Use of Three-way Catalytic Converters in Vehicles to Reduce Carbon Emissions

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Abstract

The usage of three-way catalytic converters (TWCs) as an 'end of pipe' primary capture method of combustion products from internal combustion engines is critical to reduce emissions of nitrogen oxides, carbon monoxide and volatile organic components. The performance of TWCs is discussed, evaluating kinetics, physical arrangements, and mechanisms of operation by literature survey. Specific consideration is given to experimental procedure performed in published literature.

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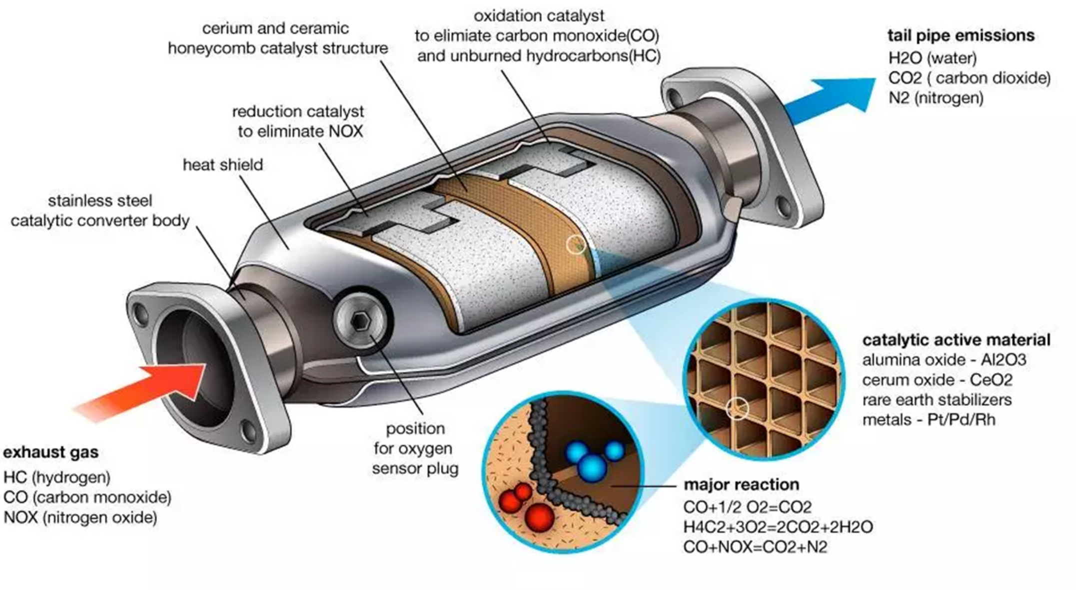
1 Introduction

One of the major contributors to global emissions particularly evident in urban settings are vehicles, which in 2020 contributed 78% of all global transport emissions [1]. For the past 100 years, the norm in automotive industry has been vehicles powered by internal combustion engines, which emit exhaust gases containing combustion byproducts; nitrogen oxides (NO_x), sulfur oxides (SO_x), partially combusted hydrocarbons. Such emissions interact with the environment when activated by UV light, causing a free radical chain reaction propagating reactive components throughout the atmosphere [2]. In 1948, Houdry noticed photochemical smog above the Los Angeles skyline and sought to resolve the pollution problem plaguing cities following the industrial revolution. To reduce photochemical smog, Houdry founded Oxy-Catalyst which invented the catalytic converter to reduced the primary pollutants emitted by vehicles, thus reducing secondary pollutants which arise on interaction of primary pollutants with the atmosphere [3]. Following the initial catalytic converter, three-way catalytic converters (TWC) were invented which was designed to capture exhaust gases by reaction with both reducing and oxidising agents. Today, it is essential to have a catalytic converter to comply with governmental restrictions on vehicle emissions.

1.1 Schematic Diagram

Figure 1: Schematic Diagram of a Catalytic Converter [4]



As seen in Figure 1, there are various considerations to the TWC unit, including physical arrangement, chemical reactions and monitoring. Critical areas will be evaluated throughout this paper with reference to literature, focusing on experimental procedure carried out in such literature. Each reaction is catalysed by a platinum group metal, with rhodium a reducing agent in the catalysing of NO_x, palladium an oxidising agent in the oxidation of carbon monoxide and platinum both oxidising and reducing agent in the reaction of non-combusted volatile organic compounds [5].

2 Catalytic Converters

2.1 Fundamental Reactions

The work of Charles aims to model the reactions which govern the behaviour of a TWC across a range of temperatures. The fundamental governing reactions are given below, taken from Charles' paper, 'Use of Electrically Heated Metal Catalytic Converter in Cold Starting To Reduce Automotive Emissions' [3].

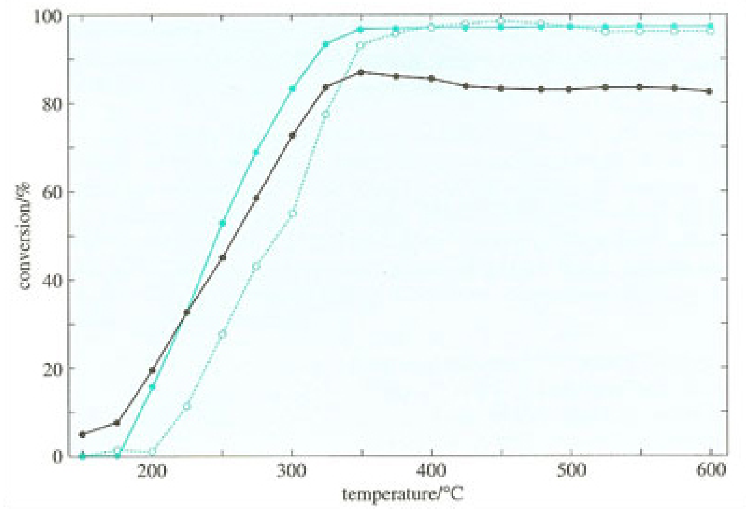
$$2\,NO_x \longrightarrow N_2 + x\,O_2 \quad (1)$$

$$2\,CO + O_2 \longrightarrow 2\,CO_2 \quad (2)$$

$$C_x\,H_{2x+2} + \frac{3\,x+1}{2}O_2 \longrightarrow x\,CO_2 + (x+1)\,H_2O \quad (3)$$

The experiment of Charles utilised a setup consisting of a gasoline-fed internal combustion engine coupled to a dynamomenter with sufficient safety measures including cooling water accounted for. Fuel consumption was measured by flow control on the fuel supply. Thermocouples measured the temperature of the inlet gas and outlet gas of the TWC, as well as catalyst bed temperature. A gas analyser was used to measure exhaust gas composition. The experiment began at idling speed of the engine at 1750 rpm for 20 seconds to normalise engine emission, and then applied a load in the form of mass to the engine for 20 seconds, repeating across a range of masses. Charles presents the findings, demonstrating the increase in engine efficiency at higher engine speed, which was inversely proportional to load. The composition of exhaust gas was significantly improved when the catalytic converter was present and catalytic converter performance was optimised when the heating element was utilised. The heating element helps to reduce emissions during the start-up period for engine operation, where catalyst bed operates at sub-optimal temperatures.
Charles' paper was a very practical example of the usage of a catalytic converter. Ning and Yan further the work of Charles with a greater look into theoretical modelling of the catalyst behaviour during start-up in their paper, 'Temperature Control of Electrically Heated Catalyst for Cold-start Emission Improvement' [6]. Ning proposes a mechanism which is dependent on stoichiometric oxygen supply and sufficient wall temperature of the catalyst unit. Bang-bang control, or on-off control, and ADRC control, a development from proportional-integral-derivative control, are proposed as optimal control mechanisms to ensure sufficient performance of a TWC. Ning focuses on control theory with specific reference to optimal kinetic performance of the catalyst bed, which is modelled as a CSTR. Ning utilises the kinetic parameters proposed by Ramanathan, which were later developed further by Ramanathan and Rao, discussed later in this paper.

Figure 2: Activity of a TWC with temperature for the simultaneous conversion of CO (black), NO_x (solid green) and propene (dotted green) [7]



The experimental results presented by Ning are achieved by simulation performed on GT-Power and Matlab/Simulink. Ideal operation is achieved when catalyst bed remains above 'light-off' temperature during preheating and post-heating. Light-off temperature is demonstrated in Figure 2, where catalyst activity has significant drop-off below a 'light-off temperature'. Operation at such temperature is not favourable and should be avoided. Ning assumes light-off occurs at 300 °C, and design of the electrically heated catalyst is centred on this assumption. Ning evaluated the performance of various controllers, which follow differing mathematical models and optimised tuning parameters of each model to match required power supply to ensure sufficient heating of the catalyst bed, finding optimal performance using both a bang-bang controller with an ADRC controller.

2.2 Langmuir-Hinshelwood Kinetic Model Selection

To accurately model catalytic converter behaviour, the correct kinetic model is critical. The work of Rao estimating kinetic parameters for a TWC suggests the Langmuir-Hinshelwood (LH) model in the paper 'Sensitivity Analysis and Kinetic Parameter Estimation in a Three Way Catalytic Converter' [8]. The LH model operates with assumptions that a species must adsorb onto a surface where the reaction takes place and that the surface reaction is the rate determining step. The model accounts for the inhibitor effects of CO, propylene and NO_x, and is the industrial standard model applied to Pd and Rh catalysts. Generally, a holistic picture of the kinetics can be ascertained with combination of LH and Arrhenius kinetics. Rao discusses the adjustable nature of LH modelling, which allows for tunable parameters, referencing applicability and historical development alongside development of suitable algorithms to solve for parameters.
The experimental model used by Rao utilised the genetic algorithm, adjusted to find the LH parameters. The major steps follow:

1. Bounds: Lower and upper bounds of kinetic parameters set, based upon an uncertainty boundary applied to literature values.
2. Number: The number of 'individuals' [number of kinetic parameters] in the 'population' [set of kinetic parameters] are set, and the number of 'generations' [iterations] decided.
3. Formatting: Initial population created, formatted into binary to allow operations of algorithm.
4. Function: Objective function evaluated for each individual in the population, which predicts outlet gas composition from catalytic converter. Outputs are compared to experimental data.
5. Iteration: A sample from each population is selected to cross-over or 'mutate' with operator-set probabilities. Greater number of iterations leads to greater convergence of parameters.
6. Optimisation: Bound values re-selected if converged value trends outside of permissible values.

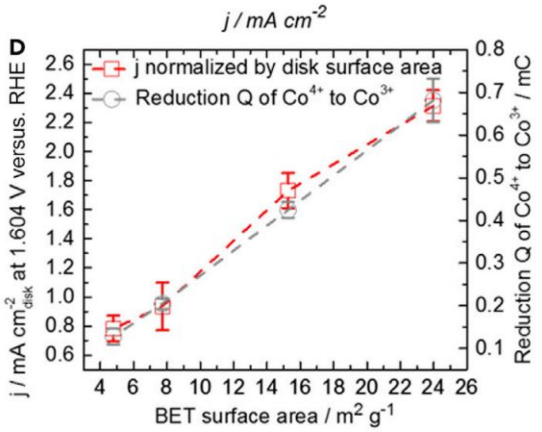
Rao notes the improvement of the GA algorithm from beginning with two sample populations which are used to form a new population with the two better halves of each sample population.
The experimental procedure followed by Rao included two 'bricks' of catalytic material, arranged in series where exhaust gas flows through channels of porous catalyst. Concentration and flow rate of exhaust gases are measured at the inlet of the first catalytic converter and the outlet of the final converter. Rao uses fundamental conservation equations utilising solid and fluid phase energy balances to solve a system of partial differential equations, finding parameters to compared to experimental data to minimise errors. On comparison to experimental data for exhaust gases, Rao predicts a kinetic model including rate constants for a TWC by identifying sensitive parameters and optimising their values. A picture of the rate profile of TWCs is achieved, including inhibition effects of concurrent reactions.

2.3 Arrangement of Catalytic Converters

2.3.1 Monoliths & Packed Bed Adsorption Units

The traditional setup of TWCs consists of catalyst material arranged across a matrix of material to maximise surface area of catalytic material. Figure 3, taken from Sun's work on the impact of surface area on catalytic activity, demonstrates the increase in performance of catalyst with Brunauer-Emmett-Teller surface area, so minimising catalyst particle size led to optimised overpotential as demonstrated in Tafel plot shown.
Both monolith structures and packed bed adsorption units (PBAU) have ceramic base structures which have catalyst material deposited on. Minimal diffusion is required since the LH mechanism is observed for surface reactions, so depth of surface is not a considerable concern. As such, the core of the spherical particles in PBAUs and the monolith structure do not follow kinetic degradation models such as the shrinking core model, instead they experience a simple decay with time as catalyst material is spent or coked. There is extensive literature modelling the kinetics of monolith structures or PBAUs, such as Schweich's 'Laboratory data for three-way catalytic converter modelling' [10]. Schweich modelled a TWC using theoretical calculations in laboratory conditions based upon the assumption the behaviour of a TWC can be reduced to a packed bed of catalyst material or a monolith with square channels. Schweich mentions the diversion from ideal behaviour of plug flow under normal operation, as well as the consideration of mass transfer alongside kinetics.

Figure 3: Activity of a TWC versus available surface area [9]



2.3.2 Hollow Fibre Adsorption Units

The work of Larkin and Hemmings on hollow fibre adsorption units (HFAU) shows very recent developments into potential future structures of TWCs in the paper 'Hollow Fibre Adsorption Unit for On-board Carbon Capture: The Key to Reducing Transport Emissions' [11]. The mechanism of combustion product capture is key to catalytic converter function. Adsorption is the primary mechanism of capture, and is proportional to available surface area of capture. The work of Hemmings sought to compare performance of hollow fibre versus packed bed adsorption units due to the reduced size and thus applicability of HFAUs in vehicles.
The HFAUs were constructed by impregnating an α-Al_2O_3 with CaO. CaO was selected due to applicability to carbon capture and availability of literature, with optimum CaO loading found by comparison of CO_2 capture over varying loading. The surface-area-to-volume of $> 3000m^2m^{-3}$ exhibited by HFAUs whilst minimising pressure drops allows for minimisation of diffusion limitations associated with gas flow. Adsorption tests were conducted at 650 °C and 1 atm, with desorption at 900 °C and 1 atm. Exhaust gases were monitored by in-line mass spectroscopy. Cyclic behaviour was analysed by repetition of adsorption/desorption cycling. Comparison between HFAU and PBAU were made by the effective capacity of CO_2 normalised by respective volume. Computational fluid dynamics (CFD) calculations were performed to determine flow regimes and velocity profiles. Boundary layer thickness was found which can help to ensure optimal gas velocity for sufficient adsorption on the HFAU.

3 Limitations of Catalytic Converters

3.1 Dependence on Expensive Materials

Inherent in the operation of catalytic converters is the usage of rare platinum group metals (PGMs) including platinum, palladium and rhodium. Such elements have supply chain management issues and require significant separation processing if recycling from existing TWCs is performed. In industry, high recovery is achieved, with around 98 % recovery for Pt and Pd and 87.5 % for Rh; the cost of recovery represents around 6.5% of the value recovered PGM from ceramic monoliths and 13.6 % for metallic TWCs. Yakoumis discusses the recovery of PGMs in automotive catalytic converters in the paper 'Real life experimental determination of platinum group metals content in automotive catalytic converters'. The total PGM concentration was found for an average 0.737 kg ceramic monolith TWC to be 2596 ppm and 7872 ppm per 0.214 kg metallic foil TWC [5]. The experimental procedure to quantitatively analyse spent TWCs began with the milling of large batches of spent catalyst material of both ceramic monolith structure and metallic structure to ascertain a representative sample. Small samples were taken at each milling stage to reduce particle size and continued onto the next milling stage, with leftover spent catalyst material sent to recycle. Sampling for further milling was repeated until a 1 kg batch consisting of particle sizes less than 160 μm was achieved. The samples were homogenised and analysed using X-Ray fluorescence spectroscopy (XRF) for precious metal content. For other present elements, atomic adsorption spectroscopy and inductive couple plasma mass spectrometry were used.
The presence of high value elements has led to issues with theft of units from cars due to resell value of full units or individual components, though Yakoumis shows the content of precious metals to be minimal - in the range of $10^3 - 10^4$ ppm.

4 Summary

The rise of alternative technologies has seen sizeable shift made towards sustainability since the integration of internal combustion engine powered vehicles into society. The addition of catalytic converters, an end-of-pipe solution to capture the combustion products before they are emitted to the environment, was critical for reducing emissions of environmentally damaging compounds. Sustainability of modern transport is in a transformative era, with the rise of electric vehicles and transition towards holistic solutions to carbon emissions in vehicles - the future of carbon capture is perhaps absent of catalytic converters. However, there remains a generation of vehicles which will continue to require the technology including sufficient knowledge of kinetics, mechanisms and fluid dynamics. Such knowledge can lead to optimal operating conditions and well-designed systems, which is demonstrated in the literature evaluated performing various methods of analysis from computational to practical analysis techniques.

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