

# A Mechanism Improvement Strategy Using Global Sensitivity Analysis

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**Abstract**—A new theoretical method based on global sensitivity analysis is developed for the systematic improvement combustion mechanisms. Applications to the combustion of methanol and butanol are presented.

## I. INTRODUCTION

Biofuels for combustion engines represent a promising renewable alternative to fossil fuels and have been the subject of great interest from both practical and fundamental scientific standpoints. While “bio”-ethanol is widely used as a blend in automotive fuels, there are strong motivations to design other biofuels. Obviously, ethanol has a great disadvantage in that it consumes “food” as a synthetic starting point. Furthermore, ethanol is not an ideal fuel since it is corrosive and possesses a relatively low energy density. We are interested in developing new techniques in the field of theoretical chemistry that will aid in biofuel design and testing.

In the present work, we suggest new methods to systematically improve chemical mechanisms are used to model the combustion of biofuels. The use of such mechanisms for the theoretical modeling of combustion is essential in designing a biofuel and establishing the proper engine operating conditions. Specifically, theoretical modeling can be used to identify the correct fuel blend (i.e. the mole fraction of various organic species and oxygen), engine temperature, and compression ratio that will minimize sooting and NO<sub>x</sub> formation, and promote ideal ignition characteristics. The chemical mechanism consists of a set of elementary chemical reaction steps and the associated reaction rate constants that represent all the chemistry within the flame. Chemical modeling consists of solving large systems of differential equations that represent the concentration of various molecular species, the thermodynamic characteristics such as temperature, and possibly transport properties within flames. The goal of a chemical kineticist is to perfect the rate constants in the mechanism so that theoretical modeling can be used as a predictive tool. For very simple fuels, such as H<sub>2</sub>, the elementary chemical steps and the associated rate constants are well established through experiment and high quality theoretical modeling. Unfortunately, for “complicated fuels” the mechanisms can include thousands of elementary chemical steps where most of the rate constants have never been measured. In mechanism generation methods, the values of such rate constants are determined by simple rules (viz. group additivity [1]) which are little more than educated guesses. Even though such mechanisms are often fitted to experiment globally, their performance can be quite poor when applied outside of the fitting regime. Our objective is to develop methods

that will systematically improve the chemical mechanism by identifying key reactions steps which are sequentially improved using high quality theoretical chemistry.

## II. METHODS

Our theoretical method consists of several interactive steps that rely on sophisticated methods of theoretical chemistry and statistics. We assume that a nominal N-reaction mechanism exists, and we focus on methodology for systematic improvement. We note that good plausible “first guess” mechanisms exist for hydrocarbon fuels up to heptane in size. Mechanisms are often developed hierarchically and oxygenated fuels (as are biofuels) are usually modeled by simply augmenting the corresponding hydrocarbon mechanism. The methanol combustion is modeled using the mechanism of Li et al [2].

**Step 1:** We identify an observable “target” that we want the theoretical mechanism to accurately reproduce. For auto-ignition in a diesel engine, a good choice of target is the ignition time delay ( $\tau$ ) which is the time required for the fuel/O<sub>2</sub> mixture to ignite under the desired (T,p) engine conditions. The “response surface” is then the target as a function of the rate constants,  $\tau(k_1, k_2, \dots, k_N)$ ; thus  $\tau$  is a very high dimensional function that is sensitive to the ignition properties.

**Step 2:** Using screening methods developed by statisticians, we identify the rate constants that most strongly influence the target. The conventional approach of chemists, local sensitivity analysis that involves computing  $\partial\tau/\partial k_i |_{\mathbf{k}=\mathbf{k}_0}$  where  $\mathbf{k}_0$  are the rate constants of the nominal mechanism, is a poor method for such screening. Instead, using techniques such as *High Dimensional Model Representation* (HDMR) for the analysis of variance (ANOVA) the functionality of  $\tau$  is decomposed into main effects (involving one variable, i.e. reaction rate constant), second order effects (involving two variables), etc.

$$\tau(k_1, k_2, \dots, k_N) = \tau_0 + \sum_i A_i(k_i) + \sum_{i \neq j} B_{i,j}(k_i, k_j) + \dots$$

Using such decompositions, the partial variances are computed, and the largest values determine the reaction that most strongly affects the target. Thus, *i*-th main effect =  $\sigma_i^2 / \sigma_{total}^2$  where the partial variance of  $\tau$  is computed using  $A_i$ , [3]. In practice, this involves numerically computing  $\tau$  at random (or quasirandom) values of the rate constants within the

hypervolume that constitute the uncertain ranges of  $k_i$ . It is critical to realize that there are two quantities that determine the magnitude of the main effect: first, the intrinsic sensitivity of  $\tau$  to the variable  $k_i$ , and second, the magnitude of the uncertainty range of  $k_i$ , i.e.  $\Delta k_i$ . For complicated fuels,  $\Delta k_i/k_i$  can be a factor of 10 or larger. Thus, a reaction for which  $\tau$  is very sensitive may nevertheless be “unimportant” (small main effect) if the corresponding  $k_i$  is known very accurately.

**Step 3:** The reaction with the largest main effect from step 2 is selected for improvement. The objective is improve the value of the rate constant (i.e. to reduce the uncertainty  $\Delta k_i$ ) so that the main effect becomes smaller. While in principle experiments may be done to find the rate constant, we shall instead use theoretical calculations to determine  $k_i$ . The barrier for the reaction in question is analyzed using quantum chemistry calculations. For many reactions we have studied previously, coupled cluster calculations, CCSD(T), provides an efficient method to approximate the solution to the electronic Schrodinger equations when implemented with an adequate basis set. We shall carry out the quantum chemistry at the highest level practical for each system. Once the saddlepoint on the potential surface has been computed, the minimum energy path is computed using a gradient following algorithm. The normal mode frequencies are computed as a function of  $s$  (the reaction coordinate) which are then used to determine the free energy function versus  $s$ . The maximum is the variational transition state (which generally does not lie at the saddlepoint). Variational transition state theory makes use of this information to give the new rate constant. The influence of tunneling may be incorporated using methods we have developed. Internal consistency checks on the quantum chemistry, combined with experience using transition state theory, yields a new presumably smaller value for  $\Delta k_i$ .

**Step 4:** Once the most important reaction rate constant (largest main effect) has been improved via Step 3, the response surface is recalculated using the new mechanism. Assuming that a good job is done in improving the rate constant, the new simulation will uncover a new reaction with the largest main effect. Step 3 is then repeated to improve that rate constant. This process continues until mechanism can account for the desired experimental properties.

### III. RESULTS

To illustrate the viability of the methods, we show results for the combustion of methanol [4]. In Fig. 1, we show the main effects for a 93 reversible reaction mechanism proposed by Dryer and co-workers. The most important reaction for ignition time delay is found to be rxn 91  $\text{CH}_3\text{OH} + \text{HO}_2 \rightarrow \text{CH}_2\text{OH} + \text{H}_2\text{O}_2$ , since the  $\text{H}_2\text{O}_2$  fragments to 2OH leading to rapid chain branching. In Fig. 2 the ignition delay time obtained for an ensemble of rate coefficients is plotted versus the value of a single rate, i.e. that for reaction 91.

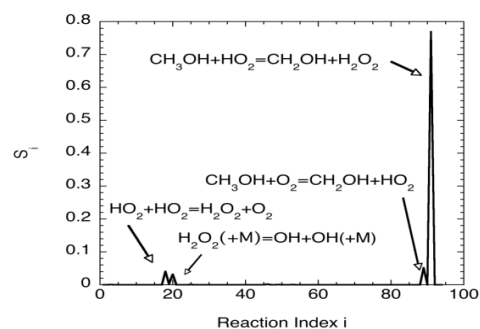


Fig. 1. The main effect,  $S_i$ , versus reaction index for the methanol combustion mechanism of Li et al.

Having identified reaction 91 as the most important step, the rate coefficient is then improved using theoretical methods. The TS barrier of the reaction was computed to be 9.6 kcal/mol and the new rate constant differed by a factor of 12 from the Li mechanism, and the uncertainty ratio fell from 12 to 1.5. Then, the new simulation revealed  $\text{CH}_3\text{OH} + \text{O}_2 \rightarrow \text{CH}_2\text{OH} + \text{HO}_2$  dominates the main effects. The quantum chemistry/TST calculation gives a new rate constant about a factor of 7 smaller than the original. After this change is included, the  $\text{HO}_2 + \text{HO}_2$  dominates.

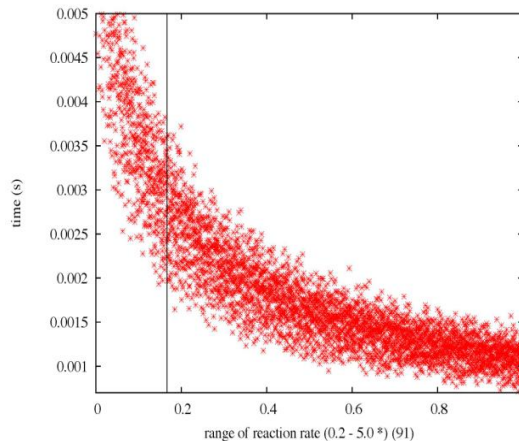


Fig. 2. Ignition delay time versus the value of the rate coefficient at 1150K for the key reaction  $\text{CH}_3\text{OH} + \text{HO}_2 = \text{CH}_2\text{OH} + \text{H}_2\text{O}_2$

For the combustion of butanol, the mechanism of Curan and coworkers [5] was employed. This mechanism consists of 1446 reversible steps and is much more challenging than the methanol case. In Fig. 3 the results of the global sensitivity analysis is presented. It is seen, in analogy to the methanol combustion, that the fuel+HO2 reaction dominates the uncertainty. We are presently engaged in improving this rate, with preliminary indications that the value at 1200 K goes down at least a factor of 3.

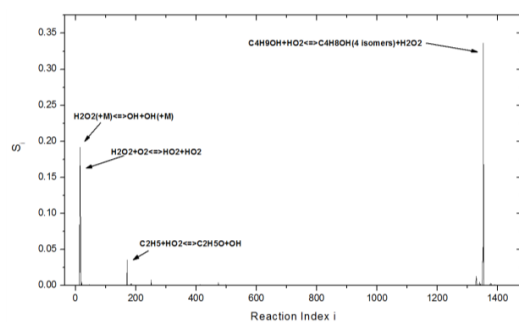


Fig. 3 The main effect,  $S_i$ , versus reaction index for the butanol combustion mechanism. Butanol+HO<sub>2</sub> emerges as the most important step for the ignition delay time.

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