

Factors Affecting Three-Way Catalyst Light-Off: A Simulation Study

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ABSTRACT

Achieving early catalyst light-off is crucial if stringent emissions standards are to be met; if light-off is late, the emissions limit could be exceeded even before the catalyst starts to work. This paper presents a detailed simulation study of the factors affecting the light-off of a TWC.

Simulation is not just faster and cheaper than vehicle testing, it also enables more insight into the factors affecting catalyst performance to be obtained. For example, changing the substrate (cell density and wall thickness) affects the rates of heat and mass transport, as well as the thermal mass of the catalyst. In a vehicle test, all three factors are changed at once, but with a simulation each of these factors can be implemented one at a time to enable the relative importance of these factors to be determined. Thus, it can be shown that while a 1200/2 substrate offers faster heat and mass transport than a 900/2, this is largely offset by the increased thermal mass, so that both substrates give similar light-off performance. Once the catalyst has warmed up, mass transport is the only factor of real importance.

Other catalyst factors considered in this study include catalyst activity, washcoat thermal mass and thickness, heat losses to the surroundings, catalyst volume and catalyst poisoning. Simulation can also be used to investigate the impact of engine calibration, something which is much easier to do by simulation than by modifying the engine calibration. In this case, the effect of exhaust temperature and stoichiometry were investigated.

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1. INTRODUCTION

Three-way catalysts (TWC) [1] have been used to control the emissions from gasoline engines since the early-/mid-1980s [1, 2, 3, 4]. The TWC is so called because it removes three pollutants, viz. CO, hydrocarbons (HCs) and NO_x. Extensive reviews of research on TWCs can be found in the literature [2, 3, 4, 5, 6, 7].

Computer simulation has become an important tool for designing aftertreatment systems, enabling a wide range of parameters and scenarios to be investigated more quickly and cost effectively than a purely experimental, "trial and error" approach [8,9]. However, modelling is more than just a substitute for vehicle / engine testing; one of the purposes of this paper is to demonstrate that modelling can also be used to improve understanding of system operation and to obtain information / insight that cannot be obtained experimentally, e.g. by enabling parameters, which in reality are linked, to be decoupled / varied independently, or by enabling outputs that cannot readily be measured experimentally to be interrogated.

Another advantage of computer simulation is that the input to the catalyst is always the same in each "experiment"; with vehicle data test-to-test variability can easily mask subtle effects, particularly when a human driver is used. However, it should be noted that in reality engine out emissions may not always be unaffected by catalyst changes, e.g. a change in substrate type or size may affect backpressure and hence engine out emissions.

Achieving early catalyst light-off is crucial if stringent emissions standards are to be met; if light-off is late, the emissions limit could be exceeded even before the catalyst starts to work. For example, Kašpar *et al.* [6] report that typical engine-out emissions during the FTP75 will exceed ULEV within 40 s and SULEV within only 3-15 s.

The aim of this study was to use computer simulation to closely examine the factors affecting TWC catalyst light-off and initial breakthroughs. With this in mind, simulations have been run to look at the impact of various design factors over the first 40 s

of the FTP75 test cycle [10]. For simplicity (and as HC is often the limiting emission when it comes to meeting the legislation), only predictions for total hydrocarbon (THC) will be presented. Trends for CO and NO_x will be similar to those obtained for THC for most of the factors considered, e.g. those factors affecting catalyst warm-up or activity; the exception to this is changing the inlet O₂ concentration, which will affect CO, THC and NO_x differently. Since catalyst performance can be very system sensitive, the magnitude and relative importance of these factors should be regarded as only being valid for this particular vehicle and exhaust aftertreatment system, rather than being generally applicable.

The rest of this paper is structured as follows. First, the TWC model used will be briefly discussed. Then the simulation results will be presented and discussed. This has been divided into three sections: i) the effect of close-coupled (CC) catalyst design parameters, ii) the effect of rear catalyst (RC) design parameters and iii) the effect of engine operation. Finally, conclusions will be drawn and the relative importance of the factors investigated assessed.

2. EXPERIMENTAL / METHODS

2.1. Vehicle Testing

The inputs to the model (exhaust gas temperature, mass flow and composition) were measured on a chassis dynamometer using a 2.3L, 2001 model-year, passenger car.

2.2. Computer Simulation

Computer simulations were carried out using a one-dimensional model for a monolith reactor, which has been described in more detail elsewhere [11]. The model treats the gas and solid (monolith) phases separately with heat and mass transfer between the gas and solid being described by correlations. The physical properties of the catalyst (channel dimensions, thermal conductivity, heat capacity, etc.) were based on values given in substrate manufacture's datasheets with allowance made for the washcoat. An account of the history of development of one-dimensional models for simulation of automotive emissions control catalysts has been written by Depcik and Assanis [12].

Langmuir Hinshelwood type rate equations [13,14] were used to describe the kinetics of each reaction. The exact form of the rate equations was decided on the basis of what best fitted the data, rather than using equations taken from the literature.

The kinetics used in the model were for catalysts with a platinum group metal (PGM) loading of 100 g ft⁻³ after 50 000 miles of use.

The reactions included in the model are listed in Table 1. The model includes oxidation of CO and H₂ (Eq. 1 and 2). Hydrocarbons (HCs) can react either via total oxidation (Eq. 3), partial oxidation (Eq. 4) or steam reforming (Eq. 5). There are

two reactions for the reduction of NO by CO; the first results in reduction of NO to N₂ (Eq. 6). The second is a combination of the reaction of CO with H₂O via the water gas shift reaction to produce H₂, which then reduces NO to NH₃ (Eq. 7). The model also included a simple description of oxygen storage. However, this had little effect on the THC predictions presented here. The model includes a small number of HCs to represent the range of reactivities and mass transport propensities of the HCs found in gasoline exhaust. Further information on the development of TWC models is given elsewhere [11].

The standard model assumed that diffusion of reactants and products through the washcoat was rapid. However, simulations were also run in which coupled diffusion and reaction in the washcoat was included (section 3.2.3). In these simulations, the coated monolith channel was assumed to have a circular cross-section and the washcoat was discretised as a series of concentric cylindrical shells. Realistic effective diffusion coefficients were used. Including washcoat diffusion considerably increased the numeric complexity of the model, so it was necessary to simplify the reaction scheme / kinetics in order to get the model to solve.

Table 1. Reactions included in the TWC model.

CO oxidation:	
$\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$	(1)
H ₂ oxidation:	
$\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$	(2)
HC total oxidation:	
$\text{C}_x\text{H}_y + (x+y/4)\text{O}_2 \rightarrow x\text{CO}_2 + (y/2)\text{H}_2\text{O}$	(3)
HC partial oxidation:	
$\text{C}_x\text{H}_y + (x/2+y/4)\text{O}_2 \rightarrow x\text{CO} + (y/2)\text{H}_2\text{O}$	(4)
HC steam reforming:	
$\text{C}_x\text{H}_y + x\text{H}_2\text{O} \rightarrow x\text{CO} + (x+y/2)\text{H}_2$	(5)
NO _x reduction:	
$\text{CO} + \text{NO} \rightarrow \text{CO}_2 + \frac{1}{2}\text{N}_2$	(6)
$2\frac{1}{2}\text{CO} + \text{NO} + 1\frac{1}{2}\text{H}_2\text{O} \rightarrow 2\frac{1}{2}\text{CO}_2 + \text{NH}_3$	(7)

Before the model is used to make predictions, it is important to validate the model against measured data to ensure that the predictions are reliable and to understand any limitations of the model. Therefore model has been validated against two sets of data. Figure 1 shows a comparison of measured and simulated CO and THC conversion over an engine bench light-off test for a single 4 × 6 in (101.6 × 152.4 mm, diameter × length) cylindrical catalyst on a 400/6-5 ceramic substrate. Figure 2 compares measured and simulated THC emissions over the

first 130 s of the FTP75 for the same catalyst system as used for the simulation study (depicted in Fig. 3) measured on the same vehicle as used for the rest of the study, but with a different engine calibration. Both figures show good agreement between measurement and simulation.

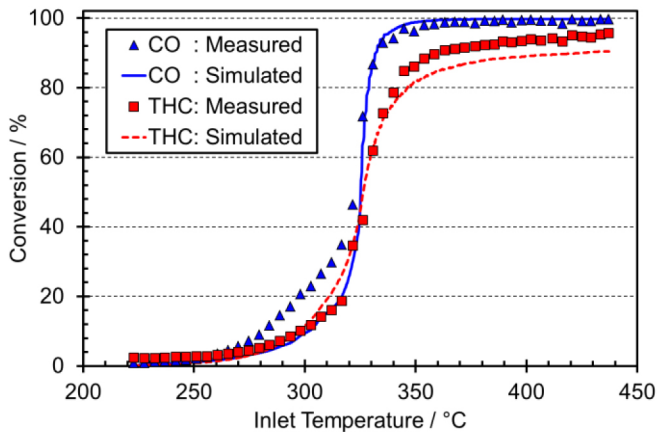


Figure 1. Model validation: Comparison of measured and simulated conversion during an engine bench light-off test. 4 × 6 in (101.6 × 152.4 mm, diameter × length) cylindrical catalyst on a 400/6.5 ceramic substrate.

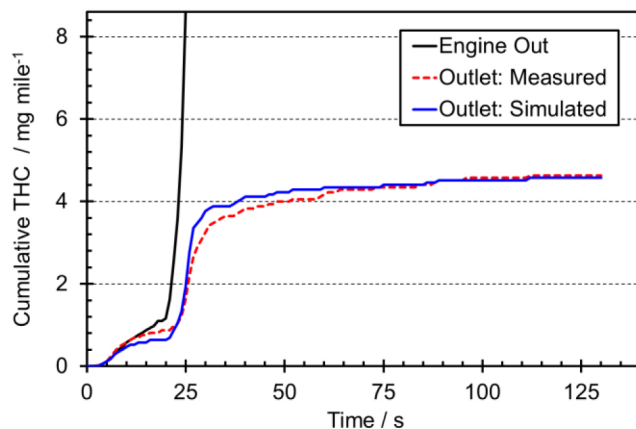


Figure 2. Model validation: Comparison of measured and simulated THC over the first 130s of the FTP75 for the system depicted in Fig. 3, but with different model inlet data to that used for the other simulations in this paper.

3. RESULTS AND DISCUSSION

3.1. Base System

The systems simulated in this study are variations of the base system depicted in Fig. 3. This consisted of a 98.4 × 90.0 mm (diameter × length) cylindrical CC catalyst (CCC) on a 600/4 (cell density in cpsi / wall thickness in thousandths of an inch) ceramic substrate followed by a 4 × 6 × 4 in (101.6 × 152.4 × 101.6 mm) oval part on a 400/4 ceramic substrate. For the purposes of the simulations, these two catalysts were assumed

to be immediately adjacent in the same can with perfectly uniform gas flow across the width of both parts.

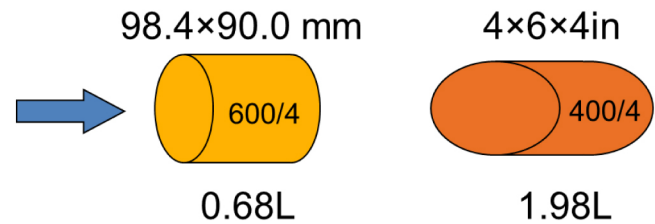


Figure 3. Schematic diagram of the system modelled. Both catalysts were assumed to be immediately adjacent in the same can. Catalyst dimensions are shown above and volumes below. All parts were ceramic.

3.2. Effect of CC Catalyst Design Parameters

3.2.1. CC Catalyst Substrate

Changing the substrate on which the washcoat is supported affects the:

- thermal mass of the catalyst
- the rate of mass transfer between the gas and washcoat
- the rate of heat transfer between the gas and the solid

The thermal mass depends on the cell density and the wall thickness of the substrate (as well as the washcoat), while heat and mass transfer depend on the hydraulic diameter¹ of the coated channels and the geometric surface area of the coated substrate; heat and mass transfer are faster with a higher geometric surface area (as the surface for transport to occur over is larger) and a smaller hydraulic diameter. For developed (Newtonian) laminar flow in the channels of the monolith, the Nusselt number (Nu) is constant [15,16] and hence it follows from the definition of Nu for this system,

$$Nu = \frac{(\text{Heat transfer coefficient})(\text{Hydraulic diameter})}{\text{Thermal conductivity}},$$

that the rate of heat transport is inversely proportional to the hydraulic diameter. By a similar argument, the rate of mass transport is also inversely proportional to the hydraulic diameter for developed laminar flow.

When the substrate is changed, all three effects are changed at once making it difficult to understand which of these effects is most important. However, with simulation these effects can be decoupled. Thus, in the next subsection (section 3.2.1.1) the effect of changing each of these factors individually will be examined to enable their effect to be investigated and understood. This information will then be applied in the following subsection (section 3.2.1.2) to understand what happens when the substrate is changed and all three effects change at once.

1. Defined as four times the channel cross sectional area divided by the channel perimeter [17].

Separating the Effects Substrate on Thermal Mass, Heat Transfer and Mass Transfer

In this section, the relative importance of thermal mass, heat transfer and mass transfer when changing the CCC substrate (from the base case of a 600/4) will be investigated by running simulations in which only one of these properties was changed to its value in another substrate, while the other two were kept at their value for a 600/4 substrate. In this way the contribution of these three effects to the improvement in emissions when the substrate is changed can be estimated. This is an example of how computer simulation can be used to gain understanding / information that cannot be obtained experimentally.

The effect of changing substrate thermal mass alone is shown in Fig. 4. This figure displays the results both in terms of cumulative THC emissions (Fig. 4 top) and instantaneous THC conversion (Fig. 4 bottom), after both the CCC and the rear catalyst. For clarity, post-CCC emissions and conversions are shown with solid lines and post-RC emissions and conversions with dashed lines. Cumulative THC emissions are expressed in mg mile^{-1} , i.e. the mass emissions divided by the distance used for calculating weighted emissions over the FTP75 (7.5 miles) and multiplying by the bag 1 weighting factor (0.43) [10]. With the base system (600/4 + 400/4), the CCC lights off at around 6 s and the RC at about 24s.

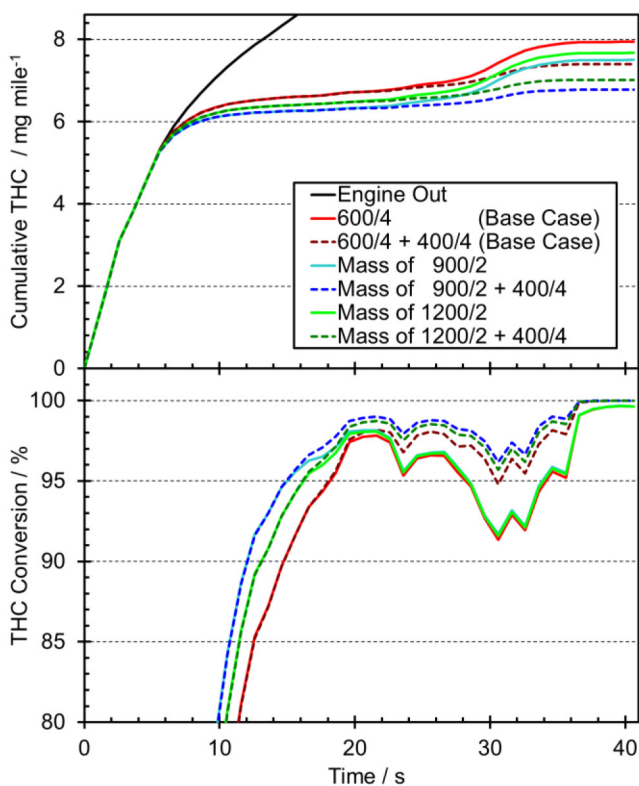


Figure 4. Predicted effect of CC catalyst substrate thermal mass alone on THC emissions displayed as cumulative emissions (top) and as conversion (bottom). All CCCs have the same heat and mass transfer as a 600/4. The post-CCC conversion line for the 900/2 lies under that for the 1200/2 after the first 20 s. (Solid line: post-CCC emissions; Dashed line: post-RC emissions)

When the thermal mass only is changed (Fig. 4), CCC light-off occurs in the order 900/2 (first) > 1200/2 > 600/4 (last), i.e. earlier light-off with the lighter catalyst. The 1200/2 gives worse performance than the 900/2 due its higher thermal mass (having the same wall thickness, but more walls). This can be seen in both the cumulative and conversion plots, but is clearer in the latter.

After CCC has warmed up (from 23 s onwards), the HC conversion after the CCC is the same for all three substrates (Fig. 4 bottom) as the catalyst temperature is much the same for all substrates. This is because the rate of heat transfer is high (see below) so the gas and solid (catalyst) temperatures become very similar after the initial catalyst warm-up. However, despite the RC substrate being the same (400/4) in all cases, the conversion after the RC still depends on the CCC substrate in this region (23-37 s) as the RC is still warming up. Post-RC conversions increase in the same order as CCC light-off (i.e. 900/2 > 1200/2 > 600/4) as the faster the CCC warms up, the more heat will reach the RC and the faster this will warm up.

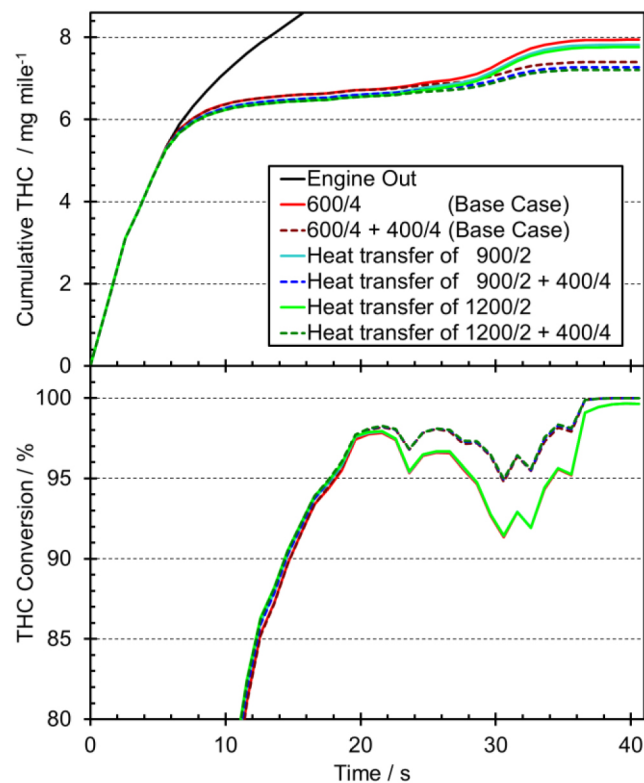


Figure 5. Predicted effect of CC catalyst substrate heat transfer alone on THC emissions displayed as cumulative emissions (top) and as conversion (bottom). All CCCs have the same thermal mass and mass transfer as a 600/4. The post-CCC conversion lines for the 600/4 and 900/2 lie under that for the 1200/2. Post-RC conversions are also overlapping. (Solid line: post-CCC emissions; Dashed line: post-RC emissions)

The effect of changing substrate heat transfer rate alone (Fig. 5) is predicted to be almost negligible after both CCC and RC; almost no difference can be seen in the predicted conversions while only small changes can be seen in the cumulative plot.

This is because the rate of heat transfer from the exhaust gas to the catalyst is already so fast with a 600/4 that increasing the heat transfer has only a slight effect.

Changing the mass transfer rate of the CCC is predicted to have a more dramatic effect (Fig. 6). CCC light-off occurs in the order $1200/2 > 900/2 > 600/4$, i.e. earlier light-off with a higher cell density due to the higher geometric surface area and smaller channel hydraulic diameter, both of which result in an increased rate of mass transfer (see above).

The CCC mass transfer rate also impacts on the size of the first major breakthrough (Fig. 6). With the 600/4, the breakthrough after the CCC starts at about 28 s, but is largely controlled by the RC. The 900/2 mass transfer rate results in a significant reduction in the size of this breakthrough and its start being delayed until 30 s. The increased conversion over the CCC results in reduced conversion over the RC. The 1200/2 mass transfer results in further reduction in the size of the post-CCC breakthrough and results in very little conversion occurring over the RC. These simulations indicate that this breakthrough is largely due to mass transfer limitation and illustrates how simulation allows the cause of the breakthrough to be understood.

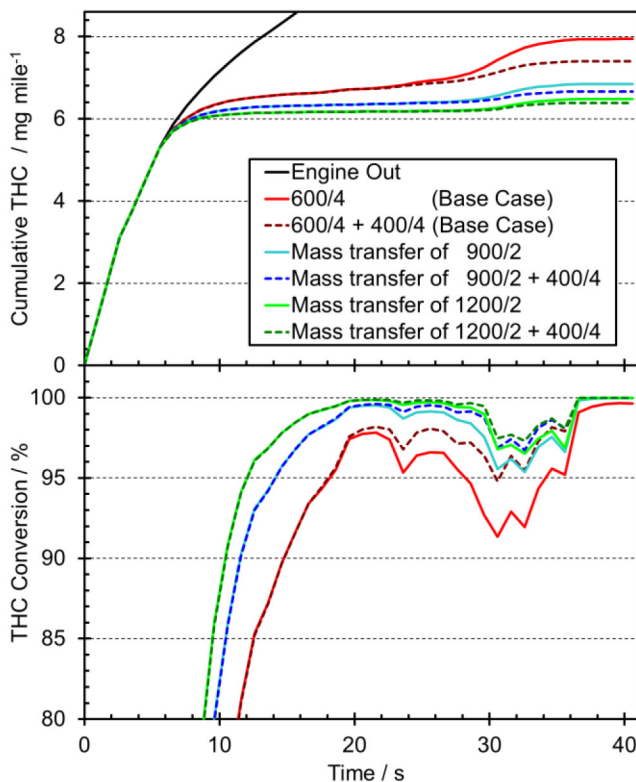


Figure 6. Predicted effect of CC catalyst substrate mass transfer alone on THC emissions displayed as cumulative emissions (top) and as conversion (bottom). All CCCs have the same thermal mass and heat transfer as a 600/4. (Solid line: post-CCC emissions; Dashed line: post-RC emissions)

After 20 s, the post-RC conversions of the 900/2 + 400/4 and 1200/2 + 400/4 systems are very similar (Fig. 6 bottom), indicating that some factor other than mass transfer is limiting the conversion with these systems in this region, particularly between 30 and 37 s where there is a drop in the conversion. In section 3.4.2 it will be shown that increasing O_2 concentration results in a higher conversion between 31 and 37 s with the base system than is achievable by increasing mass transport, indicating that O_2 availability is limiting conversion here.

Overall Effect of Changing Substrate

Changing the CCC substrate from a 600/4 to a 900/2 or a 1200/2 is predicted to result in earlier light-off and reduced breakthrough after light-off (Fig. 7) and hence considerably reduced post-catalyst emissions compared to the base system.

By looking at Fig. 7 in more detail and applying the learning from the previous subsection (section 3.2.1.1), further understanding of the effect of changing substrates can be obtained. Changing the CCC substrate from a 600/4 to 900/2 results in much earlier light-off due to reduced thermal mass (see Fig. 4) and improved mass transport (see Fig. 6). Changing the CCC substrate from a 900/2 to a 1200/2 only results in a small improvement in light-off (compared to the 900/2). This is because the improved mass transfer of the 1200/2 compared to the 900/2 is offset by the increased thermal mass of the 1200/2.

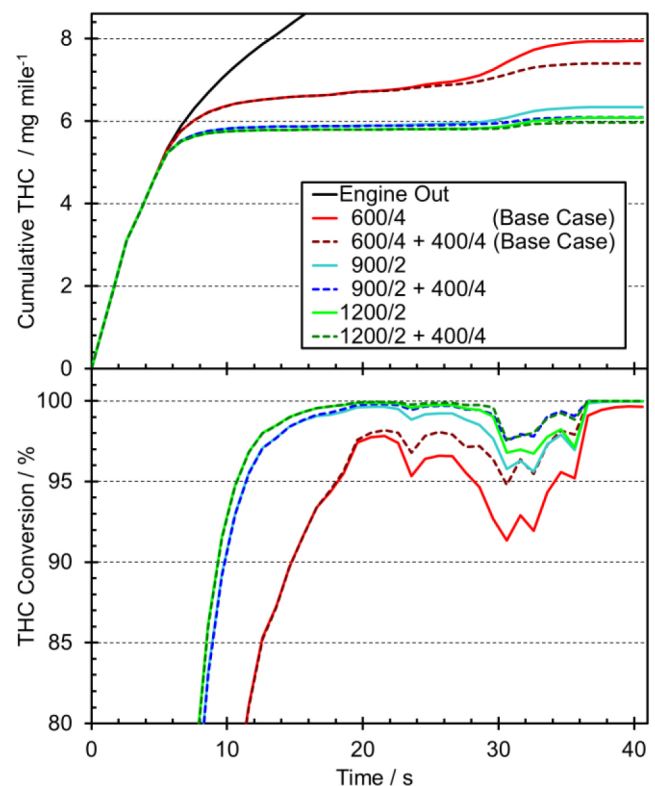


Figure 7. Predicted effect of CC catalyst substrate on THC emissions displayed as cumulative emissions (top) and as conversion (bottom). (Solid line: post-CCC emissions; Dashed line: post-RC emissions)