperature on the catalyst. While maintaining part-throttle but varying engine load and speed, the catalyst storage temperature could be manipulated between 400 and 800 °C. Storage duration was kept at 5 minutes. Earlier on it was mentioned that the disadvantages of using an engine for studying the influences on the catalyst are that it is normally not possible to change one variable alone. Therefore, changing the engine mode also changed the air/fuel ratio and this effect must be kept in mind when interpreting the results.

7.5.1 Results and discussion

See table 4 and figure 9. Figure 9 shows that maximum peak release occurs between 550 and 600 °C at which the concentrations are 660 ppm and 900 ppm respectively. The storage air/fuel ratio's are 1.04 and 1.11 respectively but several researchers (25,39,34,56) had found that storage conditions leaner than 1.05 did not result in higher peak emissions. The release reaction appear kinetically limited and does not occur for temperatures lower than 500 °C and higher than 700°C. This is in agreement with the results from others (21,26), that at high temperatures SO_2 rather than H_2S is the preferred species.

The temperature interval of 550-600°C for maximum release compares well with that found by others (33,34,37,43). It is the average operating temperature for a catalyst fitted underneath a car and thus also the most effective to cause sulphur problems.

The H_2S emission level at 600 °C are highest and was measured using several detector tubes. See figure 10. The graph confirms that the H_2S release is of shorter duration than that found after 30 minutes storage (figure 8).

7.6 H_2S RELEASE FOR VARIOUS STORAGE AIR/FUEL RATIO'S

By changing load and engine speed while maintaining exhaust temperature in the window 500-600°C ratio's it was attempted to create various air/fuel ratio's and to evaluate its effect on the storage and release mechanism.

7.6.1 Results and discussion

Several experiments were done to determine the impact of air/fuel ratio on the storage/release mechanism and their discussion is given as follows:

1 A condition slightly rich from stoichiometric (lambda = 0.98, table 5) was maintained for 10 minutes, to evaluate whether any sulphur storage and subsequent release would take place. No H_2S emissions were observed after changing to the idle engine mode, a proven H_2S release condition. Therefore the test confirmed that no sulphur storage takes place under fuel rich condition.

2 A slight change in engine load increased the air/fuel ratio to marginally lean conditions (lambda = 1.04). After 10 minutes storage at this mode, 800 ppm H_2S release was observed, confirming that a fuel-lean condition is a necessity for storage to take place. A small change in engine load produces a relatively large increase in air/fuel ratio.

3 The standard 10 minutes storage condition was followed by 10 minutes at wide-open throttle with fuel rich conditions (lambda = 0.81, table 5). No H_2S emissions were observed at this mode. This is possibly due to the high exhaust temperatures at this mode as catalyst temperatures immediately rose to 770°C. It was found in section 7.5 that no H_2S release takes place at this temperature and that that SO_2 is the preferred sulphur species. The wide-open-throttle (W.O.T.) condition was followed by a rapid deceleration to idle at 870 rpm, the standard release mode for H_2S. No H_2S was detected, confirming all sulphur had been removed under the high temperature W.O.T. condition. The wide-open-throttle also increased the space velocity in the catalyst, enhancing any high temperature effect.

4 The above (number 3) test was repeated but for a wide-open-throttle (W.O.T.) condition of only 5 minutes. The standard release (idle) mode produced a modest 50 ppm H_2S release, indicating that approximately 94 per cent of the sulphur had been removed with the shorter W.O.T. condition.

The above results show that fuel lean conditions are necessary to produce H_2S emissions. This is the reason why no emissions were noticed under closed-loop control. H_2S release occurs via SO_2 formation in the intermediate stage, and at high temperatures and space velocities mainly SO_2 emissions are produced due to kinetic limitations in the conversion reaction.

7.7 EMISSIONS AND CATALYST POISONING DEPENDENCE ON FUEL SULPHUR CONTENT

The noble metals on the catalyst coating undergo sulphur poisoning with normal use and higher sulphur fuels should therefore lead to reduced catalyst efficiencies compared to low sulphur fuels. In addition, more sulphur should lead to more storage and subsequent H_2S release.

In the following tests the above statements will be verified. To ensure that any air/fuel ratio variations would not play a role in determining the poisoning effect, the lambda sensor was reconnected. The following routine was used:

1 The fuel system was cleaned . The fuel system was drained and all fuel was replaced with the new fuel under test.

2 The catalyst was cleaned. The engine was run under full throttle in open loop condition for 30 minutes. This operation was thought to produce a sufficiently high temperature (>800°C), space velocity and fuel rich condition for any sulphur present on the catalyst, to "burn off".

3 The catalyst was poisoned with the fuel under investigation. The poisoning condition was done under closed-loop control at a fixed medium speed and low load condition for 30 minutes. The important control parameters of this test are to maintain a steady temperature between 550 °C and 600°C and a stoichiometric condition.

4 The regulated emissions are measured. Near the end of the poisoning condition the catalyst inlet and outlet exhaust are sampled and tested for CO, HC and NO_x. Conversion efficiencies are calculated.

5 Conduct the standard two-step H_2S production mode. The lambda sensor is disconnected and the two-step H_2S production mode is conducted with 15 minutes for the storage duration. Peak H_2S emissions, steady state H_2S and SO_2 emissions are measured.

6 Repeat 5

The results are given in tables 6a-c

7.7.1 H_2S peak release-results and discussion

Following the two-step H_2S production mode and 15 minutes storage, the H_2S peak concentration was measured in the manner described in section 6.2.2 using several detector tubes. Tests were repeated to obtain accurate values, see figure 11. The graph shows a definite relationship between fuel sulphur content and H_2S release. The relationship with H_2S release deteriorates for sulphur levels over 500 ppm and larger increases in fuel sulphur content only results in small increases in peak emissions. Fuel B5 has a very high sulphur content (3461 ppm) and the duplicated tests with this fuel gave two widely varying results (900 and 1600 ppm respectively).

Mogan (50) found with cars in rolling road experiments that fuels with sulphur content less than 100 ppm did not contribute to any significant H_2s emissions and therefore suggested there would be no need to reduce sulphur levels in reformulated fuels to less than 100 ppm to counteract the poisoning effects. Henk et al (43) found no difference in peak emissions for fuels with sulphur content higher than 100 but reported that the decay with higher sulphur fuels lasted longer.

See figures 12 and 13 for details on the release process using fuel B5. A possible explanation for the difference in two readings might be that, although the duration of the release condition was 15 minutes, not all sulphur had been released before the test was repeated.

Fuel B1 was re-tested after fuel B5. After the two-step mode, no H_2S was detected, indicating that the high temperature, fuel rich W.O.T. mode had been effective in removing any residual sulphur on the catalyst.

7.7.2 H_2S steady state emissions - results and discussion

Using fuels A and B1-B5 the steady state H_2S emissions were measured. Except when using fuel B5, emission levels were below 5 ppm and the discolouration on the detector tubes was marginal. Fuel B5 produced 5-7 ppm steady-state H_2S emissions under fuel rich conditions, many times lower than could be expected for this kind of fuel. Several authors have confirmed (38,43,47,48,56) that under fuel rich conditions all exhaust SO_2 is converted to H_2S and that levels agree with that calculated from the fuel content.

7.7.3 SO_2 emissions - results and discussion

Using the Draeger tubes, the SO_2 emissions were monitored for the fuels A and B5. These tests were done under both open-loop control and under closed-loop control

Fuel A with sulphur content of 386 should theoretically produce 23 ppm SO_2 at the engine outlet. Using the SO_2 detection tubes, the concentration was measured repeatedly as being less than 3 ppm.

Similarly, fuel B5 should theoretically produce engine-out SO_2 emissions of 208 ppm. The discolouration on the detector tubes was maximal 5 ppm.

The above showed the limitation of the Draeger tubes for SO_2 measurements and that results must be interpreted carefully before coming to any conclusions. There is overwhelming evidence that SO_2 are directly proportional to fuel sulphur levels and the very high H_2S emissions reported indicate that SO_2 is being stored on the catalyst.

7.7.4 Catalyst poisoning - results and discussion

The pre-and after-catalyst emissions were measured near the end of the 30 minutes of "closed-loop poisoning mode", See figure 14.

The figure shows that when using fuels B3-B5 the conversion efficiency for carbon monoxide decreases from 100 per cent to 83 per cent. The conversion of hydrocarbons is reduced from 93 to 86 per cent using fuel B3. The conversion of oxides of nitrogen is only slightly affected, with conversion efficiency being reduced to 96 per cent. Fuel B3 with 398 ppm sulphur produced a significant deterioration of catalyst performance compared to fuels with lower sulphur content.

After fuel B5 (a very high sulphur fuel), fuel B1 was re-tested. The conversion efficiency was immediately restored to 100 per cent, indicating that sulphur poisoning is a reversible process and depends solely on fuel sulphur content. The result also showed that the 30 minutes W.O.T. open-loop condition had indeed removed any sulphur from the catalyst.

The conversion efficiencies for the three regulated pollutant are compared to the sulphur content of the five fuels in figure 15. It confirms the findings of others (50,66) that most deterioration of catalyst efficiencies takes place at fuel sulphur levels above 100 ppm and and that sulphur levels higher than 400 ppm do not add to the poisoning effect. This would indicate the poisoning is capacity limited. However, the American Auto/Oil AQRP (70) found a linear effect between fuel sulphur contents less than 500 ppm and the reduction in catalyst efficiency.

7.8 GENERAL DISCUSSION

Initial tests showed that the catalyst operated satisfactory in the removal of CO, HC and NO_x from the exhaust and that it had not been poisoned during any previous (unknown) use.

Engine tests at various loads and speeds indicated that the closed-loop control was extremely effective in preventing any H_2S release. It did not, however, prevent the catalyst from becoming poisoned. This poisoning had a pronounced effect on the catalyst efficiency for CO conversion but not for NO_x conversion. Low sulphur fuels (<100 ppm) do not cause any significant poisoning of the catalyst. There seems little benefit in reducing the sulphur content of very high-sulphur fuels down to 500 ppm as most poisoning occurred between 100 and 400 ppm sulphur. Fuels with various sulphur contents showed that the poisoning effect is immediate but reversible. Literature indicates an approximately linear relationship between the poisoning effect and fuel sulphur content for levels below 500 ppm.

Many small European catalyst equipped cars operate under open-loop engine mode and the finding showed that problems were to be expected with the use of this catalyst. A two-stage H_2S production mode using open-loop control and at a catalyst temperature of 550 °C, gave high concentrations of reproducible H_2S release. Fuel storage is kinetically limited at fuel-lean conditions and results showed that longer exposure to storage condition not necessarily results in higher H_2S release concentrations but might produce high levels of H_2S for longer durations. This is in agreement with the general findings reported by others.

H_2S peak release gave values up to 700 ppm after five minutes of storage, indicating that extreme problems would have been experienced with this catalyst/engine combination under open-loop control if fitted to a car. Result with fuels with varying sulphur content showed increased H_2S peak emissions with increased sulphur content. There are confliction reports in the literature on this. Some confirm this relationship, others found that peak emission do not significantly increase for fuels with more than 100 ppm sulphur.

Results showed that no H_2S suppression technology had been used on the catalyst, supporting VW Germany's view that H_2S control can be done effectively by air/fuel control only.

Experiments with various storage temperatures found that maximum storage and subsequent release occurs at temperatures between 550 and 600 °C. This is in line with the literature.

The air/fuel ratio control is the overwhelming factor determining H_2S release. No storage takes place under fuel-rich conditions. SO_2, rather than H_2S, is the preferred sulphur species at high temperatures and space velocities. This was confirmed in experiments where no H_2S could be measured at catalyst temperatures over 800 °C.

The failure of the H_2S electronic analyser at the very beginning of the tests made it necessary to use Draeger detector tubes. These tubes provided satisfactory for most test.

Only marginal levels of steady state SO_2 or H_2S could be detected. The lack of these emissions is most likely due to the method of measurement, and is not thought to be a specific engine or catalyst behaviour.

CHAPTER EIGHT
SUMMARY AND CONCLUSIONS

8.1 SUMMARY

The research and work done for this thesis has provided some insight into the mechanism by which the sulphur content in fuel influences the emissions of automotive three-way catalysts.

Early oxidation catalysts produced higher emission of sulphate particulates and it was soon realised that there are interactions between the fuel, the engine and the catalyst that determine the tailpipe emissions. The catalyst could not be regarded as a "stick-on" device. By better control of air/fuel ratio's by placing the catalyst closer to the engine manifold for higher operating temperatures and faster light-off, and especially the use of improved catalyst formulation the sulphate emission problem was practically solved.

However, increased emission legislation required more active catalysts with higher levels of cerium oxide in the washcoat composition. This rare-earth metal is essential for providing efficient catalyst conversion efficiency under fuel rich condition for CO and HC. Bad-odour complaints with the use of those highly active catalysts proved that H_2S emissions were released from the catalyst. These emissions are produced by two means. Firstly, steady-state H_2S emissions are produced under fuel rich conditions and at normal operating temperatures. They are directly related to the fuel sulphur content and SO_2 engine emissions and are normally below the odour detection limit and do not cause any problems. This was confirmed in tests using fuels with various sulphur content. Engine emissions normally only contain SO_2, although it it possible that COS is released at very high exhaust temperatures. The second cause of H_2S is the ability of catalysts to store significant amounts of sulphur on to the catalyst under fuel lean conditions, and to release this sulphur rapidly as H_2S under fuel-rich conditions. This storage/release mechanism allows H_2S emissions many times higher than can possibly come from the fuel.

The deposits of sulphur also meant that catalysts could deteriorate (poison) when high sulphur fuels were used. This poisoning affected mainly the noble metals and occurred under fuel-rich conditions, the opposite for storage of sulphur for H_2S. Tests done in this report showed that the poisoning was immediate but reversible.

The hydrogen sulphide emission are dependant on the air/fuel control used for the engine/catalyst system. Hydrogen sulphide emissions only occur in a certain catalyst temperature interval. It has been shown that the sulphur level of a fuel plays an important role in producing steady state and peak hydrogen sulphide emissions.

8.2 CONCLUSION

The tests with a VW Digifant engine and catalyst system on a test bed have provided satisfactory results despite some problems with the hydrogen sulphide and sulphur dioxide emissions. It has been shown that the effect of sulphur on the catalyst behaviour is determined by the catalyst composition, the engine air/fuel control, and the sulphur level of the fuel used. By optimising those variables, the sulphur effects can be brought down to negligible levels.

The general conclusions that can be drawn from the experimental work discussed in this thesis are as follows;

1 The catalyst and engine combination gave good suppression of peak H_2S emission under closed loop control. Rapid changes in engine mode did not lead to the production of the distinctive odour. Experiments under closed-loop conditions indicated that any H_2S release can be controlled with an excellent air/fuel control management system.

2 Test under open-loop control gave significant levels of H_2S release. It was confirmed that sulphur storage takes place under fuel-lean conditions and that H_2S formation takes place under fuel-rich conditions.

3 The experiments confirmed that H_2S release is a kinetically limited process and that release is a maximum at catalyst temperatures between 550 and 600°C. Catalyst temperatures above 800°C and with high space velocities do not produce H_2S emission and it is thought that under these conditions SO_2 and COS are the preferred sulphur species.

4 By using fuels with varying sulphur content it was shown that higher sulphur levels do produce higher peak H_2S emissions. No relation was found between peak emission and the sulphur content of the fuel.

5 Sulphur poisoning was found to be immediate and reversible. Catalyst deterioration is recovered after reverting to low sulphur fuels. Fuels with sulphur levels above 100 ppm do not add significantly to the poisoning process. The poisoning process can not be influence by improved air/fuel control and was found the same both under open-loop and under closed-loop control.

6 Carbon monoxide emissions are most affected by sulphur poisoning. The catalyst conversion efficiency for nitrogen oxide emissions does not change significantly even for high sulphur fuels. Both findings are in agreement with literature.

7 There seems litle reason to promote the use of fuels with sulphur content less than 100 ppm. The tests showed that, at this level, little catalyst deterioration was observed and H_2S peak emissions were minimal.

CHAPTER EIGHT
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APPENDIX ONE

TABLES

Table 1 Emission and air/fuel control under closed-loop conditions

STOICHIOMETRIC CONDITIONS -TAB1

Before/ After	Speed rpm	Torque Nm	Power kW	Tin DegrC	Tout DegrC	CO %	CO2 %	NOx ppm	HC ppm	O2 %	Equi	Lambda	Fuel G/MIN	Oil DegrC	Water DegrC
B	2706	43	12	575	601	0.6	15	1600	1230	5.0	1.00	1.00			
A	2706	43	12	574	598	0.1	16	55	150	5.2	0.94	1.06	72		
Conversion						83.3	-7	97	263			1.00			
B	1008	95	10	530	546	0.5	15	1480	1230	5.1	0.99	1.01	49		
A	1004	94	10	531	547	0.0	16	800	60	5.4	0.93	1.08			
Conversion						100.0	-9	46	285			1.01			
B	1022	120	13	568	555	0.5	15	1520	1050	5.6	0.97	1.04	60	98.4	89.2
A	1025	117	13	570	555	0.0	16	1100	39	5.8	0.91	1.09			
Conversion						100.0	-5	28	289			1.04			
B	5000	127	66	920	886	0.4	16	1620	300	0.1	1.15	0.87	230	110	89
A	5008	125	66	930	890	0.0	17	850	30	0.0	1.13	0.88			
Conversion						100.0	-3	48	270			1.03			
B	2711	41	12	560	583	0.7	15	1620	1440	4.9	1.01	0.99			
A	2711	41	12	565	591	0.1	16	15	150	5.0	0.95	1.05		104.8	89.3
Conversion						84.6	-6	99	269			0.99			
B	824					0.6	15	65	1230	5.9	0.97	1.03			
A	824	6	1	412	530	0.0	16	0	93	5.8	0.92	1.09			
Conversion						100.0	-7	100	277			1.03			
B	2718	41	12	571	599	0.6	15	1550	1440	5.0	1.00	1.00	70		
A	2714	41	12	571	599	0.0	16	2	81	5.1	0.94	1.07			
Conversion						100.0	-5	100	283			1.00			
B	2710	41	12	559	580	0.6	15	1540	1500	5.1	1.00	1.00	70	104.9	90.1
A	2710	41	12	559	581	0.0	16	7	105	5.3	0.93	1.07			
Conversion						100.0	-6	100	279			1.00			
B	2695	41	12	566	590	0.6	15	1475	2070	5.5	1.01	0.99	70		
A	2695	41	12	568	592	0.1	16	3	285	5.9	0.93	1.08			
Conversion						83.3	-5	100	259			0.99			
B	2701	42	12	573	597	0.7	15	1475	2100	5.5	1.01	0.99			
A	2701	42	12	573	597	0.1	16	6	240	5.6	0.93	1.07			
Conversion						84.6	-10	100	266			0.99			
B	2710	41	12	566	594	0.6	15	1360	2070	5.7	1.01	0.99			
A	2710	41	12	567	595	0.1	16	1300	150	8.6	0.84	1.19			
Conversion						83.3	-5	4	278			0.99			

OPEN LOOP CONTROL-TAB2, p1

Before/ After	Speed rpm	Torque Nm	ower kW	Tin DegrC	Tout DegrC	CO %	CO2 %	NOx ppm	HC ppm	O2 %	Equi	Lambda	Fuel /MIN	Oil DegrC	Water DegrC
B	2700	45	13	555	551	0.2	15	1580	1050	5.6	0.95	1.05	70	104	90
A	2697	44	12	559	557	0.0	15	1580	51	6.0	0.90	1.11			
Conversion						100.0	-1	0	285			1.05			
B	820	5	0	320	480	2.0	15	58	2940	6.2	1.07	0.94		91	88.1
A						1.4	15	10	2700	6.2	1.04	0.96			
Conversion						30.0	-3	83	24			0.94			
B	2700	41	12	552	543	0.1	15	1580	900	5.0	0.96	1.04	68	102	90.6
A	2696	41	12	556	551	0.0	15	1550	108	5.5	0.91	1.09			
Conversion						100.0	-2	2	264			1.04			
B	870	7	1	310	360	1.7	15	64	2280	6.0	1.04	0.96			
A	870	7	1	310	360	1.5	15	18	1905	6.4	1.28	0.78			
conversion						14.7	-3	72	49			0.96			
B	2708	41	12	552	542	0.1	15	1550	930	5.5	0.95	1.05	68	102	90.6
A	2707	41	12	553	548	0.0	15	1550	102	5.8	0.91	1.10			
Conversion						100.0	-2	0	267			1.05			
B	2708	42	12	554	547	0.1	15	1520	870	5.7	0.94	1.06			
A				554	547	0.0	15	1550	48	6.2	0.89	1.12		105	89.6
Conversion						100.0	-2	0	283			1.06			
B	2700	44	12	558	553	0.2	15	1600	1185	5.3	0.97	1.03	70	103	90.8
A	2700	44	12	558	560	0.0	15	1600	80	5.8	0.91	1.10			
Conversion						100.0	-2	0	280			1.03			
B	3533	155	57	810	800	1.5	15	1680	1500	0.1	1.24	0.80	250	105	89.9
A	3531	151	56	822	800	1.2	16	90	540	0.1	1.19	0.84			
Conversion						17.2	-4	95	192	0.0		0.80			

Table 2a Emission and air/fuel control under open-loop condition

Table 2b Emission and air/fuel control under open-loop condition (continued)

OPEN LOOP CONTROL-TAB2, p2

Before/ After	Speed rpm	Torque Nm	ower kW	Tin DegrC	Tout DegrC	CO %	CO2 %	NOx ppm	HC ppm	O2 %	Equi	Lambda	Fuel /MIN	Oil DegrC	Water DegrC
B	1525	15	2	425	424	0.3	15	230	450	6.1	0.92	1.09	29	97.5	89.4
A				424	425	0.0	15	240	30	6.2	0.90	1.12			
Conversion						100.0	0	0	280			1.09			
B	idle														
A						0.9		10	1980	5.8					
Conversion															
B	2313	24	6	500	481	0.1	15	800	450	6.2	0.91	1.10	55	102.9	89.2
A	2313					0.0	15	800	48	6.3	0.89	1.13			
Conversion						100.0	0	0	268			1.10			
B	2700	40	11	550	550	0.1	15	1680	1065	5.4	0.96	1.04			
A	2697	40	11	552	552	0.0	15	1700	930	5.6	0.95	1.06			
Conversion						100.0	0	0	38			1.04			
B	2700	41	12	560	561	0.1	15	1620	1050	5.5	0.96	1.05			
A	2700	41	12	559	561	0.0	16	1600	93	6.2	0.90	1.12			
Conversion						100.0	0	1	273			1.05			
B	3790	75	30	690	690	0.6	16	1720	1380	6.6	0.95	1.05	76		
A	3790			707	708	0.0	16	1650	54	6.8	0.89	1.13			
Conversion						100.0	0	4	288			1.05			
B, idle	831	5	0	310	329	1.3	15	65	2190	5.8	1.03	0.97			
A, idle	831	5	0	310	387	0.9	15	25	2025	6.1	1.00	1.00			
Conversion						30.8	0	62	23			0.97			
B	3119	33	11	604	603	0.1	15	1550	660	6.5	0.90	1.11	69		
A	3125	34	11	591	583	0.0	15	1550	51	7.0	0.87	1.16			
Conversion						100.0	0	0	277			1.11			

Table 2c Emission and air/fuel control under open-loop condition (continued)

OPEN LOOP CONTROL-TAB2, p3

Before/ After	Speed rpm	Torque Nm	ower kW	Tin DegrC	Tout DegrC	CO %	CO2 %	NOx ppm	HC ppm	O2 %	Equi	Lambda	Fuel /MIN	Oil DegrC	Water DegrC
B	1933	59	12	535	558	0.6	15	1530	1446	6.2	0.97	1.04	66	90.8	90.2
A	1934	59	12	531	552	0.0	16	20	450	7.0	0.89	1.12			
						100.0	0	99	207			1.04			
	idle														
B	1995	61	13	533	543	0.4	15	1580	1380	6.0	0.96	1.04			
A	1990	60	12	539	555	0.0	16	100	45	6.0	0.91	1.10			
Conversion						100.0	0	94	290	0.0		1.04			
B	2700	41	12	558	557	0.2	15	1580	2460	7.0	0.96	1.04	70		
A	2700	41	12	562	560	0.0	15	1600	114	7.2	0.87	1.15			
Conversion						100.0	0	0	286			1.04			
B	2922	147	45	770	750	1.5	15	1500	2640	1.5	1.23	0.81			
A	2922	147	45	770	750	1.0	16	18	1125	2.5	1.10	0.91			
Conversion						36.7	0	99	172			0.81			
B	2718	43	12	563	564	0.2	15	1620	1095	5.3	0.97	1.04	70	102	90.1
A	2712	42	12	558	560	0.0	15	1620	54	6.4	0.88	1.13			
Conversion						100.0	0	0	285			1.04			
B	2591	137	37	743	734	1.2	15	1600	1170	2.3	1.12	0.89			
A	2600	139	38	743	733	0.8	16	10	360	3.7	1.02	0.98			
Conversion						34.2	0	99	208			0.89			
B	2697	41	12	561	560	0.2	15	1600	1065	5.6	0.95	1.05	70		
A	2698	41	12	561	560	0.0	15	1620	80	6.0	0.90	1.11			
Conversion						100.0	0	0	278			1.05			
B	2717	43	12	564	561	0.2	15	1580	1200	5.8	0.95	1.05			
A	2717	43	12	564	564	0.0	15	1600	78	6.2	0.89	1.12			
Conversion						100.0	0	0	281			1.05			
B	2709	41	12	557	560	0.3	15	1450	1200	6.5	0.93	1.07			
A	2709	41	12	556	558	0.0	16	1515	90	6.8	0.88	1.14			
Conversion						100.0	0	0	278			1.07			
B	2709	40	11	562	569	0.4	15	1550	1380	6.4	0.94	1.06			
A	2709			570	570	0.1	15	1550	108	6.7	0.88	1.14			
Conversion						71.4	0	0	277			1.06			
B	2710	40	11	561	568	0.4	15	1500	1110	6.5	0.93	1.08			
A				560	657	0.1	15	1550	96	7.2	0.87	1.15			
Conversion															

Table 3 H_2S release after various durations of sulphur storage

VARIOUS STORAGE DURATIONS -TAB3

Before/ After	Speed rpm	Torque Nm	Power kW	Tin DegrC	Tout DegrC	CO %	CO2 %	NOx ppm	HC ppm	O2 %	Equi	Lambda	Fuel G/MIN	Oil DegrC	Water DegrC	Comment
B	2700	45	13	555	551	0.2	15	1580	1050	5.6	0.95	1.05	70	104	90	20 minutes storage
A	2697	44	12	559	557	0.0	15	1580	51	6.0	0.90	1.11				
Conversion						100.0	-1	0	285							
B	820	5	0	320	480	2.0	15	58	2940	6.2	1.07	0.94		91	88.1	200 ppm (20 min)
A						1.4	15	10	2700	6.2	1.04	0.96				
Conversion						30.0	-3	83	24							
B	2700	41	12	552	543	0.1	15	1580	900	5.0	0.96	1.04	68	102	90.6	20 minutes storage
A	2696	41	12	556	551	0.0	15	1550	108	5.5	0.91	1.09				
Conversion						100.0	-2	2	264							
B	870	7	1	310	360	1.7	15	64	2280	6.0	1.04	0.96				600 ppm(20 min)
A	870	7	1	310	360	1.5	15	18	1905	6.4	1.28	0.78				
conversion						14.7	-3	72	49							
B	2708	41	12	552	542	0.1	15	1550	930	5.5	0.95	1.05	68	102	90.6	5 minutes storage
A	2707	41	12	553	548	0.0	15	1550	102	5.8	0.91	1.10				
Conversion						100.0	-2	0	267							
	810	7	1	Idle					0							200 ppm(5 min)
									0							
B	2708	42	12	554	547	0.1	15	1520	870	5.7	0.94	1.06				5 minutes storage
A	2708			554	547	0.0	15	1550	48	6.2	0.89	1.12		105	89.6	
Conversion						100.0	-2	-2	283							
				Idle					0							200 ppm(5 min)
									0							
B	2714	41	12	554	548	0.1	15	1520	900	5.3	0.96	1.05				10 minutes storage
A									0							
	817	6	1			1.8	15	10	2280	6.0	1.04	0.96				1200 ppm(10 min)
									0							
									0							
B	2700	44	12	558	553	0.2	15	1600	1185	5.3	0.97	1.03	70	103	90.8	5 minutes storage
A	2700	44	12	558	560	0.0	15	1600	80	5.8	0.91	1.10				
Conversion						100.0	-2	0	280							
	idle															200 ppm(5 min)
B	2700	40	11	550	550	0.1	15	1680	1065	5.4	0.96	1.04				5 minute storage
A	2697	40	11	552	552	0.0	15	1700	930	5.6	0.95	1.06				
Conversion						100.0	-3	-1	38							
	idle															660 ppm(5 min)
Thursday 18/8/94																
B	2700	41	12	560	561	0.1	15	1620	1050	5.5	0.96	1.05				30 minutes storage
A	2700	41	12	559	561	0.0	16	1600	93	6.2	0.90	1.12				
Conversion						100.0	-2	1	273							
	idle															500 ppm(30 min)

DIFFERENT STORAGE TEMPERATURES

Before/ After	Speed rpm	Torque Nm	Power kW	Tin DegrC	Tout DegrC	CO %	CO2 %	NOx ppm	HC ppm	O2 %	Equi	Lambda	Fuel G/MIN	Oil DegrC	Water DegrC	Comments
B	1525	15	2	425	424	0.3	15	230	450	6.1	0.92	1.09	29	97.5	89.4	Storage at 425 deg C
A				424	425	0.0	15	240	30	6.2	0.90	1.12				
Conversion						100.0	-2	-4	280	-0.8						
B	idle								0							Nothing detected (T=425C)
A						0.9		10	1980	5.8						
Conversion									0							
B	2313	24	6	500	481	0.1	15	800	450	6.2	0.91	1.10	55	102.9	89.2	Storage at 500 deg C
A						0.0	15	800	48	6.3	0.89	1.13				
Conversion						100.0	-1	0	268	-1.1						
	idle								0							3 ppm (T= 500C)
									0							
B	2700	40	11	550	550	0.1	15	1680	1065	5.4	0.96	1.04				Storage at 550 C
A	2697	40	11	552	552	0.0	15	1700	930	5.6	0.95	1.06				
Conversion						100.0	-3	-1	38.02	-3.7						
	idle								0							660 ppm (T=550 C)
									0							
B	3790	75	30	690	690	0.6	16	1720	1380	6.6	0.95	1.05	76			Storage at 690 deg C
A	3790			707	708	0.0	16	1650	54	6.8	0.89	1.13				
						100.0	-5	4	288.2	-3.0						
B	831	5	0	310	329	1.3	15	65	2190	5.8	1.03	0.97				33 ppm (T=690 C)
A	831	5	0	310	387	0.9	15	25	2025	6.1	1.00	1.00				
						30.8	-4	62	22.60	-5.2						
B	3119	33	11	604	603	0.1	15	1550	660	6.5	0.90	1.11	69			Storage at 604 deg C
A	3125	34	11	591	583	0.0	15	1550	51	7.0	0.87	1.16				
	idle					100.0	-2	0	276.8	-7.7						900 ppm (T=604 C)

Table 4 H_2S release after various storage temperatures

Table 5 H_2S release after various storage air/fuel ratio conditions

AIR/FUEL RATIO EFFECTS

Before/ After	Speed rpm	Torque Nm	Power kW	Tin DegrC	Tout DegrC	CO %	CO2 %	NOx ppm	HC ppm		O2 %	Equi	Lambda	Fuel G/MIN	Oil DegrC	Water DegrC	Comments
Storage at various A/F ratios																	
B	1933	59	12	535	558	0.6	15	1530	482	1446	6.2	1.02	0.98	66	90.8	90.2	
A	1934	59	12	531	552	0.0	16	20	150	450	7.0	0.95	1.05				
Conversion						100.0	-5	99	69	207	-13.8						Nothing detected
	idle																
B	1995	61	13	533	543	0.4	15	1580	460	1380	6.0	0.96	1.04				
A	1990	60	12	539	555	0.0	16	100	15	45	6.0	0.91	1.10				
conversion						100.0	-4	94	97	290	0.0						
	idle																800 ppm
Storage, then WOT, then idle																	
B	2700	41	12	558	557	0.2	15	1580	820	2460	7.0	0.96	1.04	70			10 minutes storage
A	2700	41	12	562	560	0.0	15	1600	38	114	7.2	0.87	1.15				
Conversion						100.0	-3	-1	95	286	-2.9						
B	2922	147	45	770	750	1.5	15	1500	880	2640	1.5	1.23	0.81				10 minutes WOT
A	2922	147	45	770	750	1.0	16	18	375	1125	2.5	1.10	0.91				
Conversion						36.7	-2	99	57	172	-66.7						Nothing detected
	idle																
Storage, then WOT, then idle																	
B	2718	43	12	563	564	0.2	15	1620	365	1095	5.3	0.97	1.04	70	102	90.1	10 minutes storage
A	2712	42	12	558	560	0.0	15	1620	18	54	6.4	0.88	1.13				
conversion						100.0	-1	0	95	285	-20.8						
B	1700																5 minutes WOT
A	1700																
B	idle																Then release, 50 ppm
A																	

Table 6a Catalyst poisoning and H2S release using various fuels

POISONING AND H2S USING FUELS B1-B5 -p1

Before/ After	Speed rpm	Torque Nm	Power kW	Tin DegrC	Tout DegrC	CO %	CO2 %	NOx ppm	HC ppm	O2 %	Equi	Lambda	Fuel G/MIN	Oil DegrC	Water DegrC	Comments
FUEL B1																
B	2591	137	37	743	734	1.2	15	1600	1170	2.3	1.12	0.89				20 minutes W.O.T.-open loop
A	2600	139	38	743	733	0.8	16	10	360	3.7	1.02	0.98				
Conversion						34.2	-3	99	69							
idle																No H2S detected
B	2697	41	12	561	560	0.2	15	1600	1065	5.6	0.95	1.05	70			10 minutes storage-open loop
A	2698	41	12	561	560	0.0	15	1620	80	6.0	0.90	1.11				
Conversion						100.0	-3	-1	93							
idle																No H2S detected
B	2717	43	12	564	561	0.2	15	1580	1200	5.8	0.95	1.05				20 minutes storage-open loop
A	2717	43	12	564	564	0.0	15	1600	78	6.2	0.89	1.12				
Conversion						100.0	-3	-1	94							
idle																No H2S detected
B	2718	41	12	571	599	0.6	15	1550	1440	5.0	1.00	1.00	70			30 minutes storage-closed loop
A	2714	41	12	571	599	0.0	16	2	81	5.1	0.94	1.07				
Conversion						100.0	-5	100	94							Measure poisoning
idle																No H2S detected
FUEL B2																
B	2710	41	12	559	580	0.6	15	1540	1500	5.1	1.00	1.00	70	104.9	90.1	30 minutes storage-closed loop
A	2710	41	12	559	581	0.0	16	7	105	5.3	0.93	1.07				
Conversion						100.0	-6	100	93							Measure poisoning
idle																No H2S detected
B	2709	41	12	557	560	0.3	15	1450	1200	6.5	0.93	1.07				5 minutes storage-open loop
A	2709	41	12	556	558	0.0	16	1515	90	6.8	0.88	1.14				
Conversion						100.0	-5	-4	93							
idle																No H2S detected
B	2709	40	11	562	569	0.4	15	1550	1380	6.4	0.94	1.06				15 minutes storage-open loop
A	2709			570	570	0.1	15	1550	108	6.7	0.88	1.14				
Conversion						71.4	-4	0	92							
idle																80 ppm H2S
B	2710	40	11	561	568	0.4	15	1500	1110	6.5	0.93	1.08				15 minutes storage-open loop
A				560	657	0.1	15	1550	96	7.2	0.87	1.15				
Conversion						75.0	-4	-3	91							
idle																70 ppm H2S

Table 6b Catalyst poisoning and H_2S release using various fuels (continued)

POISONING AND H2S USING FUELS B1-B5, p2

Before/ After	Speed rpm	Torque Nm	Power kW	Tin DegrC	Tout DegrC	CO %	CO2 %	NOx ppm	HC ppm	O2 %	Equi	Lambda	Fuel G/MIN	Oil DegrC	Water DegrC	Comments
FUEL B3																
B	2866	137	41	735	720	2.5	15	1250	1275	1.9	1.18	0.84	190			20 minutes W.O.T.-open loop
A	2866	137	41	735	722	1.8	15	6	960	2.6	1.12	0.89				
Conversion						28.0	-1	100	25							
B	2695	41	12	566	590	0.6	15	1475	2070	5.5	1.01	0.99	70			30 minutes storage-closed loop
A	2695	41	12	568	592	0.1	16	3	285	5.9	0.93	1.08				
Conversion						83.3	-5	100	86							Measure poisoning
idle																No H2S detected
B	2706	43	12	555	552	0.5	15	1475	2220	7.0	0.97	1.04				15 minutes storage-open loop
A	2706	43	12	571	593	0.0	16	700	90	7.3	0.87	1.15				
Conversion						100.0	-5	53	96							
idle																300 ppm H2S
B	2706	43	12	567	577	0.4	15	1520	1980	6.7	0.96	1.04				15 minutes storage-open loop
A	2708	44	12	568	577	0.0	16	1520	90	7.1	0.87	1.15				
Conversion						100.0	-4	0	95							
idle																250 ppm H2S
FUEL B4																
B	2828	129	38	733	719	1.9	15	1300	1620	1.4	1.20	0.83		102.9	89.3	20 minutes W.O.T.-open loop
A	2828	129	38	734	720	1.7	15	280	1380	2.5	1.14	0.88				
Conversion						10.5	0	78	15							
idle																No H2S detected
B	2701	42	12	573	597	0.7	15	1475	2100	5.5	1.01	0.99				30 minutes storage-closed loop
A	2701	42	12	573	597	0.1	16	6	240	5.6	0.93	1.07				
Conversion						84.6	-10	100	89							Measure poisoning
idle																No H2S detected
B	2697	41	12	561	567	0.3	15	1450	1080	5.6	0.96	1.04	70	103	88.9	15 minutes storage-open loop
A	2683	41	12	563	572	0.0	16	1450	93	5.8	0.91	1.10				
Conversion						100.0	-3	0	91							
idle																400 ppm H2S detected
B	2685	41	12	561	567	0.3	15	1450	1080	5.7	0.96	1.04				15 minutes storage-open loop
A	2690	41	12	563	572	0.0	16	1450	93	6.0	0.90	1.11				
Conversion						100.0	-3	0	91							450 ppm H2S detected
idle																

Table 6c Catalyst poisoning and H_2S release using various fuels (continued)

POISONING AND H2S USING FUELS B1-B5, p3

Before/ After	Speed rpm	Torque Nm	Power kW	Tin DegrC	Tout DegrC	CO %	CO2 %	NOx ppm	HC ppm	O2 %	Equi	Lambda	Fuel G/MIN	Oil DegrC	Water DegrC	Comments
FUEL B5																
B	2855	139	42	715	733	2.0		1150	1620	3.1		0.84				20 minutes W.O.T.-open loop
A	2854	139	42	715	733	2.0		45	1380	4.9		0.90				
Conversion						0.0		96	15							
	idle															No H2S detected
B	2710	41	12	566	594	0.6	15	1360	2070	5.7	1.01	0.99				30 minutes poisoning-closed loo
A	2710	41	12	567	595	0.1	16	1300	150	8.6	0.84	1.19				
Conversion						83.3	-5	96	93							Measure poisoning
	idle															No H2S detected
B	2710	41	12	569	570	0.4	15	1425	1260	7.8	0.90	1.11		98.1	89.3	15 minutes storage-open loop
A	2710	41	12	569	570	0.0	16	1425	75	8.4	0.84	1.20				
Conversion						100.0	-2	0	94							
	idle															900 ppm H2S peak (see fig)
B	2717	42	12	551	550	0.3	15	1425	1140	8.2	0.88	1.13				15 minutes storage-open loop
A	2716	42	12	564	568	0.0	16	1450	90	8.4	0.84	1.19				
Conversion						100.0	-4	-2	92							
	idle															1600 ppm H2S peak 8 ppm steady state
B	idle															Id;e under closed loop
A																0 ppm steady state!
FUEL B1																
B	2861	143	43	740	725											20 minutes W.O.T.-open loop
A																
	idle															No H2S detected
B	2706	41	12	573	596	0.6	15	1400	1440	4.6	1.02	0.98				30 minutes poisoning-closed loo
A	2706	41	12	574	595	0.0	16	3	105	5.5	0.93	1.08				
Conversion						100.0	-5	99.8	93							Measure poisoning
	idle															No H2S detected
B	2695	39	11	563	567	0.2	15	1420	1350	5.25	0.98	1.02		103	90.7	15 minutes - open loop
A	2695	39	11	565	568	0.0	16	30	120	5.7	0.92	1.09				
Conversion									91							
	idle															No H2S detected

APPENDIX TWO

FIGURES

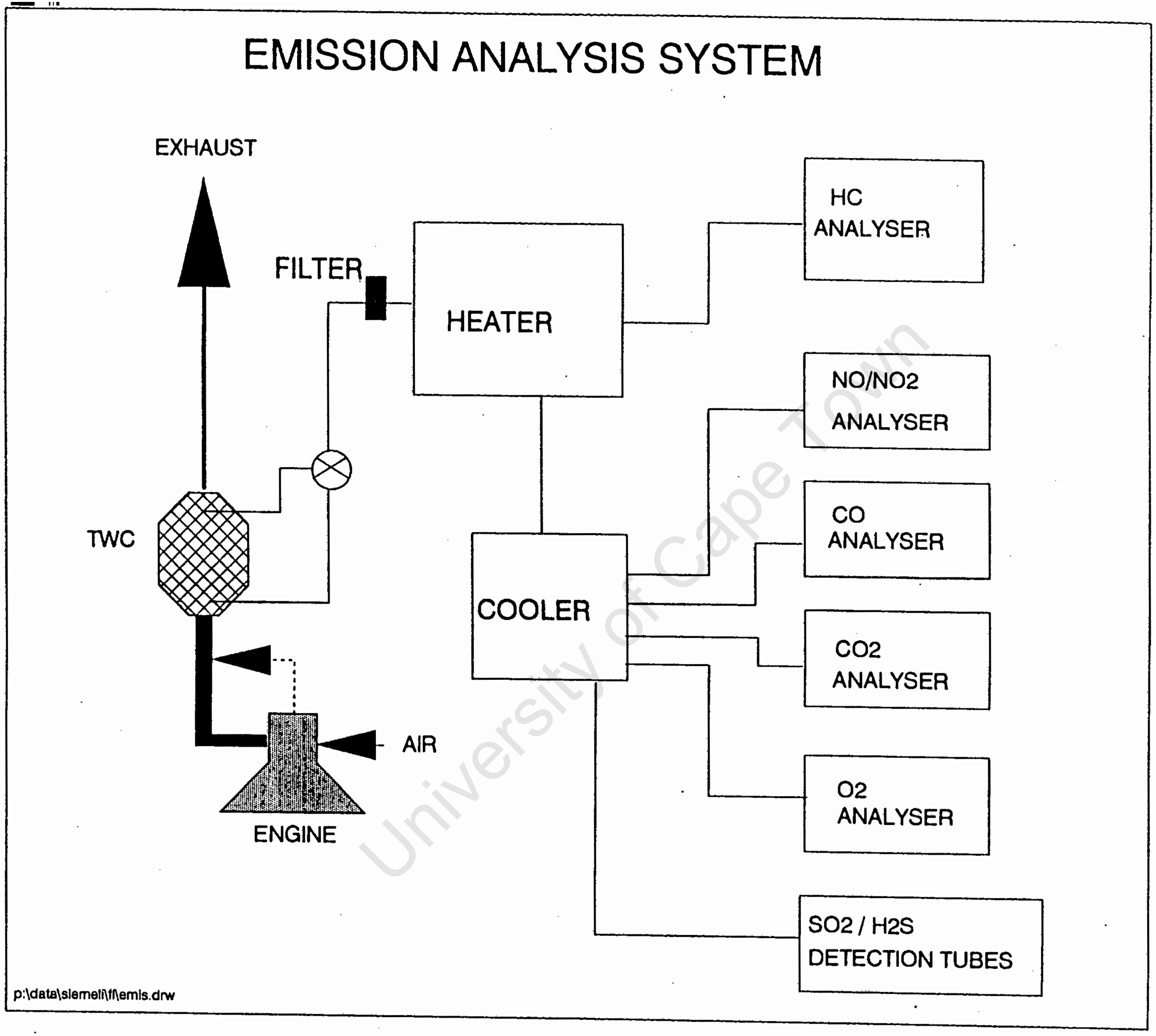
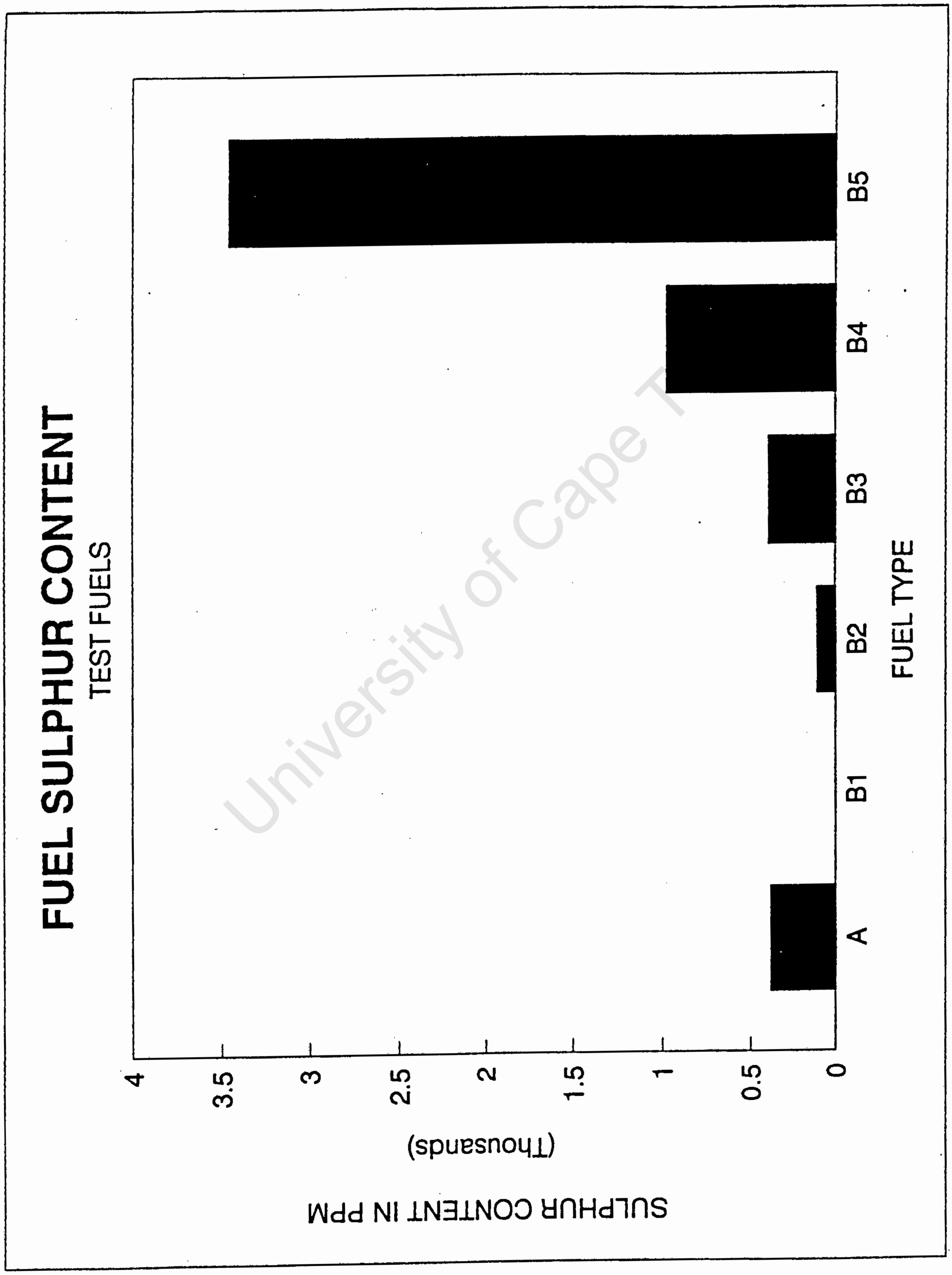


Figure 1: The emission analysis system

Figure 2: Fuel sulphur content of the various test fuels



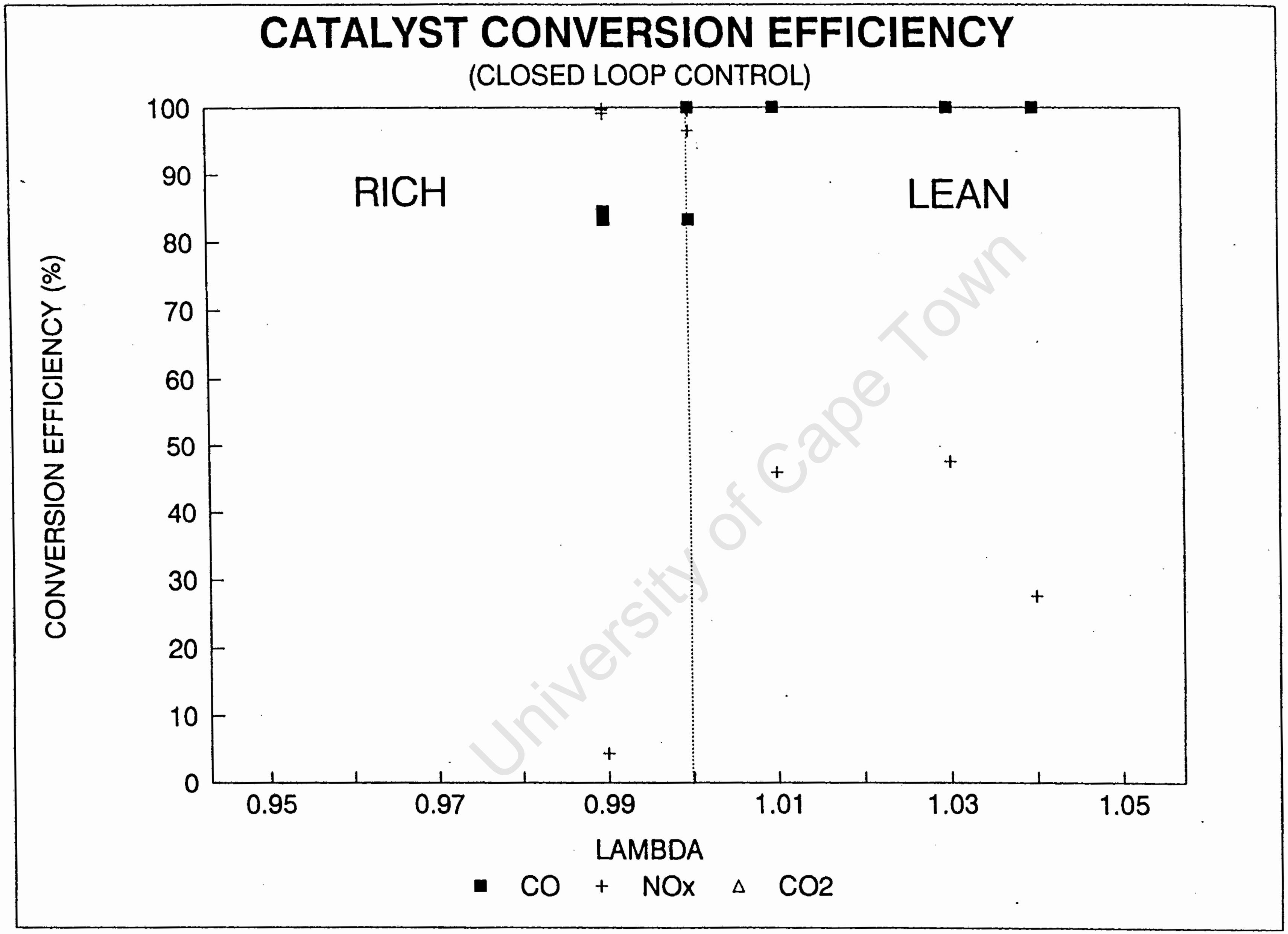


Figure 3: Catalyst efficiency under closed-loop control

Figure 4: Catalyst efficiency under open-loop control - nitrogen oxide

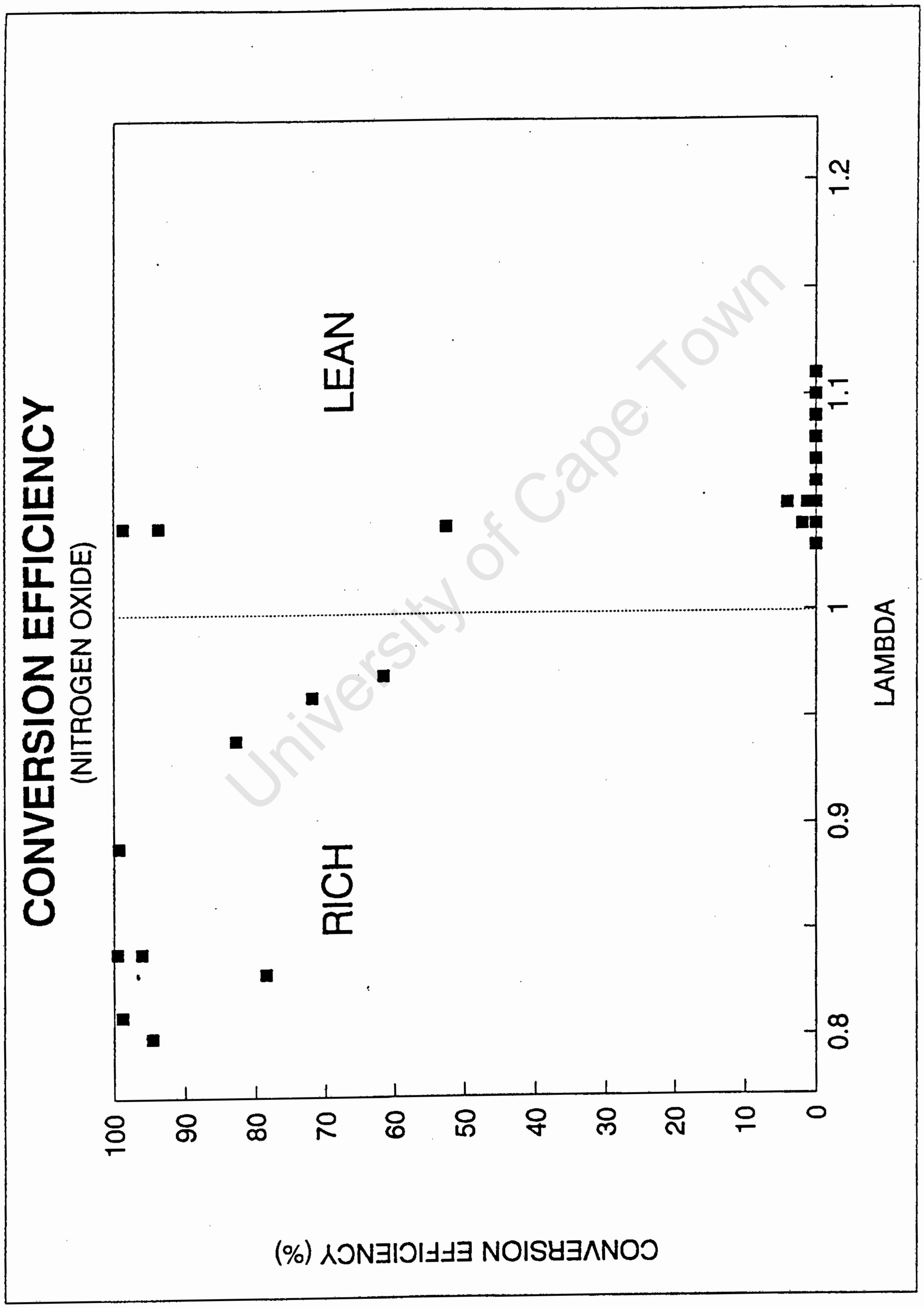
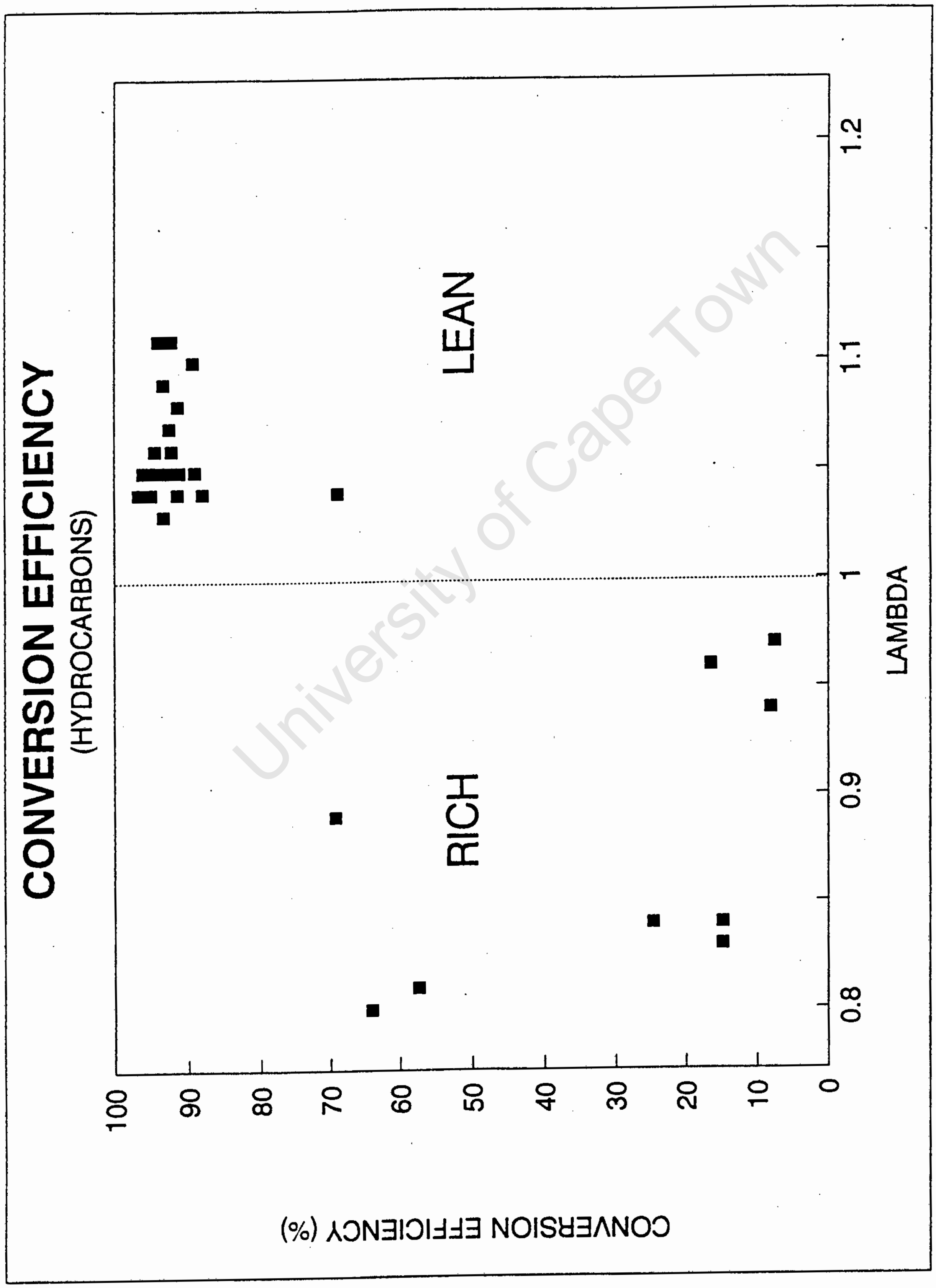


Figure 5: Catalyst efficiency under open-loop control - hydrocarbons



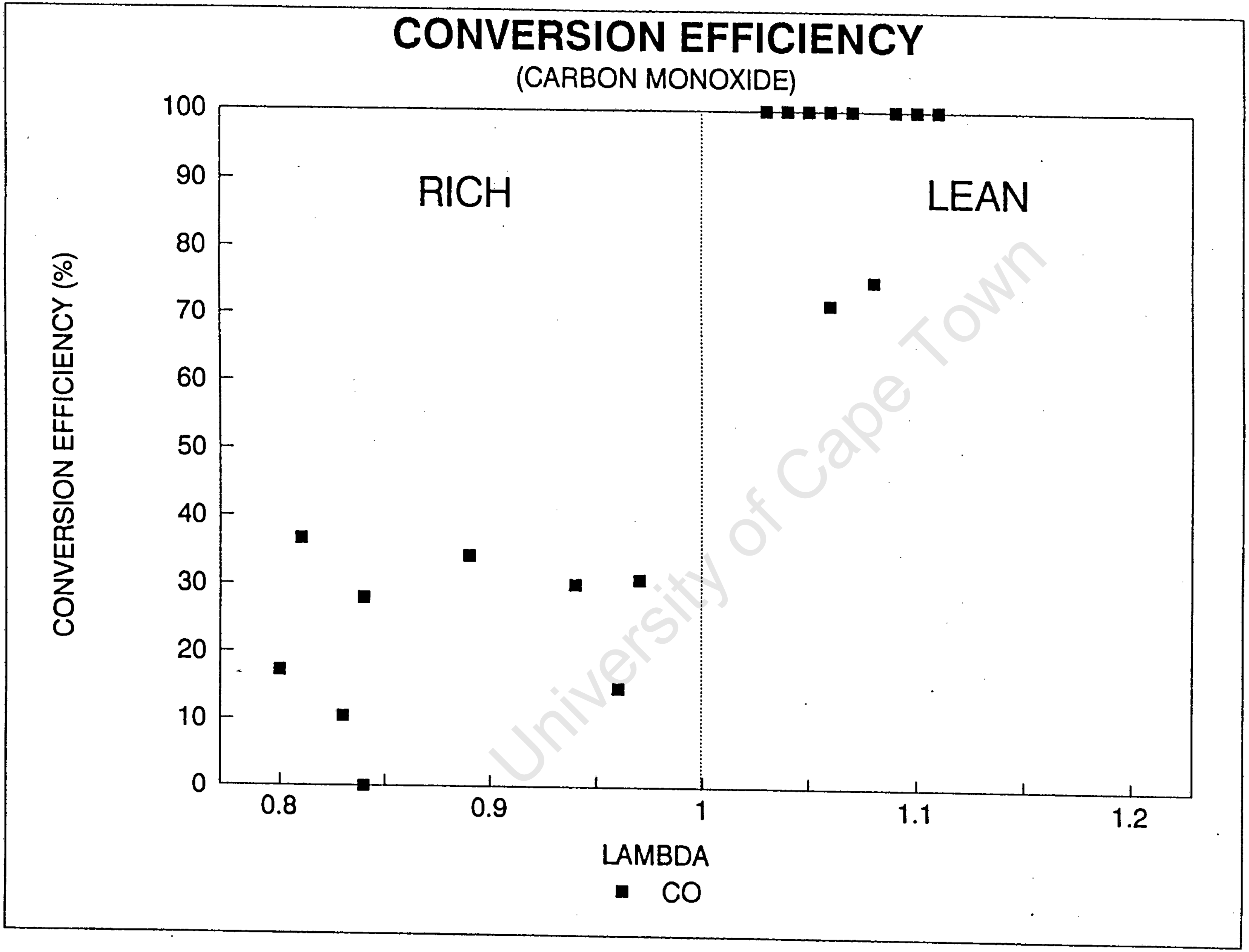


Figure 6: Catalyst efficiency under open-loop control - carbon monoxide

Figure 7: HS release for various storage durations

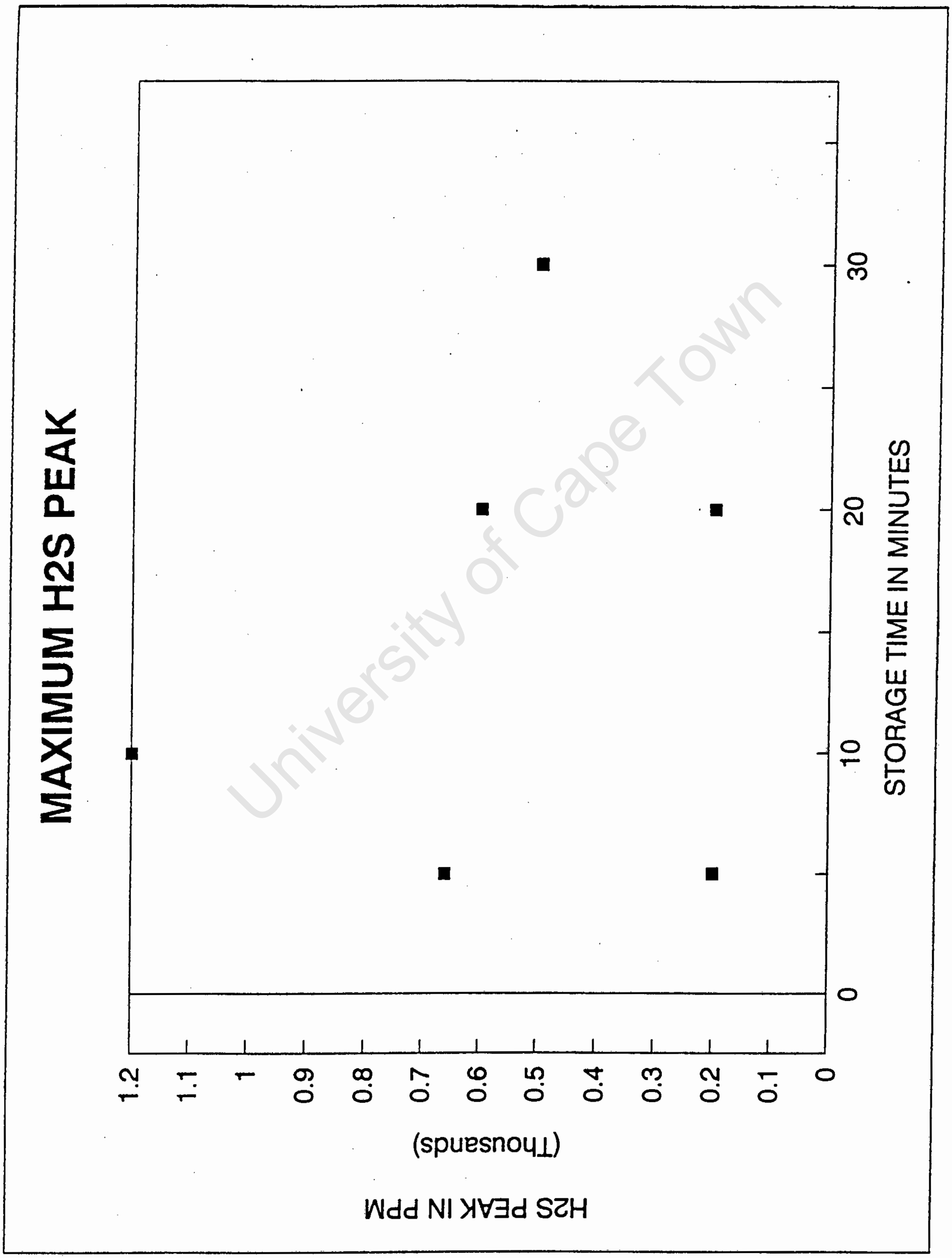
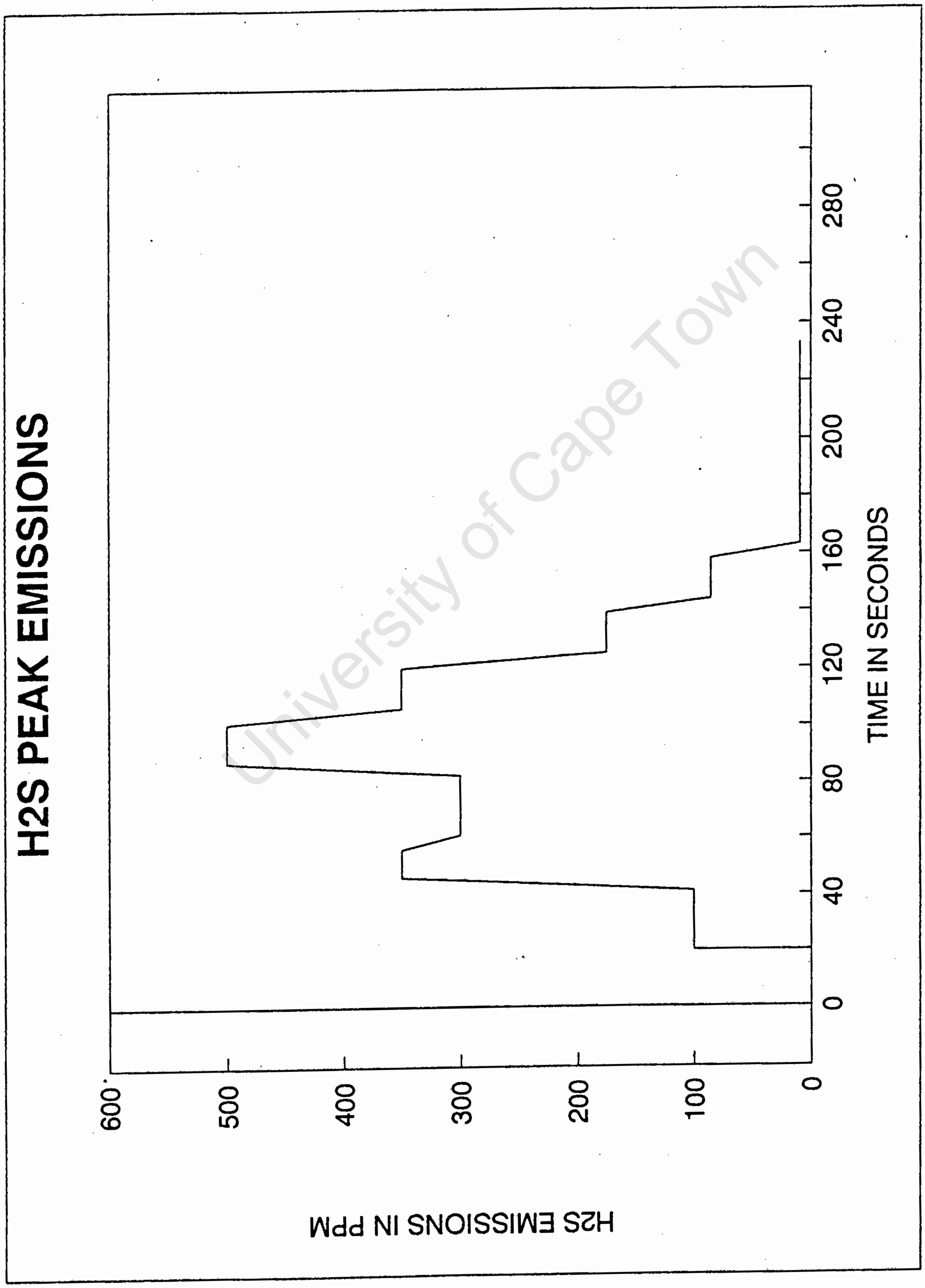


Figure 8: H_2S release after 30 minutes storage at 560°C



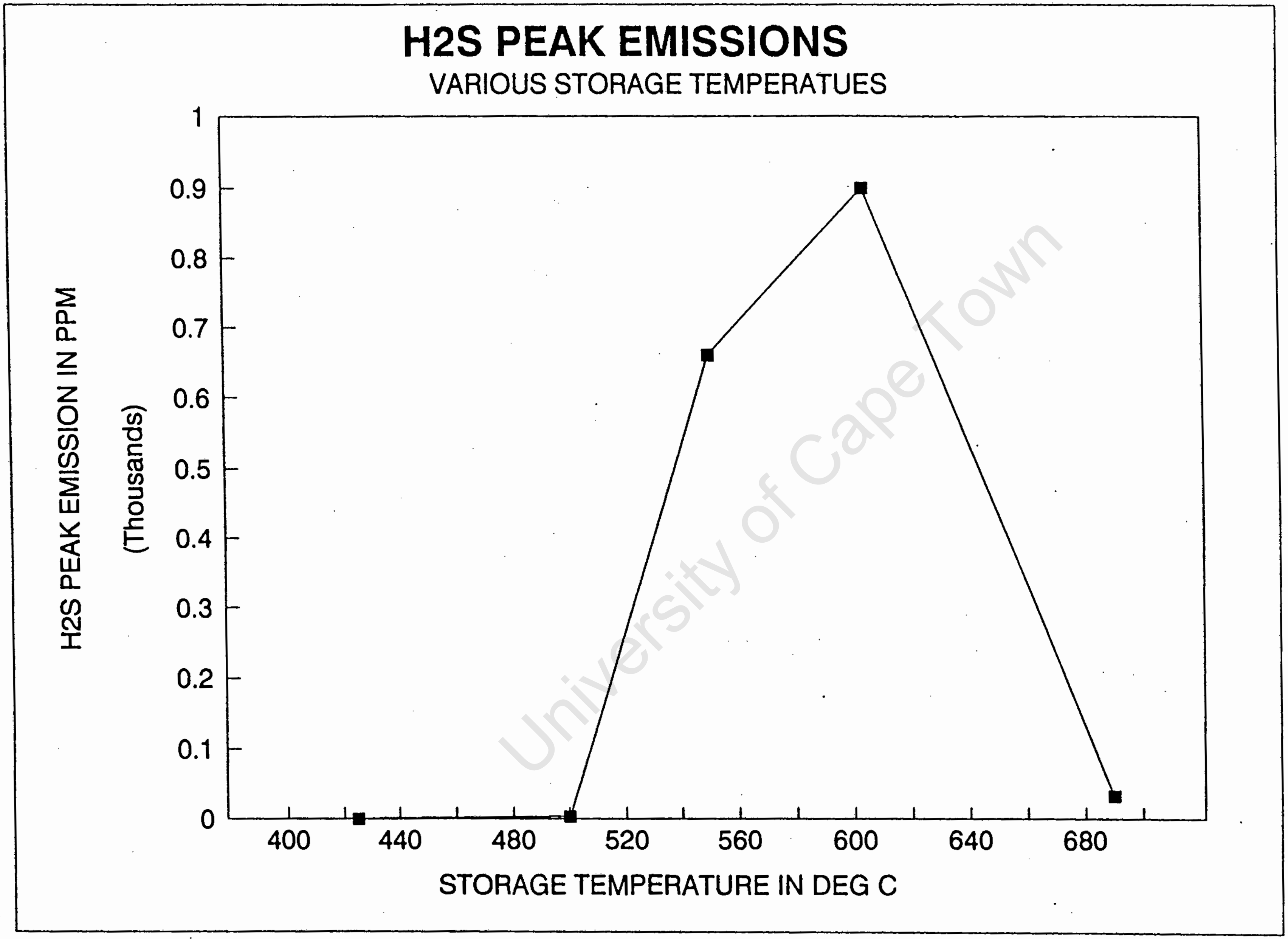
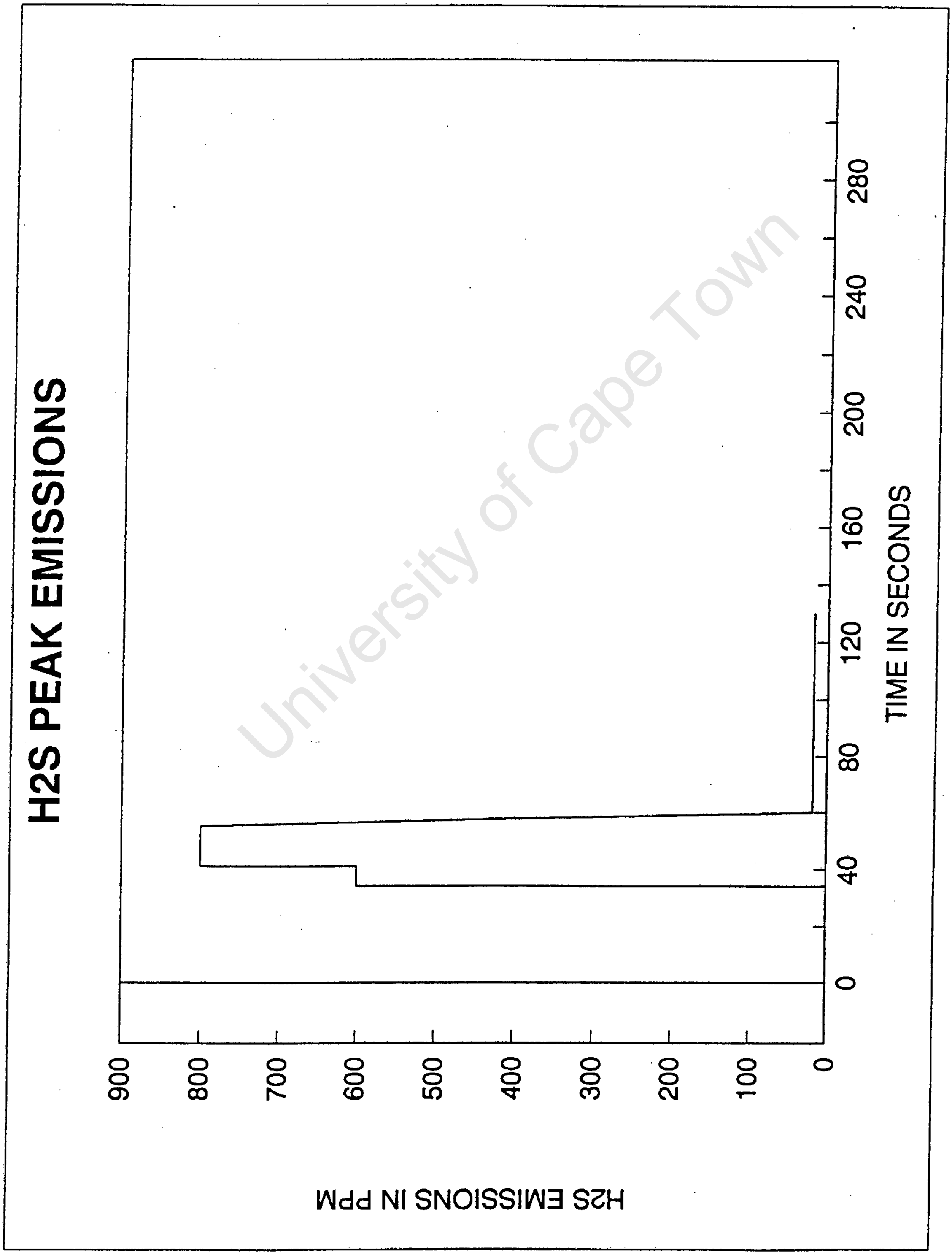


Figure 9: H_2S release after storage at various temperatures

Figure 10: H_2S release after 5 minutes storage at 600°C



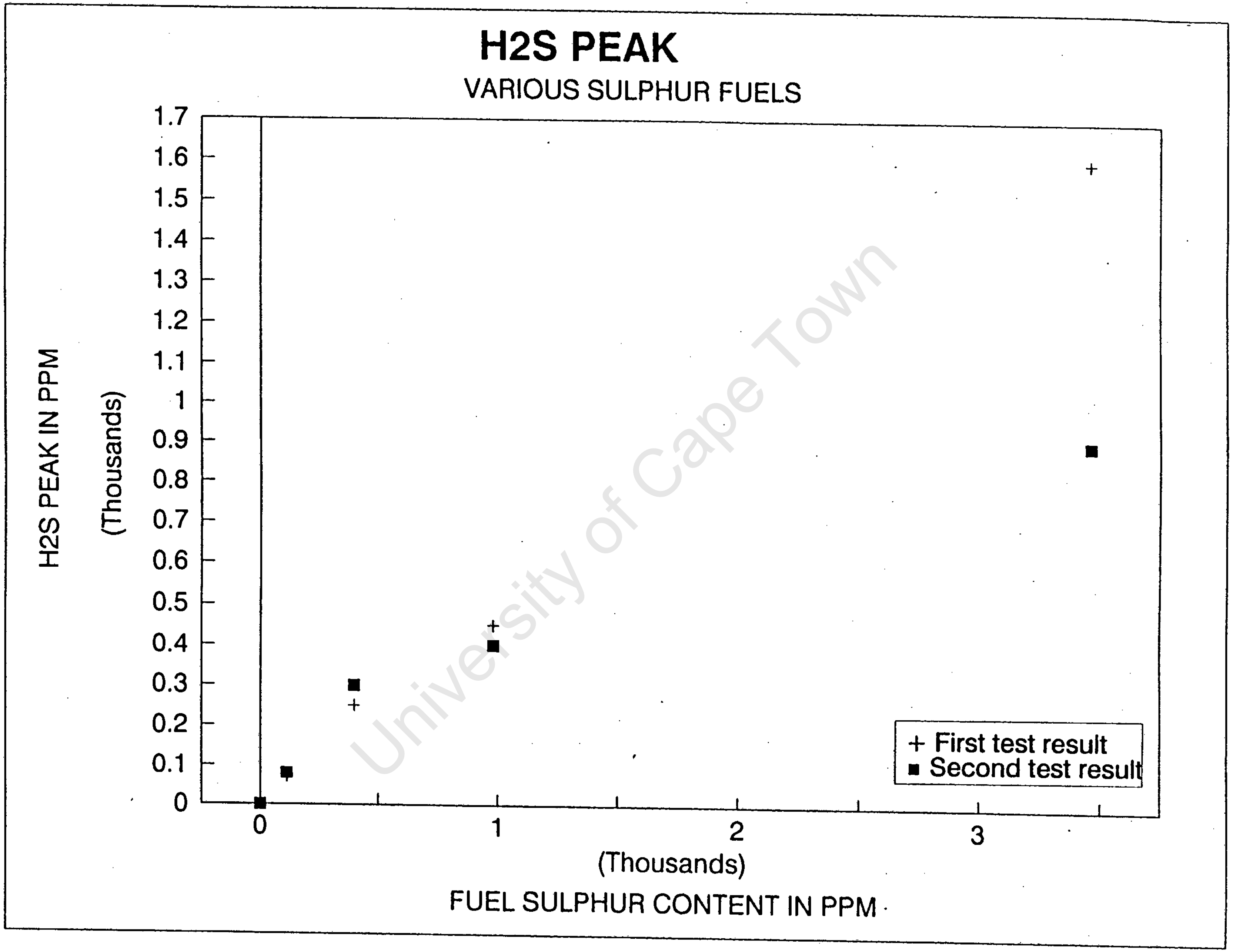


Figure 11: H_2S release using fuels with various sulphur contents

Figure 12: H_2S release after 15 minutes storage with 3461 ppm sulphur fuel

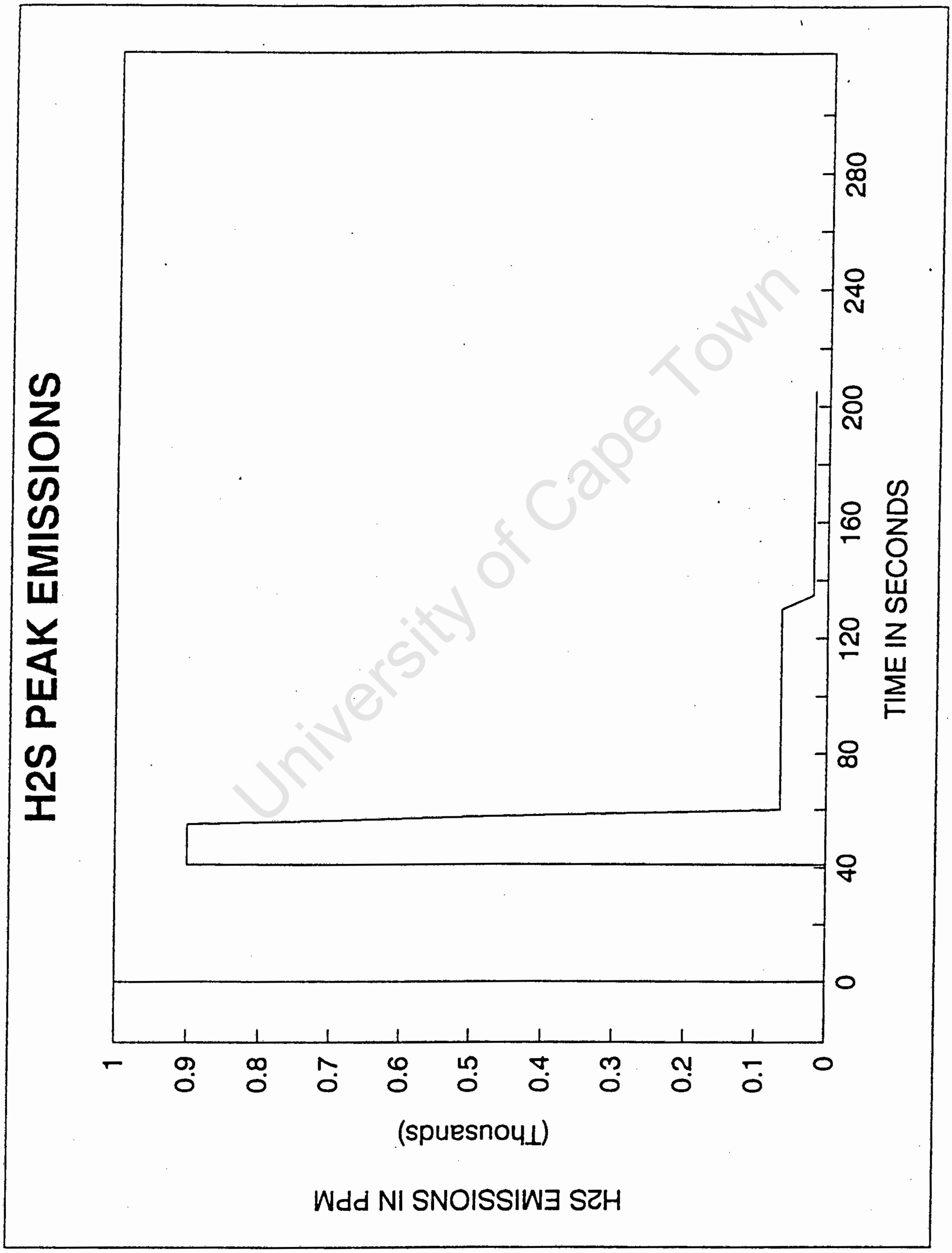
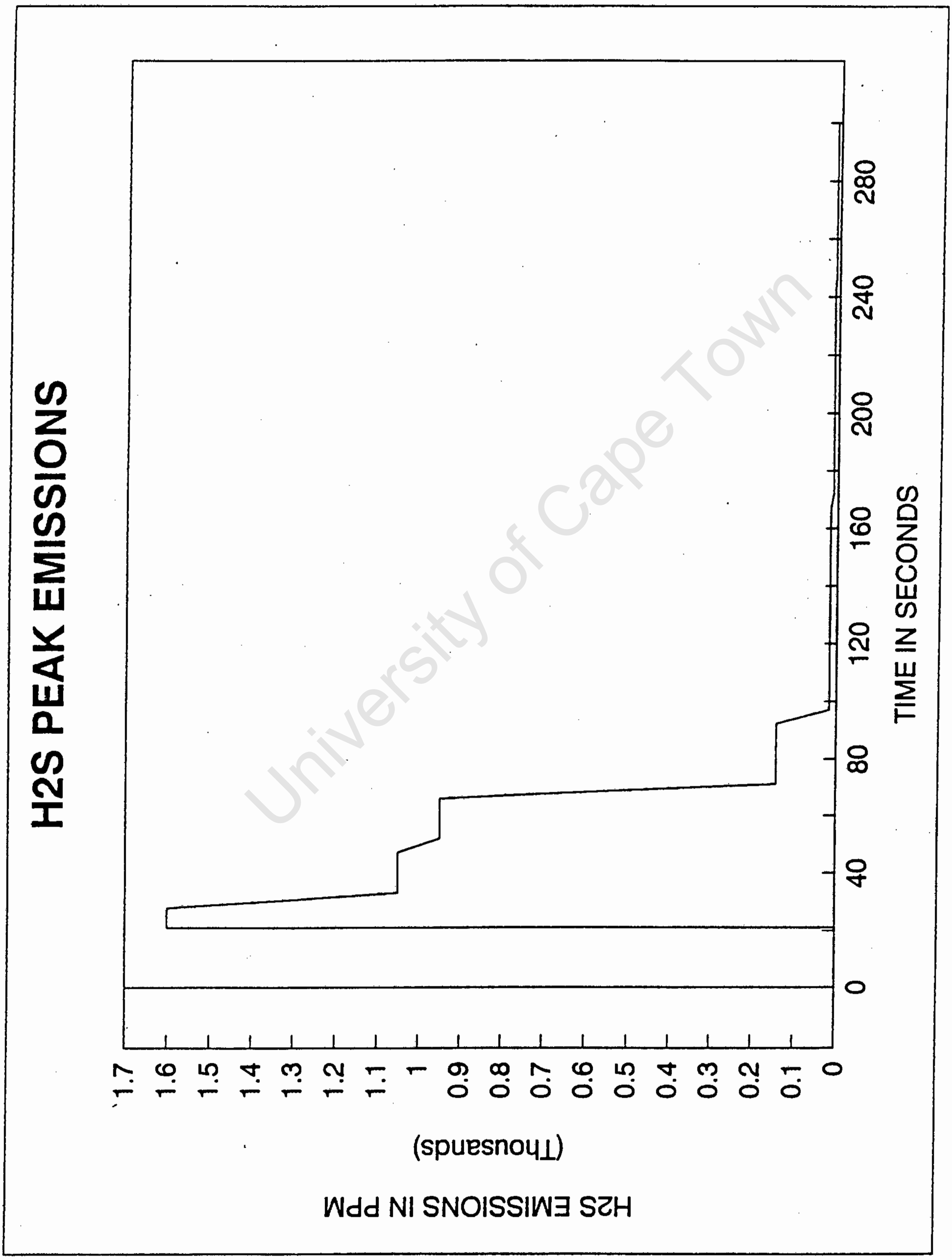


Figure 13: H_2S release after 15 minutes storage with 3461 ppm sulphur fuel (repeat)



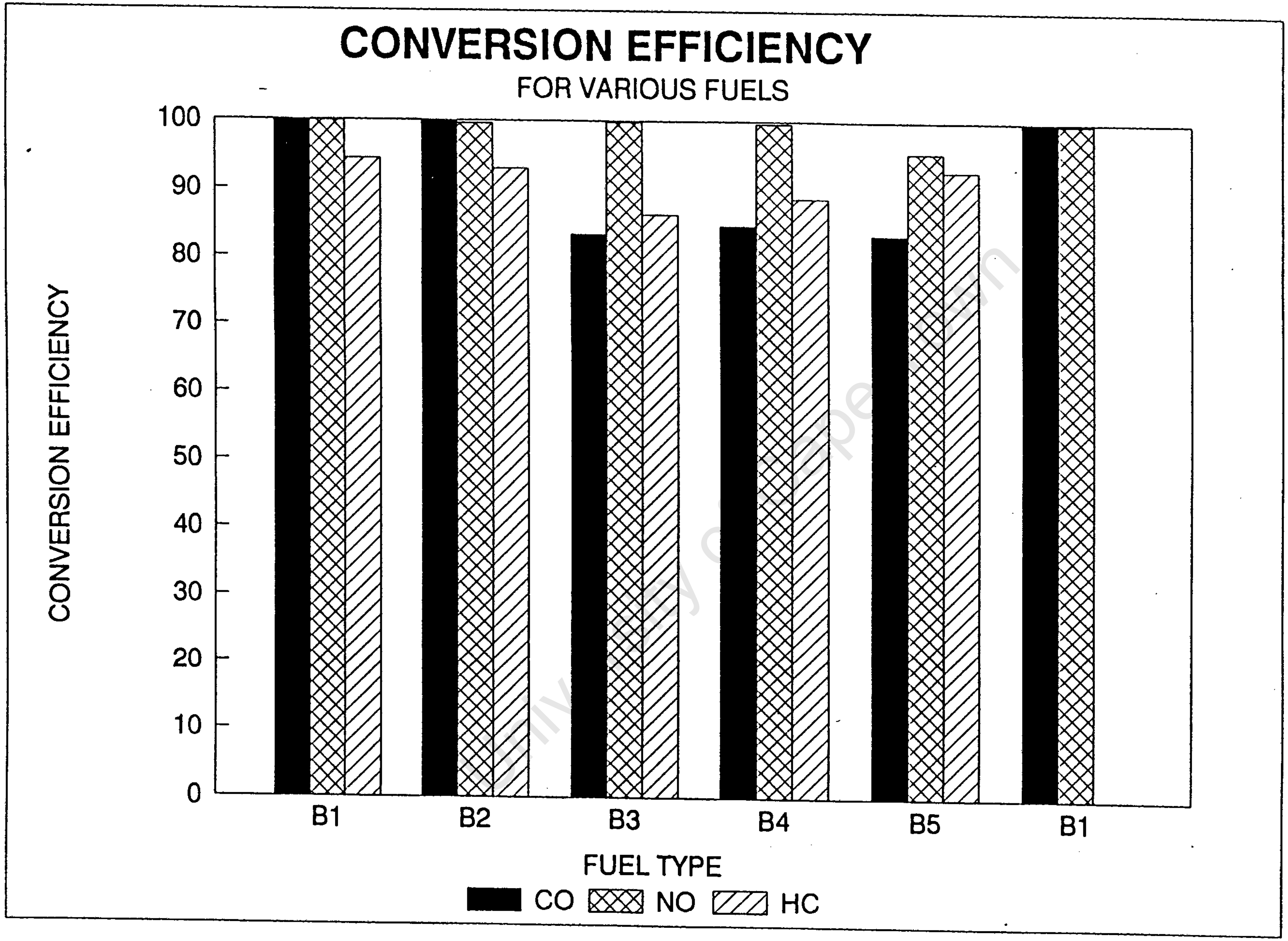


Figure 14: Catalyst conversion efficiency with various test fuels

Figure 15: Catalyst conversion efficiency as function of fuel sulphur content