Bifurcation features of mixtures containing CO and hydrocarbons in Diesel Oxidation Catalyst.

Rama Krishna Dadi, Dan Luss, Vemuri Balakotaiah^{*}
Department of Chemical and Biomolecular Engineering,
University of Houston, Houston, TX-77204

Abstract:

A model of a monolith reactor with radial gradients in the washcoat is used to study the ignition-extinction of pure CO, C₂H₆ and C₃H₆ and of their mixtures on a Pt/Al₂O₃ diesel oxidation catalyst. The ignition temperature of the individual species oxidation increases upon an increase in feed concentration of either CO or C₃H₆ and decreases upon an increase in feed concentration of C₂H₆. This is because CO, C₃H₆ have negative order kinetics and C₂H₆ has positive order kinetics. We determine the steady-state hysteresis behavior of conversion versus feed temperature during co-oxidation of CO and hydrocarbons (C₃H₆, C₂H₆). A single S-shaped bifurcation diagram of conversion versus inlet temperature is obtained during the co-oxidation of all feed mixtures of CO and C₃H₆ because the activation energies of CO and C₃H₆ are close to each other. The presence of CO in the feed inhibits the oxidation of propylene during the co-oxidation of CO and C₃H₆. In contrast, the ignition temperatures of pure CO and pure C₂H₆ are much different and CO ignites at a much lower temperature than C₂H₆. A double-S shaped

^{*} Corresponding author: Tel: +1 713 743 4318; fax: +1 713 743 4323

Email: bala@uh.edu

bifurcation diagram is obtained when hysteresis exists for both CO and C₂H₆ during the co-oxidation. The oxidation of CO present in the feed increases the catalyst temperature and this reduces the C₂H₆ ignition temperature. The separated ignition is transformed to a simultaneous ignition when the CO concentration in the feed is sufficiently high. We determine the boundary in the parameter space of feed compositions and other operating conditions that separate the simultaneous and separate ignition. The application of this result for the design of DOCs for treating exhaust gases at lower inlet temperatures is discussed.

Keywords: steady-state hysteresis, co-oxidation, separate ignition, simultaneous ignition

1. Introduction and literature review:

The diesel oxidation catalyst (DOC) is an integral part of diesel engine exhaust system that reduces the amount of harmful emissions released to the environment. DOC is the first exhaust component after the engine and is followed by diesel particulate filter and NO_x treatment units. The main functions of DOC are oxidation of CO, NO and hydrocarbons. NO oxidation has gained importance in recent years since NO₂ is an important feedstock to Lean NO_x Traps (LNT) and Selective Catalytic Reduction (SCR) reactions in the downstream units. Generally, ceramic honeycomb monolith reactors are used in DOC. However, metallic monoliths are sometimes used. Platinum group metals are used as catalyst materials in DOC as they have good oxidation performance and high thermal durability. They are deposited on thin layers of a washcoat which is adhered to the monolith walls. The washcoat thickness is in the range of 15-50µm.

Many previous studies examined the oxidation of CO and hydrocarbons and co-oxidation reactions. CO oxidation on Pt in monolith reactors has been extensively studied. Langmuir [1] proposed a micro-kinetic model for CO oxidation on Pt. Voltz et al. [2] reported that both CO and C₃H₆ are self-inhibiting and that CO inhibits C₃H₆ oxidation and vice-versa due to competitive adsorption. Salomons et al. [3] predicted ignition and extinction curves using different models for CO oxidation on Pt/Al₂O₃. Abedi et al. [4] investigated CO hysteresis behavior in a mixture with C₃H₆. Khosravi et al. [5] investigated the oxidation of carbon monoxide, nitrogen monoxide and propene and the reduction of nitrogen monoxide by propene over two diesel oxidation catalysts. A more recent study by Raj et al. [6] examined steady-state and dynamic hysteresis effects during co-oxidation of CO and C₃H₆ on Pt/Al₂O₃.

Garetto et al. [7] evaluated catalyst performance during oxidation of ethane, propane and butane on Pt supported catalysts. Harold and Luss [8] studied multiplicity features during co-oxidation of CO and C₂H₆ on a single catalytic pellet. Dadi et al. [9] studied transient hysteresis effects during co-oxidation of CO and C₂H₆ on Pt/Al₂O₃ and showed that the exotherm generated by the oxidation of CO decreases the light-off temperature of C₂H₆.

Balakotaiah and Luss [10] predicted different types of bifurcation diagrams describing the dependence of a state variable of the reactor on a design or operating variable. They presented a systematic and efficient scheme for finding parameter values corresponding to a specific number of solutions as well as different bifurcation diagrams for lumped-parameter systems in which many chemical reactions occur simultaneously [10,11]. Harold et al. [12, 13] showed that experimental multiplicity features may be used to identify the kinetic features. Ramanathan et al. [14] developed an analytical criterion for light-off in a straight channeled monolith with washcoat. Gundlapally and Balakotaiah [15] studied the effect of substrate material on the steady-state and transient performance of monolith reactors. The co-oxidation of CO and H₂ is a system in which ignition of the two components occurs in the same temperature region. Sun et al. [16] studied steady-state features during co-oxidation of CO and H₂ on a catalytic monolith washcoated with Pt/Al₂O₃. Bhatia et al. [17] used bifurcation analysis to study the effect of inlet temperature, inlet concentration and exposed Pt surface area on the multiplicity behavior. They compared the light-off curves generated using global and micro kinetic models and studied the effect of rate parameters on the region of multiplicity. Joshi et al. [18] characterized the controlling regimes during lean oxidation of CH₄ and C₃H₆ in Pt/Al₂O₃ monolith reactors. Carlsson et al. [19] studied the ignition and extinction processes during total oxidation of CO,

CH_4 and $\text{CO}+\text{CH}_4$ mixture in excess oxygen over $\text{Pt}/\text{Al}_2\text{O}_3$ and Pt/CeO_2 . The ignition and extinction of CO and CH_4 oxidation in mixture of CO and CH_4 occur in different temperature regions. A diesel oxidation catalyst is expected to oxidize CO and several hydrocarbons. In order to design efficient diesel oxidation catalysts it is important to know the ignition and extinction behavior of mixtures of CO and hydrocarbons as a function of inlet temperature, composition and space time.

The main objective of this work is to conduct bifurcation analysis (i.e. ignition and extinction behavior as a function of feed or inlet temperature) during co-oxidation of CO and hydrocarbons in a diesel oxidation catalyst. We first determine the bifurcation features of individual oxidation reactions of CO, C_3H_6 and C_2H_6 . We study the effect of various parameters such as space time or space velocity and inlet mole fraction on the ignition and extinction behavior. We then examine steady-state features during co-oxidation of mixtures of CO, C_3H_6 and CO, C_2H_6 . Two different systems are chosen to study the bifurcation features in diesel oxidation catalyst. The first system comprises reacting species whose activation energies are close to each other (CO, C_3H_6) whereas the second system is of the reacting species whose activation energies are much different from each other. The difference in the activation energies in CO- C_3H_6 system is small compared to CO- C_2H_6 system.

This paper is organized as follows. In the next section, a 1+1 D model and a model of a short monolith with gradients in the washcoat are presented. The bifurcation features of individual reactions are presented in section 3. We study ignition and extinction behavior during co-oxidation of CO and C_3H_6 in section 4 and of co-oxidation of CO and C_2H_6 in section 5. In section 6 we determine bifurcation features when all the three species are present in the

feed. The last section summarizes the main results and their possible application to the design and operation of DOCs.

2. Mathematical models

1+1 Model

The basic assumptions in the 1+1 D model include a) fully developed laminar flow, b) axial dispersion of heat and mass in fluid phase is negligible compared to convection, c) physical properties are independent of species concentration, d) pressure drop across the channel is negligible, e) gas mixture is dilute so that gas expansion effects are insignificant, f) steady-state operation, g) adiabatic reactor (or heat losses are negligible). Following the preceding assumptions, the steady-state balance equations are:

Species and energy balance in the channel:

$$\langle u \rangle \frac{\partial X_{jm}}{\partial z} = -\frac{k_c(j,z)}{R_\Omega} (X_{jm} - X_{js}); \quad j=1,2,\dots,S \quad (1)$$

$$\rho_f C_{pf} \langle u \rangle \frac{\partial T_m}{\partial z} = -\frac{h}{R_\Omega} (T_m - T_s) \quad (2)$$

Species and energy balance in the washcoat

$$c_{Tm} D_{je} \frac{\partial^2 \hat{X}_j}{\partial y^2} + \sum_{l=1}^{r_{gl}} v_{lj} R_{v,l} (T_s, \hat{X}) = 0 \quad (3)$$

$$k_w \delta_c \frac{\partial^2 T_s}{\partial z^2} + h(T_m - T_s) - \sum_{l=1}^{r_{gl}} \Delta H_l \int_0^{\delta_c} R_{v,l} (T_s, \hat{X}) dy = 0 \quad (4)$$

The boundary conditions used in solving the above set of balance equations are:

$$X_{jm}(z = 0) = X_{jm,in} \quad (5)$$

$$k_c(j)(X_{jm} - X_{js}) = -D_{je} \frac{\partial \hat{X}_j}{\partial y} \big|_{y=0} \quad (6)$$

$$\hat{X}_j = X_{js} @ y = 0 \quad (7)$$

$$\frac{\partial \hat{X}_j}{\partial y} = 0 @ y = \delta_c. \quad (8)$$

$$T_m(z = 0) = T_{m,in} \quad (9)$$

$$\frac{\partial T_s}{\partial z}(z = 0) = 0 \quad (10)$$

$$\frac{\partial T_s}{\partial z}(z = L) = 0. \quad (11)$$

Here, $X_{jm,in}$, X_{jm} and X_{js} are the inlet mole fraction, cup-mixing mole fraction in the fluid phase, and mole fraction at the fluid-washcoat interface of species j, respectively; $k_c(j)$ is the mass transfer coefficient of species j, whereas L , $\langle u \rangle$ and R_Ω denote the channel length, average fluid velocity in the channel and effective transverse length scale, respectively ($R_\Omega = \frac{A_\Omega}{P_\Omega}$; A_Ω is the channel cross-sectional area open to flow; P_Ω , channel perimeter open to flow; R_Ω is the hydraulic radius of the channel); c_{Tm} is the total molar concentration, D_{je} represents the effective diffusivity of the species j and is estimated using constant ratio with diffusivity in fluid phase, r_{gl} is the number of global reactions, v_{lj} is the stoichiometric coefficient of species j in reaction l and $R_{v,l}(T_s, \underline{\hat{X}})$ is the reaction rate (in mol/m³/s) which depends on the solid temperature (T_s) and mole fractions in the washcoat; $T_{m,in}$ and T_m are the inlet and cup-mixing fluid temperature, respectively; h refers to the heat transfer

coefficient and ρ_f, C_{pf} represent the density and specific heat capacity in the fluid phase, respectively; ΔH_l is the heat of reaction l , and S is the number of species.

Various limiting cases of the above model may be formulated depending on the values of the dimensionless groups characterizing the various (internal, external, axial and radial) gradients. A model that is particularly useful for the purpose of the current study (i.e. bifurcation analysis) is that of the so-called “short monolith” model. This limiting model is obtained by integrating the reactor equations in the axial direction and is valid when axial gradients (within the monolith) are small compared to radial gradients in the channel and washcoat [17, 20]. It reduces the computational effort and captures the qualitative features (specifically the ignition and extinction behavior) of the reactor [Remark: The main caution in using this model is that it does not retain the quantitative accuracy on the high conversion ignited branches]. We shall use this short monolith model to present and analyze the bifurcation features of mixtures. However, a comparison of this limiting model with the full model will be presented when appropriate. Further details can be found in [17, 20].

Short monolith model

The balance equations describing the short monolith model are given by

$$X_{jm,in} - X_{jm} - \frac{k_c(j) L}{\langle u \rangle R_\Omega} (X_{jm} - X_{js}) = 0, \quad (12)$$

$$c_{Tm} D_{je} \frac{\partial^2 \hat{X}_j}{\partial y^2} + \sum_{l=1}^{r_{gl}} \nu_{lj} R_{v,l} (T_s, \hat{X}) = 0 \quad (13)$$

$$T_{m,in} - T_m - \frac{h_f L}{\langle u \rangle \rho_f C_{pf} R_\Omega} (T_m - T_s) = 0, \quad (14)$$

$$h_f(T_m - T_s) - \sum_{l=1}^{r_{gl}} \Delta H_l \int_0^{\delta_c} R_{v,l}(T_s, \underline{\hat{X}}) dy = 0 \quad (15)$$

$$k_c(j)(X_{jm} - X_{js}) = -D_{je} \frac{\partial \hat{X}_j}{\partial y} \big|_{y=0} \quad (16)$$

$$\hat{X}_j = X_{js} @ y = 0 \quad (17)$$

$$\frac{\partial \hat{X}_j}{\partial y} = 0 @ y = \delta_c. \quad (18)$$

The mass transfer and the heat transfer coefficient for the short monolith model are evaluated using the asymptotic Sherwood ($Sh_{H_{1,\infty}}$) and Nusselt numbers ($Nu_{H_{1,\infty}}$) for a channel of square cross-section by the following equations (Ramanathan et al. [14]):

$$\frac{k_c(j)R_\Omega}{D_{jm}} = \frac{Sh_{H_{1,\infty}}}{4} \quad (19)$$

$$\frac{h_f R_\Omega}{k_f} = \frac{Nu_{H_{1,\infty}}}{4} \quad (20)$$

D_{jm} in Eq. 19 and k_f in Eq. 20 are the fluid phase molecular diffusivity of species j and conductivity of the fluid phase, respectively.

Kinetic model

We use a global kinetic model to study the bifurcation features. The oxidation reactions studied are:

The catalyst used in simulations is Pt supported on alumina (Pt/Al₂O₃). The loading of Pt is 90 gm/ft³ of monolith. The rate expressions for the individual reactions are [6, 7]

$$R_{CO} = \frac{\widehat{k}_1 Y_{CO}}{(1 + K_{CO} Y_{CO})^2} \quad (21)$$

$$R_{C_3H_6} = \frac{\widehat{k}_2 Y_{C_3H_6}}{(1 + K_{C_3H_6} Y_{C_3H_6})^2} \quad (22)$$

$$R_{C_2H_6} = \widehat{k}_3 Y_{C_2H_6} \quad (23)$$

In all the reactions, excess oxygen is assumed to be present and its mole percentage is taken to be 10% in all the simulations. Thus,

$$\widehat{k}_i = k_i Y_{O_2}, \quad (24)$$

with $Y_{O_2} = 0.1$. During co-oxidation of CO and C_3H_6 , mutual inhibiting terms are also present and the corresponding rate expressions are [6]

$$R'_{CO} = \frac{\widehat{k}_1 Y_{CO}}{(1 + K_{CO} Y_{CO} + K_{I,C_3H_6} Y_{C_3H_6})^2}, \quad (25)$$

$$R'_{C_3H_6} = \frac{\widehat{k}_2 Y_{C_3H_6}}{(1 + K_{C_3H_6} Y_{C_3H_6} + K_{I,CO} Y_{CO})^2}. \quad (26)$$

It should be noted that the denominators in the above rate expressions for CO oxidation and C_3H_6 oxidations are different unlike the global rate expressions derived from a mechanistic model. Raj et al. [6] showed that the second inhibition term is needed in the rate expressions of CO and C_3H_6 oxidations to account for mutual inhibition. These global rate expressions are empirical and are based on fitting the experimental light-off curves at different concentrations.

As they are validated in a previous publication [6], we do not modify them here (except for adjusting the rates for different amounts of Pt loading).

During co-oxidation of CO and C_2H_6 , the inhibition term is only due to CO adsorption.

The rate expressions during co-oxidation of CO and C_2H_6 are taken to be of the form

$$R''_{CO} = \frac{\widehat{k}_1 Y_{CO}}{(1 + K_{CO} Y_{CO})^2} , \quad (27)$$

$$R''_{C_2H_6} = \frac{\widehat{k}_3 Y_{C_3H_6}}{(1 + K_{CO} Y_{CO})^2} . \quad (28)$$

The rate expressions of CO and C_3H_6 oxidations in a mixture of CO, C_3H_6 and C_2H_6 remain the same as that of mixture containing CO and C_3H_6 . The rate expression for ethane oxidation in a mixture of CO, C_3H_6 and C_2H_6 is taken as

$$R'''_{C_2H_6} = \frac{\widehat{k}_3 Y_{C_3H_6}}{(1 + K_{CO} Y_{CO} + K_{C_3H_6} Y_{C_3H_6})^2} , \quad (29)$$

$$k_i = A_i \exp\left(-\frac{E_i}{R_g T}\right) \quad i=1,2,3 \quad (30)$$

$$K_{CO} = A_{CO} \exp\left(-\frac{\Delta H_{CO}}{R_g T}\right); K_{C_3H_6} = A_{C_3H_6} \exp\left(-\frac{\Delta H_{C_3H_6}}{R_g T}\right) \quad (31)$$

$$K_{ICO} = A_{ICO} \exp\left(-\frac{\Delta H_{ICO}}{R_g T}\right); K_{IC_3H_6} = A_{IC_3H_6} \exp\left(-\frac{\Delta H_{IC_3H_6}}{R_g T}\right) . \quad (32)$$

The values of the kinetic parameters used in the calculations are reported in Table 1. The rate expressions for individual oxidation reactions of CO and C_3H_6 and during co-oxidation are taken from the work of Raj et al. [6]. The rate expression for C_2H_6 oxidation is obtained by parameter estimation using the experimental data [7]. Fig.1 shows that data fit. For the purpose of this calculation, the full 1+1D model is used with the axial heat Peclet number defined by

$$Pe_h = \frac{\langle u \rangle L \rho_f C_{pf} R_{\Omega 1}}{k_w R_{\Omega w}} = \frac{\text{characteristic heat conduction time along the channel}}{\text{convection/space time}} \quad (33)$$

As stated earlier, axial gradients may become important at high conversion of the limiting reactant and the short monolith model may not retain quantitative accuracy. Fig.2 compares the bifurcation diagrams for ethane oxidation for short-monolith model and the full 1+1 D model with different Pe_h numbers. Fig.2 shows that although short monolith model slightly under predicts the ignition and extinction temperatures, it is able to capture the qualitative features accurately. In a nutshell, the short monolith model predicts qualitative bifurcation features with sufficient accuracy but with very low computational effort. Therefore, it is used to study the bifurcation features of individual oxidation and co-oxidation reactions. Finite difference methods are used to discretize the model equations. The full 1+1 D model is discretized using 15 points in the washcoat (y) direction and 30 points in the axial (x) direction. This leads to about 1500 algebraic equations (for a mixture containing 3 species) in as many unknowns, after discretization. Similarly, about 50 algebraic equations are obtained after the discretization of short monolith model in the washcoat (y) direction. Pseudo-arc length continuation method is used for computation of bifurcation diagrams and ignition or extinction and hysteresis loci. All the calculations are done in FORTRAN and using the package called MINPACK [Remark: While the computation of the bifurcation diagrams is straightforward, it is the computation of higher order singular points such as limit and hysteresis points, that is non-trivial and computationally demanding, especially when the number of discretized equations is large. Details of the computation of higher order singularities can be found in references 17 and 21].

3. Bifurcation features of individual reactions

CO oxidation:

It is important to know the bifurcation features of single component oxidation to understand the multiplicity features of multi-component oxidation. Therefore, we present first bifurcation features of single component oxidation starting with CO oxidation, which follows Langmuir-Hinshelwood kinetics. The parameters used in simulations are listed in Table 2. Air at an average temperature of 400K is used to estimate the values of physical parameters. Fig.3a shows that steady-state multiplicity does not exist for 500ppm of CO whereas steady-state multiplicity exists for a feed of 1 and 3% CO concentrations. This is evident from the bifurcation diagrams shown in Fig.3b, which shows the solid (catalyst) exit temperature versus fluid inlet temperature. Fig. 3a shows that the steady-state multiplicity region expands upon an increase in feed concentration of CO. This occurs because the heat released by the oxidation increases with an increase in CO feed concentration. This heat provides thermal feedback, which expands the region of steady-state multiplicity. Fig.4a shows the bifurcation set (ignition and extinction locus) for oxidation of CO at two different space times. It shows that the ignition temperature increases and the extinction temperature decreases with increase in CO feed concentration. The increased ignition temperature suggests that the effect of negative order kinetics is more pronounced than the exothermic effect generated by the CO oxidation. The extinction temperature decreases because the reactor quenches at a lower temperature when the heat generated by the oxidation of CO increases. The sensitivity of the ignition temperature to the feed concentration is much smaller than the sensitivity of the extinction temperature. Fig.4a

suggests that the region of steady-state multiplicity increases upon an increase in space-time. This is because feed stays long enough in reactor to get higher conversion. Fig. 4b shows the hysteresis locus, which is the boundary for existence of steady-state multiplicity. CO feed concentration required for steady-state multiplicity decreases upon an increase in space-time. We note that for typical space times (or space velocities) used in after-treatment ($\tau > 10$ ms or $SV < 360000 \text{ hr}^{-1}$), multiplicity exists for CO feed concentrations above 0.3%

C₃H₆ oxidation:

C₃H₆ oxidation follows Langmuir-Hinshelwood kinetics. Similar to CO oxidation, propylene does not have steady-state multiplicity for very low feed concentrations. Steady-state multiplicity expands with increase in feed concentration of C₃H₆. Fig.5 and Fig.6 show that most bifurcation features of C₃H₆ oxidation are qualitatively similar to that of CO oxidation. The main difference is in the C₃H₆ concentrations needed to obtain multiplicity. These values are about a factor of 3 to 5 times lower in magnitude than those of CO for the same space-time. This is expected based on the heats of the oxidation reaction and inhibition terms.

C₂H₆ oxidation:

Unlike CO and C₃H₆ oxidation, C₂H₆ oxidation follows positive order kinetics. Fig.7 shows that steady-state multiplicity does not exist for 500ppm of C₂H₆ but exists for a feed concentration of 1.5%. Fig.8a shows that both ignition and extinction temperatures decrease with an increase in feed concentration of C₂H₆. Fig.8b shows that feed concentration of C₂H₆ required for steady-state multiplicity to occur decreases following an increase of the space-time.

4. Bifurcation features of co-oxidation of CO and C₃H₆

Fig.9a shows that steady-state multiplicity does not exist for co-oxidation of 500ppm CO and 200ppm of C₃H₆ since hysteresis criterion is not satisfied for both CO and C₃H₆. Fig.9a also shows that light-off temperature (temperature corresponding to 50% conversion when steady-state multiplicity does not exist and the ignition temperature when steady-state multiplicity exists) is the same for both CO and C₃H₆. This is because the activation energies for both CO and C₃H₆ oxidations are very close to each other. Fig.9b shows that a single ignition and extinction exist when hysteresis exists for both CO oxidation and C₃H₆ oxidation. A single S shaped bifurcation diagram is obtained even when hysteresis exists for both CO and C₃H₆ during co-oxidation. The bifurcation diagrams show that the CO conversion is much higher than of C₃H₆ at ignition temperature. This confirms that C₃H₆ oxidation is more self-inhibiting than CO oxidation. Fig.10 shows that the ignition temperature increases with increase in C₃H₆ feed concentration. When 1% CO is introduced into the feed it delays the ignition and decreases the extinction temperature. When CO is introduced along with C₃H₆ into the feed, the catalyst temperature is increased and this can decrease the ignition temperature. However, in this case, the ignition temperature is increased when 1% of CO is introduced into the feed along with C₃H₆. This shows that inhibition due to strong CO adsorption is more pronounced than the exotherm effect generated due to CO oxidation.

5. Co-oxidation of CO and C₂H₆

The light-off temperatures of CO and C₂H₆ oxidation are much different from each other. So, co-oxidation of CO and C₂H₆ represent a system in which ignition temperatures of the reacting

species are very different from each other. Fig.11 shows that both ignition and extinction temperatures are reduced when CO is introduced into the feed. The bifurcation set in Fig.11 shows that the ignition temperature is reduced by about 80K when 1% CO is introduced into the feed. Simulations not shown here reveal that the light-off temperature of C_2H_6 is reduced by about 80K for every 1% CO added to the feed. This is consistent with a recent study by Dadi et al. [9]. The exotherm generated by the CO oxidation increases the catalyst temperature and this reduces the light-off temperature of C_2H_6 .

Hysteresis exists for CO oxidation but not for C_2H_6 oxidation when concentration of C_2H_6 is low. Since hysteresis exists only for CO oxidation, a single ignition and extinction points are observed in this case. However, an increase in the C_2H_6 feed concentration can cause hysteresis to occur for C_2H_6 oxidation. Fig.12 shows that a double S shaped bifurcation diagram with two ignitions and extinctions is obtained when hysteresis exists for both CO and C_2H_6 oxidation. In the double S shaped bifurcation diagram the first ignition and extinction correspond to CO oxidation and the second ignition and extinction correspond to C_2H_6 oxidation. Fig.12 shows that the ignition temperature of C_2H_6 oxidation is higher than that of CO oxidation during the co-oxidation of 1% CO and 1.5% C_2H_6 . However, increasing CO concentration can lead to a simultaneous ignition of CO and C_2H_6 . Fig.13 shows such a simultaneous ignition in which ignition temperatures of both CO and C_2H_6 are equal. It should be noted here that extinction temperatures for CO oxidation and C_2H_6 oxidation are different.

Fig.14 shows the phase diagram in the parameter space of CO and C_2H_6 feed concentrations with feed temperature as distinguished bifurcation variable. Hysteresis does not exist for both CO and C_2H_6 oxidation for all the (low) feed concentrations in region 1 in Fig.14. Hysteresis

exists only for C_2H_6 oxidation in region 2 and for only CO oxidation in region 3. The light-off temperature of C_2H_6 oxidation is more than CO ignition temperature in region 3 and less than CO ignition temperature in region 4. The dashed line is the boundary for separate and simultaneous ignition when hysteresis does not exist for C_2H_6 oxidation. Hysteresis exists for both CO and C_2H_6 oxidation in regions 5 and 6. In region 5, ignition temperature of C_2H_6 is higher than the ignition temperature of CO and it is opposite in region 6. Fig.12 is an example of bifurcation diagram in region 5 and Fig.13 is in region 6. The solid line separating regions 5 and 6 is the boundary for separate and simultaneous ignitions when hysteresis exists for both CO and C_2H_6 oxidation. In bifurcation theory this boundary is called the *double limit locus* [10]. A double limit locus is the locus of all parameter values for which two limit (ignition or extinction) points exists for same value of distinguished (bifurcation) variable which is feed temperature in this case. Typical composition of diesel engine exhaust falls in the regions 1,3 and 4.

Fig.15 shows the dependence of the ignition and extinction temperatures of CO and C_2H_6 oxidation on feed mole percentage of CO. It shows that CO ignition temperature increases with an increase in the CO feed concentration. However, the ignition temperature of C_2H_6 decreases upon an increase in CO feed concentration. The heat generated by the CO oxidation increases with increase in feed concentration of CO. This decreases C_2H_6 ignition temperature upon an increase in feed mole percentage of CO. Two double limit points exist in bifurcation set shown in Fig.15a. One double limit point is at a feed of 1.5% C_2H_6 and 2.2% CO and the second is at feed of 1.5% C_2H_6 and 1.3% CO. The ignition temperatures of both CO and C_2H_6 are equal at a feed of 1.5% C_2H_6 and 2.2% CO. Fig.13 shows the bifurcation diagram of this case and Fig.14 shows the boundary locus of all such points. At the other double limit point, which is obtained

at the feed composition of 1.5% C₂H₆ and 1.3% CO, the extinction temperature of ethane oxidation is equal to the ignition temperature of CO. Figs.15a and 15b show that the steady multiplicity region of C₂H₆ oxidation decreases and finally disappears upon an increase in CO feed concentration. The inhibition term, $K_{CO}Y_{CO}$, becomes more significant as the feed CO concentration is increased. At higher feed concentrations of CO, $K_{CO}Y_{CO} \gg 1$ and this results in an increase in the effective activation energy. This increase in effective activation energy is the main reason for the decrease in steady-state multiplicity region of C₂H₆ oxidation with increase in feed concentration of CO.

6. Co-oxidation of CO, C₃H₆ and C₂H₆

Fig.16 shows that during the co-oxidation of 500ppm CO, 500ppm C₃H₆ and 500ppm C₂H₆ the light-off temperature of CO and C₃H₆ is 380K and that of C₂H₆ is 640K. Thus co-oxidation of CO, C₃H₆ and C₂H₆ represents a system in which two reacting species ignite together and the third ignites at a much higher temperature. However, the light-off temperature of C₂H₆ can be reduced with an increase in the feed concentration of either CO or C₃H₆. The heat generated by the oxidation of CO or C₃H₆ increases the catalyst temperature and this decreases C₂H₆ light-off temperature. Fig.16 and Fig.17a show that ignition temperature of CO, C₃H₆ is increased from 380K to 400K as the feed concentration of CO is increased from 500ppm to 3%. This confirms that self-inhibition effect of CO is more pronounced than temperature rise effect even during the co-oxidation of CO, C₃H₆ and C₂H₆. The light-off temperature of C₂H₆ is almost equal to ignition temperature of CO and C₃H₆ when 3% CO is fed into the reactor. Similarly, light-off temperature of C₂H₆ can be made equal to the ignition

temperature of CO, C₃H₆ when 5000ppm of C₃H₆ is fed into reactor. Fig.17b shows the simultaneous ignition of all the three components for the feed composition of 500ppm CO, 5000ppm C₃H₆ and 500ppm C₂H₆. The feed concentration of CO or C₃H₆ required for the simultaneous ignition of the three components decreases with an increase in feed concentration of C₂H₆. A double S shaped bifurcation diagram can be obtained when hysteresis exists for at least one of CO or C₃H₆ and the hysteresis exists for oxidation of C₂H₆.

Fig.18 shows the boundary for separate and simultaneous ignition during co-oxidation of CO and multiple hydrocarbons. This figure shows the total adiabatic temperature rise of all the low temperature igniting species required to simultaneously ignite the species that ignite at higher temperature. In our study, the low temperature igniting species are CO and C₃H₆ and the high temperature igniting species is C₂H₆. The mole fraction of C₂H₆ in diesel engine exhaust is few hundreds ppm. Fig.18 suggests that total adiabatic temperature rise of about 280K is required to simultaneously ignite C₂H₆ with the low temperature igniting species. The exothermicity of all the low temperature igniting species can be used to decrease the ignition temperature of the late igniting species. The adiabatic temperature rise of the mixture is given by

$$\Delta T_{ad} = \sum_{i=1}^n \frac{-\Delta H_{R,i}}{\langle C_p \rangle} Y_i$$

where $\Delta H_{R,i}$ is the heat of reaction for species i oxidation, Y_i is the mole fraction of species i, and $\langle C_p \rangle$ is the average molar heat capacity of gas mixture.

The adiabatic temperature rise of the mixture containing CO and C₃H₆ is given by

$$\Delta T_{ad} = \frac{(\Delta H_{R,CO})Y_{CO}}{\langle C_P \rangle} + \frac{(\Delta H_{R,C_3H_6})Y_{C_3H_6}}{\langle C_P \rangle} \sim 9433Y_{CO} + 64200Y_{C_3H_6}$$

where Y_{CO} and $Y_{C_3H_6}$ are the mole fractions of the species in the feed.

At present, the authors are not aware of any experimental data on the co-oxidation of CO, C_3H_6 and C_2H_6 . Therefore, the simulations presented here may be used as a guide to design appropriate experiments and verify the predictions of simultaneous and separate ignitions. Further, the simulations show that the light-off characteristics of ethane oxidation are not sensitive to the denominator. This can be explained by the fact that mole fractions of CO and C_3H_6 become almost zero before ethane oxidation becomes active. Again, this can be validated or corrected by experimental data.

7. Summary and discussion

The main contribution of this work is the analysis of the ignition (light-off) and extinction characteristics of DOC with CO and HCs in the feed. We have used a short monolith model to study the bifurcation features of the oxidation and co-oxidation reactions. It has been shown in previous publications that the short monolith model can capture most of the qualitative bifurcation features. For a few selected cases, the bifurcation features of the 1+1D model are also studied and compared with the results of the short-monolith model. The short monolith model under predicts the ignition temperature and over predicts the region of steady-state multiplicity. It also under predicts the hysteresis locus i.e. it under predicts the inlet mole fraction required for steady-state multiplicity at a particular space-time. Despite these

shortcomings, the short monolith model is used to study the bifurcation features because it captures most of the qualitative features with minimal computational time.

Bifurcation analysis of individual oxidation reactions of CO, C₃H₆ and C₂H₆ and of co-oxidation reactions of CO, C₃H₆; CO, C₂H₆ and CO, C₃H₆, C₂H₆ is presented. A single S shaped bifurcation diagram is obtained at all feed concentrations of CO and C₃H₆ during co-oxidation of CO and C₃H₆. The ignition temperature increases upon an increase in feed concentration of both CO and C₃H₆ because of the inhibition terms present in denominator terms of the rate expressions. The light-off temperatures of CO and C₂H₆ are very different from each other during the co-oxidation of CO and C₂H₆. The C₂H₆ light-off temperature can be reduced due to the exotherm generated by the CO or C₃H₆ oxidation.

A diesel oxidation catalyst is expected to oxidize CO and several hydrocarbons. Each of the hydrocarbons ignites at a different temperature depending upon the kinetics. We considered here two systems, which represent many practical systems in diesel oxidation catalyst. We conducted the bifurcation analysis of three reactants system, which closely resembles the reactant systems, fed to a diesel oxidation catalyst. We used global kinetics to determine the ignition and extinction features of CO, C₃H₆ and C₂H₆ system.

The results of the present work may be used as a guide to determine the ignition/extinction behavior of more complex mixtures containing H₂, CO and several hydrocarbons. In such cases, we can lump all the species that have nearly the same ignition temperature (e.g. CO, H₂, C₃H₆) into one lump or an equivalent single species and those that have a much higher ignition temperature into a second lump.

The light-off curves for individual oxidation are validated using the experimental data. The steady-state bifurcation diagrams shown in this work give the information about ignition and extinction during individual as well as co-oxidation reactions. Few experimental studies exist in the current literature describing the extinction process. The bifurcation analysis presented here can serve as a guide for experimentally studying the ignition and extinction behavior during individual oxidation as well as co-oxidation reactions.

It should be pointed out that the main results of this work are applicable to full scale DOC systems, which are operated close to adiabatic conditions. In most laboratory reactors, heat losses are significant and hence the various bifurcations predicted here can be observed only if heat exchange with furnace is minimized, or more precisely if the characteristic heat exchange time is at least an order of magnitude larger than the space time. As shown in the literature [22], the region of hysteresis shrinks and disappears when the heat losses are significant [Remark: This reference also provides a detailed discussion of the impact of scale-up on the ignition-extinction behavior].

A major limitation of the present work is that NO oxidation is not considered. The presence of NO in the feed can inhibit CO as well as hydrocarbons oxidation. While a small amount of NO (e.g. < 50ppm) is not expected to change the main conclusions of this work, higher concentrations of NO can increase the ignition temperature of CO and hydrocarbons by about 10-20°C. Selective catalytic reduction of NO by CO and hydrocarbons can also occur and should be considered in the kinetic model and simulations. The impact of NO in the feed on the bifurcation features using both global and micro-kinetic models will be pursued in the future.

Experimental results suggest that the presence of water does not change the light-off characteristics of CO and HCs oxidations. Therefore, the effect of water is not considered in this study. However, it is a well-known fact that the water-gas-shift reaction and steam reforming reactions become important at higher temperatures. The global kinetic models used here do not account for these two reactions or the impact of water. Therefore, an obvious extension of the work presented here is to include the species NO and water along with other global reactions among the species. An alternative approach is to replace global kinetic models with micro-kinetic models that include all the species of interest as was done by Kota et al. [23] for an analogous problem of the LNT. This extension for DOC will be considered in a future publication.

Acknowledgements: This study was funded by grants from the U.S. DOE National Energy Technology Laboratory as part of the Vehicles Technologies Program DOE-NETL (DE-EE0000205) and National Science Foundation CBET 1258688.

Nomenclature

c_{Tm}	total concentration in gas phase
C_{pf}	specific heat capacity of gas
D_{je}	effective diffusivity of species j in washcoat
D_{jm}	molecular diffusivity of species j in fluid phase
h	heat transfer coefficient
$k_c(j)$	external mass transfer coefficient
k_f	fluid thermal conductivity
k_w	effective thermal conductivity of wall and washcoat
L	length of the monolith
$Nu_{H_1,\infty}$	asymptotic Nusselt number
P_Ω	channel perimeter open to flow
Pe_h	axial heat Peclet number
R_Ω	effective transverse length (channel hydraulic radius)
$R_{v,l}$	volumetric reaction rate
r_{gl}	number of global reactions
S	number of species
$Sh_{H_1,\infty}$	asymptotic Sherwood number
T_m	cup-mixing temperature
$T_{m,in}$	fluid inlet temperature
T_s	solid (catalyst) temperature
$\langle u \rangle$	average fluid velocity
X_{jm}	cup-mixing mole fraction of species j in fluid phase
$X_{jm,in}$	inlet mole fraction

X_{js}	mole fraction of species j at the fluid-washcoat interface
$\hat{X}_j$	mole fraction of species j in the washcoat
y	radial coordinate
z	axial coordinate

Greek letters

ΔH_l	heat of reaction l
δ_c	effective washcoat thickness
ρ_f	density in fluid phase
ν_{lj}	stoichiometric coefficient of species j in reaction l

References:

1. I. Langmuir, The mechanism of the catalytic action of platinum in the reactions $2\text{CO} + \text{O}_2 = 2\text{CO}_2$ and $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$. Transactions of the Faraday Society 17 (1922) 621-654.
2. S.E.Voltz, C.R. Morgan, D. Leiderman, S.M. Jacob, Kinetic study of carbon monoxide and propylene oxidation on platinum catalysts, Industrial & Engineering Chemistry Product Research and Development 12 (1973) 294-301
3. S. Salomons , R.E. Hayes, M. Votsmeier, A. Drochner, H. Vogel, S. Malmberg and J. Gieshoff, On the use of mechanistic CO oxidation models with a platinum monolith catalyst, Applied Catalysis B: Environmental, 70(1) (2007) 305-313
4. A. Abedi, R. Hayes, M. Votsmeier and W.S. Epling, Inverse Hysteresis Phenomena During CO and C_3H_6 Oxidation over a $\text{Pt}/\text{Al}_2\text{O}_3$ Catalyst, Catalysis letters 142(8) (2012) 930-935.
5. M. Khosravi, A.Abedi, R.E. Hayes, W.S. Epling, M.Votsmeier, Kinetic modelling of Pt and Pt:Pd diesel oxidation catalysts, Applied Catalysis B: Environmental 154 (2014) 16-26
6. R. Raj, M. P. Harold and V.Balakotaiah, Steady-state and dynamic hysteresis effects during lean co-oxidation of CO and C_3H_6 over $\text{Pt}/\text{Al}_2\text{O}_3$ monolithic catalyst, Chemical Engineering Journal 281 (2015) 322-333
7. T.F. Garetto, E. Rincón and C. R. Apesteguia, The origin of the enhanced activity of Pt/zeolites for combustion of C_2 – C_4 alkanes, Applied Catalysis B: Environmental 73.1 (2007) 65-72
8. M.P. Harold and D. Luss, An experimental study of steady-state multiplicity features of two parallel catalytic reactions, Chemical Engineering Science, 40.1 (1985) 39-52

9. R.K. Dadi, D. Luss, V. Balakotaiah, Dynamic hysteresis in monolith reactors and hysteresis effects during co-oxidation of CO and C₂H₆, Chemical Engineering Journal 297 (2016) 325-340.
10. V. Balakotaiah and D. Luss, Structure of the steady-state solutions of lumped-parameter chemically reacting systems. Chemical Engineering Science 37.11 (1982) 1611-1623.
11. V. Balakotaiah and D. Luss, Global analysis of the multiplicity features of multi-reaction lumped-parameter systems, Chemical Engineering Science, 39(5) (1984) 865-881
12. M.P. Harold , M. Sheintuch and D. Luss, Analysis and modeling of multiplicity features. 1. Nonisothermal experiments, Industrial & Engineering Chemistry Research, 26(4) (1987) 786-794
13. M.P. Harold , M. Sheintuch and D. Luss, Analysis and modeling of multiplicity features. 2. Isothermal experiments, Industrial & Engineering Chemistry Research, 26(4) (1987) 794-804
14. K. Ramanathan, V. Balakotaiah and D.H. West, Light-off criterion and transient analysis of catalytic monoliths, Chemical Engineering Science, 58(8) (2003) 1381-1405
15. S.R. Gundlapally and V. Balakotaiah, Analysis of the effect of substrate material on the steady-state and transient performance of monolith reactors, Chemical Engineering Science 92 (2013) 198-210
16. M. Sun, E.B. Croiset, R. R. Hudgins, P.L. Silveston and M. Menzinger, Steady-state multiplicity and superadiabatic extinction waves in the oxidation of CO/H₂ mixtures over a Pt/Al₂O₃-coated monolith. Industrial & Engineering Chemistry Research, 42(1) (2003) 37-45.

17. D. Bhatia, M.P. Harold and V. Balakotaiah, Kinetic and bifurcation analysis of the cooxidation of CO and H₂ in catalytic monolith reactors, *Chemical Engineering Science* 64.7 (2009) 1544-1558
18. S.Y. Joshi, Y. Ren, M.P. Harold and V. Balakotaiah, Experimental and theoretical investigation of controlling regimes during lean oxidation of methane and propylene on Pt/Al₂O₃ monolith reactors, *Industrial & Engineering Chemistry Research* 51(22) (2011) 7482-7492
19. P.A. Carlsson and M. Skoglundh, Low-temperature oxidation of carbon monoxide and methane over alumina and ceria supported platinum catalysts, *Applied Catalysis B: Environmental* 101.3 (2011) 669-675
20. V. Balakotaiah, N. Gupta, and D.H. West, A simplified model for analyzing catalytic reactions in short monoliths." *Chemical Engineering Science* 55.22 (2000) 5367-5383.
21. V. Balakotaiah, D. Luss and B. L. Keyfitz, Steady-state Multiplicity Analysis of Lumped Parameter Systems Described by a Set of Algebraic Equations", *Chemical Engineering Communications*. 36 (1985) 121-147
22. T. Gu and V. Balakotaiah, Impact of heat and mass dispersion and thermal effects on the scale-up of monolith reactors. *Chemical Engineering Journal* 284 (2016): 513-535.
23. A. S. Kota, D. Luss and V. Balakotaiah, Micro-kinetics of NO_x Storage and Reduction with H₂/CO/C₃H₆ on Pt/BaO/Al₂O₃ Monolith Catalysts, *Chemical Engineering Journal* 262 (2015) 541-551.

Table 1: List of kinetic parameters used in simulations

Parameters	Values	Units
A_1	$1.28 \cdot 10^{21}$	moles/m ³ /s
A_{CO}	88.59	-
A_2	$1.36 \cdot 10^{17}$	moles/m ³ /s
$A_{C_3H_6}$	2508.28	-
A_{ICO}	2090.13	-
$A_{IC_3H_6}$	323	-
A_3	$0.85 \cdot 10^{10}$	moles/m ³ /s
E_1/R_g	14422	K
$-\Delta H_{CO}/R_g$	1162	K
E_2/R_g	11306	K
E_3/R_g	9262	K
$-\Delta H_{C_3H_6}/R_g$	117	K
$-\Delta H_{ICO}/R_g$	300	K
$-\Delta H_{IC_3H_6}/R_g$	1100	K

Table2: List of constant parameters used in simulations

Parameter	Value
R_Ω	262 μm
δ_c	30 μm
L	2.54cm
$Sh_{H_{1,\infty}}$	4.364
$Nu_{H_{1,\infty}}$	4.364
ρ_f	0.87 kg/m^3
C_{pf}	1015 J/kg/K
R	8.314 J/mol/K
$D_{m,\text{CO}}$	$1.2 * 10^{-9} * T_f^{1.7} \text{ m}^2/\text{s}$ (T_f in K)
$D_{m,\text{C}_3\text{H}_6}$	$4.2 * 10^{-10} * T_f^{1.7} \text{ m}^2/\text{s}$ (T_f in K)
$D_{m,\text{C}_2\text{H}_6}$	$1.12 * 10^{-9} * T_f^{1.7} \text{ m}^2/\text{s}$ (T_f in K)

Figure1: Comparison of experimental data with model predictions for oxidation of C_2H_6 on Pt/Al_2O_3 ($\tau=0.1s$ and $C_2H_6=500ppm$)

Figure2: Comparison of the predicted bifurcation diagrams of conversion versus inlet temperature for the 1+1 D model and the short monolith model. ($\tau=0.1s$ and $C_2H_6=1.7\%$)

Figure3: Bifurcation diagrams showing the dependence of (a) conversion and (b) solid (catalyst) exit temperature on fluid inlet temperature for CO oxidation ($\tau=0.1s$).

Figure4: (a) Dependence of ignition and extinction temperatures on feed CO concentration. (b) Hysteresis locus for CO oxidation

Figure5: Bifurcation diagrams showing dependence of (a) conversion and (b) solid (catalyst) exit temperature on fluid inlet temperature during C_3H_6 oxidation for space time=0.1s

Figure6: (a) Dependence of ignition and extinction temperatures on feed C_3H_6 concentration. (b) Hysteresis locus for C_3H_6 oxidation

Figure7: Bifurcation diagrams showing dependence of (a) conversion and (b) catalyst exit temperature on fluid inlet temperature during C_2H_6 oxidation for space time=0.1s

Figure8: (a) Dependence of ignition and extinction temperatures on feed C_2H_6 concentration. (b) Hysteresis locus for C_2H_6 oxidation

Figure9: Bifurcation diagram showing dependence of conversion on fluid inlet temperature during co-oxidation of CO and C_3H_6 for space time=0.1s. (a) CO= 500ppm and C_3H_6 =200ppm. (b) CO= 1% and C_3H_6 =2000ppm

Figure 10: Dependence of the ignition and extinction temperatures on C_3H_6 feed concentration during co-oxidation of CO and C_3H_6 for space time=0.1s

Figure 11: Dependence of the ignition and extinction temperatures on C_2H_6 feed concentration during co-oxidation of CO and C_2H_6 for space time=0.1s

Figure12: Bifurcation diagram showing dependence of (a) conversion and (b) solid exit temperature on fluid inlet temperature during co-oxidation of CO and C_2H_6 for space time=0.1s

Figure13: Bifurcation showing dependence of (a) conversion and (b) solid exit temperature on fluid inlet temperature during co-oxidation of CO and C₂H₆ for space time=0.1s

Figure14: Phase diagram in the parameter space of CO and C₂H₆ feed concentrations during co-oxidation of CO and C₂H₆. Different regions of the phase diagram correspond to different types of bifurcation behavior.

Figure 15: Dependence of ignition and extinction temperatures on C₂H₆ feed concentration during co-oxidation of CO and C₂H₆ for space time=0.1s

Figure16: Bifurcation diagram showing dependence of conversion on fluid inlet temperature during co-oxidation of CO, C₃H₆ and C₃H₆ for space time =0.1s

Figure17: Bifurcation diagram illustrating the dependence of conversion on fluid inlet temperature during co-oxidation of CO, C_3H_6 and C_2H_6 for different feed compositions (a) CO 3%, C_3H_6 500ppm, C_2H_6 500ppm, $\tau = 0.1s$ (b) C_3H_6 5000ppm, CO 500ppm, C_2H_6 500ppm, $\tau = 0.1s$

Figure18: A phase diagram illustrating the boundary for separate and simultaneous ignition during co-oxidation of CO and other hydrocarbons that ignite simultaneously and another hydrocarbon having higher ignition temperature (characterized by C_2H_6)