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EXECUTIVE SUMMARY OF THE THESIS

Data-driven, class-based kinetic modeling of oxymethylene ethers combustion

LAUREA MAGISTRALE IN CHEMICAL ENGINEERING - INGEGNERIA CHIMICA

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1. Introduction

Developing kinetic mechanisms that can describe how different fuels undergo oxidation and pyrolysis is crucial in creating more efficient combustion techniques, which aim to reduce environmental impact, diversify energy sources, and utilize them in a sustainable manner. In the past two years, the scientific community has focused on developing new synthetic fuels, or e-fuels, to store excess energy from renewable sources, which are intermittent in nature. Among these e-fuels, dimethoxymethane (DMM) and higher oxymethylene ethers (OMEs) have emerged as potential alternatives to traditional fuels in diesel engines. Combustion involves a complex network of reactions with hundreds of species, and their kinetic mechanisms rely on rate constants as parameters, together with thermodynamic and transport properties associated with the species. These rate constants can be determined experimentally, calculated using quantum chemistry tools, or estimated based on analogies with similar compounds. Recent advances have led to more sophisticated theoretical methods for determining rate constants, but simply adopting the "best" parameters may not re-

sult in better model performance. This is due to multiple reasons, not least the fact that in the majority of the models, the rate parameters were estimated through analogy rules and semi-empirical correlations for the estimation of the thermodynamics and transport properties. Performing a sensitivity analysis on rate parameters allows choosing the important rate constants needing properly tuned. The tuning of the rate constants can be done manually or automatically, but recent frameworks have been developed to automate this process. However, current frameworks perturb each parameter independently and do not consider the underlying consistency between reaction classes. In this work, an optimization technique based on reaction classes was utilized, whereby the kinetic constant of each reaction class was calibrated instead of adjusting each parameter separately. This guarantees to obtain a more consistent and physically sound model. The overall optimization process has been implemented as an extended capability of `OptiSMOKE++` [1]. The methodology presented has been applied, as a case study, to the optimization of the OME_{1-4} model, selecting as the optimization targets different classes of reaction. After the

optimization, a validation over a wide range of experimental conditions has been automatically performed by exploiting a data ecosystem, SciExpeM [2], as a framework.

2. Methodology

2.1. Reaction Classes and Rate Rules

Chemical kinetics has a long-standing tradition of using reaction classes and rate rules. In fact, identifying the primary reaction classes and their corresponding kinetic parameters in the combustion mechanism of a fuel is crucial for two purposes: i) developing a comprehensive mechanism, and ii) potentially extending the reaction subset and kinetic parameters to molecules with analogous chemical structures. Species that share reactive moieties and functional groups involved in the reaction and have a resemblance in their structure are considered molecules “with similar structures”. For example, both 1-butene and 1-pentene may be subject to C-C bond fission, resulting in the ejection of a C_2H_3 radical. The expansion of a reaction set to include “similar” molecules can be systematically and consistently achieved using rate rules. These rules involve assigning reference kinetic parameters to a particular reaction type and incorporating correction factors that account for energetic, entropic, and structural effects. Depending on the work, approximately 15-30 reaction classes were identified to depict the high- and low-temperature oxidation of the fuel and its primary decomposition products, which include fuel alkyl radicals and corresponding alkenes, RO_2 , $QOOH$, O_2QOOH radicals, and cyclic ethers. The reaction classification in these studies focused on two primary aspects, which are clarified below:

- Each reaction class is generally identified by the type of species and the class type corresponding to an elementary reaction.
- Within each reaction class, different reaction types identify specific reactions associated with reference kinetic parameters which may be extended via analogy or rate rules. As an example, in the reaction class, “H-atom abstraction” by a given radical the reaction types are distinguished on the basis of the abstraction site, primary, secondary, or tertiary.

2.2. Kinetic Modeling

The kinetic mechanism describing the oxidation and pyrolysis of DMM and higher OMEs was built up following the principles of hierarchy and modularity, starting from the CRECK kinetic framework. The modules referred to H_2/O_2 and C_1-C_2 had been adopted and subsequently improved. Then the module referred to C_3 has been added too. The final kinetic mechanism examined in this work was taken from the sub-mechanism proposed by Cai et al. [3]. These were generated by adopting a reaction class-based methodology with the principle of hierarchy, in order to obtain an automatic generation process for the reactions and their kinetic parameters started from a previous work based on DMM. The detailed model finally obtained consists of 282 species and 2657 reactions. The detailed model underwent an automatic lumping procedure, obtaining a mechanism with 176 species and 2486 reactions.

2.3. Numerical optimization

The lumped mechanism, obtained as explained above, underwent a reaction class-based optimization, which was implemented in OptiSMOKE++ [1].

The OptiSMOKE++ toolbox applies heuristic optimization strategies to iteratively calibrate kinetic parameters. The optimization can be performed against experimental measurements in ideal reactors (ST, JSR or PFR) and 1-D laminar flames, by selecting different targets as well as against artificially generated data. The numerical routines employed are performed by OpenSMOKE++, while the DAKOTA toolkit handles different optimization algorithms. The objective function in optimizing a kinetic scheme is highly non-linear, which makes it difficult to use gradient-based algorithms due to the non-linearity of each kinetic constant. As a result, according to the work of several authors, a Genetic Algorithm has been applied to address the issue. OptiSMOKE++ exploits the CurveMatching framework [4] as the objective function for the minimization problem. The CurveMatching framework handles model predictions and experimental as functional data, by interpolating them with B-Splines with roughness penalty on the second derivative. The agreement is then quantified using the mean of the extended L^2 -

norm, as well as Pearson correlations in order to compare the shape of the curves and those of their first derivatives. In such a way 4 indices are defined, bound between 0 and 1, respectively indicating the worst and best similarity with experimental data.

$$d_{L2}^0(f, g) = \frac{1}{1 + \frac{\|f - g\|}{|D|}} \in (0, 1) \quad (1)$$

$$d_{L2}^1(f, g) = \frac{1}{1 + \frac{\|f' - g'\|}{|D|}} \in (0, 1) \quad (2)$$

$$d_p^0(f, g) = 1 - \frac{1}{2} \left\| \frac{f}{\|f\|} - \frac{g}{\|g\|} \right\| \in (0, 1) \quad (3)$$

$$d_p^1(f, g) = 1 - \frac{1}{2} \left\| \frac{f'}{\|f'\|} - \frac{g'}{\|g'\|} \right\| \in (0, 1) \quad (4)$$

where $\|f\| = \sqrt{\int_a^b f(x)^2 dx}$, and D is the intersection between the domains of the two functions. For each dissimilarity measure, the minimum value is zero, indicating minimal dissimilarity between f and g . In order to set the maximum value of the two dissimilarity measure to 1, f and g are divided by the maximum value of the experimental curve f and f' and g' by the maximum value of the first derivative of the experimental curve f' .

Moreover, in order to take into account the experimental uncertainty, when available, it is possible to adopt a bootstrap evaluation procedure. Thus a synthetic score index of the CurveMatching will be computed as reported in Equation 5 and the global objective function assumes the form reported in Equation 6.

$$CM_i = \frac{d_{i,L2}^0 + d_{i,L2}^1 + d_{i,p}^0 + d_{i,p}^1}{4} \in (0, 1) \quad (5)$$

$$Obj = \frac{1}{N} \sum_i \left(1 - \frac{1}{N_b} \sum_j^{N_b} CM_{i,j} \right) \quad (6)$$

The original toolbox proposed by Furst et al. [1] treats all the parameters of the selected rate constants according to the modified Arrhenius expression where the logarithmic form is adopted.

$$\ln(k) = \ln(A) + \beta \ln(T) - \frac{E_a}{R} \frac{1}{T} \quad (7)$$

Hence to each rate is assigned an uncertainty factor (f_r) in the form of:

$$f_r = \frac{k_{max} - k_0}{\ln(10)} = \frac{k_0 - k_{min}}{\ln(10)} \quad (8)$$

The parameters undergoing the optimization are the pre-exponential factor A , temperature exponent β , and the activation energy E_a . They are considered continuous random variables, usually assumed to be uniformly or normally distributed. Furthermore, during the optimization, they are subjected to non-linear constraints derived from Equation 8. Sets of Arrhenius parameters violating the constraints are excluded by applying a penalty function.

Leveraging the fact that all the reactions belonging to a specific class of reaction share a common reference parameter, the idea is to optimize only the three Arrhenius parameters for the reference kinetic and after that scale the reaction rate of the other reactions belonging to the same class accordingly. So after the optimization of kinetic parameters for the reference reaction of the class, the parameters for the other reactions belonging to the same class are scaled by employing the following rules:

$$f_{scaling}^A = \frac{\ln(A_{opt})}{\ln(A_{ref})} \quad (9)$$

$$f_{scaling}^\beta = \beta_{opt} - \beta_{ref} \quad (10)$$

$$f_{scaling}^{\frac{E}{R}} = \left(\frac{E}{R} \right)_{opt} - \left(\frac{E}{R} \right)_{ref} \quad (11)$$

The Equations above reflect the idea that if there is a relationship between the reference kinetic parameter and the parameter of a reaction belonging to a reaction class by a factor of two, then once the reference kinetic parameter is optimized this proportion must be retained, and this must be true for all the three Arrhenius parameters. Moreover, it is worth underlying that the scaling factors are assigned apriori since they are specifically conceived by the kinetic modeler and so they have to remain constant.

3. Results and Discussion

In this section, the optimization of the selected reaction classes is applied to the lumped mechanism for the combustion of OME₁₋₄, obtained as explained in section 2.2. The optimization was

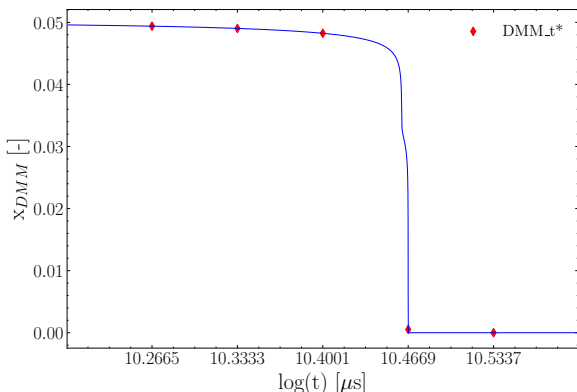


Figure 1: Times chosen for the local sensitivity analysis for DMM $\phi = 1$, $P = 10\text{atm}$, $T = 600\text{K}$.

carried out against ignition delay time experiments from the works of Gillespie [5] and Cai et al. [3]. Then, the performances of the optimized mechanism were tested against the lumped and the detailed mechanism with respect to the experimental data. All the validation was done exploiting SciExpeM [2] as a framework and the CurveMatching for assessing the performances.

3.1. Selection of the classes

The proposed methodology for mechanisms optimization aims at improving the reference parameters for the selected classes of reaction considering all target datasets and parameters, simultaneously.

In order to perform the optimization, the classes of reactions have been identified by performing a local sensitivity analysis at different times based on the DMM conversion in a ST reactor. The range examined is $\phi = 1$, $P = 10\text{atm}$, $T = 600 - 1300\text{K}$. After performing local sensitivity analyses at each temperature, the indexes are normalized and the highest absolute value of each reaction is selected to avoid duplicates. This summary of the sensitivity analysis is then provided by PySMOKEPostProcessor (see Figure 2). In order to avoid altering the lumped species, only the most sensitive reactions involving DMM as a reactant have been selected. From this analysis seven H-abstraction reactions by different radicals have emerged as the most sensitive ones (see Figure 1 and 2). A summary of the reaction classes optimized in this work is reported in Table 1.

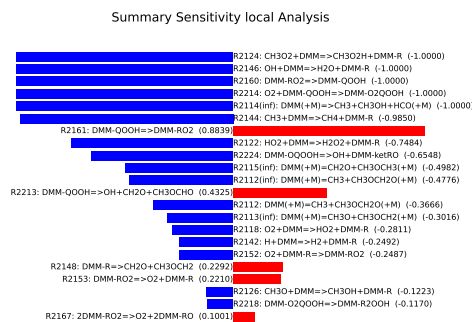


Figure 2: Summary of the local sensitivity analysis for DMM $\phi = 1$, $P = 10\text{atm}$, $T = 600 - 1300\text{K}$.

3.2. Model Optimization and Validation

All mechanisms were finally validated against a wide range of experiments, including IDTs in STs, speciations in JSRs and Plug Flow Reactors, and LFSs. Figure 3 shows the comparison between the detailed, lumped and optimized model against the experimental measurements for OME_1 from the work of Gillespie [5]. It is clear from the plot that the optimized model has better performance than the lumped one, recovering the error introduced by the latter with respect to the detailed model itself. The two datasets with equivalence ratios equal to 0.5 and 1 were not employed during the optimization. However, the model still reproduces quite reasonably the trends and its performances are still good. The DMM rates were consistently used as the reference kinetic parameters throughout the process. To validate the proposed procedure, Figure 4 displays three distinct datasets for OME_2 as a fuel, each at a pressure of 20bar and varying equivalence ratios. The datasets for equivalence ratios of 0.5 and 1 were not utilized in the optimization process. Although the model performs well overall, the set at $\phi = 1$ exhibits some inaccuracies, likely attributable to the limited number of experimental datasets used during optimization. More rigorous constraints on the process would undoubtedly improve the results. Similarly, Figure 5 illustrates the same considerations for OME_3 . For this specie two datasets were utilized as optimization targets, specifically IDT at $P = 10 - 20\text{bar}$ and $\phi = 1$. When examining the results obtained at $\phi = 2$,

Reaction Class	Summary
H-abstraction by OH	$OH + OME_n \rightarrow H_2O + OME_n - R$
H-abstraction by H	$H + OME_n \rightarrow H_2 + OME_n - R$
H-abstraction by O	$O + OME_n \rightarrow OH + OME_n - R$
H-abstraction by HO_2	$HO_2 + OME_n \rightarrow H_2O_2 + OME_n - R$
H-abstraction by O_2	$O_2 + OME_n \rightarrow HO_2 + OME_n - R$
H-abstraction by CH_3	$CH_3 + OME_n \rightarrow CH_4 + OME_n - R$
H-abstraction by CH_3O_2	$CH_3O_2 + OME_n \rightarrow CH_3O_2H + OME_n - R$

Table 1: Summary of the H-abstraction reaction classes used within the optimization.

it was observed that the overestimation in the medium temperature range was partially recovered, and the underestimation introduced by the lumped mechanism was significantly corrected. Given the lack of experimental data, the optimization target was the experimental dataset of OME_4 at $\phi = 1$. Despite this constraint, the optimized model surpasses the detailed model (as seen in Figure 6).

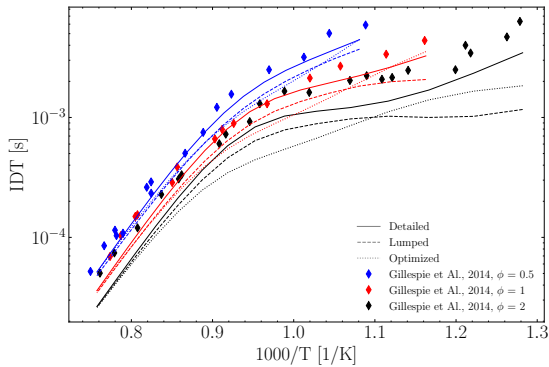


Figure 3: IDTs of DMM at $P = 3.5bar$ and $\phi = 0.5 - 2$. DMM and O_2 are diluted in 99% Ar.

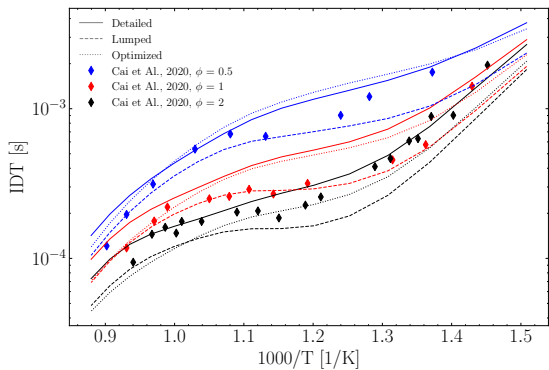


Figure 4: IDTs of OME_2 at $P = 20bar$ and $\phi = 0.5 - 2$. OME_2 is diluted in Air.

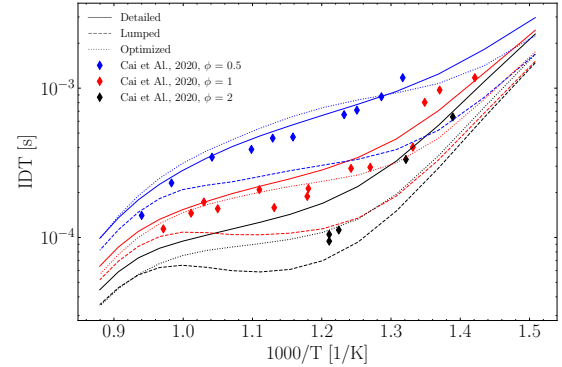


Figure 5: IDTs of OME_3 at $P = 20bar$ and $\phi = 0.5 - 2$. OME_3 is diluted in Air.

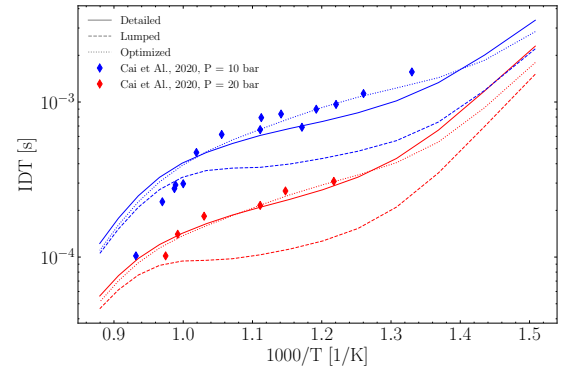


Figure 6: IDTs of OME_4 at $P = 10 - 20bar$ and $\phi = 1$. OME_4 is diluted in Air.



Figure 7: Average CM index for the three mechanisms examined per fuel.

Class	Species	Lumped			Optimized		
		A	β	Eatt/R	A	β	Eatt/R
H-abstraction by OH	OME_1	$8.52 \cdot 10^2$	3.21	-1860.85	$4.58 \cdot 10^2$	3.17	-1866.21
	OME_2	$2.91 \cdot 10^2$	3.33	-2002.62	$1.58 \cdot 10^2$	3.29	-2149.56
	OME_3	$5.20 \cdot 10^2$	3.27	-1926.05	$2.76 \cdot 10^2$	3.23	-2008.48
	OME_4	$8.22 \cdot 10^2$	3.22	-1870.32	$4.40 \cdot 10^2$	3.18	-1891.45
H-abstraction by H	OME_1	$1.30 \cdot 10^6$	2.44	4826.49	$4.11 \cdot 10^6$	2.38	4570.93
	OME_2	$1.57 \cdot 10^6$	2.31	4915.92	$4.56 \cdot 10^6$	2.25	4719.35
	OME_3	$4.55 \cdot 10^6$	2.20	4986.44	$1.33 \cdot 10^7$	2.15	4863.01
	OME_4	$8.26 \cdot 10^6$	2.15	5010.74	$2.68 \cdot 10^7$	2.09	4858.39

Table 2: Kinetic constant parameters for H-abstraction by OH and H, for the nominal mechanism and the optimized one.

4. Conclusions

In this work, an optimization methodology was applied to calibrate the reaction rate of different classes of reaction. The presented method resulted in a kinetic mechanism consistent with the underlying chemistry, while also achieving good agreement with experimental data, including data points not included in the optimization process. The methodology largely reduces the number of parameters to be considered and therefore it is applicable even in the case where a large number of important reactions are present. The methodology allows the discovery and calibration of parameters that are difficult to obtain with computational chemistry tools or experimental measurements, or which have not been studied yet. The optimization results are summarized in Figure 7 in terms of CM index per each model and each fuel. Some refinements can be envisioned in the next future: first of all, the optimization can be extended to the remaining reaction classes of OMEs, thus extending the number of degrees of freedom of the system. The scaling factors are the crucial element for both optimization and generation. By utilizing the sensitivity analysis method proposed, the most sensitive reactions can be identified, and the mechanism can be appropriately categorized.

References

[1] Magnus Fürst, Andrea Bertolino, Alberto Cuoci, Tiziano Faravelli, Alessio Frassoldati, and Alessandro Parente. Optismoke++: A

toolbox for optimization of chemical kinetic mechanisms. *Computer Physics Communications*, 264:107940, 2021.

- [2] Edoardo Ramalli, Timoteo Dinelli, Andrea Nobili, Alessandro Stagni, Barbara Pernici, and Tiziano Faravelli. Automatic validation and analysis of predictive models by means of big data and data science. *Chemical Engineering Journal*, 454:140149, 2023.
- [3] Liming Cai, Sascha Jacobs, Raymond Langer, Florian vom Lehn, Karl Alexander Heufer, and Heinz Pitsch. Auto-ignition of oxymethylene ethers (omen, n = 2–4) as promising synthetic e-fuels from renewable electricity: shock tube experiments and automatic mechanism generation. *Fuel*, 264:116711, 2020.
- [4] Matteo Pelucchi, Alessandro Stagni, and Tiziano Faravelli. Chapter 15 - addressing the complexity of combustion kinetics: Data management and automatic model validation. In Tiziano Faravelli, Flavio Marenti, and Eliseo Ranzi, editors, *Mathematical Modelling of Gas-Phase Complex Reaction Systems: Pyrolysis and Combustion*, volume 45 of *Computer Aided Chemical Engineering*, pages 763–798. Elsevier, 2019.
- [5] Fiona Rita Gillespie. An experimental and modelling study of the combustion of oxygenated hydrocarbons. *National University of Ireland*, 2014.