Characterisation and Modelling of the Reactions in a Three-Way PdRh Catalyst in the Exhaust Gas from an Ethanol-Fuelled Spark-Ignition Engine


Published in:
Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
Link to publication record in Queen’s University Belfast Research Portal

Publisher rights
Copyright 2018 SAGE. This work is made available online in accordance with the publisher’s policies. Please refer to any applicable terms of use of the publisher.

General rights
Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The Research Portal is Queen's institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact openaccess@qub.ac.uk.

Download date: 17. Apr. 2021
Characterisation and Modelling of the Reactions in a Three-Way PdRh Catalyst in the Exhaust Gas from an Ethanol-Fuelled Spark-Ignition Engine

C. McAtee¹, G. McCullough¹*, D. Sellick², A. Goguet³*

1. School of Mechanical and Aerospace Engineering, Queen’s University Belfast, BT9 5AH, UK
2. Jaguar Land Rover Limited, Abbey Road, Whitley, Coventry CV3 4LF, UK
3. School of Chemistry and Chemical Engineering, Queen’s University Belfast, BT9 5AG, UK

* Corresponding authors: g.mccullough@qub.ac.uk; a.goguet@qub.ac.uk

Abstract:

This work investigated and modelled the performance and characteristics of automotive catalytic converter formulations when subjected to a synthetic exhaust gas mixture representative of that emitted by an ethanol-fuelled spark-ignition engine. A synthetic gas reactor and exhaust gas emissions analysers were used to assess the catalytic activity, the products distribution and chemical mechanisms exhibited by a commercial catalytic converter formulation when exposed to ethanol containing gas mixtures. A commercially available after-treatment modelling platform named Axisuite was used to simulate the catalyst performance. This software was used to assign the pre-exponential frequency factor and activation energy variables within the rate equations. A set of global kinetic coefficients for the relevant reactions was established and is reported.

1. Introduction

Fossil fuel derived hydrocarbons (HCs) have been the primary source of energy for internal combustion engines for many years. Fluctuating crude oil prices, the desire for energy security and the increased desire for sustainable fuel sources, has driven the exploration for alternative fuel sources. Alcohols such as ethanol (C₂H₅OH) and methanol (CH₃OH) can be used in spark-ignition (SI) engines, and can be produced from various renewable sources.
Additionally, the presence of oxygen in alcohol fuels is advantageous as the emissions of carbon monoxide (CO) and unburned hydrocarbons are lower in comparison with traditional gasoline-fuelled engines (1, 2). Alcohol fuels have a higher octane rating than that of gasoline, which facilitates an increase in compression ratio in an engine optimised for alcohol fuel usage. The increased compression ratio improves thermal efficiency and provides a further reduction of pollutant emissions (3, 4). \( \text{C}_2\text{H}_5\text{OH} \) can either be used as an oxygenate source in gasoline (up to 10 vol%), without modification to engine components or operating parameters, or as the main fuel component in blends such as E85. The use of alternative fuels alters the engine out gas composition compared to that seen for gasoline fuelled vehicles. However, vehicles that use alternative liquid fuels still need to comply with the same emissions legislation as those vehicles fuelled by gasoline only.

Investigations into the effect of fuel \( \text{C}_2\text{H}_5\text{OH} \) content on exhaust composition reveal an increase in oxygenated species emissions, particularly \( \text{C}_2\text{H}_5\text{OH} \) and acetaldehyde (\( \text{CH}_3\text{CHO} \)) (5, 6, 7, 8, 9). However, there is wide variation in reported results, which may be due to various reasons such as engine set-up, test conditions and whether the engine has been optimised for operation using E85 fuel. While numerous researchers have studied the kinetics of the combustion of ethanol within the cylinder, and therefore predicted the emissions resulting from this combustion (10), investigation of the reaction pathways within catalytic converters is limited.

The after-treatment system applied to a SI engine is in the form of a three-way catalytic converter (TWC) which contains platinum (Pt), palladium (Pd) and rhodium (Rh). Whilst E85 combustion can result in lower emissions of regulated pollutants such as CO, the generation and catalytic conversion of pollutants such as \( \text{CH}_3\text{CHO} \) requires increased understanding.

The activity of noble metal catalysts for \( \text{C}_2\text{H}_5\text{OH} \) and \( \text{CH}_3\text{CHO} \) control has been reported by several researchers. Maunula et. al (11) reported that PtRh and PdRh TWC formulations
displayed similar overall conversion efficiencies. However, PtRh showed a higher total hydrocarbon (THC) conversion efficiency and greater durability.

Lupescu et al. (7) studied the mechanism of C₂H₅OH conversion and subsequent CH₃CHO formation over zeolite catalysts/traps. The authors attribute CH₃CHO formation to partial oxidation of C₂H₅OH as shown in Equation 1, followed by methane (CH₄) formation which was attributed to the breakdown of CH₃CHO as shown in Equation 2.

\[
\text{C}_2\text{H}_5\text{OH} + \frac{1}{2} \text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O} \quad \text{Eq. 1}
\]

\[
\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO} \quad \text{Eq. 2}
\]

There is some discussion in the literature on the mechanisms by which CH₃CHO and CH₄ are generated from C₂H₅OH. Some assign CH₃CHO formation to CH₄ partial oxidation (7),(11),(12). An alternative mechanism is the dehydrogenation of C₂H₅OH to form CH₃CHO and H₂ as shown in Equation 3.

\[
\text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2 \quad \text{Eq. 3}
\]

The dehydrogenation and decomposition reactions have been observed at temperatures as low as 80°C (13, 14).

Physical testing of catalyst performance can be cost and time intensive which makes the use of modelling tools to predict catalyst behaviour very attractive. The requirement of a catalytic converter model is to accurately simulate the performance of the catalytic converter through mathematical representation of the physical and chemical processes that occur within it. These processes include mass transfer, heat transfer, and the surface reactions associated with the chemical reactions of interest. While numerous catalyst models have been reported in the literature, such as those by Kuo et al. (15), Voltz et al. (16) and Montreuil et al. (17),
limited information is available regarding the reactions that occur on a catalyst exposed to the exhaust gas of an ethanol-fuelled SI engine.

Stepanek et al. (12) reported a global kinetic model which incorporated rate equations as derived from experimental synthetic bench testing. The authors described reaction pathways in oxygen rich exhaust gases which included partial oxidation of C₂H₅OH, a reduction and oxidation mechanism with nitric oxide (NO), adsorption and desorption of C₂H₅OH on zeolites and oxidation of CH₃CHO. The experimental work carried out included light-off performance tests where the conversion performance of the catalyst was measured. The kinetic parameters extracted from experimental data were presented and incorporated within a two-dimensional catalyst model.

Due to the oxygen rich nature of the gas feeds used by Stepanek et al., the kinetic parameters are not applicable to a TWC fitted to a SI engine using ethanol containing fuel. There is a lack of available data regarding the behaviour and simulation of a TWC exposed to stoichiometric ethanol-fuelled engine exhaust gas species.

The work reported in this paper focuses on clarifying the chemical reaction pathways for a TWC exposed to ethanol-fuelled engine exhaust gas species, and defining the promoting and inhibiting species for each key reaction to allow the definition of kinetic rate equations.

2. Experimental Setup

The catalyst samples were supplied by Jaguar Land Rover (JLR) and had a precious metal loading of 150 g ft⁻³ or 50 g ft⁻³ (Pd and Rh in a ratio of 29:1 in both cases) and 600 cpsi cell density. Cores of 30mm diameter and 75mm length were removed from a full sized brick for analysis.
A synthetic gas reactor (Horiba SIGU 2000) was used to assess the performance of the catalyst samples. This reactor allows both gas and liquid HCs to be introduced to the gas mixture and also has the ability to simulate closed loop air-fuel ratio (AFR) perturbation in an SI engine via separate perturbation mass flow controllers. The sample outlet gases were analysed using a Horiba 6000FT FTIR analyser for HC speciation, and a Horiba MEXA 7170 (CO, CO₂, O₂, THC and NOₓ). Further details on the experimental equipment used in this study are available in McAtee et al. (18).

A typical temperature profile for activity testing is reported in Figure 1. The procedure of using a warm up temperature ramp followed by two subsequent measurement temperature ramps was established in previous work to ensure that the catalyst surface is in the same condition prior to each test (19), thereby improving the repeatability of the measurements.

![Figure 1 Temperature Profile for Activity Testing](image)

The tests conducted included individual performance tests for C₂H₅OH, CH₃CHO, C₃H₆, C₃H₈ and CO. Following this, each HC was tested in the presence of CO on the basis that CO typically has a strong inhibiting effect on HC oxidation. All tests were performed at stoichiometric O₂ conditions and the O₂ concentration was calculated accordingly for each test. All tests were performed at a space velocity of 50,000 h⁻¹. Finally, a full gas mixture was
tested which also included NO and CH₄. The concentrations of each gas are shown in Table 1. In all cases nitrogen (N₂) was used as the balance gas.

<table>
<thead>
<tr>
<th>Gas Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₅OH</td>
<td>300ppm</td>
</tr>
<tr>
<td>CH₃CHO</td>
<td>100ppm</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>150ppm</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>100ppm</td>
</tr>
<tr>
<td>CO</td>
<td>0.5%</td>
</tr>
<tr>
<td>NO</td>
<td>400ppm</td>
</tr>
<tr>
<td>CH₄</td>
<td>150ppm</td>
</tr>
<tr>
<td>CO₂</td>
<td>12%</td>
</tr>
<tr>
<td>H₂O</td>
<td>5%</td>
</tr>
</tbody>
</table>

In addition to the activity tests performed using the synthetic gas reactor, the thickness of the channel wall and the washcoat were measured for modelling purposes using a JOEL 6500 scanning electron microscope.

3. Experimental Results

3.1 Ethanol-Oxygen Variation Tests

The impact of O₂ on the dehydrogenation, decomposition and oxidation of C₂H₅OH was assessed at three stoichiometric ratios as shown in Table 2. The O₂ concentrations were calculated on a stoichiometric basis i.e. a C₂H₅OH:O₂ molar ratio of 1:3 was required to achieve full conversion.

<table>
<thead>
<tr>
<th>C₂H₅OH Concentration</th>
<th>O₂ : C₂H₅OH</th>
<th>O₂ Concentration (vol.%)</th>
</tr>
</thead>
</table>
The first step in ethanol conversion was expected to be the formation of CH$_3$CHO, the experimental results of which are in Figure 2. For all three ethanol concentrations explored, an increase in CH$_3$CHO concentration was observed until about a third of the inlet C$_2$H$_5$OH was converted, which typically occurred at 150 - 175°C. In all cases the O$_2$ : C$_2$H$_5$OH ratio had little to no impact on the reaction profile which suggests that CH$_3$CHO is predominantly formed via dehydrogenation, rather than the partial oxidation, of C$_2$H$_5$OH.
Figure 2 CH₃CHO Formation from a) 150 ppm, b) 300 ppm, c) 1000 ppm C₂H₅OH Inlet at Stoichiometric Ratios of 0.6, 1.0 and 1.5

Evolution of CH₄ was also observed, which is reported in Figures 3 to 5. A peak CH₄ make of 50 ppm was observed at all stoichiometric ratios when 150 ppm of ethanol was fed (Figure 3) to the catalyst, meaning that approximately two thirds of the inlet C₂H₅OH was converted
to CH$_3$CHO and CH$_4$. When the oxygen concentration was decreased (i.e. ratio of 0.6), CO was evolved coupled with sustained CH$_4$ generation at higher temperatures.

![Figure 3 Formation Trends for a) CH$_4$ and b) CO with 150 ppm C$_2$H$_5$OH Inlet at Stoichiometric Ratios of 0.6, 1.0 and 1.5](image)

Doubling the ethanol feedgas concentration to 300 ppm (Figure 4) led to a similar trend (i.e. CH$_4$ and CO evolution at low oxygen conditions). Increasing the ethanol concentration to 1000 ppm (Figure 5) further illustrates the formation of CH$_4$ and CO via the decomposition of CH$_3$CHO (Eq. 2). A key feature of these results is that significant quantities of CH$_4$ and CO remain unreacted at temperatures in the range 300 – 500 °C when the stoichiometric ratio is set at 0.6. The reason for this trend is that, while temperature of the catalyst is sufficient to promote oxidation of CH$_4$ and CO, there is insufficient oxygen in the feed gas to permit both of these reactions to proceed to completion.
Figure 4 Formation Trends for a) CH₄ and b) CO with 300 ppm C₂H₅OH Inlet at Stoichiometric Ratios of 0.6, 1.0 and 1.5
3.2 Inhibition factors to ethanol conversion

To construct the kinetic equations for each of the reactions involving C₂H₅OH it was necessary to understand the interactions between each compound. Using the component concentrations given in Table 1, the conversion of C₂H₅OH in the presence of the other compounds separately was probed. The only significant inhibitors to C₂H₅OH conversion were found to be CO and NO, which is consistent with the findings of previous studies of hydrocarbon reaction kinetics (17). To investigate their effect in greater detail, the tests were repeated at different CO (0.5, 1 and 1.5 vol %) and NO (400, 1000 and 1500 ppm) concentrations.
3.3 The inhibition effect of CO

Figure 6 shows that only a relatively low concentration of CO is required to produce an inhibiting effect for both C₂H₅OH and THC conversion. The role of CO can be explained further by examining the formation trends for CH₃CHO and CH₄ as reported in Figure 7. The presence of CO resulted in greater CH₃CHO formation and shifted the generation of CH₄ to higher temperatures, confirming that the presence of CO has an inhibiting effect on the decomposition of CH₃CHO to form CH₄. Moreover, the fact that the formation of CH₄ continued to a higher temperature in the presence of CO indicated that it also inhibited CH₃CHO oxidation. These results also showed that CO does not significantly inhibit C₂H₅OH dehydrogenation and hence can be omitted from its kinetic rate equation.

![Figure 6](image-url)
3.4 The inhibition effect of NO

The presence of NO did not significantly affect the dehydrogenation of C₂H₅OH as shown by the conversion efficiency graphs in Figure 8. While a small increase in light-off temperature was evident when 400ppm NO was added to the feed gas, increasing the NO concentration to 1500ppm had no additional impact on this reaction. Peak C₂H₅OH conversion efficiency was also unaffected by the presence of NO, regardless of its concentration. However, the presence of NO did inhibit the subsequent decomposition of CH₃CHO and formation of CH₄, seen in Figures 9(a) and 9(b) respectively. While the temperature at which CH₃CHO formed, 100-150 °C in Figure 9(a), was unaffected by NO, the temperature at which it decomposed increased as NO was added to the feed gas. This trend is confirmed by the formation of CH₄ seen in Figure 9(b), which
occurred at increasing temperatures as the concentration of NO was increased. The temperature at which CH₄ oxidised also increased in the presence of NO.

Figure 8 C₂H₅OH Conversion Curves in the Presence of Varying Concentrations of NO

(a) CH₃CHO Formation in the presence of NO

(b) CH₄ Formation in the presence of NO

Figure 9 CH₃CHO (a) and CH₄ (b) formation curves in the Presence of Varying Concentrations of NO
3.5 Summary of catalyst characterisation

The effects of the reactants and products on the C₂H₅OH and CH₃CHO reactions were:

- C₂H₅OH dehydrogenation to form CH₃CHO is little affected by CO or NO.
- CO and NO inhibit both CH₃CHO decomposition and CH₃CHO oxidation.
- There is no inhibiting effect for CH₃CHO, C₃H₈, C₃H₆ and CH₄.

Based on the above results, the general pathway for conversion of C₂H₅OH over this PdRh catalyst is believed to be:

1. C₂H₅OH dehydrogenation forming CH₃CHO
2. CH₃CHO decomposition to form CH₄ and CO at low temperatures (below ~ 200 °C)
3. when the catalyst temperature is sufficiently high, the majority of the CH₃CHO is fully oxidised. Due to the observation of prolonged formation of CH₄, it is reasonable to conclude that the decomposition of CH₃CHO continues alongside CH₃CHO oxidation.

It is difficult to draw conclusions on the direct full oxidation of C₂H₅OH; if it occurs at a temperature higher than that of the CH₃CHO oxidation then its evaluation would be challenging. Consequently, a kinetic equation is included for the full oxidation of C₂H₅OH for modelling purposes with the assumption that the reaction is inhibited by CO and NO.

4. Formulation of Kinetic Equations

The model used to simulate the behaviour of the catalyst sample was Axisuite by Exothermia (20). This commercially available software is used by the sponsoring company to model various catalyst formulations and so it was the preferred choice of simulation tool in which to add the new reactions. The Axicat module of Axisuite was used in this study as the
The sample under investigation was a flow-through TWC. The module requires catalyst specification data including precious metal loading and geometric dimensions. The inlet gas concentrations, which are specified by the user, can be constant as required for synthetic gas reactor testing, or derived from transient drive cycle emissions data taken from on-engine tests. Temperature profile and mass flow rate data are also essential requirements. The module requires catalyst specification data including precious metal loading, geometric dimensions and cell density. C$_2$H$_5$OH and CH$_3$CHO are not included in the standard gas species configuration of Axisuite and, at the authors’ request, these were added by Exothermia to a specially devised reaction scheme. This allowed for implementation of the required C$_2$H$_5$OH and CH$_3$CHO reactions and kinetic parameters. The structures of the standard kinetic equations in Axicat are based on the standard Langmuir-Hinshelwood expressions traditionally used to represent the surface reaction rates within catalysts (16, 17). These expressions include the promotional and inhibiting compounds and their respective kinetic coefficients for each reaction. Axisuite contains 35 pre-programmed inhibition parameters. Ten additional inhibition rate values were added to this standard list in order to incorporate the requirements of the new C$_2$H$_5$OH and CH$_3$CHO reactions. This provided maximum flexibility with respect to derivation of the coefficient values for each new reaction. The sequence of reactions proposed from the experimental work are summarised in Table 3, and are described in Equations 4 – 7.

To achieve acceptable agreement between experimental and theoretical temperature predictions at catalyst sample exit, the heat transfer coefficients were tuned until good agreement with the SIGU 2000 synthetic gas generator temperature profile was achieved. The parameters modified to achieve this were the canning density, canning thermal capacity, insulation thermal conductivity and density.

<table>
<thead>
<tr>
<th>Step no.</th>
<th>Description</th>
<th>Reaction</th>
<th>Eq.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ethanol dehydrogenation</td>
<td>$C_2H_5OH \rightarrow CH_3CHO + H_2$</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>Acetaldehyde decomposition</td>
<td>$CH_3CHO \rightarrow CH_4 + CO$</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>Acetaldehyde oxidation</td>
<td>$CH_3CHO + 2.5O_2 \rightarrow 2CO_2 + 2H_2O$</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>Ethanol oxidation</td>
<td>$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$</td>
<td>7</td>
</tr>
</tbody>
</table>
The kinetic equation for ethanol dehydrogenation, Equation 8, is relatively simple as the other compounds in the feed gas do not introduce an inhibiting effect.

\[
r_{C_2H_5OH_{dehydro}} = \frac{k^r_{C_2H_5OH_{dehydro}}[C_2H_5OH]}{(1 + k^{inh}_{C_2H_5OH_{1}}[C_2H_5OH])}
\]

Eq. 8

The \(C_2H_5OH\) inhibition term refers to \(C_2H_5OH\)'s self-inhibition and in this case it is the only inhibiting factor.

CO and NO inhibit \(CH_3CHO\) decomposition, and as per the previous equation, a \(CH_3CHO\) self-inhibition term is also required as shown in Equation 9.

\[
r_{CH_3CHO_{dec}} = \frac{k^r_{CH_3CHO_{dec}}[CH_3CHO]}{(1 + k^{inh}_{CO_{1}}[CO])(1 + k^{inh}_{NO_{1}}[NO])(1 + k^{inh}_{CH_3CHO_{1}}[CH_3CHO])}
\]

Eq. 9

CO and NO inhibit \(CH_3CHO\) oxidation, whereas \(CH_3CHO\) and \(O_2\) promote it. Allowance for these effects is made in Equation 10.

\[
r_{CH_3CHO_{ox}} = \frac{k^r_{CH_3CHO_{ox}}[CH_3CHO][O_2]}{(1 + k^{inh}_{CO_{2}}[CO])(1 + k^{inh}_{NO_{2}}[NO])(1 + k^{inh}_{CH_3CHO_{2}}[CH_3CHO])}
\]

Eq. 10

The definition of the \(C_2H_5OH\) oxidation kinetic equation is more challenging as it was not possible to observe the direct oxidation of \(C_2H_5OH\) from the experimental data. However, including an expression allows for flexibility with respect to simulation work. It is assumed that the inhibitors of \(C_2H_5OH\) oxidation would be CO and NO as shown in Equation 11.

\[
r_{C_2H_5OH_{ox}} = \frac{k^r_{C_2H_5OH_{ox}}[C_2H_5OH][O_2]}{(1 + k^{inh}_{CO_{3}}[CO])(1 + k^{inh}_{NO_{3}}[NO])(1 + k^{inh}_{C_2H_5OH_{2}}[C_2H_5OH])}
\]

Eq. 11
The repetition of gas species in various inhibition functions was introduced to allow maximum flexibility in the investigation of the pre-exponential and activation energy coefficients for each reaction. This approach allowed assessment of the effect of each inhibition function on individual reactions. This is particularly helpful where chain-reactions occur such as CH$_3$CHO decomposition which is heavily dependent on the preceding C$_2$H$_5$OH dehydrogenation reaction.

Note that both rate constants and inhibition coefficients are represented using an Arrhenius dependence as described in Equation 12.

$$k_i = Ae^{\left(\frac{E_a}{RT}\right)} \quad i = \text{species}$$  \hspace{1cm} \text{Eq. 12}

5. **Kinetic Parameter Optimisation**

5.1 **Single Component Test Simulation**

The kinetic expressions defined in Section 4 were fed into the reaction schemes of Exothermia's Axisuite after-treatment modelling package. Initially, the C$_2$H$_5$OH only tests (150, 300, 1000 ppm concentrations) were simulated to produce the promoting kinetic coefficients for C$_2$H$_5$OH dehydrogenation and oxidation, CH$_3$CHO decomposition and oxidation without the inhibition of compounds such as CO and NO. Additionally, the self-inhibition kinetic coefficients were required, specifically $k_{\text{C}_2\text{H}_5\text{OH},1}^{\text{inh}}$ (C$_2$H$_5$OH self-inhibition) for C$_2$H$_5$OH dehydrogenation, $k_{\text{CH}_3\text{CHO},1}^{\text{inh}}$ (CH$_3$CHO self-inhibition) for CH$_3$CHO decomposition, $k_{\text{C}_2\text{H}_5\text{OH},2}^{\text{inh}}$ (C$_2$H$_5$OH self-inhibition) for C$_2$H$_5$OH oxidation and $k_{\text{CH}_3\text{CHO},2}^{\text{inh}}$ (CH$_3$CHO self-inhibition) for CH$_3$CHO oxidation. As previously stated some repetition of gas species with different kinetic coefficients occur to allow for maximum flexibility i.e. one kinetic coefficient affects only one reaction. It should be noted that it was the goal of the authors to achieve consistency of coefficients for each gas species. For example, $k_{\text{CH}_3\text{CHO},1}^{\text{inh}}$ and $k_{\text{CH}_3\text{CHO},2}^{\text{inh}}$
would consist of the same pre-exponential and activation energy values as they both refer to the self-inhibition of CH₃CHO.

The determination of the kinetics parameters was achieved through a manual iterative process. Once each simulation had been matched, a process of convergence was undertaken in order to identify trends in the coefficients and eventually converge on a set of coefficients which produced acceptable correlation across the set of simulated and measured data. The process began with the initial estimation of C₂H₅OH dehydrogenation kinetic coefficient values for the 300ppm C₂H₅OH only test, which was then compared with those values obtained for the 1000ppm C₂H₅OH only simulation.

To determine the pre-exponential and activation energy values for the C₂H₅OH dehydrogenation reaction an estimation was made whilst the coefficients for subsequent reactions were set to zero. Although the rate of disappearance of C₂H₅OH and the concentration of CH₃CHO are also affected by the subsequent CH₃CHO decomposition reaction, this approach was the least complex method of making an initial estimation of the dehydrogenation coefficients. This prediction was then compared to the measured data and the kinetic parameters adjusted iteratively to minimise the error between the two. This process was repeated for CH₃CHO formation and then CH₄ formation. This sequence was repeated until kinetic parameters for all three reactions simultaneously produced simulated data that matched the measured data. After some alteration of the kinetic coefficients, a good correlation was achieved for each of the concentration traces as shown in Figure 10. Other kinetic parameters involved in reactions such as the oxidation of CO, CH₄, C₃H₆ and C₃H₈ were kept at the default values and so only the values of the new kinetic terms are reported here.
The simulation and experimental results were not an exact match (as expected) as self-inhibition was not included at this stage. The values of the kinetic parameters obtained during this phase of the process are summarised in Table 4.

The coefficients established in the 300ppm simulation were then used for the 1000ppm simulation to assess the output in comparison with its corresponding experimental results as shown in Figure 11.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k^0$ (s$^{-1}$ or m$^3$ mol$^{-1}$ s$^{-1}$)</th>
<th>$E'$ (J mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$H$_5$OH Dehydrogenation</td>
<td>4.0 x 10$^9$</td>
<td>35,000</td>
</tr>
<tr>
<td>C$_2$H$_5$OH Oxidation</td>
<td>3.5 x 10$^{20}$</td>
<td>101,000</td>
</tr>
<tr>
<td>CH$_3$CHO Decomposition</td>
<td>9.0 x 10$^8$</td>
<td>29,000</td>
</tr>
<tr>
<td>CH$_3$CHO Oxidation</td>
<td>3.0 x 10$^{18}$</td>
<td>92,000</td>
</tr>
</tbody>
</table>
It was clear that the coefficients established using the 300ppm C$_2$H$_5$OH data were not directly transferable to the 1000ppm test which highlighted the need for self- and cross-inhibition terms to be included.

Temperature differences between the simulated and measured data for CH$_3$CHO and CH$_4$ formation were observed. For example the disappearance of CH$_3$CHO and the peak formation of CH$_4$ in the simulated data occur at a lower temperature than observed.
experimentally (Figure 11 b and c). This is caused by the absence of CH₃CHO self-inhibition which is required in its decomposition as well as oxidation reactions. Additionally, when considering tests which incorporate other compounds such as CO and NO, further alteration was required to take their inhibiting effects into account.

Using data reported in literature as a starting point for the inhibition coefficients (12,13), an optimization of the parameters through an iterative process was carried out using the C₂H₅OH + CO, C₂H₅OH + NO and C₂H₅OH only data as objective functions. A set of values was established that provided the most agreeable compromise with respect to the difference between simulated and measured data. An example of the quality of the match between the experimental data and the simulation is reported in Figure 12 for the case 300ppm C₂H₅OH only experiments.
Figure 12 1000ppm C₂H₅OH Only Test Simulated and Measured Data using 300ppm Derived Coefficients and new Inhibition Coefficients
5.2 Full Mixture Test Simulation

The full mixture test was used to refine the kinetic coefficients obtained thus far, based on their best fits between overall simulation performance and the range of experimental tests (Tables 5 and 6).

Table 5 Final Kinetic Promotional Coefficients

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( k^{0r} ) ((\text{s}^{-1} \text{ or } \text{m}^3 \text{ mol}^{-1} \text{ s}^{-1}))</th>
<th>( E^r ) ((\text{J mol}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_2\text{H}_5\text{OH} ) dehydrogenation</td>
<td>(3.6 \times 10^{11})</td>
<td>48,500</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CHO} ) decomposition</td>
<td>(1.4 \times 10^{9})</td>
<td>25,200</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CHO} ) oxidation</td>
<td>(5.65 \times 10^{18})</td>
<td>84,400</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_5\text{OH} ) oxidation</td>
<td>(9.5 \times 10^{18})</td>
<td>108,000</td>
</tr>
</tbody>
</table>

Table 6 Final Kinetic Inhibition Coefficients

<table>
<thead>
<tr>
<th>Inhibition Parameter and Corresponding Gas Species</th>
<th>( k^{0\text{inh}} ) ((\text{m}^3 \text{ mol}^{-1}))</th>
<th>( E^{\text{inh}} ) ((\text{J mol}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_2\text{H}_5\text{OH} ) dehydrogenation</td>
<td>Self-inhibition ( k^{\text{inh}}_{\text{C}_2\text{H}_5\text{OH} \cdot 1} )</td>
<td>(4.1 \times 10^{2}) (-2460)</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CHO} ) decomposition</td>
<td>Self-inhibition ( k^{\text{inh}}_{\text{CH}_3\text{CHO} \cdot 1} )</td>
<td>(6.8 \times 10^{3}) (-6950)</td>
</tr>
<tr>
<td></td>
<td>Inhibition by CO ( k^{\text{inh}}_{\text{CO} \cdot 1} )</td>
<td>65.5  (-7990)</td>
</tr>
<tr>
<td></td>
<td>Inhibition by NO ( k^{\text{inh}}_{\text{NO} \cdot 1} )</td>
<td>(1.9 \times 10^{2}) (-17150)</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CHO} ) oxidation</td>
<td>Self-inhibition ( k^{\text{inh}}_{\text{CH}_3\text{CHO} \cdot 2} )</td>
<td>(6.8 \times 10^{3}) (-6950)</td>
</tr>
<tr>
<td></td>
<td>Inhibition by CO ( k^{\text{inh}}_{\text{CO} \cdot 2} )</td>
<td>65.5  (-7990)</td>
</tr>
<tr>
<td></td>
<td>Inhibition by NO ( k^{\text{inh}}_{\text{NO} \cdot 2} )</td>
<td>(4.79 \times 10^{5}) 31036</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_5\text{OH} ) oxidation</td>
<td>Self-inhibition ( k^{\text{inh}}_{\text{C}_2\text{H}_5\text{OH} \cdot 2} )</td>
<td>(4.1 \times 10^{2}) (-2460)</td>
</tr>
<tr>
<td></td>
<td>Inhibition by CO ( k^{\text{inh}}_{\text{CO} \cdot 3} )</td>
<td>65.5  (-7990)</td>
</tr>
<tr>
<td></td>
<td>Inhibition by NO ( k^{\text{inh}}_{\text{NO} \cdot 3} )</td>
<td>(4.79 \times 10^{5}) 31036</td>
</tr>
</tbody>
</table>

The result of using these parameters in the full ethanol mix test show good correlation between the simulated and measured data (Figures 13-16).
Figure 13 Concentration Traces from Full E85 Exhaust Mixture Simulation and Measured
Figure 14 CO Conversion Simulated and Measured, Full Mixture

Figure 15 C₃H₆ Simulated and Measured, Full Mixture

Figure 16 THC Simulated and Measured, Full Mixture
6. Model Validation using 50 g/ft³ PdRh catalyst

A final model validation using an identical PdRh automotive catalyst, with the exception of the overall precious metal loading being reduced to 50 g ft⁻³, was carried out in order to confirm that the reaction pathways derived using the 150 g ft⁻³ sample could be transferred.

The experimental results and simulations are reported in Figures 17 to 20. The disappearance of \(\text{C}_2\text{H}_5\text{OH}\) in the simulation is predicted at a slightly lower temperature than measured and is a result of \(\text{CH}_3\text{CHO}\) formation and subsequent decomposition (Figure 17). The disappearance of \(\text{CH}_3\text{CHO}\) is also simulated to start at a lower temperature than measured which appears to be due to excessive \(\text{CH}_4\) formation and full oxidation. As a result, the onset of the THC conversion (Figure 20) is predicted to occur at a lower temperature than what was measured; the high temperature (>250°C) conversion corresponds with the \(\text{CH}_4\) conversion behaviour observed over the same temperature range.

The prediction of the CO, \(\text{C}_3\text{H}_6\) and THC conversions, shown in Figures 18-20 respectively, are also in good agreement with the measured data. Considering that no attempt was made at further tuning the parameters defined using the 150 g ft⁻³ sample, the correspondence between the experimental data and the simulated results is remarkable.
Figure 17 50g/ft³ PdRh Sample Full Mixture Simulated and Measured Comparison
Figure 18 50g/ft³ CO Conversion Simulated and Measured Comparison

Figure 19 50g/ft³ C₂H₆ Conversion Simulated and Measured Comparison

Figure 20 50g/ft³ THC Conversion Simulated and Measured Comparison

7. Conclusions

The performance of a PdRh automotive catalyst was evaluated when subjected to a range of concentrations of C₂H₅OH and CH₃CHO at varying stoichiometric ratios, and the effect of O₂ concentration on the dehydrogenation and decomposition reactions was clarified. The inhibiting compounds to these reactions were determined along with the effect of their concentrations. Analysis of CH₃CHO formation using various C₂H₅OH inlet concentrations and stoichiometric ratios showed that:
- C₂H₅OH dehydrogenation is independent of O₂ concentration
- CO and NO were found to be the main inhibiting compounds to CH₃CHO decomposition, CH₃CHO oxidation and C₂H₅OH oxidation.
- C₂H₅OH dehydrogenation was not significantly affected by the presence of CO or NO.

The experimental work provided a suitable structure for the derivation of the kinetic equations required to develop a simulation of the reactions. An iterative manual optimization process was used to derive a set of global kinetics parameters representative of the catalyst performance when exposed to exhaust gas from E85-fuelled SI engine. The kinetic parameters were validated by using a lower loading PdRh catalyst, which showed remarkably good correlation, confirming that the model can be used to describe the behaviour of PdRh catalysts when exposed to E85 exhaust effluents. It is particularly noteworthy that the formation of CH₄ via the decomposition of CH₃CHO results in full conversion of THC being delayed until the catalyst inlet temperature reaches approximately 600 °C.

**Nomenclature**

**Symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Pre-exponential frequency factor</td>
<td>s⁻¹</td>
</tr>
<tr>
<td>Ea</td>
<td>Activation energy</td>
<td>J mol⁻¹</td>
</tr>
<tr>
<td>i</td>
<td>Gas species</td>
<td></td>
</tr>
<tr>
<td>kₘᵢₙh</td>
<td>Inhibition rate constant</td>
<td>m³ mol⁻¹</td>
</tr>
<tr>
<td>kₘᵢʳ</td>
<td>Promotional rate constant</td>
<td>m³ mol⁻¹</td>
</tr>
<tr>
<td>kᵣ₉C₂H₅OH₅OHdehyd</td>
<td>C₂H₅OH promotional coefficient dehydrogenation</td>
<td>s⁻¹</td>
</tr>
<tr>
<td>kᵣ₉C₂H₅OH₉ox</td>
<td>C₂H₅OH promotional coefficient oxidation</td>
<td>m³ mol⁻¹ s⁻¹</td>
</tr>
<tr>
<td>kᵣ₉CH₃CHO₉dec</td>
<td>CH₃CHO promotional coefficient decomposition</td>
<td>s⁻¹</td>
</tr>
<tr>
<td>kᵣ₉CH₃CHO₉ox</td>
<td>CH₃CHO promotional coefficient oxidation</td>
<td>m³ mol⁻¹ s⁻¹</td>
</tr>
</tbody>
</table>
Reaction rate $r$ 
$C_2H_5OH$ dehydrogenation rate of reaction $r_{C_2H_5OH\ dehydro}$ 
$C_2H_3CHO$ decomposition rate of reaction $r_{CH_3CHO\ dec}$ 
$C_2H_3CHO$ oxidation rate of reaction $r_{CH_3CHO\ ox}$ 
$C_2H_5OH$ oxidation rate of reaction $r_{C_2H_5OH\ ox}$ 
$C_2H_5OH$ dehydrogenation self inhibition coefficient $k_{C_2H_5OH\ _1}^{inh}$ 
$C_2H_5OH$ oxidation self inhibition coefficient $k_{C_2H_5OH\ _2}^{inh}$ 
$CH_3CHO$ decomposition self inhibition coefficient $k_{CH_3CHO\ _1}^{inh}$ 
$CH_3CHO$ oxidation self inhibition coefficient $k_{CH_3CHO\ _2}^{inh}$ 
$CH_3CHO$ decomposition – CO inhibition coefficient $k_{CO\ _1}^{inh}$ 
$CH_3CHO$ oxidation – CO inhibition coefficient $k_{CO\ _2}^{inh}$ 
$C_2H_5OH$ oxidation – CO inhibition coefficient $k_{CO\ _3}^{inh}$ 
$CH_3CHO$ decomposition – NO inhibition coefficient $k_{NO\ _1}^{inh}$ 
$CH_3CHO$ oxidation – NO inhibition coefficient $k_{NO\ _2}^{inh}$ 
$C_2H_5OH$ oxidation – NO inhibition coefficient $k_{NO\ _3}^{inh}$ 
Universal gas constant $R$ 
Surface temperature $T$ 
concentration of a reactant $X$yn 

**Abbreviations and Acronyms**

AFR Air fuel ratio

cpsi Cells Per Square Inch

E85 85% Ethanol and 15% Gasoline Fuel

FTIR Fourier Transform Infrared Spectroscopy

HC Hydrocarbon

JLR Jaguar Land Rover

PdRh Palladium and Rhodium Catalytic Converter Formulation

PtRh Platinum and Rhodium Catalytic Converter Formulation

ppm Parts Per Million

ppmC Parts Per Million Carbon
SI  Spark Ignition
TWC  Three-way Catalyst
THC  Total Hydrocarbons

Chemical Symbols

CH₄  Methane
C₂H₆  Propylene
C₃H₈  Propane
CH₃CHO  Acetaldehyde
CH₃OH  Methanol
C₂H₅OH  Ethanol
CO  Carbon monoxide
CO₂  Carbon dioxide
H₂  Hydrogen
H₂O  Hydrogen
N₂  Nitrogen
NO  Nitric oxide
NOₓ  Oxides of nitrogen
O₂  Oxygen
Pd  Palladium
Pt  Platinum
Rh  Rhodium

Acknowledgements

This work was supported by the Department of Education and Learning, and the authors would like to thank Jaguar Land Rover for financial support.

References


20. www.exothermia.com [viewed on 13 Nov 2018]