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Supplementary Materials

Optimization of Kinetic Mechanism for Ethylene Combustion Based on Machine Learning

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Table S1. IDT and LFS measurements of ethylene-oxygen mixtures.

Type	Author	Year	*T*(K)	*P*(atm)	*φ*	Diluents	DataPoints
IDT	Mathieu [1]	2015	1181–1808	0.89–2.15	0.5–2.0	AR	53
	Colket [2]	2001	1125–1414	4.83–7.89	0.5–1.0	AR	27
	Kalitan [3]	2005	1115–1754	0.94–3.26	0.5–1.0	AR	79
	Deng [4]	2017	1090–1600	1.2–10	1	AR	26
	Shao [5]	2018	1095–1317	15.5–63.3	1.0–2.0	AR	33
	Wan [6]	2019	721–1307	0.97–20.54	0.5–2.0	N_2	116
LFS	Egolfopoulos [7]	1991	298	0.5–2.0	0.45–2.2	N_2	52
	Huo [8]	2019	298	0.75–10.0	0.6–1.8	N_2	41
	Wang [9]	2024	298–358	1.0	0.7–2.0	N_2	28
	Marco [10]	2021	298	1.0	0.7–2.0	N_2	14
	Ma [11]	2021	298	1.0–5.0	0.7–1.5	N_2,HE	35
	Konnov [12]	2008	298	1.0	0.6–1.8	N_2	81
	Ravi [13]	2015	298	1.0	0.6–1.8	N_2	9
	Kumar [14]	2008	298–470	1.0	0.5–1.4	N_2	40
	Huo [15]	1998	298	0.5–4.0	0.8–1.6	N_2	35

Based on the species selection in the minimized methane kinetic mechanism [16] and detailed kinetic mechanisms, CH_2 and CH were introduced as additional species to the minimized ethylene kinetic mechanism. Relevant elementary reactions and their kinetic parameters that do not involve new species were collected. Where original parameters followed a three-parameter Arrhenius format, these were converted to a two-parameter form (A, E_a) and parameter fitting was performed across the temperature range of 300-3000 K. The resulting kinetic parameters were presented in Table S2.

Table S2. Compilation of kinetic parameters.

No.	Reactions	*A* / ($cm^3 \cdot mol^{-1} \cdot s^{-1}$)	E_a / ($cal \cdot mol^{-1}$)	References
1	$C_2H_4 + O <=> CH_2 + CH_2O$	2.81×10^{13}	5625	[17]
2		2.80×10^{13}	5624	[11]
3	$C_2H_2 + O <=> CH_2 + CO$	1.47×10^{13}	4250	[17]
4		1.47×10^{13}	4250	[18]
5		1.47×10^{13}	4250	[11]
6	$CH_2 + OH <=> CH + H_2O$	5.89×10^{13}	5777	[18]
7		5.21×10^{12}	9580	[11]
8	$CH_2 + O_2 <=> CO_2 + 2H$	2.27×10^{12}	1110	[17]
9		4.54×10^{12}	1110	[11]
10	$CH_2 + O_2 <=> CO + H + OH$	1.40×10^{9}	1110	[17]
11		6.58×10^{12}	1491	[18]
12	$CH_2 + O_2 <=> CO_2 + H_2$	2.63×10^{12}	1491	[18]
13	$CH_2 + O_2 <=> HCO + OH$	1.28×10^{13}	1734	[16]
14	$CH + OH <=> HCO + H$	3.00×10^{13}	0	[11]
15	$CH + OH <=> CO + H + H$	3.40×10^{12}	690	[11]
16	$CH + O_2 <=> HCO + O$	6.32×10^{13}	577	[18]
17		1.60×10^{13}	910	[11]
18	$CH + O <=> CO + H$	4.00×10^{13}	0	[18]

The proposed modification schemes and their predicted errors were presented in Table S3. Furthermore, given that prediction errors for IDT typically exceed those for LFS in kinetic mechanisms, and considering the lower computational cost of IDT simulations, genetic algorithm was employed to individually optimize IDT predictions for the nine schemes exhibiting the smaller total mean relative errors. The optimization boundaries for the pre-exponential factors are set to multiplicative factors of 0.1–10 relative to their initial values, while those for activation energies are set to additive offsets of ±5000 cal/mol from initial values. Among all modification schemes, Scheme 6 demonstrated high prediction accuracy with the addition of only the CH_2 species and two associated elementary reactions. Following optimization specifically targeting IDT, optimized mechanism of this scheme maintained low average relative error in IDT predictions and exhibited superior performance in balancing predictive accuracy and mechanism size. Consequently, Scheme 6 was selected for comprehensive optimization of the 28-step minimized ethylene kinetic mechanism proposed in this study.

Table S3. Mechanism modification schemes and corresponding prediction errors.

No.	New Reactions No.	Mean Relative Error of IDT	Mean Relative Error of LFS	Total Mean Relative Error	Mean Relative Error of IDT (Post Single-IDT Optimization)
1	1, 8,	0.7753	0.2847	0.5400	/
2	1, 10,	0.5907	0.3876	0.4933	/
3	1, 13,	0.7004	0.2709	0.4944	/
4	3, 10,	0.4957	0.3932	0.4465	/
5	3, 12,	0.4142	0.2383	0.3299	0.3246
6	3, 13,	0.3761	0.2575	0.3192	0.2926
7	1, 3, 8, 10,	0.7669	0.3889	0.5856	/
8	1, 3, 8, 13,	0.7147	0.3041	0.5178	/
9	1, 3, 10, 13,	0.6892	0.2934	0.4994	/
10	1, 3, 12, 13,	0.6435	0.2616	0.4604	/
11	4, 9, 11, 12, 16	0.3810	0.2382	0.3125	0.2951
12	4, 9, 11, 13, 16	0.3757	0.2593	0.3199	0.2989
13	4, 9, 12, 13, 16	0.3786	0.2434	0.3138	0.2948
14	4, 9, 11, 12, 16, 18,	0.3810	0.2380	0.3125	0.2933
15	4, 9, 11, 13, 16, 18,	0.3767	0.2591	0.3203	0.2929
16	4, 9, 12, 13, 16, 18,	0.3786	0.2433	0.3137	0.2966
17	2, 5, 7, 9, 14, 15, 17	0.7796	0.4008	0.5980	/
18	2, 5, 7, 11, 14, 15, 17	0.7409	0.4008	0.5778	/
19	2, 5, 7, 12, 14, 15, 17	0.4418	0.2322	0.3413	0.2865
20	2, 5, 7, 13, 14, 15, 17	0.6894	0.2933	0.4995	/

Calculation of weighting coefficients for the objective function optimization employed the α-method. This method establishes a system of linear equations based on the minima of each component objective function f_i

within the feasible domain F and an initially introduced parameter α Solving this system determines the corresponding weighting coefficients.

For the case of two component objective functions (i=2), the computational procedure of this method is as follows:

First, find the minimizers of the component objective functions f_1 and $f_2$within the feasible domain F, denoted as x_1*和 x_2*. If x_1*≠x_2*, calculate:

$$f_{11}=f_1(x_1^*) \tag{S1}$$

$$f_{12}=f_1(x_2^*) \tag{S2}$$

$$f_{21}=f_2(x_1^*) \tag{S3}$$

$$f_{22}=f_2(x_2^*) \tag{S4}$$

Construct the following system of linear equations involving the parameter α and the weighting coefficients λ_1, λ_2:

$$\begin{cases} \lambda_1 f_{11} + \lambda_2 f_{21} = \alpha \\ \lambda_1 f_{12} + \lambda_2 f_{22} = \alpha \\ \lambda_1 + \lambda_2 = 1 \end{cases} \tag{S5}$$

Solve the above system of linear equations, yielding the unique solution:

$$(\lambda_1, \lambda_2) = \frac{e^{\mathrm{T}} A^{-1}}{e^{\mathrm{T}} A^{-1} e}, \ \alpha = \frac{1}{e^{\mathrm{T}} A^{-1} e} \tag{S6}$$

where:

$$A = \begin{pmatrix} f_{11} & f_{12} \\ f_{21} & f_{22} \end{pmatrix}, \ e = \begin{pmatrix} 1 \\ 1 \end{pmatrix} \in \mathrm{R}^2 \tag{S7}$$

The mean relative error of IDT was defined as the first objective function f_1, and the mean relative error of LFS was defined as the second objective function f_2. Using this method, the weighting coefficients for 26-step minimized ethylene kinetic mechanism are set to (λ_1, λ_2) = (0.5, 0.5), and the weight coefficients for 28-step minimized ethylene kinetic mechanism are set to (λ_1, λ_2) = (0.3, 0.7).

This study collected five detailed mechanisms from the past few decades for comparative analysis. Table S4 lists all the mechanisms and provides information about their size.

Table S4. Mechanism information.

Mechanism	Species	Reactions	References
Aramco3.0	581	3037	[19]
CRECK	114	1999	[20]
UCSD	57	268	[18]
USC2.0	111	784	[21]
Ma	45	401	[11]

Figure S1 shows the distributions of relative errors. As shown in the figure, the UCSD mechanism demonstrated the best predictive capability for IDT, while its performance in predicting LFS was slightly inferior to the other four mechanisms. Although all the detailed mechanisms achieved relatively accurate predictions for both IDT and LFS, the UCSD and Ma mechanisms are significantly smaller in size compared to the others. Since this work is focused on the minimized ethylene kinetic mechanism, the UCSD and Ma mechanisms were selected for further validation in subsequent analysis.

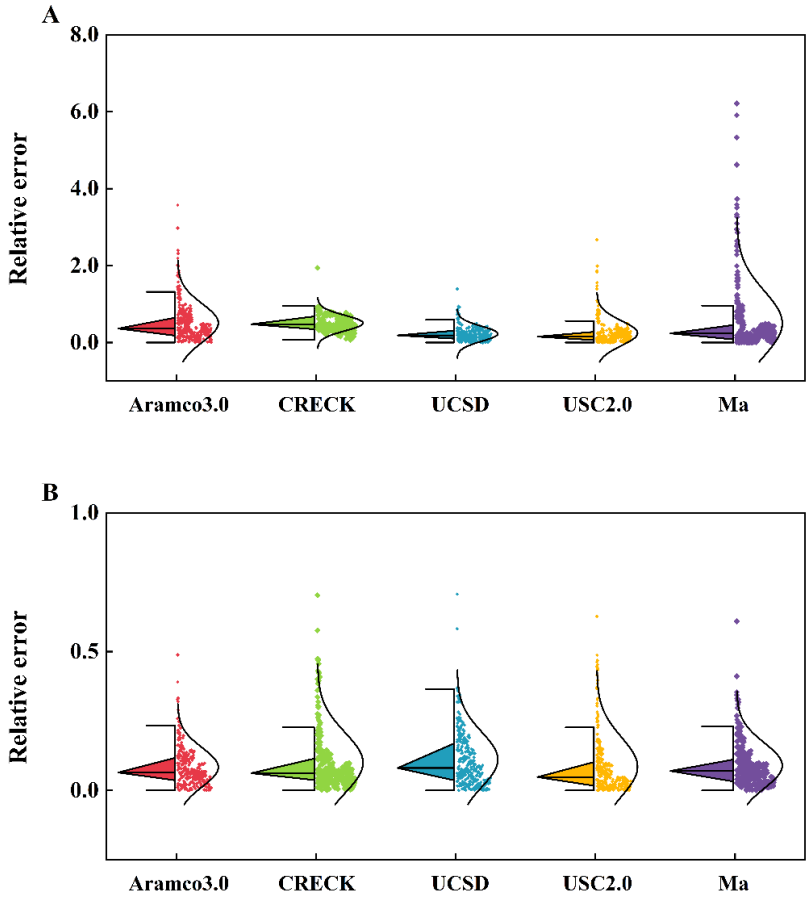

Figure S1. Box plots of the relative errors in predicted IDT(A) and LFS(B) by the detailed mechanisms.

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