Modelling of Three Way Catalysts for Control

First Year Report

By
S. Cornelius
Sidney Sussex College

Supervisor : **Professor K. Glover**

Department of Engineering
University of Cambridge
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> To travel hopefully is better than to arrive, and the true success is to labour.
>
> *(R. L. Stevenson "El Dorado" in "Virginibus Puerisque")*

To Mum and Dad for thirty years, and Gran and Pop for sixty!

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Chapter 1

Introduction

1.1 Summary

This first year report is for the Control Group in the Cambridge University Engineering Department. It examines some of the phenomena associated with vehicle emissions, from the formation of the pollutants in the engine to their removal in the three way catalyst.

Much of the first months in Cambridge were spent on courses and in study groups, there has been no summary of those here.

Chapter 2 gives a background to spark ignition engines, and the formation and affects of vehicle pollution. The function of catalysts, particularly the three way catalyst used in automotive pollution control are examined to illustrate the complexities of modern catalytic converters.

Chapter 3 presents some of the physical and thermodynamic considerations of modelling three way catalytic converters. Modelling approaches appearing in the literature are critically examined.

Chapter 4 Introduces the work which it is hoped leads towards a PhD thesis.

Chapter 2

Catalysts and Converters

2.1 Introduction

Catalytic converters are devices used to reduce the pollutant effects from motor vehicles. Catalyst systems were first introduced in 1975 [7] and have continuously been researched and improved to keep emission levels within legislative bounds.

This chapter examines the function of catalysts in automotive pollution control. An overview of the factors involved illustrates the complexities of modern catalytic converters.

Discussion starts with a background on *spark ignition* (SI) engines, this being the type used in the Cambridge University Engineering Department (CUED) engine cell room. Then we will look at the types of pollution formed during engine operation and explain the need for catalytic after-treatment.

The first sections rely heavily on Heywood's book *Internal Combustion Engine Fundamentals* [15]. Most of the catalyst details are sourced from Perry's *Chemical Engineers Handbook* [21] and Bond's *Heterogeneous Catalysis: Principles and Application* [6]. Pollution description and effects are found in Elsom's *Atmospheric Pollution: A Global Problem* [12].

2.2 Engines

Car engines perform the function of converting *chemical energy* which is stored in the fuel into *mechanical energy* to drive the vehicle. The energy is released by oxidising the fuel inside the engine.

Over the past thirty years, with the increasing awareness of environmental concerns, the factors governing motor vehicle engine design and operation have come to include reducing fuel consumption and controlling the emissions which contribute to air pollution.

The engine used in the project is a production fuel injected 1.8 litre 4-stroke Ford Zetec engine with modified exhaust gas recirculation (EGR) control system.

2.2.1 Engine Basics

Fuels used in modern petrol engine are mixtures of many hydrocarbons. Fuel is mixed with air prior to entering the engine and is burned in the engine cylinders releasing heat and kinetic energy.

The amount of oxygen required to oxidise the hydrocarbon mixture to carbon monoxide or carbon dioxide and water with no remaining oxygen or hydrocarbon molecules is known as the *stoichiometric* ratio of air to fuel. The stoichiometric *air/fuel ratio* (AFR) for typical SI engine fuels is around $14.5 kg_{air}/kg_{fuel}$. An important parameter in characterising a mixture of fuel and air is the *relative air/fuel ratio* λ:

$$\lambda = \frac{AFR_{actual}}{AFR_{stoich}} \tag{2.1}$$

Note that some American authors prefer to use the *fuel/air equivalence ratio* ϕ where

$$\phi = \lambda^{-1} \tag{2.2}$$

A combustion mixture is called *rich* if there is excess fuel ($\lambda < 1$) and *lean* if there is excess air ($\lambda > 1$).

2.2.2 Best Conditions for Engine Operation

Modern engines are usually operated at close to stoichiometric. Maximum power operation requires slightly rich mixtures as the extra fuel helps to keep the engine cool (operating lean in this situation will cause high NO_x formation). At part-load conditions (cruising on a motor way) can handle lean mixtures. Rich operation is necessary in *cold starting* an engine as at this condition only part of the fuel vapourises, and it is the vapour/air ratio that determines proper combustion.

2.2.3 Pollutant Formation and Effects

On drive cycles, typical of the "average" drive, most of the emissions from SI engines occur during cold start [14], and *transient driving conditions* such as acceleration and deceleration [20]. During steady state warmed-up driving modes the engine produces relatively low pollution levels and the catalytic after-treatment system is very efficient.

In engine exhaust there are currently three categories of pollutant gases which are legislated against, these being unburned or partially burned *hydrocarbons* (HC), *carbon monoxide* (CO) and the *oxides of nitrogen* (NO_x), specifically nitric oxide (NO) and nitrogen dioxide (NO_2). The effects and approximate amounts of these compounds exiting an SI engine are presented in Table 2.1. For passenger cars with less than six passengers the EC 96 allowed emission levels are HC + NO_x = 0.5g/km and CO = 2.2g/km [1], note that there may be more current legislative levels.

There are other secondary pollutant effects; for example *photochemical smog* is formed by a series of reactions involving hydrocarbons, nitrogen oxides and oxygen catalysed by sunlight – See [12, p38] for a complete discussion. This form of pollution can affect plant growth, irritate eyes and even affect pulmonary functions.

Note that currently nitrous oxide, commonly known as laughing gas (N_2O) is not legislated against though it is thought to have a destructive effect on stratospheric ozone concentrations. In addition, particulate emissions are not legislated for in SI engines even though there are health concerns especially with respect to respiratory irritation [1].

There are many ways that that hydrocarbon molecules escape being burned in the engine. The two main contributions to hydrocarbon pollution are gas being forced into crevices in the combustion chamber which are too narrow for the flame to penetrate, and gas being absorbed into the lubricating oil on the walls

Emission	**Amount**	**Effect**
HC	3000ppm	precursor to photochemical smog, carcinogenic and mutagenic, longer chains are toxic, irritant, odour.
CO	1-2%	highly toxic to humans, a concern in enclosed spaces. Causes headaches, dizziness, lethargy and death by affecting the body's ability to absorb O_2.
NO_x	500-1000ppm	irritant to human respiratory tract, toxic. Oxidation to nitric acid causes acid rain, promotes photochemical smog, greenhouse gases.

Table 2.1: The effects and amounts of main automotive pollutants

of the cylinder. These unburned hydrocarbons leave the crevices or desorb from the oil in the expansion stroke, and leave with the exhaust. CO forms during the combustion process in rich fuel-air mixtures where there is insufficient oxygen to completely oxidise the carbon in the fuel to CO_2. NO forms in the high temperature burned gases which do not achieve chemical equilibrium.

It must be noted that the most perfectly built engine, running at ideal conditions, will still produce pollutants far in excess of values that can be legally emitted.

It was mentioned in Section 2.2.2 that engines run better with a slightly rich mixture. Figure 2.1 shows how the pollutant concentrations vary with λ, indicating that slightly lean mixtures give the best overall emissions characteristics. Note, however, that an engine running too lean will *misfire* and enable more hydrocarbons to pass through unburned.

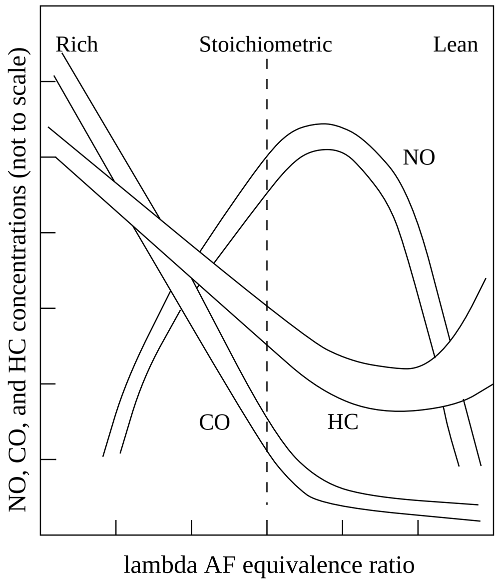

Figure 2.1: Variation of NO, HC and CO concentrations in a spark ignition engine with λ. Adapted from [15, figure 11-2]

2.3 What are Catalysts?

There are two broad classes of catalyst, these being *homogeneous*, where the catalyst forms a homogeneous phase with the reaction mixture, and *heterogeneous* where the catalyst exists as a distinct phase from the reaction mixture. For this project we are interested in heterogeneous catalysts, specifically the reactions of the exhaust gas on a solid surface.

Prior to any discussion it is important to distinguish between two fundamental concepts which are relevant to catalytic reactions. *Chemical thermodynamics* governs whether or not a reaction will proceed, and also determines the extent to which the reaction will proceed (this is known as *chemical equilibrium*). Once thermodynamics has determined that a reaction can occur, *chemical kinetics* governs how fast the equilibrium is approached.

2.3.1 Properties of Catalysts

In relation to automotive emission control the most important properties of the catalyst are that it *increases the rate of reaction*, and that it remains *chemically unchanged at completion* of the reaction. Other properties of catalysts are that the *reaction rate is proportional to the catalyst concentration* (for a surface reaction, concentration is equivalent to the number of *active sites* available for molecules to adsorb and, thus, for reaction to take place). A catalyst exhibits *selectivity* if there exists the possibility of more than one reaction. That is, the catalyst speeds up a certain reaction over the other possible reactions thus increasing the yield of that product. It must be stressed that the position of chemical equilibrium does not change in a catalysed reaction as this is a property of thermodynamics not kinetics, so to increase the yield of a certain substance, product must be taken out before equilibrium is reached.

Increased rate of reaction

The fundamental principle of a catalyst is the lowering of the *activation energy barrier* as seen in Figure 2.2. This is achieved by changing the *reaction mechanism* (the path taken from reactants to products). For example, in many of the reactions that we are interested in, the formation of the products involves *bond dissociation* in one or more of the reactants; thus the reaction in the homogeneous gas phase is unlikely to occur as the activation energy is prohibitively high. On the catalyst surface, however, the energy of dissociation of certain species is much reduced (especially diatomics such as O_2 and H_2 which proceed with a activation energy near zero) [18].

The kinetic parameters (rate coefficient k, activation energy E and the order of reaction) depend sensitively to the path followed, and the introduction of a catalysed pathway changes not only the values of these parameters, but also their significance [6]. The paper by Montreuil et al. [19] illustrates that slight differences in catalyst formulation cause variation in kinetic parameters (and thus speed of reaction). Knowledge of the kinetic parameters for a reaction can sometimes help in understanding the reaction mechanism.

Conservation of Catalyst

It is important that the catalyst is not consumed during operation. The reaction pathway may be made up of a number of elementary steps. For example a reaction may proceed by the two elementary reactions:

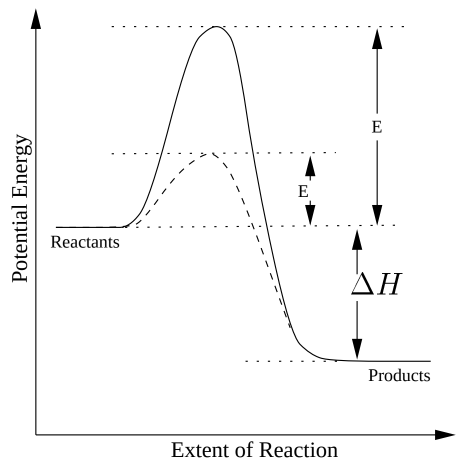

Figure 2.2: Potential energy profile for an exothermic reaction. The dashed line shows the lower activation energy needed in a catalysed reaction. Adapted from [6, fig. 1.1]

step 1	$A + C$	$\rightarrow$	AC
step 2	$AC + B$	$\rightarrow$	$D + C$
overall reaction	$A + B$	$\rightarrow$	D

The catalyst represented by C forms an *intermediate product* with A; however, C is returned to its original form at the end of step two and the only observable reaction product is D.

It must be noted that the knowledge of the overall kinetics does not define the whole reaction mechanism. There may be fast intermediate steps between reactants and products which, because they are not *rate determining* (or rate limiting or rate controlling) are not observed.

2.3.2 Catalyst Poisoning

A poison is a substance that appreciably reduces the catalytic reaction rate. In this work the most important poisoning effects to be aware of are the *masking* of active sites (this can occur by a molecule adsorbing so strongly to the catalyst surface that it cannot be easily released), and *physical blockage* of pores or covering of active sites.

2.3.3 Reaction Steps

A typical heterogeneous catalytic reaction involves the following five elementary steps [2, 6, 21], which are illustrated in Figure 2.3:

1. *Mass Transport* of reactants from bulk fluid to surface

2. *Adsorption* of reactants onto the surface

3. *Surface Reaction*

4. *Desorption* of products from the surface

5. *Mass Transport* of products from surface to bulk fluid

Each step represents a physical or chemical *resistance*. In heterogeneous catalytic reactions the rate controlling step may be a complex relation between two or more of the above five steps. This is thought to be due to interaction between physical and chemical processes [21].

The *rate of reaction* is limited by the slowest of these elementary steps. Steps 1 and 5 involve a *mass diffusion* process and are governed by Fick's law of diffusion [11]. If either of these steps are slowest then the process is *diffusion limited* or *mass-transport limited*. Steps 2, 3 and 4 can be lumped together to constitute the "chemical reaction". If step 2, 3 or 4 is the slowest then the process is *reaction limited*.

The rate limiting step may change depending on the reaction conditions. The rate of each step is a function of temperature; thus, over a range of temperatures the rate limiting step and, therefore, the equation governing the rate, may change [8]. For the catalyst at low temperature the chemical reaction rate is slower than mass transfer, but at high temperature the chemical rate becomes much greater and the overall process becomes mass transfer limited [4].

2.4 Three Way Catalysts (TWC)

Three Way Catalytic Converters were introduced to car exhaust systems by Volvo in 1977 [14] and have become the most commonly used converter. TWC is so

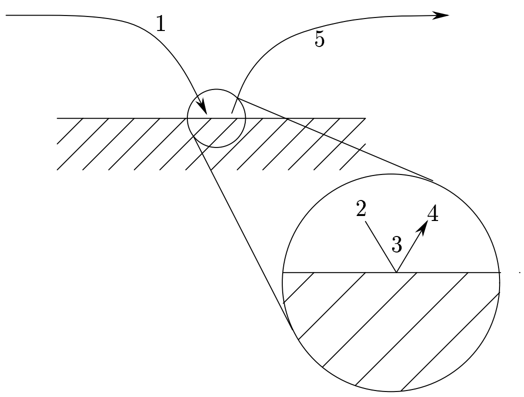

Figure 2.3: Elementary steps in a surface reaction

called because of its ability to convert each of the three pollutant classes (CO, NO_x and HC) to less harmful compounds (CO_2, N_2 and H_2O) in a single catalyst bed.

Catalytic converters operate under an enormous range of conditions. The *cold start* temperature in some countries can be well below 0^oC, in sustained high load operation the temperature in the catalyst can be over 900^oC. The *light-off temperature* is around 300^oC. At the light-off temperature the catalyst is sufficiently activated such that 50% of the pollutants are removed, below this the catalyst is inactive and effectively all the pollutants from the engine pass into the atmosphere. 80% of weighted emissions result from the *warm up* period before the catalyst has achieved light off [14]. At around 900^oC damage can occur to the catalyst in the form of sintering of the noble metals.

2.4.1 Physical Description

The type of converters of interest have a *monolithic* structure. The converter consists of a honeycomb ceramic *substrate* with many parallel square channels through which passes the exhaust gas with laminar flow. A *washcoat*, usually of Al_2O_3 and *ceria* (Ce_2O_3), covers the insides of the channels. The washcoat has a very fractal structure, which has a surface area around ten times that of the geometric surface area of the inside of the channels. This provides a greater surface for the dispersion of *precious metal catalyst* - on which the chemical reaction takes place. Small particles of the noble metal are desired so that the largest surface area per volume (and thus lowest cost) can be achieved.

Chemical and Operational Considerations

Rhodium, Platinum and *Palladium* are the three commonly used precious metals in automotive catalysts. Figures for 1996 precious metal usage in automotive catalytic converters are as follows: 56.1 tonne Pt (which was 40% of the worlds production), 68.1 tonne of Pd, and 12 tonne of Rh [18]. Rhodium is very active for NO_2 reduction. Platinum is a good oxidiser and is lead tolerant. Palladium also has good oxidising characteristics but is poisoned by lead; however Pd has much better high temperature stability and a lower light off temperature than Pt.

As well as increasing the available surface area for reaction, the washcoat has two other important properties. First, it stabilises the precious metals which have a tendency to sinter into larger particles at high temperature, thus, reducing the reaction surface area (this is part of a phenomena known as *aging*). Second, the ceria provides *oxygen storage* by itself undergoing a series of redox reactions, [3] which are thought to be, for CO,

$$O_2 + 2Ce_2O_3 \rightarrow 4CeO_2 \tag{2.3}$$

$$CO + 2CeO_2 \rightarrow CO_2 + Ce_2O_3 \tag{2.4}$$

Aging is the reduction in oxygen storage capacity (OSC) with usage. OSC increases in aged catalysts with increasing temperature (650-753K). This form of catalyst deterioration mainly affects transient emissions [16], however, it also delays light-off [20, p576].

Efficient removal of all three pollutants requires the presence of an *oxidising atmosphere* to convert CO and the hydrocarbons and a *reducing atmosphere* to convert NO_x. The oxygen storage property of the ceria helps overcome these two conflicting conditions. In lean exhaust there is excess oxygen available; this excess is stored in the catalyst until it saturates the OSC. Conversely, if more O_2 is needed than is available, the ceria will give up oxygen provided it still has some stored [7, 8]. Aimard et al. [3] notes that "The importance of the OSC comes from its close relation to the CO/NO_x conversion efficiency: OSC estimation is a way of monitoring TWC efficiency". Figure 2.4 comprises of data from the CUED test engine, it shows evidence of oxygen storage [13].

Figure 2.5 shows that there is a narrow window of AFR around stoichiometry in which the conversion of all three pollutants is high [3, p1119]. AFR must be

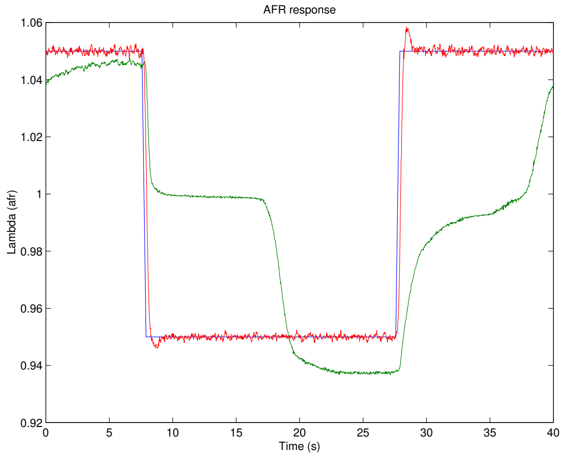

Figure 2.4: A lean to rich, then rich to lean step in λ. The converter inlet response follows the step inputs quite well. The converter outlet λ holds at stoichiometry for a time, indicating oxygen is being used from the storage. On the rich to lean step the response also holds around stoichiometry indicating that oxygen is being stored in the ceria.

close to stoichiometric for good catalytic operation, however as explained above this is not so for engines [5, 14, 15].

To meet emissions targets it will be necessary to improve the engine management system to operate an even closer λ window [14]. Experiments indicate a "considerable widening of the air/fuel ratio window where all three pollutants are effectively removed, with cyclic variation of the fuel flow" [15, p656].

2.5 Considerations

There are many conflicting considerations in optimising for the minimum overall cost of an automotive exhaust system. The primary concern is meeting emission limits for the life of the catalyst - and ensuring that the catalyst life be as long as possible.

A great majority of car emissions are produced during transient driving modes, therefore these are focused on as the most likely areas in which improvements can be made [20]. For instance, it is known that reduction of hydrocarbons emitted before light-off and a reduction of NO_x during acceleration are important to improved emission performance [4].

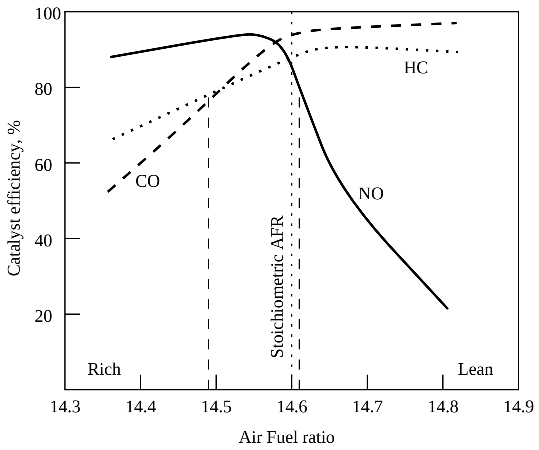

Figure 2.5: Conversion efficiency for NO, CO and HC in a TWC with AFR, note the narrow band with high conversion for all three pollutants. Adapted from [15, figure 11-57].

The engine should operate slightly rich for cold start and for good transients but should run at stoichiometry or lean for good pollutant conversion in the converter. A strategy employed is to modulate the AFR so that the average is at the stoichiometric ratio. Pattas et al. [20, p569] states that "The chemisorption and storage of oxygen by cerium during lean engine operation and its release during rich conditions has been recognised as one of the major phenomena affecting catalyst's behaviour during vehicle acceleration and deceleration. Furthermore, this effect significantly influences the converter's efficiency during operation under modulated A/F ratio".

The desired goals are having a low light-off temperature and reaching the light-off temperature as quickly as possible. One method of achieving quick light-off is by placing the catalyst near the exhaust manifold, however, the catalyst also needs to operate below a certain temperature to avoid rapid aging damage.

Chapter 3

Models and Modelling

3.1 Introduction

In this chapter the physical and thermodynamic considerations are presented to demonstrate the complex phenomena to be modelled in a TWC. Several modelling approaches are examined and some of the models appearing in the literature are critically discussed.

3.2 Models

Some of the reasons given in the literature for the development of catalyst models include the high expense of experiments, the analysis of thermal and conversion characteristics [10], the improvement of TWC design [9], control, and on board diagnostics (OBD). Baba et al. [4] uses a model for predicting the temperature and concentration fields inside the converter, and optimising heating patterns.

The usefulness of a model depends on the simplifications and assumptions used. Generally, complex distributed models are used in numerical simulations for *design* of catalytic converters and exhaust systems; slightly simplified models are used in the *analysis* of conversion efficiency or oxygen storage and for long term simulation; grossly simplified models which can run in real time are often used for *control* and *diagnostics* purposes.

3.3 Modelling Catalytic Converters

3.3.1 Physical Considerations

The physical and chemical interactions in the catalytic converter are numerous and quite complex. Gottberg et al. [14, p355] has an excellent section on phenomena that might be considered, classified in the four groups: *flow, heat transfer, mass transfer,* and *chemical reactions*, which has been extended here.

Flow: Velocity distribution over converter inlet plane, i.e. over different channels, flow regime and boundary layer characteristics in each channel, entrance effects of gas flow, molar and thermal expansion due to chemical reactions, dispersion, i.e. deviation from ideal plug flow, axial dispersion of gas-phase species, lateral variation of gas-phase temperature.

Heat Transfer: Heat balances. Considered in the bulk gas phase: gas flow transport, convection, conduction. Considered in solid (substrate + washcoat) phase: axial and radial conduction, radiation - important at high temperatures, heat loss to atmosphere.

Mass Transfer: Material balances. Considered in the gas phase: bulk flow transport, convection (velocity dependent), diffusion. Considered within the washcoat particles: diffusion coupled with chemical reactions, oxygen storage.

Chemical Reactions: Have effects on both the material and energy balances. Effects on composition (and velocity): adsorption (from gas phase to surface site), surface reactions (redox), desorption (from surface site to gas phase), homogeneous gas phase reactions (may occur at high temperature). Effects on temperature (and velocity): heat of adsorption, heats of reaction. Reaction rates.

3.3.2 A Modelling Approach

This section presents balance equations and a few chemical reactions that are common to much of the work found in the literature. For the monolithic catalyst, balances of energy and reaction species in the bulk fluid and at the reaction surface during the exothermic chemical reactions must be included [10].

Mass Balance in bulk fluid

$$\varepsilon\frac{\delta \mathrm{X_{g,i}}}{\delta \mathrm{t}} + \mathrm{v_g}\frac{\delta \mathrm{X_{g,i}}}{\delta \mathrm{z}} = \mathrm{k_{m,i}S(X_{g,i} - X_{s,i})}|_{\mathrm{x,y}} \tag{3.1}$$

Heat Balance in bulk fluid

$$\varepsilon\rho_{\mathrm{g}}\mathrm{Cp_g}\frac{\delta \mathrm{T_g}}{\delta \mathrm{t}} + \mathrm{v}\rho_{\mathrm{g}}\mathrm{Cp_g}\frac{\delta \mathrm{T_g}}{\delta \mathrm{z}} = -\mathrm{hS(T_g - T_s)}|_{\mathrm{x,y}} \tag{3.2}$$

Mass Balance at surface

$$(1-\varepsilon)\frac{\delta \mathrm{X_{s,i}}}{\delta \mathrm{t}} = \mathrm{k_{m,i}S(X_{g,i} - X_{s,i})} = \mathrm{R_i}(\bar{\mathrm{X}}_{\mathrm{s}}, \mathrm{T_s})|_{\mathrm{x,y}} \tag{3.3}$$

Heat Balance at surface

$$\begin{aligned}(1-\varepsilon)\rho_{\mathrm{s}}\mathrm{Cp_s}\frac{\delta \mathrm{T_s}}{\delta \mathrm{t}} &= \lambda_{\mathrm{s}}(1-\varepsilon)\left(\frac{\delta^2 \mathrm{T_s}}{\delta \mathrm{x}^2} + \frac{\delta^2 \mathrm{T_s}}{\delta \mathrm{y}^2} + \frac{\delta^2 \mathrm{T_s}}{\delta \mathrm{z}^2}\right) + \mathrm{hS(T_g - T_s)} \\ &\quad -\mathrm{h_{amb}S_{ext}(T_s - T_{amb})} + \sum_{\mathrm{i=1}}^{\mathrm{m}}(-\Delta\mathrm{H})_{\mathrm{i}}\bar{\mathrm{R}}_{\mathrm{i}}(\bar{\mathrm{X}}_{\mathrm{s}}, \mathrm{T_s}) \end{aligned} \tag{3.4}$$

There are many *chemical reactions* that occur in the TWC. Some reactions that are common are:

$$\mathrm{CO} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{CO_2} \tag{3.5}$$

$$\mathrm{C_3H_6} + \tfrac{9}{2}\mathrm{O_2} \rightarrow \mathrm{3CO_2 + 3H_2O} \tag{3.6}$$

$$\mathrm{NO_2} \rightarrow \mathrm{N_2} + \tfrac{1}{2}\mathrm{O_2} \tag{3.7}$$

$$\mathrm{2CO + 2NO} \rightarrow \mathrm{N_2 + 2CO_2} \tag{3.8}$$

$$\mathrm{2H_2 + 2NO} \rightarrow \mathrm{2H_2O + N_2} \tag{3.9}$$

These are only representative, for instance very little C_3H_6 actually exists.

The *Arrhenius equation* accounts for the temperature dependence of the reaction rate expression. There are other more complex models based on collision theory, however for simple reactions it is sufficiently accurate [21].

$$k = Ae^{\frac{-E}{RT}} \tag{3.10}$$

Where A is the *frequency factor* and E is the *activation energy* - the average energy level which the reactants must have in order for the reaction to proceed (see figure 2.2). Activation energy can be affected by pressure and, as discussed in section 2.3.1, catalysts.

Rates of Reaction of species i are usually expressed a function of the temperature and the species concentration raised to an index that is dependent on the catalyst formulation [19].

$$R_i = \frac{k_i X_i^{\alpha} X_j^{\beta} ...}{G} \tag{3.11}$$

Here G is an inhibition factor which represents the effect of overcrowding of molecules at the surface. Many differing schemes for G exist and no consensus exists. An example being [10, 20, p3.179,p569]:

$$G = T(1 + K_1 X_{CO} + K_2 X_{C_3H_6})^2 (1 + K_3 X_{CO}^2 X_{C_3H_6}^2)(1 + K_4 X_{NO}^{0.7}) \tag{3.12}$$

The *Langmuir-Hinshelwood* mechanism is often used as the kinetic model for low order surface reactions. It is used to determine the relationship between the surface kinetics and the apparent kinetics in the reaction. The assumptions are that the surface reaction is the rate determining step and that the *Langmuir isotherm* is applicable to the adsorption of all gases involved in the reaction, competing for the same surface sites [2, 18].

An adsorption isotherm is a constant temperature equilibrium measurement of the variation of surface coverage of the adsorbate with pressure in the gas phase.The assumptions of the Langmuir isotherm are that the surface is homogeneous, that all adsorption sites are identical, and that the adsorption energy at a site is independent of the occupancy of other sites, and only one adsorbed species can occupy a site (i.e. only a monolayer can be formed) [18, p20-21].

These phenomena are a set of closely coupled partial differential equations coupled with another PDE for temperature, these should be solved simultaneously [10, p3.177], which is quite taxing on CPU time.

The models described are often simplified to aid in understanding, or to lower CPU time when used for simulation and control. Depending on the assumptions, the final model may neglect such things as axial diffusion of mass and heat, chemical reactions in the gas phase [10]. Sometimes time derivative terms ($\frac{\delta}{\delta t}$) are ignored turning PDEs into ODEs or the heat exchange between the substrate and the surroundings at the inlet and outlet is neglected.

A common simplification is *spatial discretisation.* This discretisation can be first-order,"tanks-in-series", with each tank being considered as a CSTR (continuous stirred tank reactor) [14, 20] or, even simpler, a zero-order - a "black box" model where measurements are only taken on the inlet and outlet (i.e. only one tank).

Another common simplification is known as *reactant aggregation* where "similar" chemical species are lumped together and represented by a single "pseudo-species". For example all hydrocarbon species may be considered together, and are commonly characterised by propylene (C_3H_6). Alternatively hydrocarbons might be lumped into three categories - fast burning, slow burning and inert [19]. Even further aggregation is to "lump" all the reducing species together and all of the oxidising species together [3].

Once a model is simplified a certain set of initial conditions and boundary conditions such as the inlet gas temperature and concentration of the feedgas is given.

3.4 Models in the Literature

A sample of the models appearing in literature are reviewed in this section. Each, except Brandt et al. [7] and Shafai et al. [22] was created from first principles and then simplified as described in the previous section. The major differences are the assumptions used, how they are simplified and whether or not an oxygen storage sub-model is incorporated. In the context of the proposed work, a simple model with oxygen storage is important: "the introduction of an oxygen storage sub-model along with a fully transient mass balance equation at the washcoat enhances the capability of the model to be used towards fuel control optimisation." [20, p572]. Many models are too complicated for long term simulation and do not take OSC into account [3].

Chen et al. (1988) [10] This is a good and comprehensive model which accounts for transverse heat flux and non-uniform gas flow distribution. However, it has a few weaknesses such as not including an oxygen storage component and using the assumption that there is uniform aging throughout the entire monolith, even though it states that gas maldistribution might poison the centre region to a greater extent (p3.185). Another possible problem is that only Pt catalysed oxidation is accounted for. This is attributed to lack of kinetic data, which may have improved in the ten years since the papers publication. The model seems to be useful in predicting temperature profiles in the converter, though no experimental validation is presented in the paper.

Katashiba et al. (1991) [17] describes a simple model of a TWC and includes a model of the oxygen storage system to determine the "excess oxygen ratio" (EOR):

$$\mathrm{EOR} = \frac{\int_0^{\mathrm{T}} \mathrm{Q_{in}[O_2]dt}}{\mathrm{OSC}} \tag{3.13}$$

The possible control variables for the TWC are fluctuations in amplitude and frequency of the AFR. There is a relationship between these parameters and maximum conversion efficiency of the TWC which could be maximised with independent variation of the amplitude and frequency. They propose a sophisticated fuel control system to make full use of the oxygen storage effect in the TWC. The conversion characteristics of their model are experimentally validated with a set-up of ten small TWC in series. This type of set-up may be beneficial for the work proposed in the following chapter.

Gottberg et al. (1991) [14] considers the complete exhaust flow system from the engine to the end of the main underfloor catalyst as a chemical reactor. A simplified flow model (one axial space dimension) with a relatively advanced chemical kinetic model with five chemical species and independent adsorption/desorption and reaction rates. The model suffers two weaknesses - there is no oxygen storage in the model and there is excessive computational time, thus is unsuitable for control purposes.

Montreuil et al. (1992) [19] has a one-dimensional balance approach but uses an extremely complex set of thirteen reactions. The kinetic constants for a specific catalyst formulation were determined experimentally to be used in the model.

A problem with the kinetic information detailed is that it is only relevant for a single catalyst formulation and new data will have to be generated as catalyst technology changes. However, the parameters are probably a good initial approximation.

Pattas et al. (1994) [20] provides an excellent overview of transient TWC modelling. Steady-state models can not be used in modelling all of the transient phenomena occurring in a TCW.

The modelling rationale is to "establish and understand critical behaviour trends involved in engine emission control system optimisation", pointing out that emission and performance improvements should not endanger the longevity of the catalytic converter.

This model uses a reaction scheme of five equations plus an additional reaction included in the oxygen storage sub-model based on a reversible version of reaction Equation 2.3.

The overall oxygen storage dynamics are

$$\frac{dO_{Ce}}{dt} = \theta k_{O_2} X_{s,O_2} \left(1 - \frac{O_{Ce}}{O_{Ce,max}}\right) - \frac{O_{Ce}}{\tau_{rel}} \tag{3.14}$$

This is possibly a useful oxygen storage model.

Aimard et al. (1996) [3] includes models of varying degrees of simplification for different purposes - the design of AFR controllers, and On Board Diagnostics (OBD) systems. The low-complexity model identified gives an account of the relationship between oxygen storage and AFR which is "useful in real-time control or diagnostic applications". The model accounts for transient thermal and conversion efficiency and oxygen storage capacity (OSC).

Oxygen storage is included as two extra equations (see Equations 2.3 and 2.4 involving oxygen storage and release on ceria.)

The simulation compares quite well to the experimental results.

Baba et al. (1996) [4] extends the model of Chen et al. to develop an axisymmetric two dimensional model.

He uses a model to produce an overall rate constant k_s which can be represented by the two limiting process rates:

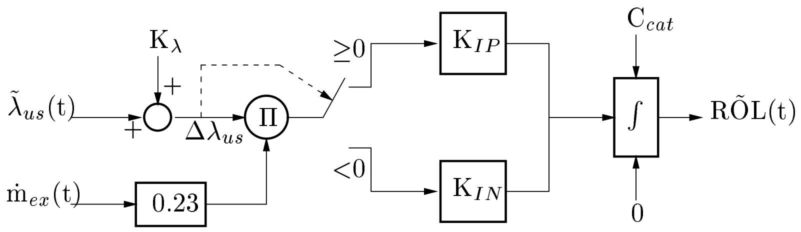

Figure 3.1: TWC model of Shafai et al.

$$\frac{1}{k_s} = \frac{1}{k_{mt}} + \frac{1}{k_{chem}} \tag{3.15}$$

The phenomelogical explanation behind this is discussed in section 2.3.3.

Two representative groups are used for hydrocarbons; propylene (C_3H_6) for "fast oxidising hydrocarbons" (86% of the HC) and methane (CH_4) for "slow oxidising hydrocarbons" (14% of the HC).

This paper is interesting in that it illustrates the huge maldistribution of species concentrations in both the axial and radial directions during warm-up. A new loading pattern (distribution of the precious metals) through the converter brick is suggested, with the outer region of the front section receiving six times the normal loading, the inner section the same loading as in a normal brick and the back section of the brick only half as much as normal. Though this might work well for a green cat in a laboratory it might not be so good in practice.

Shafai et al. (1996) [22] presents the TWC as an oxygen storage device only. An indirect adaptive control system is also presented.

Most control strategies use a stoichiometric AFR control of the mixture before TWC. To achieve an effective improvement in emissions control, the dynamic behaviour of the TWC should also be considered.

The converter is modelled as a limited integrator for control purposes with the upper limit indicating (C_{cat}) that the storage is full and the lower limit (0) indicating that the storage is empty (i.e. that there is no oxygen available to be released for oxidation).

Three parameters are used for the emptying and filling of the storage. The parameters K_{IP} and K_{IN} are time variable. They vary due to both temperature changes and changes in the OSC caused by the aging of the TWC.

An adaptive control scheme is able to estimate and control the relative oxygen level (ROL) in the TWC very well by measuring upstream and downstream AFR. They define $\tilde{\text{ROL}}$ as the stored oxygen mass relative to the current OSC.

As I see it, the strengths of Shafai's model are:

- It accounts for OSC
- Aging affects are included with the changing parameters K_{IP} and K_{IN}
- It is simple enough for controller design

The weaknesses being:

- It is zero-order and thus ignores spatial variation along the converter
- It doesn't capture some of the oxygen storage trends (see below)

Brandt et al. (1997) [7, 8] offer two similar papers that develop a simple TWC model which is dynamic and is hoped to be used for controller design. Rather than use the material and energy balance approach outlined above a "phenomenological model" has been produced which can be tuned to different data sets depending on the experimental setup. One reason given for this is that the catalyst formulation may have changed by the time all of the kinetic parameters needed, for the given catalyst, are determined. The model captures transient oxygen storage and thermal characteristics of the TWC, and the steady state conversion efficiencies.

The model comprises of three sub models, which look at:

- The steady state efficiency
- An oxygen storage mechanism
- The thermodynamics of catalyst warm-up

The oxygen storage model is similar to the one in Shafai et al. but is an improvement in that it captures the phenomena of the stoichiometric plateau (see figure 2.4) by including nonlinear storage and release terms.

Oxygen storage sub-model

$0 \leq \Theta \leq 1$ is the fraction of oxygen storage sites occupied in the catalyst. The oxygen storage capacity is modelled as a limited integrator:

$$\dot{\Theta} = \begin{cases} \frac{1}{\mathrm{C}} * \rho(\lambda_{\mathrm{FG}}, \Theta, \mathrm{MAF}) * 0.21 * \mathrm{MAF} * \left(1 - \frac{1}{\lambda_{\mathrm{FG}}}\right) & 0 \leq \Theta \leq 1 \\ 0 & \text{otherwise} \end{cases} \tag{3.16}$$

where

C is the effective catalyst capacity

MAF is the mass air flow rate

ρ describes the oxygen exchange between the gas and the catalyst:

$$\rho(\lambda_{\mathrm{FG}}, \Theta, \mathrm{MAF}) = \begin{cases} \frac{1}{\mathrm{f_V(MAF)}} \alpha_{\mathrm{L}} f_{\mathrm{L}}(\Theta) & \lambda_{\mathrm{FG}} > 1 \\ \frac{1}{\mathrm{f_V(MAF)}} \alpha_{\mathrm{R}} f_{\mathrm{R}}(\Theta) & \lambda_{\mathrm{FG}} < 1 \end{cases} \tag{3.17}$$

Where $0 \leq f_L \leq 1$ represents the fraction of oxygen from the feedgas sticking to a site in the catalyst, and $0 \leq f_R \leq 1$ representing the fraction of oxygen being released from the catalyst and recombining with the feedgas. f_L and f_R vary with the fraction of occupied sites (and potentially velocity). Conversion efficiency is dependent gas velocity as well as on the feedgas AFR and the temperature of the catalyst.

The paper suggests that in addition to Equations 2.3 and 2.4, that in catalysts which use palladium, a secondary storage reaction is:

$$PdO \leftrightarrow 2Pd + O_2 \tag{3.18}$$

In the conclusion Brandt suggests that it may be useful to use a cascade of similar models to include some of the distributed characteristics of the converter.

3.5 Conclusion

It is the final two models (Brandt et al. [7] and Shafai et al. [22]) that are of most interest as they concentrate on the oxygen storage ability of the catalyst. The work proposal outlined in the next chapter will focus on these models, though Katashiba et al. [17] and Pattas et al. [20] have storage models that may also be of interest.

The others models presented, due to their complexity, are difficult to use for control purposes.

Chapter 4

Proposed Work

4.1 Introduction

The vast amount of literature available indicates that there is much research being done on the control of automotive emissions. The CUED is well equipped to make further contributions in this field.

In this final chapter I will justify my position as a PhD student by outlining the areas in which I can make a significant contribution to the field of knowledge. It is my objective to produce work that, in addition to having sufficient academic content, is practical and serves a useful purpose in controlling emissions from vehicle engines.

4.2 Proposal

For the remainder of my time at Cambridge I wish to develop a theory on catalyst modelling which can be used in controller development. Initially I propose to more thoroughly examine the current literature to investigate the *validity* of a simple oxygen storage model, as compared to more complex distributed models. In particular, I will look at what we call "Shafai's" [22] (or "Geering's") and "Brandt's" [7, 8] models (as discussed in the previous chapter). If these models are found to be invalid then I will develop a model suitable for our purposes.

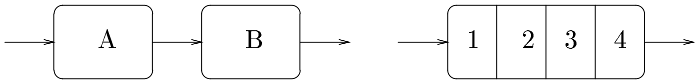

Figure 4.1: The theory could be used for: (a) Physically separated systems, (b) Spatial discretisation of a single catalyst bed

The theory I propose will look at a *"multi-bucket"* (i.e. tanks-in-series type of model) being simply a cascade of Shafai's or Brandt's model. This concept of representing a TWC by a cascade of simple blocks is mentioned in the conclusion of Brandt et al. [7, 8].

There will be at least two applications for a multi-bucket model theory. First, it can be applied when there are physically two catalysts bricks, as is seen in some exhaust systems. Second, the theory will be relevant when you think of a single converter brick as a spatially discretised object, as in Figure 4.1. Shafai's model as it stands seems to be inappropriate if there are two physically separate catalysts.

4.3 Questions and Answers

I will address the following questions (and ones that subsequently arise during research).

- Do we need to include detailed chemistry in our model or can we do without it and just use an oxygen storage model?
- Is this multi-bucket model better/more appropriate than Shafai/Brandt's "single bucket" models, or, are previous models sufficient for our purposes?
- The model will be more realistic than Shafai's and Brandt's in that it includes, to some extent, spatial variation along the catalyst. Does this matter?
- Robustness issues: Will such a model help understanding of how a catalyst works under damage conditions? If so, how?
- Can we, to some extent, control gas composition to any particular section of the catalyst and still meet emissions constraints? If so, can we characterise

the gas flow into the catalyst i.e. what are the feed-gas requirements? Are these likely to change over the catalyst life?

- Can we make each section (bucket) of the catalyst work more evenly so that aging will occur at a more uniform rate. Will this increase catalyst longevity?

- How can this model be used in relation with an AFR controller?

4.4 Experimental

Details of equipment available, what can be measured and some response times:

- UEGO sensors measure λ both into and out of the converter: 20-300ms rise time.

- Fast FID (flame ionisation detector) measure hydrocarbon concentration both into and out of the converter: 3-4ms transport delay and 3-4ms rise time.

- FNO_x use chemiluminescence to measure NO_x concentration both into and out of the converter: 3-4ms transport delay and 3-4ms rise time.

- Kistler piezo electric pressure transducers measure the pressure in each of the four engine cylinders: approximately 100kHz bandwidth.

- We have access to the standard measurements in EEC (electronic engine control) such as MAF (mass air flow) and manifold pressure.

- Thermocouples measure the temperature inside the catalyst. More of these can easily be placed along the converter body.

- Engine load from the dynometer.

- A slow response Horiba analyser can detect NO_x, CO, HC, λ, etc.

- Engine data logging.

- Drive cycle simulation software on a PC.

- The Department of Chemistry have equipment that can determine the TWC surface area. They also will be able to help in the characterisation of gases.

The model chosen must be able to describe phenomena such as the stoichiometric plateau seen in Figure 2.4. This initially suggests that Brandt's model may be the most appropriate. The model chosen will be implemented in a suitable simulation package such as SIMULINK.

Currently, we can examine the effects of oxygen storage over the converter as a whole, but not in individual sections. Experiments looking at oxygen storage of this zero-order system can be carried out immediately. However, to validate the one-dimensional multi-bucket model a converter with sensors along the body will need to be constructed. Initially it may be simpler to validate the model by constructing two physically separate catalyst bricks and measuring between them. A potential problem may be placing the sensors along the body without altering the catalyst operation too greatly. Ideally it is desired to be able to measure AFR, pollutant concentrations and temperature at points along the converter body.

4.5 Time frame

The first couple of months will be spent in a detailed examination of the oxygen storage and other models to get a more thorough understanding of catalytic converter processes. This time will also be spent becoming familiar with the experimental setup in the engine laboratory. The chosen model will be implemented in SIMULINK and refined by the end of 1998. The following 18-24 months will be experimental work and using the model. I plan to finish experimental work by the early months of 2000 and to have submitted the completed thesis by the end of the third year.

4.6 Additional Work

An application that a multi-bucket model theory could feasibly extend to is examining the effect of differential aging/OSC/conversion efficiency across the radius of the converter. This would be done by setting up in "buckets" in parallel. The justification for this is that damage visually appears to occur to a greater extent along the axis rather than at the perimeter of the converter cross section. Conversion is variable radially [4], as mentioned in [10] there is a maldistribution of poisoning of the catalyst. A possible explanation for this is that the casing acts as a heat sink, inhibiting the outer regions of the converter to heat up to as high a temperature than in the centre and thus causing different aging/OSC/conversion effects.

4.7 Summary

The potential importance of a "multi-bucket" theory is that damage from aging occurs at a different rate along the converter body, the OSC is probably different at the front end of the catalyst than at the back (and the middle will be different again). A multi-bucket model will to some extent capture these effects. The model will be more realistic than a zero order model, but will still be simple enough for control design.

Potential benefits of this work include increasing the knowledge of the workings of catalytic converters, especially in transient oxygen storage. This theory will be a step towards developing an emissions control scheme that explicitly includes the catalyst rather than assuming that it is a passive after-treatment device. Also, the work may help reduce the cost of exhaust system production.

This type of cascade system will give an opportunity of examining feedback sensors along the converter which may lead to better OBD systems, however the extra expense of the sensors will have to be justified in production vehicles.

.1 Nonmenclature

Cp specific heat, J/kg.K

E activation energy, J

G inhibition factor

h heat transfer coefficient between flow and substrate, J/m^2.s.K

$\mathbf{k}_m$ mass transfer coefficient, m/s

Δ**H** heat of combustion, J/kg

R Universal gas constant, J/mol.K

$\mathbf{R}_i$ Rate of reaction of species i

S geometric surface area per unit reactor volume, m^2/m^3

t time, s

T temperature, K

v average flow velocity along channels, m/s

X concentration

x,y axes perpendicular to the flow direction

z coordinate along flow direction, m

Greek

α, β kinetic indicies

ϵ void fraction of monolith

λ relative air/fuel ratio

λ_s thermal conductivity of solid, J/m.s.K

ρ density, kg/m^3

subscripts

amb ambient

ext external

g gas phase

i species

s surface

.2 Abbreviations

AFR Air/Fuel Ratio

CUED Cambridge University Engineering Department

CPU Central Processing Unit

CSTR Continuous Stirred Tank Reactor

EEC Electronic Engine Control

EGR Exhaust Gas Recirculation

EOR Excess Oxygen Ratio

HC Hydrocarbons

MAF Mass Air Flow

NO_x Nitrous Oxides (NO, NO_2)

OBD On Board Diagnostics

ODE Ordinary Differential equation

OSC Oxygen Storage Capacity

PDE Partial Differential Equation

ROL Relative Oxygen Level

SI Spark Ignition (engine)

TWC Three Way Catalyst

.3 notes

This final section consists of notes and observations gained from various meetings and talks with people. Information here may not be correct!

Richard Lambert:

- TWC re-oxygenation occurs at low temperature (perhaps as low as room temperature).
- The reaction paths for adsorption and desorption of oxygen onto the ceria are different: to fill the oxygen store, oxygen can go straight into the ceria or diffuse to the ceria via the platinum. To empty the storage the oxygen atoms must diffuse to the platinum surface before desorbing. Shafai's model uses the assumption that the capability of the TWC to store oxygen differs from its capability to release oxygen and Pattas et al. [20, p569] notes the experimentally observed fact that the rate of oxidation of the storage component is faster than its rate of reduction.

The TWC actually stores more components than just oxygen but the oxygen storage model represents this [8].

Krishnan Balakrishnan:

- Can measure total surface area using BET method.
- Can use X-ray diffraction to compare the average size of the Ce particles, as an estimate of sintering. Ceria sinters as well as the nobel metals.
- They will be able to get a rough idea (trends) in surface area and compare relative reactivity between samples with X-ray photospectroscopy.
- The front of the samples that they have are tri-metallic and the back are bi-metallic.

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