THREE-WAY CATALYST BEHAVIOR UNDER CONDITIONS OF TRANSIENT AIR-FUEL FLUCTUATIONS

by

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Beginning with the 1975 model year most passenger vehicles sold in the United States have been equipped with catalytic converters for use as exhaust gas aftertreatment devices. The use of catalysts has allowed the automobile manufacturers to meet government mandated standards for allowable emission levels of the three regulated pollutants, carbon monoxide (CO), hydrocarbons (HC), and oxides of nitrogen (NO_x). These standards follow a timetable in which the allowable levels decrease in succeeding years and as a result the control systems required to meet the standards have become increasingly complex. For example, with the exception of some applications for California, most current systems employ catalysts only for HC and CO control (via oxidation to CO_2 and H_2O) with the NO_x being controlled via engine modifications. In the future, however, catalysts for NO_x removal (via reduction to N_2) will be required. Three-way catalysts (TWC) are capable of simultaneously removing all three pollutants and are thus of prime importance in future automotive emission control systems.

The desired reactions (CO and HC oxidation and NO_x reduction) are all thermodynamically favorable. However, efficient three-way catalyst operation requires that the exhaust gas mixture be maintained at a composition in which the concentrations of the oxidizing and reducing species are approximately equivalent. This "chemically correct" composition is referred to as the stoichiometric point and is obtained by careful control of the air to fuel ratio (A/F) input to the engine.

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Steady-State TWC Behavior: The steady-state conversion efficiencies of three-way catalysts show a very pronounced dependence on A/F. Lean of the stoichiometric point (excess air) the CO and HC efficiencies are high while the NO_x conversion drops rapidly to zero, reflecting the fact that O_2 is preferred to NO as an oxidizing agent. Rich of stoichiometry (excess fuel) the NO_x efficiency is high with CO and HC limited by the amount of available oxidizing species. Under steady-state conditions we have found that water gas shift and steam reforming reactions are not significant. In addition, as the A/F ratio is made richer, NO_x reduction tends to yield NH_3 rather than N_2 as the product and this is undesirable. This strong dependence of catalyst efficiency on A/F leads to the definition of the A/F "window", which is the range of air-fuel ratios around stoichiometry over which CO, HC, and NO_x efficiency is greater than a given value (say 80% efficiency).

Transient TWC Behavior: Vehicle operation is inherently a transient process and it is unrealistic to expect that perfect A/F control can be achieved. In addition, A/F control is usually achieved via a limit cycle feedback arrangement, thus A/F ratio will vary about some mean value with an amplitude and frequency characteristic of the particular control and fuel metering system employed. Three-way catalyst behavior under conditions where the A/F is modulated may be quite different than in the steady-state. Specifically, the width of the A/F window is significantly broadened. The most commonly accepted explanation for this window broadening is the phenomenon known as oxygen storage. Here the catalyst is assumed to possess components which can be easily oxidized and reduced so that, as the A/F is modulated through stoichiometry, the excess oxygen and NO present during the

lean portion of the cycle is stored for use in oxidizing the excess reducing species during the rich excursions.

Oxygen Storage Model: We have developed a simple model for TWC behavior under conditions where the inlet A/F ratio varies periodically with time. This model involves the superposition of the steady-state catalyst characteristics and the transient oxygen storage process. The storage is modeled using a single CSTR in which a finite number of surface sites (the storage capacity) store, via first order reactions, O_2 and NO during lean portions of the cycle. In turn these are reduced by CO, HC, and H_2 when the A/F ratio becomes rich. Thus six parameters are used, one storage capacity and five first order rate constants. Parameter values are obtained for a given catalyst by fitting the model to a series of laboratory tests in which a pulse technique is used to characterize the storage process.

Model Application: A series of engine dynamometer experiments were carried out in which the catalyst efficiency was determined for sinusoidally varying A/F over a wide range of modulation amplitudes and frequences. The model was then applied to these tests using the storage parameters determined from laboratory experiments. Satisfactory agreement between model predictions and experimental results was found for cases in which the mean A/F was lean of stoichiometry and the amplitude of modulation was small. For rich mean A/F, however, the predicted CO and HC efficiencies were substantially lower than those observed experimentally. Other models were then examined. In particular, the limiting case of infinite storage rates and capacity was studied. Even for this limiting case the rich side CO and HC efficiencies were underpredicted.

Non-Oxygen Storage Effects: The initial results of applying our oxygen storage model show that the transient behavior of three-way catalysts cannot be explained solely on the basis of oxygen storage. Some means of CO and HC removal other than oxidation by O_2 or NO must be available under transient operation. The most obvious candidates are the steam reforming and water gas shift reactions. This hypothesis was tested in another series of engine dynamometer experiments by looking for the presence of H_2 at the TWC outlet. No significant H_2 was found for steady-state conditions or for the modulated A/F cases in which the A/F never passes through stoichiometry. However for cases in which the mean A/F is rich and the modulation amplitude large enough such that oxidizing conditions are present for a portion of the cycle, a large amount of shift and reforming reactions are observed. This then serves to explain the discrepancies found in our initial application of the oxygen storage model.