A STUDY OF HOMOGENEOUS METHANOL OXIDATION KINETICS USING CSP

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The homogeneous oxidation of methanol in air at constant pressure is examined using data generated by the method of computational singular perturbation (CSP). At any moment in time, the number of exhausted fast modes and the radicals (sometimes called the intermediaries) are computationally identified. The participation index, which quantifies the participation of any elementary reaction to an equations of state of the radicals, along with the importance index, which quantifies the importance of any elementary reaction to a particular species of interest, are computed and used to assess the sensitivities of the solution to the reaction rate constants. Every elementary reaction is classified so that it either belongs to the equilibrium set which contains fast reactions already equilibrated among themselves, and/or the rate-controlling set which contains reactions controlling the current rate of activities, or neither of the above sets—in which case it is superfluous. A number of numerical experiments were performed to verify the assessments: (a) the relative effectiveness of the reaction rate constants of two reactions (#16, #160) in breaking up the fuel indicated by the importance index is verified, (b) that fuel breakup in an early time period can actually be slowed down by increasing the reaction rate constants of certain fuel breakup reactions (#156, #159) is verified. Numerical experiments also showed that species identified as radicals responded instantly to sudden changes in reaction rates, while the non-radicals responded more smoothly. The overall response of the unknowns to perturbations is always consistent with the CSP-derived effective stoichiometric coefficients. In addition, a minimum set of species is constructed with the help of the CSP data. This minimum set, which trims the original full set of 30 species to 15 species, generates numerical solutions in excellent agreement with solutions obtained with the full set.

Introduction

The present paper studies the constant pressure oxidation of methanol in air. The full kinetics mechanism, taken from Egolfopoulos, Dv and Law's [EDL], consists of 30 species and 173 reversible elementary reactions. A partial list of the elementary reactions is given in Appendix I. The case of a fuel lean (equivalence ratio = 0.6) mixture at 1 atmosphere will be considered. The initial state of the system is taken to be: \( T(0) = 1027^\circ \text{C}, Y[	ext{CH}_3\text{OH}]/(0) = 0.00779, Y[\text{O}_2]/(0) = 0.01950, Y[\text{N}_2]/(0) = 0.9724 \), where \( T \) is temperature and \( Y \) is mass fraction. The calculation is performed in a Chemkin environment, and the resulting numerical solution is analyzed using the data generated by the method of computational singular perturbation (CSP) developed by the authors.4,5,6

Figs. 1a and 1b show the time evolution of four species: similar plots for all the other species and the temperature are readily available. The oxidation of \( \text{CH}_3\text{OH} \) can be described as a four-stage process. The first stage, \( 0.00 \text{ seconds} < t < 0.05 \text{ seconds} \), is an incubation period in which certain radicals are created. The breakup of the fuel occurs in the second stage, \( 0.050 \text{ seconds} < t < 0.079 \text{ seconds} \). The third stage, \( 0.079 < t < 0.081 \), consists of the very rapid conversion of \( \text{CO} \) to \( \text{CO}_2 \). The conversion of the remaining \( \text{CO} \) to \( \text{CO}_2 \) takes place in the fourth stage, \( 0.081 < t < 0.130 \), with progressively slower rates. The integration of the kinetics equations is straightforwardly performed by a CSP ODE solver which, in addition to generating solutions of guaranteed user-specified accuracy, also generates a set of CSP data. Each time interval between markers shown in Figs. 1a, b covers 24 integration time steps selected by the CSP code.

Preliminary Discussions

The conventional derivation of a simplified model requires that the "radicals" and fast reactions in the reaction system be somehow identified, and the
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interpret the sensitivity information\textsuperscript{10-12} of the reaction system. The CSP method performs the above tasks routinely using a programmable computational algorithm, and can generates time-resolved simplified models without the need of intuition and experience. A brief summary of the CSP method is given in Appendix II.

The Identification of Radicals

Including temperature, the system of ODEs of the [EDL] full mechanism consists of 31 unknowns and 173 reversible elementary reactions. Let $y = [y^1, y^2, \ldots, y^{31}]$ be a column vector of the $N = 31$ unknowns. Let $F^+_k(y) > 0$ and $F^-_k(y) < 0$ be the forward and backward reaction rates of the $k$-th elementary reactions, where $k = 1, 2, \ldots, R$ with $R = 173$. In general, the governing equations can be written in the following compact form:

$$\frac{dy}{dt} = g(y) = s_k(F^+_k - F^-_k), \quad (2.1)$$

where $s_k$ is called the stoichiometric vector of the $k$-th elementary reaction, and the summation convention is used. Since this is a 31-dimensional system, the solution is expected to have 31 "modes." These modes are ordered by CSP according to their speed: mode #1 being the fastest and mode #26 being the slowest. Modes #27 to #31 are constants and do not evolve with time; they represent the conservation of energy, the conservation of C, H, and O atoms and the inertness of N$_2$. In addition, CSP computationally determines $M$, the number of exhausted fast modes (see Appendix II). Fig. 2 shows $M$ vs. time. Each of the exhausted fast modes is associated by CSP with either a quasi-steady approximation (for a certain radical species) or a partial-equilibrium approximation (for a certain set of fast reactions). In the present paper, we shall call a species a radical when it can accurately be computed to terms of the other "major species" from certain approximate "equations of state" derived by CSP. More will be said on this in §4 later. The identification of these radicals was achieved by the use of $Q(m; t)$, the "radical pointer" of each of the $m$ exhausted modes, as described in Appendix II.

The following information is obtained from the CSP data for each of the four stages:

First Stage ($0.00 < t < 0.05$ seconds), $M = 14$. The following 14 species are identified as radicals: CH$_3$, C$_2$H$_5$, CH$_3$CO, HCO, H, CH$_2$, C$_2$H$_3$, CH$_2$OH, HCCO, O, CH, C$_2$H, CH$_3$O, OH.

Second Stage ($0.05 < t < 0.079$ seconds), $M = 15$. HCO joins the above, making a total of 15 radicals. The breakup of the fuel is in full swing.
of the relations of the type
\[ \frac{dx}{dt} = f(x, y, z) \]

\[ \frac{dy}{dt} = g(x, y, z) \]

\[ \frac{dz}{dt} = h(x, y, z) \]

with \( x, y, z \) being the state variables and \( f, g, h \) being continuous functions. The vector \( \mathbf{x} = (x, y, z) \) represents the state of the system at time \( t \).

**Third Stage** (0.079 < \( t < 0.081 \) seconds), \( M = 12 \). This is a most active period in which things happen very rapidly. Three exhausted modes become alive again, and \( \text{CH}_3, \text{H}, \text{O} \) are temporarily removed from the list of radicals.

**Fourth Stage** (0.081 < \( t < 0.130 \) seconds), \( M = 15-24 \). After the frenzied activities in the third stage, \( \text{CH}_3, \text{H}, \text{O} \) rejoins the list of radicals. As the fourth stage progresses, \( M \) increases from 15 to 24, mostly as the results of extinction of the carbon-related species (CO and \( \text{CO}_2 \) excluded). The remaining non-carbon related radicals in this late period are \( \text{O}, \text{H}, \text{OH}, \text{HO}_2 \) and \( \text{H}_2\text{O}_2 \).

**The Simplified Model at \( t = 0.0345 \)**

We shall demonstrate in some detail the procedures for extracting information about the reaction system using the CSP data in one typical moment in time. At \( t = 0.0345 \), when the fuel is breaking up and \( \text{HO}_2 \) is not yet a radical but is about to peak, CSP determined \( M = 14 \), and generated 14 approximate "equations of state":

\[ f^m(y) = 0, \quad m = 1, \ldots, 14 \]

Each of these equations of state can be physically interpreted either as a quasi-steady approximation or a partial-equilibrium approximation. Samples of these 14 equations of state, suitably normalized, are displayed below:

**Exhausted Mode #1 \([\text{CH}_3] \):**

\[ F^{20} = F^{33} + F^{32} + F^{163} + \ldots \]

\[ 0.50 = 0.43 + 0.05 + 0.01 + \ldots \]

**Exhausted Mode #5 \([\text{H}] \):**

\[ F^{13} + F^{53} + F^{3} = F^{106} + F^{12} + F^{38} + F^{157} + F^{11} + F^{9} + \ldots \]

\[ 0.35 + 0.14 + 0.02 = 0.23 + 0.08 + 0.08 + 0.06 + 0.02 + 0.02 + \ldots \]

**Exhausted Mode #13 \([\text{CH}_2\text{O}] \):**

\[ F^{160} + F^{157} = F^{43} + \ldots \]

\[ 0.42 + 0.08 = 0.48 + \ldots \]

Each exhausted mode is identified by the radical pointer \( Q(m, i) \) described in Appendix II with a specific species which shall be referred to as a radical. The left and right hand sides of (4.2a, b, c) are the rates of production and consumption of the identified radical. The terms on each side are ordered in descending order of magnitude; sufficient terms are kept so that the total contribution of the omitted terms is below a user-specified threshold.

The numbers displayed below each term is the participation index, \( P^r \), which is defined in Appendix II and measures the significance of the \( k \)-th reaction to the \( m \)-th exhausted fast mode.

In addition, CSP derives the following simplified model:

\[ \frac{dy}{dt} = c_k (P^k_+ - P^k_) \]

where \( c_k \) is called the effective stoichiometric vector of the \( k \)-th reaction. Mathematically, it is the projection of the original stoichiometric vector \( s_k \) in the currently active slow subspace. Samples of these 31 equations are displayed below:

\[ \frac{d[\text{CH}_4]}{dt} = c_{17}^{17} F^{16} + c_{160}^{17} F^{160} + c_{129}^{17} F^{29} + c_{43}^{17} F^{43} + c_{168}^{17} F^{168} + c_{224}^{17} F^{224} + c_{197}^{17} F^{197} + \ldots \]

\[ [\text{CH}_4] = Y^{17} \]
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\[ \frac{d[H]}{dt} = c_I^{16}F_{i}^{16} + c_{10}^{15}F_{i}^{15} + c_{10}^{14}F_{i}^{14} + \ldots \]

\[ [H] = \gamma_{15} \] (4.4b)

\[ \frac{d([CH_3OH])}{dt} = c_{15}^{15}F_{i}^{15} + c_{10}^{15}F_{i}^{10} + c_{10}^{14}F_{i}^{40} + \]
\[ + c_{10}^{16}F_{i}^{33} + c_{10}^{17}F_{i}^{28} + c_{10}^{18}F_{i}^{23} + \]
\[ - 0.40 - 0.16 + 0.12 \]
\[ - 0.05 + 0.05 + 0.05 \]
\[ \ldots \]

\[ [CH_3OH] = \gamma_{15} \] (4.4c)

where the coefficients \( c_i \) (the \( i \)-th element of \( \mathbf{c} \)) are provided by CSP numerically. The numbers displayed below each term in (4.4c) is the importance index, \( I_{15} \), a measure of the significance of the \( i \)-th reaction to the simplified equation for CH_3OH. The definition of \( I_{15} \) is given in Appendix II. Again, the terms on the right hand side are ordered in descending magnitude; sufficient terms are kept so that the total of the omitted terms is below a user-specified threshold. Note that the solution of these 31 equations automatically satisfies the 14 approximate equations of state given symbolically by (4.1) and explicitly by (4.2). Once may freely replace the differential equation for any radical, such as (4.4b), by its equation of state, in this case (4.2b).

It is interesting to compare the CSP derived simplified model equations with the original equations. For \([CH_3OH] \), the original equation is:

\[ \frac{d([CH_3OH])}{dt} = \frac{32}{\rho} \left( F_{i}^{109} + F_{i}^{106} + F_{i}^{157} + \ldots \right) \] (4.5a)

where \( \rho \) is total mass density. Using the CSP-computed numerical values for \( C_{i}^{15} \), the simplified equation for \([CH_3OH] \) is:

\[ \frac{d([CH_3OH])}{dt} = \frac{32}{\rho} \left( 2.25F_{i}^{16} + 1.19F_{i}^{16} + 0.75F_{i}^{16} + 0.94F_{i}^{23} + \ldots \right) \] (4.5b)

The terms in (4.5a, b) are ordered in descending magnitude. In contrast to (4.5a) where each term involves methanol as a participant in a reaction, only reactions \#160 and \#162 in (4.5b) directly involve methanol. Similar observation can be made for all the simplified equations. For example, none of the seven reactions listed in the CSP-derived (4.4a) for \([CH_4] \) involves CH_4. Theoretically, the difference between the right hand side of the original and the CSP-derived simplified equations is some linear combinations of the equations of state given symbolically by (4.1) and explicitly by (4.2). Even though the CSP-derived simplified equations frequently do not make chemical sense at first glance, our experience is that they usually make sense upon further reflections. Computationally, solutions obtained from the CSP-derived simplified equations and from the full equations agree within user-specified bounds.

Similar information can be obtained for any moment in time.

The Importance Index

The importance index \( I_{i} \) defined in Appendix II measures the importance of the \( i \)-th reaction to the \( i \)-th unknown. Figs. 3a and 3b show \( I_{i} \), the importance index for CH_3OH, for reactions which do and do not involve CH_3OH, respectively. These two graphs provide concise information on the rate-controlling reactions for the breakup of CH_3OH. By inspection, Fig. 3a, b show that reaction \#16 is the most effective reaction in both the first and the second stages, even though it does not directly involve CH_3OH. It is seen to be somewhat more effective than reactions \#160 and \#162 which do. A numerical experiment was performed by increasing the rate constants for reactions \#160 and \#160 by a factor of 2.5 in the first stage. The computed time histories of CH_3OH confirmed the above qualitative prediction.

In addition, Fig. 3a shows that reactions \#156 and \#159, which chemically consume CH_3OH, have positive importance indices in the 0.00 \( \leq t \leq 0.03 \) period: \( I_{156} > 0 \) and \( I_{159} > 0 \). In other words, they effectively contribute positive terms in the first stage to the right hand side of (4.4c) -- a somewhat counter-intuitive prediction. Another numerical experiment was performed in which the rate constants for reactions \#156 and \#159 were simultaneously doubled. The resulting data shows that the breakdown of CH_3OH was indeed slowed and delayed in the first stage, again confirming the CSP expectation. In the third stage, however, faster \#156 and \#159 do favor the breakup of CH_3OH, as indicated also by Fig. 3a.

Classification of Reactions

The left hand side of (4.1) consists of positive and negative terms which nearly cancel each other. Separating the positive and negative terms and placing them across an equal sign as is done in (4.2) for each of the exhausted modes, we can pick out reactions which participate most significantly on each side using the participation index, \( P_{i}^{\pm} \), defined and
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![Diagram](image)

Fig. 3. (a) Importance Index for CH$_3$OH, $I_x^*$, vs. time—for reactions involving CH$_3$OH. (b) Importance Index for CH$_2$OH, $I_x^*$, vs. time—for reactions not involving CH$_3$OH.

The reactions which only belong to the equilibrated set define via (4.1) the so-called slow subspace which may be visualized as a (N-M)-dimensional "surface" on which the N-dimensional solution point $y(t)$ moves. Changing the rate constants in the equilibrated set changes the surface, but does not change the speed of the motion. The reaction which only belong to the rate-controlling set control the speed of the motion of $y(t)$, but do not affect the surface on which it moves. The reactions which belong to both sets affect both Numerical experiments were performed by perturbing the reaction rate of reactions #15 in a step-function manner for $t \geq 0.0345$. Since #15 belongs only to the rate-controlling set, the response of $y(t)$ to this abrupt perturbation is smooth and agree qualitatively with the CSP expectations, additional numerical experiments were performed by perturbing the reaction rate of reaction #160 which belongs to both sets. The response of $y(t)$ is again in qualitative agreement with the CSP expectations: some radicals respond discontinuously, all major species respond smoothly. Such information can be very useful in reaction-path analysis.

The Minimum Set of Species

Normally, one is usually interested only in the time history of a few species in a reaction system. Using the data generated by CSP, it is straight-forward to use the CSP data to identify the minimum set of unknowns (species) which includes an user-specified species of interest. The following minimum set which includes CH$_3$OH is obtained for the time interval studied: CH$_3$OH, CH$_2$O, H, H$_2$O, CH$_4$, CH$_3$, H$_2$, H$_2$O, CH$_2$OH, CO, O, H$_2$O, HCO, N$_2$, O$_2$, OH. The solution of this minimum set of 16 species (plus temperature) system is in excellent agreement with the solution computed from the full reaction system. Comparison of results obtained for CO and H are shown in Fig. 1b.

Conclusions

Neither of the authors are knowledgeable about chemical kinetics in general, and about methanol...
oxidation in particular. The above information are presumed by us to be informative, and are obtained routinely using the CSP data generated by the CSP code. Because of limitation of space, only part of the available information is included here. The method is clearly useful for the study of massively complex systems when intuition and experience are lacking and conventional analysis is untenable.

Appendix I

Selected Elementary Reactions From Full Kinetics Mechanism of [EDL]

A1 Basic CSP Concepts and Data:

The basic CSP idea is to split the N-dimensional space of the vector \( g \) into two subspaces, a fast and a slow subspace:

\[
g = g^{\text{fast}} + g^{\text{slow}},
\]

where \( g^{\text{fast}} \) is spanned by a set of \( M \) linearly independent column basis vectors \( a_m \) (\( m = 1, 2, \ldots, M \)). CSP provides an algorithm\(^2\) to determine \( M \) and to compute for this set of \( a_m \) along the trajectory of the solution \( y(t) \), together with a set of row vectors \( b^n \) which is ortho-normal to \( a_m \): \( b^m \cdot a_n = \delta_{mn} \), \( m, n = 1, 2, \ldots, M \).

The time-resolved values of \( M \), the basis vectors \( a_m \) and \( b^n \) appropriately ordered in ascending time scales, are the basic CSP data.

A.2 Using the Basis Vectors:

The fast subspace, being \( M \)-dimensional, contains \( M \) fast reaction modes, or simply modes. For chemical kinetics problems, these modes are usually decaying modes; i.e., they tend to become exhausted. When \( g^{\text{fast}} \) falls below some user-specified threshold for \( t \geq t_M \), we have:

\[
g^{\text{fast}} = 0,
\]

which yields \( M \) algebraic relations between the elements of \( y \). In other words, \( M \) equations of state,
where the $k$ in numerator is not summed and the $r$ in the denominator is summed over the 173 reactions. As defined, the maximum magnitude of $P_{2,k}^{m}$ is 0.50. In the present study, terms in (A3.1) are ordered in descending magnitude of its $P_{2,k}^{m}$, and sufficient terms are kept so that the the positive and negative sums are at least 0.48 and $-0.48$, respectively.

Similarly, not all reactions in (A2.4a) contribute equally to $g^{low}$. The importance index, $I_i$, is introduced to assess the degree of importance of the $k$-th reaction to the $i$-th element of y:

$$I_{i,k} = \frac{c_{i}^{(k)}P_{2}^{(k)}}{|c_{i}^{(k)}[F_{i}^{+} + F_{i}^{-}] + |b^{m} \cdot \delta g_{i}^{m}|}$$

(A3.3)

the $k$ and $i$ indices on the right hand side are treated as before. Again, terms in (A2.4a) are order in descending magnitude of $I_{i,k}$ so that the sum of $I_{i,1}$ is above some user-specified value (the present paper used 0.9).

In addition, CSP associates with every exhausted mode one or more unknowns which are the "fast" variables responsible for the rapid decay of the mode. The diagonal dimensionless elements of the $N \times N$ matrix $a_{m}b_{m}^{(k)}$ (no summation on $m$), denoted by $Q(m, i)$, are called the radical pointers of the $m$-th exhausted mode on the $i$-th species. The $i$-th species is said to be a fast variable or a radical for the $m$-th exhausted mode if $Q(m, i)$ is not a small number in comparison to unity. The species with the largest $Q(m, i)$ is identified as the radical for the $m$-th exhausted mode in this paper. If duplication occurs, the next largest pointer is used. The $M$ relations $f^{m}(y) = 0$ can be used to solve algebraically for these $M$ radicals in terms of the others. If the "wrong" species are identified as radicals, the solutions of the $M$ relations are not accurate and can not be trusted.

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\[ \text{(A3.1)} \]

\[ \text{(A3.2)} \]

COMMENTS

F. A. Williams, University of California at San Diego, USA. I have two questions for which I think your response would help to clarify thinking. First, how does your method or methods invoking manifolds differ from earlier analyses in which reduced chemistry was identified computationally through asymptotics? Second, since diffusion introduces a new dimension in which two-point boundary value problems arise, that can exhibit boundary layers and shock layers, is there a reasonable chance of being able to extend these automatic methods to such problems? This second problem must be solved for application to flames.

Author’s Reply. On the difference between CSP and “computationally identified” reduced chemistry models: CSP not only can produce the reduced chemistry “mechanism,” (a smaller set of reactants and reactions), but also the full set of simplified governing equations, the solution of which automatically satisfies the algebraic equation of state which are also automatically generated. The CSP data can readily be used to generate ad hoc analytical models.

On the difference between CSP and asymptotics methods: CSP needs no intuitive estimates of order of magnitudes. It needs no hints on which species can be assumed to be in quasi-steady state and which reaction can be assumed in partial-equilibrium. It is designed to be used in dimensional form, and no dimensionless small parameter (ε) needs to be identified by the investigator. The CSP algorithm of “refinement” of fast basis vectors can be used to confirm the validity of any asymptotic theory (which required informed guessing of the fast modes), and when used numerically it can be recursively applied to obtain “higher-order” accuracy results.

On the effects of diffusion: I am currently working to include the effects of diffusion. The effects of transverse diffusion—diffusion across streamlines—can be included relatively easily. Diffusion along streamlines, which can be of major importance in flames, is much more difficult, precisely because of its two-point boundary value nature.