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Jéssica Fernanda Rebelo

**Benchmarking Ethanol Combustion Mechanisms: Predictive Performance Gaps
in Ignition, Flame Speed, and Species Profiles**

Joinville
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This Master's dissertation was evaluated and approved by an examination committee
consisting of the following members:

Rafael de Camargo Catapan, Dr.
Federal University of Santa Catarina

Agenor De Noni Junior, Dr.
Federal University of Santa Catarina

Juan Miguel Mantilla Gonzalez, Dr.
National University of Colombia

We hereby certify that this is the **final and original version** of the thesis, which has
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This work is dedicated to my family and friends.

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"The important thing is not to stop questioning; curiosity has its own reason for existing".

(EINSTEIN, A)

ABSTRACT

The growing concerns about climate change have intensified the efforts to reduce greenhouse gas (GHG) emissions, leading to the investment in renewable fuels. Among the alternatives, ethanol stands out as the most viable solution, whether used as pure fuel or as a fuel additive. To fully explore the benefits of ethanol as a biofuel in internal combustion engines (ICEs), accurate kinetics mechanisms for its oxidation and pyrolysis are required. However, although chemical kinetics and mechanism development has advanced significantly, current models retain inherent limitations, and their accuracy varies significantly with simulation conditions. But while numerous works are related to the development and assessment of chemical kinetics mechanisms for ethanol, a quantitative evaluation of these mechanisms, addressing their strengths and weaknesses, is still absent from the literature. Therefore, this work addresses this gap by evaluating seven mechanisms (Aramco v3.0, Mittal, Creck, LLNL, San Diego, Zhang, PCRL) and comparing them against experimental data from shock tube (ST), jet-stirred reactor (JSR), and laminar flame speed (LFS). All simulations employed the Cantera-Python interface, using a brute-force sensitivity analysis (BFSA) to identify key reactions and the root mean square (RMS) % method to quantify predictive uncertainties. Arrhenius parameters for dominant reactions were evaluated to identify possible sources of disparity. The results demonstrate that the PCRL mechanism is optimal for predicting flame speeds and species, while the Zhang mechanism performs best for ignition. The Mittal mechanism also demonstrated a good performance overall. However, all mechanisms failed to predict CO, CO₂, H₂O, and O₂. The results directly impact the predictive simulations of pollutants and underscore the need for a thorough revision of carbon oxidation pathways in future kinetics models. Consequently, this study not only provides a guide for mechanism selection but also directs future research toward the critical knowledge gaps preventing truly predictive modeling of ethanol combustion.

Keywords: ethanol, ignition delay times, laminar flame speed, detailed chemical kinetics, combustion modelling

RESUMO EXPANDIDO

RESUMO

A preocupação crescente com as mudanças climáticas intensificou os esforços para reduzir as emissões de gases de efeito estufa (GEE), levando ao investimento em combustíveis renováveis. Entre as alternativas, o etanol destaca-se como a solução mais viável, seja usado como combustível puro ou como aditivo. Para explorar plenamente os benefícios do etanol como biocombustível em motores de combustão interna (MCIs), são necessários mecanismos cinéticos precisos para sua oxidação e pirólise. No entanto, apesar dos avanços significativos na cinética química e no desenvolvimento de mecanismos cinéticos, os modelos ainda apresentam limitações inerentes, e a sua precisão varia significativamente dependendo das condições de simulação. Embora inúmeros trabalhos estejam relacionados ao desenvolvimento e avaliação de mecanismos cinéticos químicos para o etanol, ainda falta na literatura uma análise quantitativa desses mecanismos, abordando seus pontos fortes e fracos. Portanto, este trabalho preenche essa lacuna avaliando sete mecanismos (Aramco v3.0, Mittal, Creck, LLNL, San Diego, Zhang, PCRL), comparando-os com dados experimentais de tubos de choque, reator de mistura por jatos e velocidade de chama laminar. A interface Cantera-Python foi aplicada em todas as simulações, utilizando a análise de sensibilidade de força bruta (BFSA) para identificar reações chave, e o método da raiz média quadrática (RMS) % para quantificar as incertezas preditivas. Os parâmetros de Arrhenius das reações dominantes foram avaliados para identificar possíveis fontes de disparidade. Os resultados demonstram que o mecanismo PCRL é o mais adequado para prever velocidades de chama e concentrações de espécies, enquanto o mecanismo de Zhang apresenta o melhor desempenho para tempos de atraso da ignição. O mecanismo de Mittal também demonstrou um bom desempenho geral. Entretanto, todos os mecanismos falharam em prever as concentrações de CO, CO₂, H₂O e O₂. Esses resultados impactam diretamente as simulações preditivas de poluentes e resalta a necessidade de uma revisão aprofundada das rotas de oxidação do carbono em futuros modelos cinéticos. Consequentemente, este estudo não apenas fornece um guia para a seleção de mecanismos, mas também direciona pesquisas futuras para as lacunas de conhecimento críticas que impedem a modelagem verdadeiramente preditiva da combustão do etanol.

Palavras-chave: etanol, tempo de atraso de ignição, velocidade de chama laminar, mecanismos cinéticos detalhados, modelagem de combustão

INTRODUÇÃO

Os motores de combustão interna (MCIs) são o principal método de propulsão de veículos (HEYWOOD, 2018). No entanto, embora os combustíveis fósseis sejam amplamente conhecidos por emitir uma grande quantidade de gases de efeito estufa (GEE), os combustíveis derivados do petróleo ainda predominam frente aos biocombustíveis. Neste contexto, os biocombustíveis, em especial os álcoois derivados de biomassa, ganham destaque. Dentre essas alternativas, o etanol surge como a solução mais viável para (MCIs) no Brasil, devido à sua capacidade de reduzir emissões de NO_x , sua alta octanagem e seu custo competitivo (MENDIBURU et al., 2022).

Para explorar plenamente o potencial do etanol, é essencial uma compreensão detalhada de sua combustão por meio de modelagem cinética. No entanto, os mecanismos cinéticos para etanol disponíveis na literatura frequentemente possuem validação restrita a condições específicas, carecendo de uma avaliação sistemática e abrangente em múltiplos regimes de combustão, tais como tempos de ignição, velocidades de chama e perfis de espécies químicas. Adicionalmente, estudos comparativos existentes geralmente se concentram em parâmetros isolados, deixando uma lacuna: a falta de um guia do usuário que quantifique a acurácia e identifique as melhores aplicações de cada mecanismo.

Este trabalho preenche essa lacuna realizando uma avaliação sistemática e multi-paramétrica de sete mecanismos de combustão de etanol amplamente utilizados (Aramco v3.0, Mittal, Creck, LLNL, San Diego, Zhang, PCRL). Através da comparação com dados experimentais de diferentes configurações (tubos de choque, reator de mistura por jatos e velocidade de chama laminar), da quantificação de incertezas utilizando do método da raiz média quadrática (RMS) %, bem como análise de sensibilidade de força bruta, este estudo visa (i) identificar os modelos mais confiáveis para regimes específicos, (ii) delimitar suas faixas de aplicação e (iii) destacar prioridades para o refinamento futuro de mecanismos cinéticos.

OBJETIVO

O objetivo principal deste trabalho é realizar um *benchmark* de mecanismos detalhados de combustão de etanol e avaliar sua acurácia preditiva para tempos de atraso da ignição, velocidades de chama laminar e perfis de concentração de espécies químicas em uma faixa específica de temperaturas (700–1250 K), pressões (1–50 atm) e razões de equivalência ($\varphi = 0,3$ –1,55).

OBJETIVOS ESPECÍFICOS

Para atingir o objetivo principal, propõem-se os seguintes objetivos específicos:

- **Objetivo 1:** Desenvolver uma base de dados experimental referente à combustão etanol-ar - **Atividade Relacionada:** Coletar e organizar dados experimentais de tempo de atraso de ignição, velocidade de chama laminar e concentrações de espécies na combustão etanol-ar disponíveis na literatura.
- **Objetivo 2:** Compilar uma base de dados de modelos cinéticos detalhados para etanol. - **Atividade Relacionada:** Revisar e selecionar mecanismos cinéticos detalhados recentes para cinética do etanol disponíveis na literatura;
- **Objetivo 3:** Comparar o desempenho dos mecanismos selecionados (por intermédio das simulações de tempo de atraso de ignição, velocidade de chama e perfis de espécies) por comparação direta com a base de dados experimental. - **Atividade Relacionada:** Realizar simulações numéricas sistemáticas utilizando a interface Cantera-Python, para obter previsões numéricas para cada modelo cinético detalhado utilizado neste trabalho e subsequentemente comparar com os valores experimentais para atraso de ignição, velocidade de chama laminar e perfis de espécies.
- **Objetivo 4:** Avaliar os mecanismos cinéticos. - **Atividade Relacionada:** Realizar análise de sensibilidade com a interface Cantera-Python, para identificar as reações mais importantes nas condições selecionadas;
- **Objetivo 5:** Identificar os mecanismos com melhor desempenho para cada alvo (atraso de ignição, velocidade de chama laminar e perfis de espécies) - **Atividade Relacionada:** Quantificar estatisticamente as incertezas das previsões.
- **Objetivo 6:** Identificar lacunas de desempenho e fornecer recomendações para o desenvolvimento futuro de mecanismos. - **Atividade Relacionada:** Destacar condições (ex.: baixa temperatura) e espécies com desempenho insatisfatório, propondo refinamentos específicos.

METODOLOGIA

A metodologia adotada neste trabalho compreendeu as seguintes etapas principais:

AVALIAÇÃO QUANTITATIVA DOS MECANISMOS

Para quantificar a discrepância entre os mecanismos e os dados experimentais, foi utilizado o método estatístico da raiz média quadrática (RMS) %. Esta métrica permite avaliar a magnitude média das incertezas entre valores simulados e experimentais.

MECANISMOS CINÉTICOS INVESTIGADOS

Foram avaliados sete mecanismos cinéticos detalhados para a combustão de etanol: LLNL (2004), Creck (2012), Mittal (2014), San Diego (2016), Zhang (2018), Aramco v3.0 (2018) e PCRL (2020).

BASE DE DADOS EXPERIMENTAL

Para avaliar a incerteza dos mecanismos, compilou-se uma base de dados experimentais a partir da literatura especializada, abrangendo:

- Tempos de ignição em tubos de choque (789–1234 K, 25–51 atm);
- Velocidades de chama laminar (298–358 K, 1 atm);
- Perfis de concentração de espécies em reator de mistura por jatos (890–1250 K, 1 atm).

MODELAGEM COMPUTACIONAL

As simulações foram realizadas utilizando a interface Cantera-Python, abrangendo três tipos de sistemas reativos:

- Tempos de ignição em reator homogêneo adiabático a volume constante;
- Velocidades de chama laminar livremente propagante;
- Perfis de concentração em reator de mistura por jatos.

ANÁLISE DE SENSIBILIDADE

Realizou-se análise de sensibilidade de força-bruta para identificar as reações limitantes que mais influenciam nas discrepâncias. As condições avaliadas foram:

- Tempos de ignição (30 atm, $\phi = 1.0$, 800 K e 1200 K);
- Velocidades de chama laminar (1 atm, 358 K, $\phi = 0.70$ e 1.55).

As constantes de taxa foram perturbadas por fatores de 0.5 e 2.0 para avaliar seu impacto nas variáveis de interesse.

RESULTADOS E DISCUSSÃO

A avaliação sistemática dos sete mecanismos cinéticos revelou desempenhos distintos conforme o parâmetro de combustão analisado:

DESEMPENHO DOS MECANISMOS

Tempos de Ignição (IDT):

- **Mecanismo Zhang:** melhor desempenho global (RMS: 15–311%);
- **Aramco, Creck, Mittal e PCRL:** boa precisão em altas temperaturas;
- **LLNL e San Diego:** subestimaram sistematicamente os atrasos de ignição;
- Reações de abstração de H nos sítios α e β por radicais $\text{HO}_2^\bullet$ identificadas como críticas.

Velocidade de Chama Laminar (LFS):

- **PCRL:** mais preciso (RMS: 6,24–9,49%);
- **Zhang:** bom desempenho (RMS: 7,98–11,05%);
- **San Diego:** superestimou velocidades em misturas pobres;
- **LLNL:** subestimou velocidades em misturas ricas.

Perfis de Espécies em JSR:

- Todos os mecanismos reproduziram adequadamente o consumo de $\text{C}_2\text{H}_5\text{OH}$;
- **PCRL:** melhor precisão global para espécies oxidadas;
- **Dificuldade generalizada** em prever CO , CO_2 , H_2O e O_2 ;
- Maiores discrepâncias acima de 1150 K.

PRINCIPAIS FONTES DE DISCREPÂNCIA

A análise de sensibilidade e comparação de parâmetros de Arrhenius identificou:

- Parâmetros divergentes para reações de abstração de hidrogênio por $\text{HO}_2^\bullet$;
- Tratamento inadequado da decomposição de H_2O_2 em mecanismos antigos;
- Omissão de vias de oxidação de acetaldeído em alguns mecanismos;
- Eficiências de terceiro corpo inconsistentes em reações dependentes da pressão.

RECOMENDAÇÕES PARA SELEÇÃO

- **Multi-propósito:** Mecanismo de Zhang, o qual obteve desempenho balanceado em atrasos de ignição, chamas e espécies;
- **Velocidade de chama:** PCRL;
- **Tempo de atraso de ignição:** PCRÇ, Zhang, Aramco, Creck ou Mittal;
- **Aplicações limitadas:** LLNL e San Diego.

CONCLUSÃO

Este trabalho avaliou o desempenho de sete mecanismos de combustão de etanol através da análise comparativa de tempos de ignição, velocidades de chama laminar e perfis de concentração de espécies em reator de mistura por jatos. Os resultados demonstraram que o mecanismo de Zhang apresenta o melhor desempenho para previsão de tempos de ignição, enquanto o mecanismo PCRL destaca-se como o mais adequado para velocidades de chama laminar e perfis de espécies. Os mecanismos LLNL e San Diego mostraram limitações significativas, principalmente devido a taxas de abstração de hidrogênio subestimadas e incerteza na cinética de decomposição de H_2O_2 .

A análise de sensibilidade identificou que as vias mediadas por $\text{HO}_2^\bullet$ e a decomposição de H_2O_2 são os principais fatores responsáveis por discrepâncias em baixas temperaturas, enquanto reações relacionadas à produção/consumo de radicais livres e liberação de calor são críticas para as chamas. Um dos achados mais significativos deste trabalho foi a constatação de que todos os mecanismos, incluindo os mais detalhados, apresentam dificuldades em prever adequadamente as concentrações de O_2 , H_2O , CO_2 e CO , revelando uma lacuna fundamental no entendimento das vias de oxidação completa do carbono.

Estes resultados não representam apenas discrepâncias numéricas, mas possuem implicações diretas para a simulação preditiva da formação de poluentes. O estudo fornece um guia para seleção de mecanismos cinéticos de acordo com a aplicação desejada e direciona esforços futuros para o refinamento de vias de baixa temperatura mediadas por $\text{HO}_2^\bullet$ e da cinética de oxidação do carbono, utilizando cálculos teóricos de alto nível e experimentos em condições elevadas de pressão.

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LIST OF ABBREVIATIONS AND ACRONYMS

BFSA	brute-force sensitivity analysis
C.F. Tw-F	counterflow twin-flame
CSTR	continuously stirred tank reactor
CVB	constant volume bomb
CVR	constant volume reactor
GHG	greenhouse gas
GSA	global sensitivity analysis
ICEs	internal combustion engines
IDT	ignition delay times
JSR	jet-stirred reactor
LBV	laminar burning velocity
LFS	laminar flame speed
PFR	plug flow reactor
PSR	perfectly stirred reactor
RCM	rapid compression machine
RMS	root mean square
ST	shock tube

LIST OF SYMBOLS

σ_k	lennard-jones collision diameter
ε	depth of the intermolecular potential
$\bar{\mu}_k$	dipole moment of species k
A	pre-exponential factor
β	temperature exponent
E_a	activation energy
$\dot{m}$	mass flow rate
ρ	density
V	reactor volume
Y_{kin}	inlet mass fraction of species k
Y_k	mass fraction of each species k
$\dot{\omega}_k$	molar production rate of species k
W_k	molecular weight of species k
K	number of species
φ	equivalence ratio

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1 INTRODUCTION

Transportation heavily relies on ICEs, which are the primary method of propulsion for vehicles (HEYWOOD, 2018). While fossil fuel combustion is widely known to emit a greater quantity of greenhouse gases GHG when compared to biofuels, petroleum-derived fuels still dominate. However, oil's share of total energy demand fell below 30% in 2024 for the first time in half a century (INTERNATIONAL ENERGY AGENCY, 2024). This decline reflects not only the rise of electric vehicles but also, the growing adoption of biofuels, particularly biomass-derived alcohols such as methanol, ethanol, propanol, butanol, and pentanol. Despite the potential of these biofuels, they still face limitations associated with their use in ICEs.

Methanol, for instance, requires additives like n-pentanol to stabilize blends with diesel. Additionally, while methanol's high oxygen content improves combustion efficiency and reduces soot emissions, diesel/n-pentanol/methanol blends exhibit longer ignition delays and shorter combustion durations, leading to concentrated heat release. Also, these blends produce higher NO_x emissions (CHEN, H. et al., 2019). Butanol, though less hygroscopic than ethanol, struggles with oxidation stability and material compatibility. There is also a need to develop life cycle assessments and cost-benefit analyses (CELEBI; CENGİZ; AYDIN, 2025). Further, propanol, while less studied, shares similar challenges in energy density and scalability.

In contrast, ethanol stands out as the most viable biomass-derived alcohol for ICEs in Brazil. Ethanol reduces NO_x emissions, offers a high octane rating (OR) to prevent engine knock, and enhances combustion efficiency due to its oxygen content. Moreover, the ethanol derived from sugarcane in Brazil boasts the most competitive pricing, ranging from 0.20 to 0.30 per liter (USD) (MENDIBURU et al., 2022).

To fully leverage the potential of ethanol described above, a deep understanding of its combustion is necessary, which is facilitated by kinetic modeling techniques. These tools reduce the cost and time compared to experimental tests (WESTBROOK, Charles K. et al., 2005). The combination of theory, experiments, and simulation enables qualitative and quantitative predictions for many combustion situations of practical relevance (KOHSE-HÖINGHAUS, 2021). To achieve the full potential of these tools, a fundamental first step for kinetic modelers is to select an appropriate chemical kinetic mechanism. However, while detailed mechanisms for ethanol combustion are available in the literature, their validation often remains limited to narrow experimental ranges. For example, the San Diego mechanism was validated almost exclusively for ignition delay times (IDT) in ST at lower to moderate pressures ($p \leq 4.6$ bar) and LFS at atmospheric pressure. Hence, it lacks validation against the data from a JSR and a rapid compression machine (RCM), which are the essential regimes to capture low-temperature chemistry. Similarly, widely used mechanisms, such as the LLNL and Mittal models,

were not validated in a RCM. Even highly detailed mechanisms such as Aramco and Creck exhibit validations that do not systematically explore all combinations of parameters. The Aramco mechanism, for instance, was validated over 100 conventional and alternative fuels, but has not been rigorously tested for ethanol under extreme conditions, such as high pressures (e.g., > 20 atm) and rich equivalence ratios ($\varphi > 2.0$). In the same way, PCRL, although validated at high pressures ($p = 80$ bar) in ST, is not validated for species profiles.

Moreover, comparative studies commonly focus on isolated combustion parameters. For example, the works of Peter S. Veloo et al. (2010a) and Noorani, Akih-Kumgeh, and Bergthorson (2010) evaluated LFS and IDT, respectively, while Choudhary et al. (2021a) focused exclusively on ethanol pyrolysis in a JSR. Similarly, although studies like the one from Ranzi et al. (2012) have advanced laminar flame speed analyses and Buttgen et al. (2024) have explored IDT in RCM, these works did not integrate multi-regime data (e.g., low-temperature oxidation, high-pressure) or contrast different mechanisms. As a result, kinetic modelers lack a comprehensive 'user's guide' to these mechanisms, making it difficult to select the most robust model for a given simulation regime.

To date, no study has conducted a systematic, multi-parameter evaluation of ethanol combustion mechanisms against different experimental setups while quantifying both predictive accuracy (via uncertainty metrics) and identifying dominant kinetic pathways. This study addresses these gaps by performing a benchmark study of seven ethanol combustion mechanisms (Aramco v3.0, Mittal, Creck, LLNL, San Diego, Zhang, PCRL) against experimental data from ST, JSR, and LFS configurations. Through BFSA and uncertainty quantification via RMS %, this work aims to (i) identify the most reliable models for specific combustion regimes, (ii) delineate their applicability ranges, and (iii) highlight areas for future mechanism refinement.

1.1 OBJECTIVES

To address the gaps identified above, this research, conducted in the Graduate Program in Mechanical Engineering and Sciences at the Federal University of Santa Catarina, establishes the following objectives.

1.1.1 Main Objective

The main objective of this work is to benchmark detailed ethanol combustion mechanisms and evaluate their predictive accuracy for ignition delay times (IDT), laminar flame speeds (LFS), and species concentration profiles across a specific range of temperatures (700–1250 K), pressures (1–50 atm), and equivalence ratios ($\varphi = 0.3$ –1.55).

1.1.2 Specific Objectives

To achieve the main objective, the following specific objectives are proposed:

- **Objective 1:** To obtain an experimental ethanol-air combustion database. - **Related Activity:** To collect and organize experimental data on IDT, LFS, and species concentrations on ethanol-air combustion available in the literature.
- **Objective 2:** To obtain an ethanol detailed kinetics models database. - **Related Activity:** Review and select recent detailed kinetics mechanisms for ethanol kinetics available in the literature;
- **Objective 3:** To compare the performance of the selected mechanisms (through IDT, LFS, and species profiles) by direct comparison to the experimental database. - **Related Activity:** Performing systematic numerical simulations by using the Cantera-Python interface, to obtain numerical predictions for each detailed kinetics model used in this work and then comparing to the experimental values for IDT, LFS, and species profiles.
- **Objective 4:** To evaluate the kinetic mechanisms. - **Related Activity:** Performing sensitivity analysis with Cantera-Python interface, to identify the most important reactions under the selected conditions;
- **Objective 5:** To identify the best-performing mechanisms for each target (IDT, LFS, and species profiles) - **Related Activity:** Statistically quantify prediction uncertainties.
- **Objective 6:** To identify performance gaps and provide recommendations for future mechanism development. - **Related Activity:** Highlight underperforming conditions (e.g., low-temperature) and species, proposing targeted refinements.

1.2 OUTLINE OF THE DOCUMENT

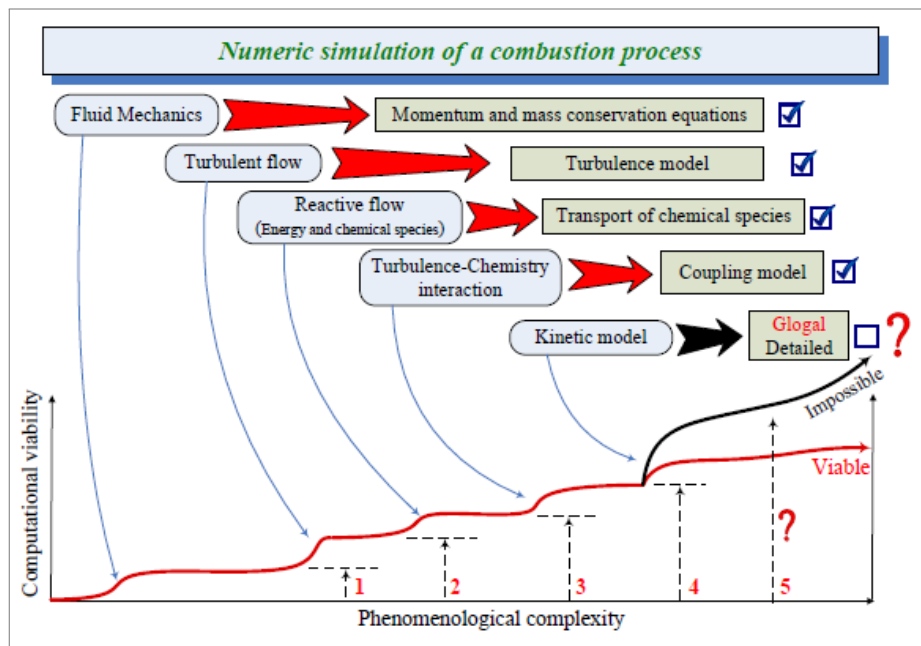
The manuscript follows a five-chapter structure, beginning with Chapter 1, which introduces the research context, problem statement, justification, and objectives. Chapter 2 reviews ethanol combustion chemistry, presents the fundamental combustion experiments and computational techniques, and also analyses existing ethanol mechanisms and their validation scopes, concluding with a state-of-the-art review. Chapter 3 describes the research methodology and design employed in this work. In Chapter 4, the results are presented and discussed. Lastly, Chapter 5 provides the conclusions and recommendations for future works, followed by references and appendices.

2 LITERATURE REVIEW

2.1 FUNDAMENTALS OF CHEMICAL KINETICS

The numerical modeling of reacting fluid flows requires solving conservation equations related to mass, momentum, energy, and the concentration of chemical species. These transport equations were addressed in an earlier work by Leonel Rincón Cancino (2009) and will not be revisited in this document. Nonetheless, in complex systems that exhibit varying time and length scales, the stiffness of species conservation equations pose significant challenges, complicating both numerical integration and spatial discretization (STEFAN, 2013). Thus, the ability to derive a numerical solution within the limits of available computational resources hinge on the phenomenological complexity of the system, as noted by Leonel Rincón Cancino (2009). Figure 1 depicts the inverse relationship between phenomenological complexity and computational feasibility.

Figure 1 – Computational viability related to the phenomenological complexity in the numerical simulation of a combustion process



Source: Leonel Rincón Cancino (2009)

Based on this, it is clear that the selection of the chemical kinetics mechanism significantly affects the effectiveness of numerical simulations. This is mostly because these kinetics mechanisms describe the chemical process using several hundreds or even thousands of reaction steps (TURÁNYI; TOMLIN, Alison S., 2014). The reaction mechanisms, in this case, are an assembly of elementary reactions together with their

rate coefficients. They describe how the reactions take place at the molecular level, with bonds being broken or formed (HEGHES, 2007).

The fundamental concepts of chemical kinetics mechanisms include *elementary reactions*, which represent single molecular events where reaction orders align with stoichiometric coefficients (FOGLER, 2016); *reaction rates* that follow temperature-dependent Arrhenius behavior (WARNATZ; MAAS; DIBBLE, 2006); *thermodynamic properties* typically described by NASA polynomial formulations (GOODWIN; MOFFAT; SPETH, 2015); *transport properties* essential for molecular transport in reacting flows (KEE; COLTRIN; GLARBORG, 2005); and *stoichiometric relationships* that define fuel-oxidizer composition through the equivalence ratio (TURNS et al., 1996).

These fundamental principles are extensively covered in combustion and chemical kinetics literature; thus, the detailed explanation and mathematical formulations are not in the scope of this work, but can be found in the referenced works. They build the necessary foundation for understanding fuel oxidation processes. However, despite this, each fuel will have its own unique chemistry. Based on this, the following section focuses on ethanol combustion, correlating its unique molecular structure and oxygenated nature with the reaction pathways and kinetic behavior.

2.2 CHEMISTRY OF HYDROCARBONS AND ETHANOL OXIDATION

The oxidation of hydrocarbons initiates through a temperature-activated perturbation of the molecule's energy field. It progresses via distinct pathways: (1) hydrogen abstraction, (2) cleavage of C–C bonds at primary or secondary carbon atoms, or (3) cleavage of C–O bonds in the case of oxygenated compounds. These pathways unfold either through isomerization, leading to the formation of various sub-structures, or through collisions with active radical species (CANCINO, Leonel Rincón, 2009).

In all cases, combustion processes are composed of chain reactions, which begin with the generation of chemical radicals that perpetuate the reaction sequence until stable molecules are formed. The intricate chain reaction process in oxidation is categorized into four fundamental steps: chain initiation, chain propagation, chain branching, and chain termination (TURNS et al., 1996). An example of these steps in the combustion mechanism within an H_2/O_2 system is detailed in Table 1.

As it can be seen, in the chain initiation step, stable species undergo a reaction and form a reactive species —specifically, two hydroxyl radicals. The subsequent propagation step involves this reactive species reacting with a stable species, resulting in the production of water and another reactive species, namely, the hydrogen radical (WARNATZ; MAAS; DIBBLE, 2006).

The chain branching reactions, conversely, generate two radicals while consuming only one (TURNS et al., 1996). This increase in the number of reactive species ($H^\bullet$, $OH^\bullet$, $O^\bullet$) can potentially lead to an explosion. In combustion, these branching

Table 1 – Most important reactions with respect to ignition in the H₂/O₂ system.

	Reaction	Type
(0)	$\text{H}_2 + \text{O}_2 \rightarrow \text{OH}^\bullet + \text{OH}^\bullet$	<i>chain initiation</i>
(1)	$\text{OH}^\bullet + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}^\bullet$	<i>chain propagation</i>
(2)	$\text{H}^\bullet + \text{O}_2 \rightarrow \text{OH}^\bullet + \text{O}^\bullet$	<i>chain branching</i>
(3)	$\text{O}^\bullet + \text{H}_2 \rightarrow \text{OH}^\bullet + \text{H}^\bullet$	<i>chain branching</i>
(4)	$\text{H}^\bullet + \text{O}_2 + \text{M} \rightarrow \text{HO}_2^\bullet + \text{M}$	<i>chain termination</i>

Source: Adapted from Warnatz, Maas, and Dibble (2006).

reactions generate a large number of radicals, causing rapid fuel decomposition. At low pressures, the reaction remains steady (HEGHES, 2007).

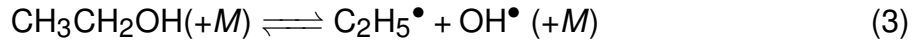
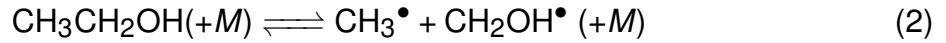
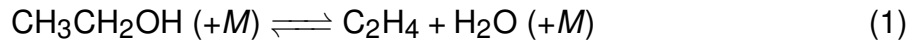
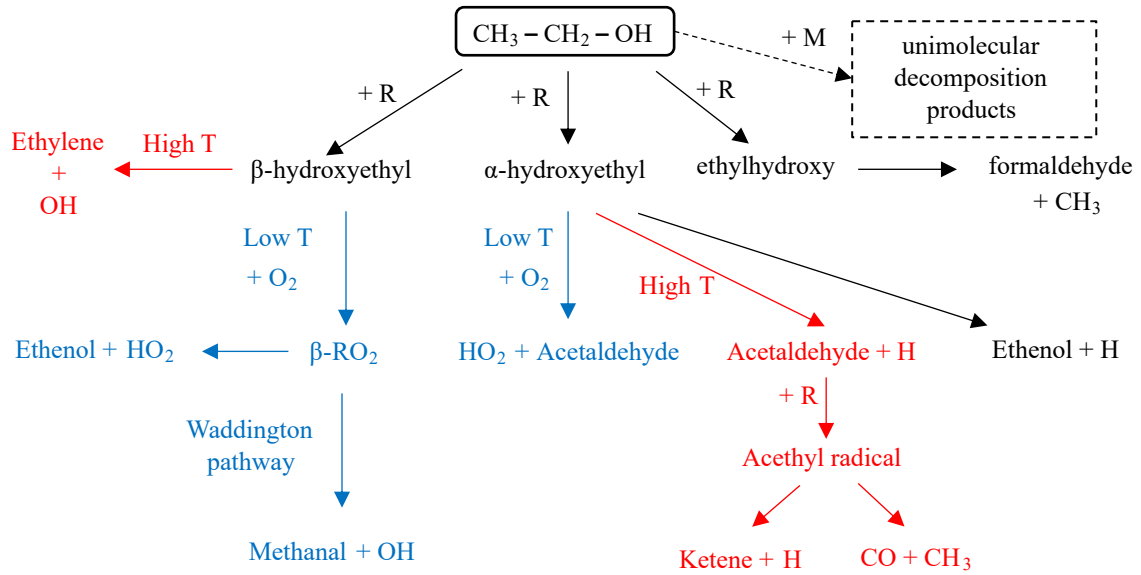
In the final stage, chain termination, the elimination of these free radical carriers occurs through various processes, such as radical-radical combination or radical-molecule reactions (WANG, H., 2015). M can be any gas (a third body needed to carry off the excess energy). The termolecular reaction leading to destruction of H[•] becomes important as the pressure is raised. At high pressures, Reaction 4 removes H atoms and reduces the rate of chain branching, resulting in a steady reaction (HEGHES, 2007).

The ignition delay time, which will be discussed in the next sections, is influenced by the balance between chain-branching and chain-terminating processes. In contrast, radical-radical reactions are crucial in flames due to the high concentrations of radicals present in a fully developed flame front. During combustion, the hydrocarbon fuel is targeted by H[•], O[•], and OH[•] radicals. This leads to the formation of alkyl radicals, which subsequently break down into smaller alkyl radicals and alkenes (HEGHES, 2007).

The kinetics of hydrocarbon oxidation exhibit temperature dependence. As a result, certain pathways and reactions assume greater significance at lower temperatures, while others become prominent only at higher temperatures (CURRAN, 2019a). However, the scarcity of experimental data represents a challenge to assign rate coefficients to all elementary reactions in the kinetic models. Consequently, researchers make estimations for similar reactions, introducing the concept of reaction classes (HANTOUCHE; SARATHY, S. Mani; KNIO, 2018). Reaction classes are kinetic generalizations that modelers use to make informed estimates of rate constants, especially for reactions lacking experimental evidence (HERBINET; DAYMA, 2013). The oxidation of alcohols like ethanol proceeds through several key reaction classes, which are discussed below. The general reaction pathway for ethanol combustion in premixed flames, batch reactors, stirred and flow reactors is presented in Figure 2.

At high temperatures (above 1500 K), and under fuel-rich or pyrolysis conditions, the thermal decomposition of ethanol is supposed to proceed through dehydration reaction Equation (1), C–C bond-scission Equation (2), or C–O bond scission Equation (3) (SARATHY, S. Mani et al., 2014):

Figure 2 – Reaction path diagram for ethanol combustion, where R denotes a radical. Low-temperature pathways are shown in blue..



The three aforementioned reactions belong to reaction class 1, unimolecular alcohol decomposition. Previous studies of Park, Zhu, and Lin (2002), Sivaramakrishnan et al. (2010), Choudhary et al. (2021a), and Choudhary et al. (2021b) have indicated Equation (2) as the most important reaction during combustion of ethanol, while Equation (1) is only important at low temperatures and pressures. It is important to note that Equation (1) is a four-center molecular elimination of water, and that the structure of the product alkene affects the global reactivity of the alcohol (SARATHY, S. Mani et al., 2014).

At intermediate and high temperatures, H-abstraction reactions control ethanol oxidation. There is a consensus in the literature regarding the importance of H-atom abstraction reactions, particularly class 2 reactions, in determining fuel reactivity. Thus, H-atom abstractions influence the ignition delay times, as well established by Pelucchi et al. (2016) and Hashemi, Jakob M Christensen, and Glarborg (2018). Indeed, Hantouche, S. Mani Sarathy, and Knio (2018) noted that uncertainties in H-atom abstraction reactions significantly impact the ignition delay time (τ_{ignition}).

S. M. Sarathy et al. (2009), Dagaut, S. M. Sarathy, and Thomson (2009), S. Mani Sarathy et al. (2014), Pelucchi et al. (2017), and Hantouche, S. Mani Sarathy, and Knio

(2018) all emphasize that H-atom abstraction reactions are the major consumption pathway of fuels. Considering the molecule of the fuel, H-abstraction can proceed from different locations, leading to distinct subclasses based on the abstracting radical or the location of the H-atom site (HANTOUCHE; SARATHY, S. Mani; KNIO, 2018). For ethanol, Peter S. Veloo et al. (2010a) and S. Mani Sarathy et al. (2014) note that hydrogen abstraction can occur from the alpha (α), beta (β), or hydroxyl sites. This results in three different isomers of $C_2H_5O^\bullet$ radicals (HASHEMI; CHRISTENSEN, J. M.; GLARBORG, 2018):

- $CH_3CH^\bullet OH$ (α -hydroxyethyl);
- $CH_2^\bullet CH_2OH$ (β -hydroxyethyl);
- $CH_3CH_2O^\bullet$ (ethoxy).

Notably, the α carbon site is vulnerable due to its proximity to the hydroxyl group, as discussed by Rotavera and Taatjes (2021) and Rawadieh et al. (2019). According to (ZHAO et al., 2019), abstraction from α site dominates not only in kinetics, but in thermodynamics as well. The activation entropy of this reaction is lower due to the stronger hydrogen bond, which results in slower reaction rate of H-abstraction from this particular site. Indeed, Nghia (2020) has demonstrated that at temperatures of 298 to 2000 K, abstractions of the hydroxyl site have only a very small contribution. However, as temperature increases, the contribution of the α channel decreases. The abstracting radicals are small species like $H^\bullet$, $OH^\bullet$, $HO_2^\bullet$, $CH_3O_2^\bullet$, $CH_3O^\bullet$, $CH_3^\bullet$, $C_2H_5^\bullet$, with $OH^\bullet$ radicals being the most important abstractors of hydrogen atoms (SARATHY, S. Mani et al., 2014).

At low to intermediate temperatures, hydroperoxy ($HO_2^\bullet$) radicals are crucial to derive the low-temperature oxidation and auto-ignition of hydrocarbons (RAWADIEH et al., 2019). Primary alcohols such as ethanol demonstrate the same trend, as well established in the works of Song Cheng et al. (2020), and Hashemi, Jakob M Christensen, and Glarborg (2018). The works of Changyoul Lee et al. (2012), and Heghes (2007), indeed highlight the crucial role of these radicals within these temperature ranges. The importance of $HO_2^\bullet$ radicals at high-pressure conditions is further demonstrated by Leonel Rincón Cancino (2009).

H-atom abstractions trap the hydroperoxy radicals into hydrogen peroxide H_2O_2 , which are stable molecules at low temperatures (HEGHES, 2007). As temperature increases, H_2O_2 molecules dissociate to form 2 $OH^\bullet$ radicals (LEE, C. et al., 2012). The resulting $OH^\bullet$ radicals enhance ethanol reactivity and restore oxidation capacity. As a result, ignition delay times are sensitive to the kinetics of H-atom abstraction reactions by $HO_2^\bullet$ radicals over a wide temperature range (HEGHES, 2007).

Another important radical abstractor at intermediate temperatures is the methylperoxy ($CH_3O_2^\bullet$) radical, which is commonly important in the decomposition of species which produce high concentrations of methyl radicals (CURRAN, 2019b). Recently, Shi

et al. (2020) found that, at temperatures lower than 1000 K, the dominant channels of abstractions of hydrogen atoms by CH_3O_2 are those producing $\text{CH}_3\text{O}_2\text{H} + \text{CH}_3\text{CH}^\bullet\text{OH}$.

At lower temperatures, reactions between α -hydroxyethyl and β -hydroxyethyl with O_2 become important. The reaction between $\text{CH}_3\text{CH}^\bullet\text{OH}$ and O_2 will most likely produce acetaldehyde and hydroperoxy radicals ($\text{HO}_2^\bullet$), due to a very low energy molecular elimination pathway (SILVA et al., 2009a). Ethenol, also known as vinyl alcohol, is the other possible product of this particular reaction, as presented in the mechanism of Hashemi, Jakob M Christensen, and Glarborg (2018). However, Silva et al. (2009a) highlights that the major pathway is the one leading to acetaldehyde. This corroborates with the findings of Zádor et al. (2009), which demonstrated that the product of a reaction between α -hydroxyethyl and O_2 is indeed ethanal + HO_2 . Xi et al. (2021a) contributes by demonstrating that $\text{CH}_3\text{CH}^\bullet\text{OH} + \text{O}_2$ can also produce $\text{CH}_3\text{CH}(\text{OO})\text{OH}$ and $\text{CH}_3\text{CHO} \cdots \text{HO}_2^\bullet$, although $\text{CH}_3\text{CHO} \cdots \text{HO}_2^\bullet$ is eventually dissociated to acetaldehyde. They emphasize that at high temperatures and low pressures, production of aldehyde is more likely to occur, followed by vinyl alcohol. Formation of $\text{CH}_3\text{CH}(\text{OO})\text{OH}$ and $\text{CH}_3\text{CHO} \cdots \text{HO}_2^\bullet$ are important at relatively low temperatures and high pressures, as well as at high pressures and elevated temperatures.

Conversely, Zádor et al. (2009) concluded that reactions between $\text{CH}_2^\bullet\text{CH}_2\text{OH}$ and O_2 will produce $\text{OOCH}_2\text{CH}_2\text{OH}^\bullet$, which quickly decomposes through a Waddington pathway to $2\text{CH}_2\text{O} + \text{OH}^\bullet$. Waddington-type reaction pathways in alcohol oxidation sustain the oxidation process through chain propagation, but compete with chain-branching reactions, thereby inhibiting the overall reactivity at low temperatures (SARATHY, S. Mani et al., 2014). Zádor et al. (2009) also report that the other possible pathway is a concerted elimination producing is vinyl alcohol + $\text{HO}_2^\bullet$. However, according to S. Mani Sarathy et al. (2014), these β -channels are less important in combustion systems because hydrogen abstractions strongly favor the α site at lower temperatures, as discussed above.

Due to the dominant role of reactions between α -hydroxyethyl and O_2 , Changyoul Lee et al. (2012) observed that at temperatures between 775-1300 K and pressures lower than 85 bar, a sustained $\text{OH}^\bullet$ production from the RO_2 and QOOH chemistry is not possible, therefore, the peroxide chemistry can be neglected under such conditions.

At high temperatures, the three isomers produced by the majority of H-abstractions are decomposed primarily by β -scission reactions (HAYES; BURGESS; MANION, 2015). β -scission of C–C and C–H bonds yields unsaturated alcohols or alkenes (i.e., C=C bonds). Conversely, β -scission of the O–H bonds produces an aldehyde (i.e., C=O bond). The radicals can also isomerize, although in most relevant combustion conditions they are preferably decomposed (SARATHY, S. Mani et al., 2014).

The ethoxy radical mostly dissociates to formaldehyde (CH_2O) and methyl radical ($\text{CH}_3^\bullet$) (HASHEMI; CHRISTENSEN, J. M.; GLARBORG, 2018). But acetaldehyde

(CH₃CHO) and H[•] radical can also be produced (LIU, B. et al., 2022). The O–H bond scission of the (α -hydroxyethyl) radical also yields acetaldehyde, and is in competition with the C–H bond scission which favors the production of ethenol (C₂H₃OH) (SARATHY, S. Mani et al., 2014).

Differently, (β -hydroxyethyl) radical is mostly decomposed to ethylene by C–C bond scission (LEPLAT et al., 2011a). Additionally, according to the work of S. Mani Sarathy et al. (2014), a small fraction of ethenol can also be produced.

The carbonyl intermediates, in this case formaldehyde (methanal) and acetaldehyde (ethanal) will eventually lead to the major products of combustion. The two works of Peter S. Veloo et al. (2013) and P.S. Veloo et al. (2013) explain the destruction pathways of aldehydes. According to them, H-atoms can be abstracted from aldehydes via the weakly bound aldehydic (H–C=O) site, followed by α -scission to form CO and an alkyl radical.

The acetaldehyde produced via decomposition of the (α -hydroxyethyl) radical is reported to form the acetyl radical (CH₃CO[•]), which then dissociates to CO and CH₃[•]. A minor pathway of acetaldehyde consumption proceeds via abstraction from the methyl group leading to ketene production (SARATHY, S. Mani et al., 2014). Carbon monoxide will also be produced through methanal (HASHEMI; CHRISTENSEN, J. M.; GLARBORG, 2018).

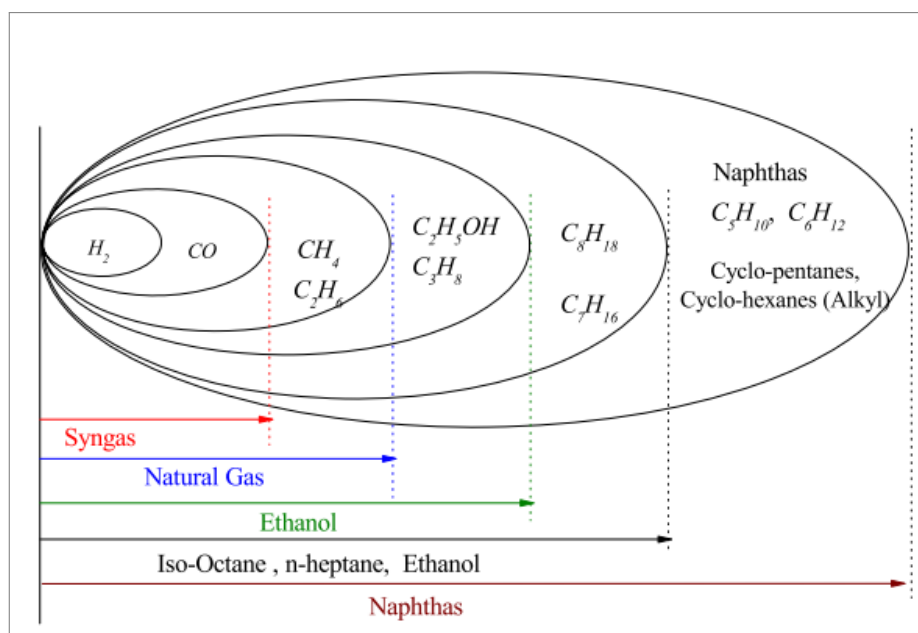
Enols are also a common intermediate in dehydrogenation pathways of alcohols. Ethenol is formed either by the α -hydroxyethyl or β -hydroxyethyl radicals, as discussed earlier. According to the work of Dames and Golden (2013), these enols can isomerize to aldehydes (and aldehydes can isomerize to enols as well). There is also a possibility to isomerization to ketones. This is known as enol-keto tautomerism (SARATHY, S. Mani et al., 2014).

Additionally, hydrocarbon oxidation follows a hierarchical process, graphically depicted in Figure 3. Thus, the intricate mechanisms governing the combustion of more complex fuels seamlessly integrate sub-mechanisms tailored specifically for simpler fuel molecules (WESTBROOK, Charles K.; DRYER, Frederick L., 1981).

This principle is also applicable to ethanol. Therefore, its mechanism is compiled by initiating with sub-mechanisms for oxidation of small hydrocarbons and alcohols, in this case methanol (SARATHY, S. Mani et al., 2014). The model also include a complete H₂ oxidation mechanism (HEGHES, 2007). The most important elementary steps are the ones that provide chain-branching and propagation, previously demonstrated in Table 1.

Having established ethanol combustion chemistry, it is also important to acknowledge that to accurately evaluate the accuracy of kinetics models across different combustion regimes, it is important to validate the numerical models with experimental results. This study foccus on three fundamental experimental configurations: IDT, LFS,

Figure 3 – Hierarchy of kinetics models for hydrocarbons oxidation



Source: Leonel Rincón Cancino (2009)

and species concentration in a JSR.

2.3 FUNDAMENTAL COMBUSTION EXPERIMENTS

The preceding section provided a summary of fundamental concepts of chemical kinetics. Going further on the understanding of fuel combustion, several experimental approaches are commonly used for evaluating combustion processes and species. This includes static reactors, stirred reactors, plug flow reactor (PFR), ST, laminar flames, and a RCM (HAYES; BURGESS; MANION, 2015).

Static reactors operate as closed systems with no mass inflow or outflow, ensuring a homogeneous mixture (FOGLER, 2016). An example is the Batch Reactor or constant volume reactor (CVR). In static reactors, the progress of reactions can be observed by measuring the change in pressure or by detecting concentrations as a function of time for one or several species (KEE; COLTRIN; GLARBORG, 2005).

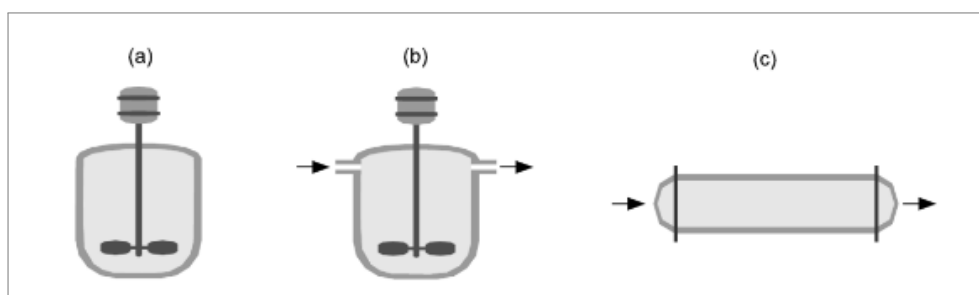
Conversely, PFR, continuously stirred tank reactor (CSTR), and perfectly stirred reactor (PSR) are open systems with continuous flow (FOGLER, 2016). PFR reactors are an example of flow reactors, which aim to achieve a plug-flow situation, where composition and temperature are uniform over the cross section of the reactor (KEE; COLTRIN; GLARBORG, 2005). In such reactors, the diffusive transport in the flow direction is also absent (FOGLER, 2016).

PSR reactors (also referred to as CSTR in chemical engineering terminology), on the other hand, can be characterized as stirred reactors. They are idealizations

where gases mix instantaneously and perfectly, leading to uniform temperature and composition throughout the reactor volume (CUOCI, 2019). A close approximation of a CSTR or a PSR reactors is the JSR, which indeed exhibits efficient gas phase mixing. This particular reactor it is commonly used to examine gas-phase oxidation and the thermal decomposition of fuels (HERBINET; DAYMA, 2013).

An illustration of the differences between these reactors can be seen in Figure 4:

Figure 4 – Ideal Reactors: (a) Batch Reactor, (b) CSTR, (c) PFR



Source: Caccavale et al. (2010)

The fundamental combustion properties investigated using these experimental systems include the homogenous IDT, premixed LFS, and product species distributions from gas-phase oxidation and/or pyrolysis (SARATHY, S. Mani et al., 2014).

The experimentally measured IDT is reproduced by spatially homogeneous adiabatic simulations with constant volume (a part of the shock tube experiments) or the volume is a function of time (other shock tube experiments and all RCM measurements) (SU et al., 2024). In a ST, the fuel-oxidizer mixture is placed in a steel tube, typically 5–10 m long and 5–10 cm in diameter, divided by a diaphragm into a high-pressure driver section (inert gas) and a low-pressure driven section (fuel–oxidizer mixture). When the diaphragm ruptures, a shock wave compresses the gas, rapidly raising its temperature and pressure. Ignition occurs after a short delay, depending on radical concentrations. The IDT is then defined as the elapsed time between compression and ignition (SZANTHOFFER, ANDRAS, 2022).

The RCM, on the other hand, reproduces the compression process of an internal combustion engine in a controlled, single-stroke experiment. Its operation consists of rapidly compressing the reaction chamber with the fuel-oxidizer mixture in a process relatively close to adiabatic compression (SUNG, C.-J.; CURRAN, 2014). Both facilities provide essential experimental data for evaluating and validating chemical kinetic mechanisms.

From a kinetics point of view, IDT is a property that can be correlated with cetane and octane numbers, serving as an indicator of fuel reactivity (TURNS et al., 1996). According to Leonel Rincón Cancino (2009) and Heghes (2007), the delay is marked

by the presence of a radical pool. Hence, the competition between chain-branching and chain-terminating controls the chemistry (HEGHES, 2007). In this context, there is a consensus in the literature regarding the importance of H-atom abstraction reactions, in determining fuel reactivity. Thus, H-atom abstractions influence the ignition delay times, as well established by Pelucchi et al. (2016) and Hashemi, Jakob M Christensen, and Glarborg (2018).

Beyond IDT, flame measurements provide complementary insights into combustion reactivity and propagation phenomena. Such analysis serves as a basis to turbulent combustion, and it also contains the fundamental information on the reactivity, diffusivity, and exothermicity (LEE, H.; JIANG; MOHAMAD, 2014). Indeed, most of the heat release in practical engines, such as gasoline, diesel, and gas turbines is produced by flames (EGOLFOPOULOS, F. et al., 2014).

Flames are typically categorized as: (i) premixed flames, where fuel and oxidizer are mixed first and burner later, or (ii) non-premixed, when combustion and mixing occur simultaneously (WARNATZ; MAAS; DIBBLE, 2006). The magnitude of LFS is affected by chemical kinetics, thermodynamic and transport properties of species (ZHENG et al., 2024).

The flame structure consists of a mixture of intermediate species leading to chain branching or chain termination (VELOO, P. S. et al., 2010a). Indeed, in this regard, the detailed work of CK Law and CJ Sung (2000) states that the flame structure can be described at three levels of detail. At the hydrodynamic level, the flame is treated as an interface that separates two thermodynamic states of unburnt and burnt gases in complete thermodynamic equilibrium. The following level is transport-dominated. At this level, the flame now has a finite thickness, with a preheat zone where diffusion and convection gradually raise the gas temperature until ignition occurs. The reaction is then concentrated in a thin reaction sheet. The relation between thermal and concentration profiles depends on the Lewis number.

At the third and most detailed reaction level, the reaction sheet is expanded to reveal the reaction rate profile. Here, diffusion dominates over convection. Overall, the one-dimensional flame structure can therefore be considered to consist of two distinct zones, a narrow reaction zone at which reaction and diffusion rates balance each other, and a thick preheating zone where convection and diffusion dominate and balance each other (KIYMAZ, 2023).

Various experimental techniques have been developed to measure laminar burning velocities (KONNOV, A. A. et al., 2018):

- **Spherical flame method:** The premixed fuel-air mixture is ignited at the center of a confined chamber, and flame speed is determined from flame radius vs. time (constant pressure) or pressure-time history (constant volume).
- **Counterflow/stagnation flame method:** A steady, flat, premixed flame is

stabilized in a stagnation flow field created by impinging two jets (twin-flame) or a jet onto a plate.

- **Heat flux method:** A flat flame is stabilized on a perforated plate burner, where the gas velocity at adiabatic conditions equals the LFS.
- **Burner method (Bunsen/nozzle):** A conical flame is anchored on a burner rim, with LFS derived from flow velocity and cone angle ($S_L = u \cdot \sin \alpha$) or from volumetric flow rate and flame surface area.

Other methods include annular stepwise diverging tubes and externally heated diverging channels (KONNOV, A. A. et al., 2018). In all cases, a flame is operated at low-pressure conditions and a reaction mixture of interest flows through it (HAYES; BURGESS; MANION, 2015).

Radical species play crucial roles in flame propagation. Xu et al. (2017) emphasizes the critical role of $\text{OH}^\bullet$ radicals in high-temperature flame combustion, serving as indicators of combustion intensity, while Lu et al. (2023a) underscores the importance of $\text{H}^\bullet$ radicals for flames. Hence, $\text{H}^\bullet$ and $\text{OH}^\bullet$ radicals are the main elements that increase the laminar flame speed. Indeed, Aghsaee et al. (2015) defines $\text{OH}^\bullet$ radicals as responsible for 50% of ethanol depletion, ensuring their role in chemically reacting systems.

The works of F N Egolfopoulos and C K Law (1990), Jinhua Wang et al. (2012), Al-Hamamre and Yamin (2013), Xu et al. (2017), and Ye et al. (2018b) highlight the reaction $\text{H}^\bullet + \text{O}_2 \rightleftharpoons \text{O}^\bullet + \text{OH}^\bullet$ as very sensitive to flames. Aghsaee et al. (2015) corroborates this statement, describing $\text{OH}^\bullet$ formation as mainly dominated by this particular reaction. Indeed, as previously stated, this is most important elementary reaction in combustion systems.

Earlier studies by Charles K Westbrook and Frederick L Dryer (1984) have already established that the radical species pool is evolved among $\text{OH}^\bullet$, $\text{O}^\bullet$, and $\text{H}^\bullet$ by the following reactions:



Moreover, to determine the kinetic and mechanistic information, product formation at various average residence times and temperatures can be measured (HAYES;

BURGESS; MANION, 2015). Commonly, those properties can be accessed through flow and JSR reactors, defined earlier in this section.

The numerical simulation of these experimental configurations using different kinetic mechanisms involve the use of specialized software tools and algorithms, depending on the desired outputs. Therefore, the following section will present the computational methods and tools for simulating chemical kinetics mechanisms.

2.4 COMPUTATIONAL TECHNIQUES

Numerous software tools are available for the analysis of chemical mechanisms, mechanism reduction, 0D homogeneous reactor, and 1D laminar flame simulations. Among the notable options are CHEMKIN, Cantera, Cosilab, and FlameMaster. It is important to note that both CHEMKIN and Cosilab require the acquisition of a user license. FlameMaster, on the other hand, is available upon request and uses a format distinct from the widely adopted CHEMKIN format for input files (KONG, 2015). Consequently, Cantera emerges as the most fitting choice and has been selected for use in this particular work.

2.4.1 Cantera, An Object-Oriented Software for Chemical Kinetics, Thermodynamics and Transport Problems

Cantera is a versatile suite of object-oriented software tools designed for solving problems related to chemical kinetics, thermodynamics, and transport processes. It provides a range of object types representing phases of matter, interfaces between phases, reaction managers, and reactor networks for both time-dependent and steady one-dimensional reacting flows (GOODWIN; MOFFAT; SPETH, 2015).

Cantera supports multiple programming languages, including Python, Matlab, C++, and Fortran 90, making it a flexible and powerful choice for researchers and engineers involved in modeling and simulating complex systems (FELDEN, 2015).

The architecture of Cantera necessitates an input file in the (*.yaml*) format, and this file serves as a critical descriptor of the system. The file contains information about the involved phases, elements, species, and reactions (SALLAM; SRIVASTAVA, 2023). A representative structure of the input file is illustrated in Figure 5.

In the "phases" section of the data file, Cantera offers details regarding the elemental and molecular composition of each phase. The *thermo* keyword is employed to specify the thermodynamic model utilized for a given phase, along with the corresponding coefficients. In this work, the NASA7 model is employed, as described in preceding sections. The data file also includes a *transport* entry, where the transport model is explicitly stated. For the present work, the chosen model is the mixture-average. Additionally, for each species, supplementary fields provide information on the molecule's ge-

Figure 5 – General format of the input file

```

units: {length: cm, quantity: mol, activation-energy: kcal/mol}

phases:
- name: gas
  thermo: ideal-gas
  # Additional fields come after this

species:
- name: A
  # Additional field come after this
- name: B
  # Additional field come after this
- name: C
  # Additional field come after this

reactions:
- equation: A + B <=> C + D
  # Additional field come after this
- equation: A + C <=> 2 D
  # Additional field come after this

```

Source: Adapted from Sallam and Srivastava (2023)

ometry, diameter (σ_k), well-depth (ε), dipole ($\bar{\mu}_k$), polarizability, rotational-relaxation, and other relevant parameters (GOODWIN; MOFFAT; SPETH, 2015). An illustrative example of these sections employing a detailed kinetic mechanism is provided in Figure 6.

Figure 6 – Illustration of Thermo and Transport Sections in a Detailed Kinetic Mechanism

```

- name: HCCO
  composition: {C: 2, H: 1, O: 1}
  thermo:
    model: NASA7
    temperature-ranges: [298.0, 1000.0, 4000.0]
    data:
      - [2.25172, 0.017655, -2.37291e-05, 1.72758e-08, -5.06648e-12, 2.00594e+04,
        12.4904]
      - [5.62821, 4.08534e-03, -1.59345e-06, 2.86261e-10, -1.94078e-14, 1.93272e+04,
        -3.93026]
  transport:
    model: gas
    geometry: nonlinear
    diameter: 2.5
    well-depth: 150.001
    rotational-relaxation: 1.0

```

Source: Author, 2024

The final section of the data file provides information about the reactions that will occur in the system. In this section, parameters A , β and E_a are enclosed within square

brackets. For three-body reactions, additional information on third-body efficiencies is included, as depicted in Figure 7 (SALLAM; SRIVASTAVA, 2023).

Figure 7 – Illustration of Reaction Section in a Detailed Kinetic Mechanism

```
- equation: H + OH + M <=> H2O + M # Reaction
  type: three-body
  rate-constant: {A: 6.1e+22, b: -3.32, Ea: 120.79}
  efficiencies: {Ar: 0.38, CO: 1.9, CO2: 3.8, H2: 3.0, H2O: 0.0, N2: 2.0,
                O2: 1.5}
```

Source: Author, 2024

Cantera also provided a reactor network module capable of simulating reactors. The three main types are (SALLAM; SRIVASTAVA, 2023): (i) ideal gas reactor (IdealGasReactor), which is a constant volume reactor meant for ideal gas mixtures. In such a reactor, the energy equation is solved in terms of the temperature; (ii) constant pressure reactor (ConstPressureReactor), that maintains the pressure at a certain value for the mixture, using enthalpy as the state variable; and (iii) ideal gas constant pressure reactor (IdealGasConstPressureReactor), at which a constant pressure maintains the reactor for ideal gas components. It also has enthalpy as the state variable.

Cantera also enables the inclusion of flow devices. They are components that connect reactors and manage the mass transport between different reactor units (GOODWIN; MOFFAT; SPETH, 2015). The common flow devices used are the *wall*, *reservoir*, *mass flow controller* and the *valve* (SALLAM; SRIVASTAVA, 2023).

The specific governing equations defining Cantera's reactor models are derived and described below (GOODWIN; MOFFAT; SPETH, 2015). The mass conservation and species equations are common to all reactor types. They are derived as follows:

$$\frac{dm}{dt} = \sum_{in} \dot{m}_{in} - \sum_{out} \dot{m}_{out} + \dot{m}_{wall} \quad (8)$$

$$m \frac{dY_k}{dt} = \sum_{in} \dot{m}_{in} (Y_{k,in} - Y_k) + \dot{m}_{k,gen} - Y_k \dot{m}_{wall} \quad (9)$$

where $\dot{m}_{k,gen} = V\dot{\omega}_k W_k + \dot{m}_{k,wall}$ represents the total rate of generation of species k .

The main differences between reactor types can be seen in the energy equations, state variables, and volume behavior, as summarized in Table 2.

Cantera also enables computation of combustion characteristics like IDT, LFS, and species concentration profiles. Ignition, for example, can be defined by tracking the temperature rise as an indicator of combustion (SALLAM; SRIVASTAVA, 2023). For hydrocarbons and oxygenates, ignition is usually identified based on monitoring

Table 2 – Comparison of Cantera reactor models - key differences

Reactor Type	State Variables	Volume Behavior	Energy Equation
Ideal Gas Reactor	m, V, T, Y_k	Variable	$mc_v \frac{dT}{dt} = -p \frac{dV}{dt} + \dot{Q} + \sum_{in} \dot{m}_{in} \left(h_{in} - \sum_k u_k Y_{k,in} \right) - \frac{pV}{m} \sum_{out} \dot{m}_{out} - \sum_k \dot{m}_{k,gen} u_k$
Constant Pressure Reactor	m, H, Y_k	Variable	$\frac{dH}{dt} = \dot{Q} + \sum_{in} \dot{m}_{in} h_{in} - h \sum_{out} \dot{m}_{out}$
Ideal Gas Constant Pressure Reactor	m, T, Y_k	Variable	$mc_p \frac{dT}{dt} = \dot{Q} - \sum_k h_k \dot{m}_{k,gen} + \sum_{in} \dot{m}_{in} \left(h_{in} - \sum_k h_k Y_{k,in} \right)$

the change of pressure or the concentrations of species $\text{OH}^\bullet$, $\text{CH}^\bullet$, or CO_2 (SU et al., 2024). In both cases, the same cantera script can be used.

In the present work, the IDT is calculated numerically by tracking the hydroxyl radical ($\text{OH}^\bullet$) concentration during CVR simulations. The IDT is defined as the time required for the $\text{OH}^\bullet$ mole fraction to reach its maximum value:

$$\tau_{ign} = t(\max([\text{OH}^\bullet])) \quad (10)$$

LFS calculations, on the other hand, use Cantera's *FreeFlame* module, which solves the steady-state conservation equations for mass, energy, and species. This computation directly yields the fundamental parameter (S_L^0), representing the adiabatic, unstretched laminar flame speed (GOODWIN; MOFFAT; SPETH, 2015).

Finally, to compute species profiles, Cantera enables to simulate the JSR as a PSR operating under steady-state conditions. Based on this, the study of chemical kinetics across a wide temperature range while maintaining constant residence time is allowed.

For such, the JSR is modeled as an *isothermal, constant-volume IdealGasReactor* and uses the following classes:

- **Reservoir**: Models the inlet and outlet reservoirs with a constant state.
- **IdealGasReactor**: Represents the perfectly stirred reactor with an ideal gas mixture.
- **MassFlowController**: Controls the mass flow rate from the inlet reservoir to the reactor.
- **Valve**: Models the outlet valve, maintaining reactor pressure.
- **ReactorNet**: Integrates the system of reactors to steady state.

The governing equations for species conservation at steady state are:

$$\frac{\dot{m}}{\rho V} (Y_{kin} - Y_k) + \frac{\dot{\omega}_k W_k}{\rho} = 0 \quad (k = 1, \dots, K) \quad (11)$$

where $\dot{m}$ is the mass flow rate, ρ is density, V is reactor volume, Y_{kin} is inlet mass fraction of species k , Y_k is mass fraction of species k , $\dot{\omega}_k$ is molar production rate of species k , W_k is molecular weight of species k , and K is the number of species.

In summary, Cantera is a robust software for modeling chemical kinetics, thermodynamics, and transport processes in reacting systems. The framework enables evaluation of fundamental combustion properties, including IDT, LFS, and species concentration profiles across various reactor configurations. Cantera also facilitates computational analyses such as sensitivity studies, which systematically identify the elementary reactions and kinetic parameters that have the most influence on the combustion behavior of several fuels. These insights are valuable for multiple applications, including uncertainty quantification of kinetics models and the development of reduced chemical mechanisms. The theory behind sensitivity analyses will be described in the following section.

2.5 ANALYSIS OF REACTION MECHANISMS

As established in earlier sections, chemical kinetics mechanisms follow a hierarchical process. However, in many cases, kinetic parameters of the elementary reactions are not determined from experiments or theoretical calculations; they are estimated (TOMLIN, Alison S, 2013). This leads to uncertainties on the mechanisms. To improve accuracy, kinetic modelers often find it difficult to know which parameters should be prioritized. In highly detailed mechanisms, with hundreds of species and thousands of reactions, the task seems almost impossible.

Therefore, methods that help in the determination of parameter importance can help us to focus our efforts on those parameters with the biggest influence on predictions (TURÁNYI; TOMLIN, Alison S., 2014). For this reason, methods like sensitivity analysis have been developed (TOMLIN, Alison S, 2013). Sensitivity analysis is used to reveal the control parameters in the model, therefore, providing information about its structure (TURÁNYI, 1997).

2.5.1 Sensitivity Analysis

The term *sensitivity analysis* defines a collection of mathematical methods that can be used to explore the relationships between the values of the input parameters of a mathematical model and its solutions (TURÁNYI; TOMLIN, Alison S., 2014).

In combustion processes, the rates of elementary reactions can differ greatly. Some reactions are rate-limiting; therefore, it is crucial to have accurate rate coefficient values. Conversely, reactions that are not rate-limiting occur so fast that the precision of their rate coefficients has minimal impact on the outcomes of mathematical modeling (HEGHES, 2007).

The sensitivity analysis method quantifies how changes in the rate constants of individual reactions within a kinetics model affects the overall system. It essentially measures the system's responsiveness to variations in these parameters. This respon-

siveness is observed through the magnitude of alterations in species concentration or reaction rates. The sensitivity coefficient, a key outcome of this analysis, quantifies the impact of that particular reaction on the system's dynamics, offering insights into its significance within the larger framework.

To choose a sensitivity analysis method, different factors need to be accounted for: the research purpose, the computational cost of energy models, the number of input variables, the analyst's time for a project, as well as the familiarity with the sensitivity methods (TIAN, 2013).

Several authors have reviewed and applied sensitivity analysis on the evaluation of kinetics models. Important insights of this method and the mathematical approach can be found on the works of Rabitz, Kramer, and Dacol (1983); Turányi (1990a), Alison S. Tomlin et al. (1992), Griffiths (1995), Leonel Rincón Cancino (2009), Alison S. Tomlin and Turányi (2013), and Turányi and Alison S. Tomlin (2014). In this work, the mathematical development that will be presented below follows the description of Griffiths (1995) and Leonel Rincón Cancino (2009).

2.5.1.1 Local Sensitivity Analysis

Local sensitivity analysis examines how small perturbations around specific parameter values in the input space, influence the model output (MORIO, 2011).

Considering the non-linear mass conservation equation represented in Equation (12), where k and c are the rate coefficient and species concentration vectors, respectively, and N is the number of chemical species, the solution can be achieved with the specification of the component values for the vector k . The concentration vector c is a function of the parameter vector as well as time ($c(k,t)$).

$$\frac{dc_i}{dt} = f(k,c), \quad i = 1, \dots, N \quad (12)$$

The first-order sensitivity coefficient with respect to species c_i represents the change in a species concentration c_i at time t owing to a change in the j^{th} rate parameter k_j (or the j^{th} component of any parameter vector, in general), and is defined as demonstrated in Equation (13).

$$\frac{\partial c_i}{\partial k_j}(k,t) = \frac{c_i(k_j + \Delta k_j, t) - c_i(k_j, t)}{\Delta k_j} \quad (13)$$

The gradient and its second-order counterpart, represented in Equation (14) convey quantitative information about the solution in the vicinity of the operating point.

$$\frac{\partial^2 c_i}{\partial k_j^2} \quad (14)$$

Hence, the linearized response of the sensitivity with respect to time throughout the reaction data set is given by Equation (15), in which J_{ij} is the Jacobian matrix defined as seen in Equation (16).

$$\frac{d}{dt} \left[\frac{\partial c_i}{\partial k_j} \right] = \sum_l J_{il} \frac{\partial c_l}{\partial k_j} + \frac{\partial f_i}{\partial k_j} \quad (15)$$

$$J_{il} = \frac{\partial f_l}{\partial c_i} \quad (16)$$

Equation (15) must be solved by numerical integration to calculate the deviations in $c_i(t)$ as a result of the changes in k . However, in combustion reactions, the ordinary differential equations describing the species concentration over time are normally stiff, and the computational cost is high. Hence, the sensitivity coefficients can be normalized using the following expression:

$$\omega_{ij} = \frac{\partial \ln c_i(t)}{\partial \ln k_j} \quad (17)$$

The order of magnitude of ω_{ij} gives the relative importance of the j^{th} reaction in influencing the concentration of species i at time t . Setting each k_j to zero and calculating the corresponding sensitivities, ω_{ij} indicates the significance of the j^{th} reaction. If all coefficients ω_{ij} for the j^{th} reaction are very small, in relation to the higher value, then the j^{th} reaction may be regarded as unimportant. Conversely, if one or more of the normalized sensitivities ω_{ij} are large, then the j^{th} reaction is said to be determining for the i^{th} species.

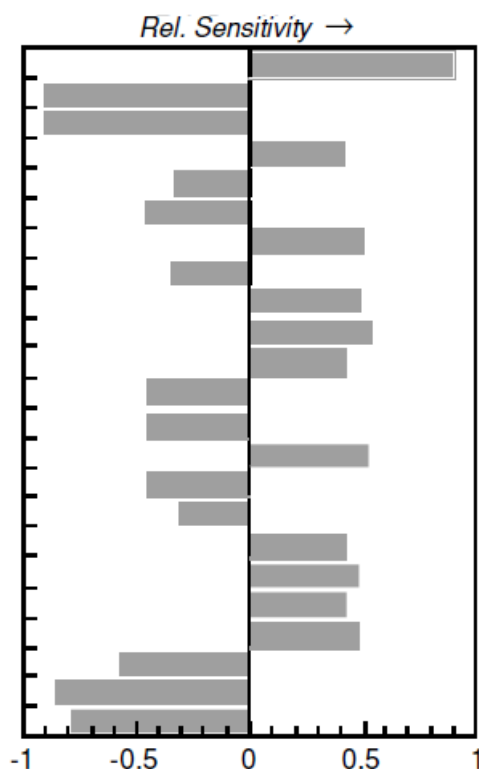
This type of analysis is called local sensitivity analysis because the parameter perturbation studied is quite small, whereas a global method would include a perturbation corresponding to the parameter uncertainty (TURÁNYI, 1990b). This is the simplest method, and it remains very useful, especially due to its low computational cost, simple implementation, and easy interpretation (TIAN, 2013). However, one limitation associated with this method is that it ignores non-linear cross interactions among the input parameters of various reactions (ROY, Sharodia et al., 2026).

2.5.1.2 Brute-Force Sensitivity Analysis

Another method for sensitivity analysis is the brute-force method, which is simply based on modification of one or several parameters (BENDTSEN; GLARBORG; DAM-JOHANSEN, 2001). In this case, the sensitivity matrix is calculated using finite-difference approximations (TURÁNYI; TOMLIN, Alison S., 2014). The application of this method involves calculating the sensitivities normally, and after, obtain new sensitivities, but this time, with a perturbation in the reaction parameters, one by one (BONINI et al., 2022; CANCINO, Leonel Rincón, 2009).

Such a method requires solving the kinetic system of ODEs $(m + 1)$ times, where m is the number of parameters, making it computationally expensive for large mechanisms. An example of a typical bar diagram generated from a sensitivity analysis can be found in Figure 8.

Figure 8 – Example of a typical bar diagram generated from a sensitivity analysis at a specific elapsed time during the ignition delay in a shock tube.



Source: (WARNATZ; MAAS; DIBBLE, 2006)

However, one limitation associated with the use of the brute-force method is its computational demand when analysing all reactions of a large reaction set (BENDTSEN; GLARBORG; DAM-JOHANSEN, 2001).

2.5.1.3 Global Sensitivity Analysis

In contrast to local sensitivity analysis, global sensitivity analysis (GSA) considers the whole variation range of the inputs (SALTELLI; CHAN; SCOTT, 2000). According to Morio (2011), GSA focuses on analyzing the variance of the model output (Y) and assesses how input variability propagates through the system to affect the variance output. This methodology enables researchers to determine which input parameters

contribute most significantly to output uncertainty through the computation of *Sobol indices*.

The mathematical idea is decomposing the total variance (MORIO, 2011):

$$\text{Var}(Y) = \sum V_i + \sum V_{ij} + \sum V_{ijk} + \dots \quad (18)$$

Where V_i = variance from parameter i alone, V_{ij} = variance from interaction between parameters i and j . From this decomposition, we get two key indices:

- **First-order index:** $S_i = \frac{V_i}{\text{Var}(Y)}$ - Main effect of parameter i
- **Total-effect index:** $S_{Ti} = \frac{V_i + \text{all interactions}}{\text{Var}(Y)}$ - Total effect including interactions

These indices range from 0 (no influence) to 1 (dominant influence). When $S_{Ti} \gg S_i$, strong parameter interactions are indicated. To estimate the Sobol indices, Monte Carlo or Quasi-Monte Carlo methods are used, though these can be computationally demanding for expensive models (CHENG, K. et al., 2020). Alternative approaches include the Morris method for screening and surrogate-based methods for efficiency (TURÁNYI; TOMLIN, Alison S., 2014).

However, the GSA methods are not so easy to implement (TIAN, 2013). Indeed, they are less common than their local counterparts, partly because GSA is computationally expensive (DAVIS; SKODJE; TOMLIN, Alison S., 2011).

2.6 STATE-OF-THE-ART

In the last decades, ethanol has emerged as a promising alternative to conventional fuels. This biofuel is derived from the fermentation of sugars present in various biomasses and exhibits properties that allow its use in internal combustion engines. Ethanol is an octane number enhancer and an oxygen carrier. Also, its use in engines is associated with the reduction of carbon monoxide and soot emissions (FRASSOL-DATI et al., 2010).

The chemical structure of ethanol includes the presence of a hydroxyl group attached to a hydrocarbon chain, as stated by S. Mani Sarathy et al. (2014). This structural feature provides unique thermochemical and reaction kinetics properties compared to traditional hydrocarbons.

The study of ethanol oxidation has been ongoing for decades, with both experimental and numerical methods contributing to its understanding. Experimental investigations cover diverse combustion properties and setups, ranging from IDT in ST; laminar burning velocity (LBV) in constant volume bomb (CVB); LFS in counterflow twin-flame (C.F. Tw-F) configurations, counterflow premixed flames, and flat flame burn-

ers. Additionally, the studies also include species profiles obtained through JSR or flow reactors.

For a consolidated overview, Table 3 summarizes some of the published experimental works on ethanol oxidation.

Table 3 – Summary of published experimental work involving ethanol oxidation.

Reference	Parameters Analyzed	φ	T [K]	P [Bar]	Experimental Setup
(NATARAJAN; BHASKARAN, 1981) ^b	IDT	0.5, 1.0, 2.0	1300-1700	1.0-2.0	ST
(GÜLDER, 1982) ^a	LBV	0.7-1.4	300-500	1.0-8.0	CVB
(DUNPHY; SIMMIE, 1991) ^a	IDT	0.25-2.0	1080-1660	1.8-4.6	ST
(NORTON; DRYER, F., 1992) ^a	Species Profiles	1.18	1020-1120	1.0	Flow Reactor
(EGOLFOPOULOS, F. N.; DU; LAW, C. K., 1992) ^b	LBV		298-453		C.F. Tw-F
	IDT	0.8-1.8	1090	1.0	ST
	Species Profiles	0.81-1.0	1300-1600		Flow Reactor
(DAGAUT, P; BOETTNER, JC; CATHONNET, M, 1992) ^b	Species Profiles	0.3, 0.6, 1.0, 2.0	770-1220	10	JSR
(CURRAN et al., 1992) ^b	IDT	0.25 - 1.5		2.3	
		0.1-4.0	1100-1900	3.5	ST
		0.15-2.4		4.5	
(MARINOV, 1999) ^b	LFS	0.6-1.4	298-453	1.0-2.0	C.F. Tw-F
	IDT	0.5-2.0	1300-1700	1.0-3.4	ST
	Species Profiles	0.2-2.0	1000-1200	1.0	JSR
(LI et al., 2007) ^b	Species Profiles	0.3-1.4	800-950	3.0-12	Flow Reactor
(LI, Juan; KAZAKOV; DRYER, Frederick L, 2004) ^b	Pyrolysis	**	1045-1080	1.7-3.0	Flow Reactor
(SAXENA; WILLIAMS, F. A., 2007) ^b	IDT	0.5-2.0	1300-1700	1.0-4.6	ST
	LBV	0.6-1.7	298-453	1.0	C.F. Tw-F

Continued on the next page

Table 3 – Continued from Previous Page.

Reference	Parameters Analyzed	ϕ	T [K]	P [Bar]	Experimental Setup
(CANCINO, L. R. et al., 2010) ^b	IDT	1.0	650-1220	10, 30, 50	ST
		0.3	650-1220	30	
		1.0	650-1600	10, 30, 50	
		0.3	650-1600	30	
		0.25-2.0	1200-1600	2.0-4.6	
(VELOO, P. S. et al., 2010b) ^a	LFS Extinction Strain rates	0.7-1.5	343	1.0	Counterflow Premixed flame
(LEPLAT et al., 2011a) ^b	Species Profiles	0.75, 1.0,	500-1800 890-1250	0.05 1.0	Low Pressure Premixed Flame JSR
		1.25			
		0.25, 0.5, 1.0, 2.0			
(KONNOV, A.; MEUWISSEN; DE GOEY, 2011a) ^a	LFS	0.65-1.55	298, 308, 318, 328, 338, 348, 358	1.0	Flat Flame Burner
(MITTAL et al., 2014) ^a	IDT	0.3-1.0	825-985	10-50	RCM
(MATHIEU et al., 2019a) ^a	IDT	0.5, 1.0, 2.0	938-1615	1.3-53	ST

- ^a: Experimental

- ^b: Experimental and Numerical.

On the numerical side, researchers have developed several detailed kinetic mechanisms based on experimental findings, whether from their own work or that of others.

Early investigations by Natarajan and Bhaskaran (1981) concentrated on the ignition characteristics of ethanol-oxygen mixtures in shock tubes (ST). They proposed a model for high-temperature ethanol oxidation, comprising 56 elementary reactions. Dunphy, Patterson, and Simmie (1991), on the other hand, significantly contributed to the understanding of ethanol oxidation by developing a detailed kinetic mechanism with 97 elementary reactions.

Later on, the kinetic parameters suggested by Norton and FL Dryer (1992) for the ethanol sub-mechanism in their experimental work were applied and optimized in the numerical studies conducted by F. N. Egolfopoulos, Du, and C. K. Law (1992), focusing on counterflow twin-flame burners (C.F. Tw-F), and Curran et al. (1992). Simultaneously,

Dagaut, P, Boettner, JC, and Cathonnet, M (1992) proposed a comprehensive kinetic reaction mechanism for ethanol pyrolysis and oxidation.

A few years later, Marinov (1999) from the Lawrence Livermore Laboratory (LLNL) expanded on some of the aforementioned ethanol studies. They introduced a kinetic model for ethanol oxidation, developed to calculate laminar flame speed (LFS) ethanol oxidation profiles from jet-stirred reactors (JSR) and turbulent flow reactors. The compiled mechanism consisted of 56 species and 351 reversible reactions, and is known as LLNL mechanism.

An interesting characteristic of the LLNL mechanism is that it is an extension of the previous studies by Borisov et al. (1992) and Norton and FL Dryer (1992), highlighting the complexity of the molecular structure of ethanol, with emphasis on the presence of three distinct hydrogen atom sites and how this feature influences product distribution during combustion at different temperatures. The three works emphasized the importance of accurate branching ratio assignments for proper determination of reaction products.

The main contributions of the work of Marinov (1999) include:

- Importance of the $\text{C}_2\text{H}_5\text{OH} + \text{O}_2 \longrightarrow \text{Products}$ reactions for ignition delay times;
- Importance of H-atom abstractions for accurate prediction of ethanol-air flame speeds;
- Significance of the $\text{C}_2\text{H}_5\text{OH} + \text{OH}^\bullet \longrightarrow \text{Products}$ reaction and its branching ratio selection for JSR and turbulent flow reactors.

Since the mechanism was based on high-temperature conditions, it faced challenges in accurately predicting low-temperature conditions. The latest update of the model was in 2004.

Marinov's model was subsequently updated by Li et al. (2007) and Saxena and Forman A. Williams (2007) to enhance predictions and minimize uncertainties, resulting in mechanisms that provided reasonable predictions for various combustion parameters. Another detailed kinetic model was later developed by L. R. Cancino et al. (2010), focusing on laminar flame speed calculations.

In contrast, the Creck mechanism developed by the CRECK Modeling Group at Politecnico di Milano is a highly detailed model. Its assessment follows a hierarchical approach, commencing with C0-C4 species. The model underwent primary validation using laminar flame speeds and incorporates species such as cycloalkanes, aromatics, oxygenated alcohols, $\text{C}_3\text{H}_6\text{O}$ isomers, ethers, and methyl esters (METCALFE et al., 2013).

Researchers at the Combustion Chemistry Centre at the University of Galway have significantly contributed to understanding the kinetics of oxygenated fuels through the development of the Aramco mechanisms, named after their sponsor, Saudi Aramco.

The initial release, Aramco 1.3, developed by Metcalfe et al. (2013), serves as the foundational kinetic model for numerous studies. An example is the mechanism of Mittal et al. (2014). The model consists of refined rate constants for reactions involving ethanol with hydroperoxyl radicals and ethanol with methyl peroxy radicals. The branching ratio of OH• radicals abstracting from the three sites of the ethanol molecule also underwent modification. The validation includes flow reactors, shock tubes, JSR, and flame studies.

The relatively short San Diego mechanism can also be used to simulate ethanol combustion. Similar to LLNL, the model was developed to represent high-temperature combustion (SAXENA; WILLIAMS, F. A., 2007). The rate parameters in Saxena's model are an enhancement over those of Juan Li, Kazakov, and Frederick L Dryer (2004), which are, in turn, a refinement of Marinov's previously described mechanism. Validation included autoignition in a shock tube, measurement of laminar burning velocities, and observation of diffusion-flame extinction.

Later, in 2016, Aramco v2.0 emerged (BURKE, U. et al., 2016). This mechanism starts with an H₂/O₂ sub-mechanism, followed by a C₁ sub-mechanism, and has grown to include larger carbon species such as ethane, ethylene, acetylene, allene, propyne, propene, n-butane, isobutene, 1-butene, and 2-butene, and oxygenated species.

Aramco v3.0 was the latest update of the mechanism. Although it includes the ethanol sub-mechanism from earlier versions, this kinetic model was developed to include comprehensive low- and high-temperature reaction mechanisms specific to diene chemistry (ZHOU et al., 2018).

The Aramco mechanism v1.3 was the base for an additional mechanism presented in the work of Zhang et al. (2018). Their research explored the low-temperature reactivity of ethanol using dimethyl ether (DME) as a radical extractor. The experimental data used for validation include ignition delay times, JSR, and flow reactors.

Recently, Shrabanti Roy and Askari (2020) proposed a new kinetic mechanism for ethanol oxidation, the PCRL-Mech1. The model was generated by the Reaction Mechanism Generator (RMG), developed by Gao et al. (2016). RMG describes molecules using adjacency lists that contain information such as atom index, atomic element, unpaired electrons, lone pairs, formal charge, bonds, and the atom at which the element is bonded, as well as the type of bond (i.e., single, double, triple, or benzene). These adjacency lists are also used to describe functional groups, where atomic elements are replaced by group atom types. There is also an indication of the reacting atoms. In RMG, all groups are ordered in hierarchical trees that begin with more general groups and descend to more specific groups, namely, "child" groups. These child groups can be understood as subsets of the parent nodes above them. They are more specific and more exclusive than the parents. The reactions are generated by one group from each tree with the use of templates, for example, (C_{pri}, O_{pri}, rad).

RMG generates elementary reactions based on reaction families, which can

be understood as templates describing the reaction sites and the recipe for the new bond connectivity. Each reaction family has its hierarchical tree of rate estimation rules, which assigns kinetics between reaction sites according to their closest-matching functional groups. The algorithm also deals with isomers, calculating the thermodynamic parameters for each resonance isomer. It iterates over all isomers, and then at the end chooses the thermochemistry of the isomer with the most stable enthalpy to represent the thermochemistry for the overall species (GAO et al., 2016).

Once built, the mechanism of Shrabanti Roy and Askari (2020) was tested with different reaction libraries or combinations of reaction libraries for H_2/O_2 and $\text{C}_1\text{--C}_4$ mechanisms. Then, 35 combinations were simulated, and ignition delay times results were compared with experimental data. Later, seven important conditions were evaluated, with the final mechanism being a combination of Aramco 2.0 (BURKE, U. et al., 2016), Burke H_2O_2 (BURKE, M. P. et al., 2012), and GRI-Mech 3.0 (SMITH et al., 1999).

PCRL-Mech1 is now available for calculations under various operating conditions. Validation across a range of experimental setups, including shock tubes, rapid compression machines (RCM), constant volume combustion chambers (CVCC), flow reactors, JSR, and counterflow flames ensures the accuracy and reliability of this model.

All these kinetic models are chronologically summarized in Table 4.

Table 4 – Detailed kinetics models for ethanol combustion.

Mechanism	Year	Number of Species	Number of Reactions	References
Natarajan and Bhaskaran	1981	27	56	(NATARAJAN; BHASKARAN, 1981)
Dunphy <i>et al.</i>	1991	30	97	(DUNPHY; PATTERSON; SIMMIE, 1991)
Egolfopoulos <i>et al.</i>	1992	35	195	(EGOLFOPOULOS, F. N.; DU; LAW, C. K., 1992)
Curran <i>et al.</i>	1992	**	**	(CURRAN et al., 1992)
Dagaut <i>et al.</i>	1992	**	39	(DAGAUT, P; BOETTNER, JC; CATHONNET, M, 1992)
LLNL	2004	57	393	(MARINOV, 1999)
Li <i>et al.</i>	2007	39	228	(LI et al., 2007)
Saxena and Williams	2007	57	288	(SAXENA; WILLIAMS, F. A., 2007)
Cancino <i>et al.</i>	2010	136	1136	(CANCINO, L. R. et al., 2010)
Leplat <i>et al.</i>	2011	38	252	(LEPLAT et al., 2011a)
Creck	2013	339	9781	(METCALFE et al., 2013)
Lee <i>et al.</i>	2012	44	279	(LEE, C. et al., 2012)
Mittal	2014	113	710	(MITTAL et al., 2014)
San Diego	2016	57	268	(WILLIAMS, F., 2016)
Aramco v3.0	2018	581	3037	(ZHOU et al., 2018)

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Table 4 – Continued from Previous Page.

Mechanism	Year	Number of Species	Number of Reactions	References
Zhang	2018	433	1004	(ZHANG et al., 2018)
Hashemi <i>et al.</i>	2018	20	38	(HASHEMI; CHRISTENSEN, J. M.; GLARBORG, 2018)
PCRL-1	2020	67	1016	(ROY, Shrabanti; ASKARI, 2020)

All these sophisticated mechanisms provide a comprehensive understanding of ethanol combustion. It is important to note that no single mechanism is universally accepted as each has been validated over limited experimental ranges. Therefore, kinetics modelers need to choose the *important* properties and parameters needed to describe the chosen physical phenomenon (BLUROCK; BATTIN-LECLERC, 2013).

This leads to the need of a systematic evaluation to assess the performance of different mechanisms across different combustion regimes. Hence, the following chapter details the methodology employed in this work to evaluate and compare seven ethanol kinetics mechanisms under specific conditions, and the respective key important parameters already discussed: IDT, LFS, and species concentration profiles.

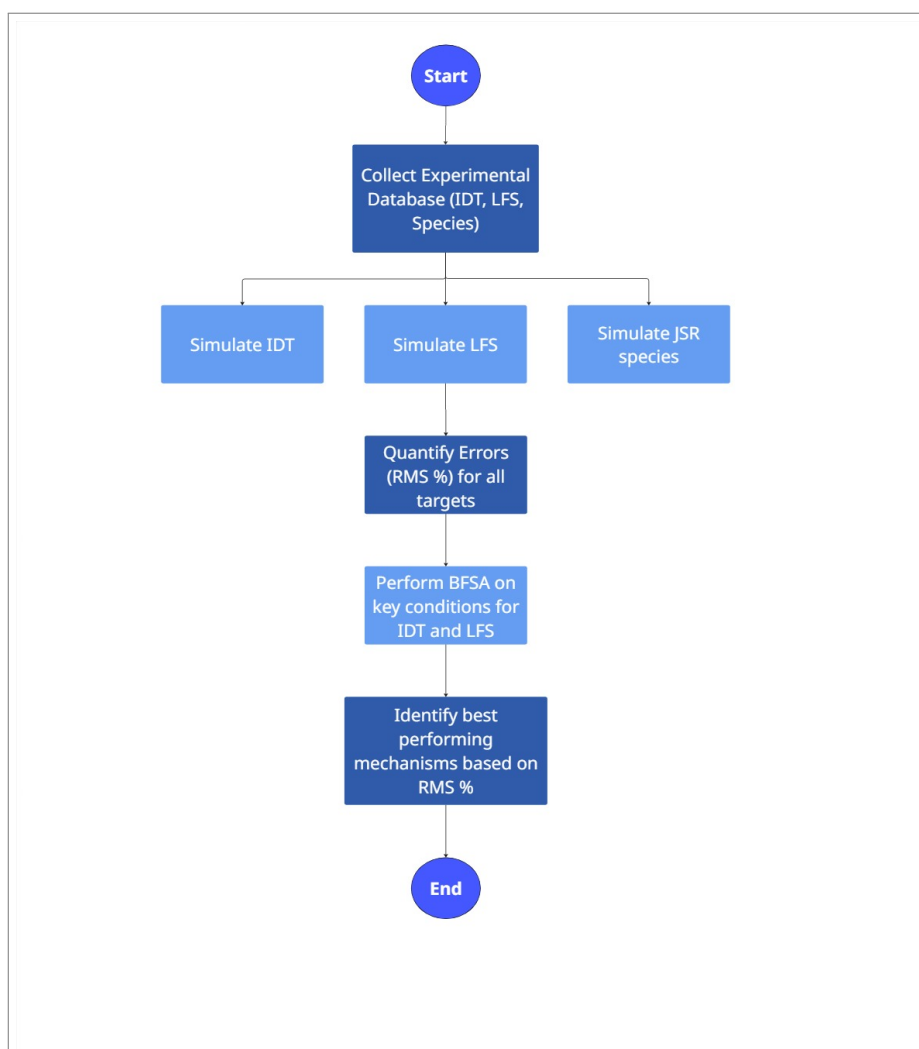
3 METHODOLOGY

In this chapter, a comprehensive overview of the methodology is provided, detailing the analytical and numerical processes applied in this work.

3.1 IMPLEMENTATION

Figure 9 depicts the flowchart of the main stages of the methodology applied. The stages employed are briefly explained below, with further elaboration provided throughout this chapter.

Figure 9 – Process flowchart



3.1.1 Metrics

To evaluate the disparity between the mechanisms and experimental data, a quantitative criteria was applied, following the methodology used in the work of Neves

et al. (2022). The method chosen was the root mean square (RMS) expressed as a percentage (RMS %). This statistical approach is, according to Karunasingha (2022), used for model fitting (optimal parameter selection of a given model), model validation, model selection, and model comparisons. It measures the average magnitude of the uncertainty between the two sets of data points, as demonstrated in Equation (19), Equation (20), and Equation (21).

$$\text{RMS} = \sqrt{\frac{1}{N} \sum_{i=1}^N (Q_{\text{sim},i} - Q_{\text{exp},i})^2} \quad (19)$$

$$\text{RMS (\%)} = \frac{\text{RMS}}{\bar{Q}_{\text{exp}}} \times 100 \quad (20)$$

$$\bar{Q}_{\text{exp}} = \frac{1}{N} \sum_{i=1}^N Q_{\text{exp},i} \quad (21)$$

Where N is the number of experimental data points, $Q_{\text{sim},i}$ and $Q_{\text{exp},i}$ are the i -th simulated and experimental values, respectively, and $\bar{Q}_{\text{exp}}$ is the mean of the experimental values. The pseudocode for this method can be found in A.1.

3.2 COMPUTATIONAL MODELING

For the development of this study, three kinds of simulations of reactive systems were performed: (i) ignition delay time simulation on a homogeneous adiabatic constant volume reactor, (ii) laminar free propagating flame speed, and (iii) species concentration profiles in a jet-stirred reactor (JSR). All the simulations were carried out on a Windows operating system with 8GB RAM and a Core-i5 processor, utilizing the Cantera-Python interface (GOODWIN; MOFFAT; SPETH, 2015). The in-house simulation code was developed by the Combustion Research Group at LABMCI/UFSC, and it was adapted by the author of this dissertation for specific purposes. The following sections will delve into the chosen mechanisms, experimental conditions, and how computational modelling was used for optimization.

3.2.1 The investigated mechanisms

7 detailed combustion mechanisms published over the past decades were considered in this work. The numerical models chosen can be found in Table 5. The mechanism identifiers were created by using the traditional short name or combining the names of the first author or the research group.

Table 6 lists all the investigated mechanisms and provides information about the type of experiments used for validation. The experiments include ignition delay times in shock tubes (IDT-ST) and rapid compression machines (IDT-RCM), jet-stirred reactor

Table 5 – Detailed kinetics models for ethanol combustion used in this work.

Mechanism	Year	Elements number	Species number	Reactions number	References
Mittal	2014	6	113	710	(MITTAL et al., 2014)
LLNL	2004	4	57	393	(MARINOV, 1999)
San Diego	2016	6	58	268	(WILLIAMS, F., 2016)
Creck	2012	6	339	9781	(METCALFE et al., 2013)
Aramco v3.0	2018	6	404	3037	(ZHOU et al., 2018)
PCRL	2020	14	67	1016	(ROY, Shrabanti; ASKARI, 2020)
Zhang	2018	6	433	1004	(ZHANG et al., 2018)

(JSR) data, flow reactor (FR) experiments, laminar burning velocities (LBV), and burner-stabilized flame (BSF) measurements.

Table 6 – Experiment types of ethanol combustion measurements at which the mechanisms were originally validated by their developers. Mark ✓ indicates the mechanism was validated against the corresponding type of experiments.

Mechanism ID	Experiment types of mechanism validation					
	IDT ST	IDT RCM	JSR	FR	LBV	BSF
Mittal	✓	✓	✓	✓	✓	✓
LLNL	✓	-	✓	✓	✓	✓
San Diego	✓	-	-	-	✓	✓
Creck	✓	-	✓	✓	✓	✓
Aramco v3.0	✓	✓	✓	✓	✓	-
PCRL	✓	✓	✓	✓	✓	✓
Zhang	✓	✓	-	-	-	-

For further information about the experimental ranges used to validate each mechanism, please refer to Table 29, Table 30, Table 31, Table 32, Table 33, Table 34, and Table 35.

3.2.2 Collection of experimental data

This section deals with the collection of experimental measurements for ethanol. In the present study, experimental data were obtained from the works of L. R. Cancino et al. (2010), Peter S. Veloo et al. (2010a), A.A. Konnov, Meuwissen, and de Goey (2011a), Leplat et al. (2011b), and Mathieu et al. (2019b). The experimental conditions used for validation can be found in Table 7.

Table 7 – Experimental data of ethanol combustion reported in the literature used in this work

Experimental Conditions					
Author	T [K]	p [atm]	p [kPa]	φ	
Ignition Delay Time					
(MATHIEU et al., 2019a)	990-1125	25±1.5	2533±152	1.0	
(MATHIEU et al., 2019a)	945-1085	51±2.5	5168±253	1.0	
(CANCINO, L. R. et al., 2010)	900-1223	9.5±1.3	964±132	1.0	
(CANCINO, L. R. et al., 2010)	789-1197	30±1.2	3040±122	1.0	
(CANCINO, L. R. et al., 2010)	841-1234	49.3±2.0	4994±202	1.0	
(CANCINO, L. R. et al., 2010)	912-1183	32.4±2.5	3282±253	0.3	
Laminar Flame Speed					
(KONNOV, A.; MEUWISSEN; DE GOEY, 2011a)	298, 318	1.0	101.3	0.65-1.55	
(KONNOV, A.; MEUWISSEN; DE GOEY, 2011a)	338, 358	1.0	101.3	0.65-1.55	
(VELOO, P. S. et al., 2010a)	343	1.0	101.3	0.70-1.50	
Species Concentration					
(LEPLAT et al., 2011b)	890-1250	1.0	101.3	1.0	

Ignition delay times were measured in ST. Ethanol laminar burning measurements were collected from different experimental configurations: spherical bomb tests (MATHIEU et al., 2019b) and the flat adiabatic flame technique using heat flux burners (KONNOV, A.; MEUWISSEN; DE GOEY, 2011a). Species profiles were recorded using a fused silica jet-stirred reactor (JSR) (LEPLAT et al., 2011a). The concentration of species includes measurements of CO, CO₂, H₂O, C₂H₅OH, and O₂.

For additional details, Table 8 provides an overview of the initial condition ranges for the collected data points, categorized by experiment type, along with the corresponding number of data points.

Table 8 – Summary of the experimental data on ethanol combustion sorted according to experiment types and techniques (see text for the abbreviation).

Experiment types	T [K]	p [atm]	p [kPa]	φ	No. of data points
IDT-ST	789–1234	25–51	2533–5170	0.3, 1.0	52
JSR	890–1250	1.0	101	1.0	29
LBV	298, 318, 338, 343, 358	1.0	101	1.0	78

3.2.3 Sensitivity Analysis

To identify the rate-limiting reactions and understand the chemical behavior of the system under the conditions of this study, the BFSA was employed. The selection of this method was based on the following considerations specific to this work:

- The computational cost of BFSA is manageable for the scope of this study. This contrasts with more complex approaches like GSA, which would be computationally expensive for the seven mechanisms;
- BFSA provides direct and interpretable results through sensitivity coefficients, facilitating clear comparison across different mechanisms;
- BFSA has well-established precedent in combustion kinetics literature for mechanism evaluation and refinement, as demonstrated in the works of Ols-son and Andersson (1987), Rui Li et al. (2019), Shrabanti Roy and Askari (2020), Liang et al. (2020), Bonini et al. (2022), and Chunxia Chen et al. (2022), ensuring methodological reliability.

This step aims to determine the primary sources of discrepancy within the mechanisms and the experimental data used in this study, identifying the reactions with the most influence on the target outputs, i.e, IDT, and LFS. The results from this sensitivity analysis can be further used to elucidate the reaction pathways and rate parameters that require more attention in the development or refinement of chemical kinetics mechanisms. The BFSA was applied to all seven mechanisms. For each reaction, the rate constant was perturbed by a factor of 0.5 and 2.0, respectively. The result change in the interest output parameter was then calculated for a specific set of initial conditions:

- For IDT, the analysis was conducted at a pressure of 30 atm for a stoichiometric mixture $\varphi = 1.0$ and two temperatures, 800 K and 1200 K.
- For LFS, the analysis was conducted at atmospheric pressure (1 atm) and an unburned gas temperature of 358 K. To evaluate the chemistry of both lean and rich conditions: $\varphi = 0.70$ and $\varphi = 1.55$.

This approach enables the identification of key reactions whose kinetics can influence the model predictions across the range of conditions relevant to this study.

4 RESULTS AND DISCUSSION

4.1 IGNITION DELAY TIMES

In previous chapters, it was established that the ignition delay time is influenced by the balance between chain-branching and chain-terminating processes. Therefore, in this section, experimental IDT data is compared with simulations performed in Cantera, followed by a discussion of the results. The predicted ignition delay times for C_2H_5OH as a function of temperature are found in Figure 10 for different pressures and equivalence ratios.

Figure 10 – Comparison of ethanol ignition delay time for different mechanisms. (a) and (b), the symbols represent the experimental results of Mathieu et al. (2019b). (c) to (f), the symbols represent the experiments of L. R. Cancino et al. (2010)

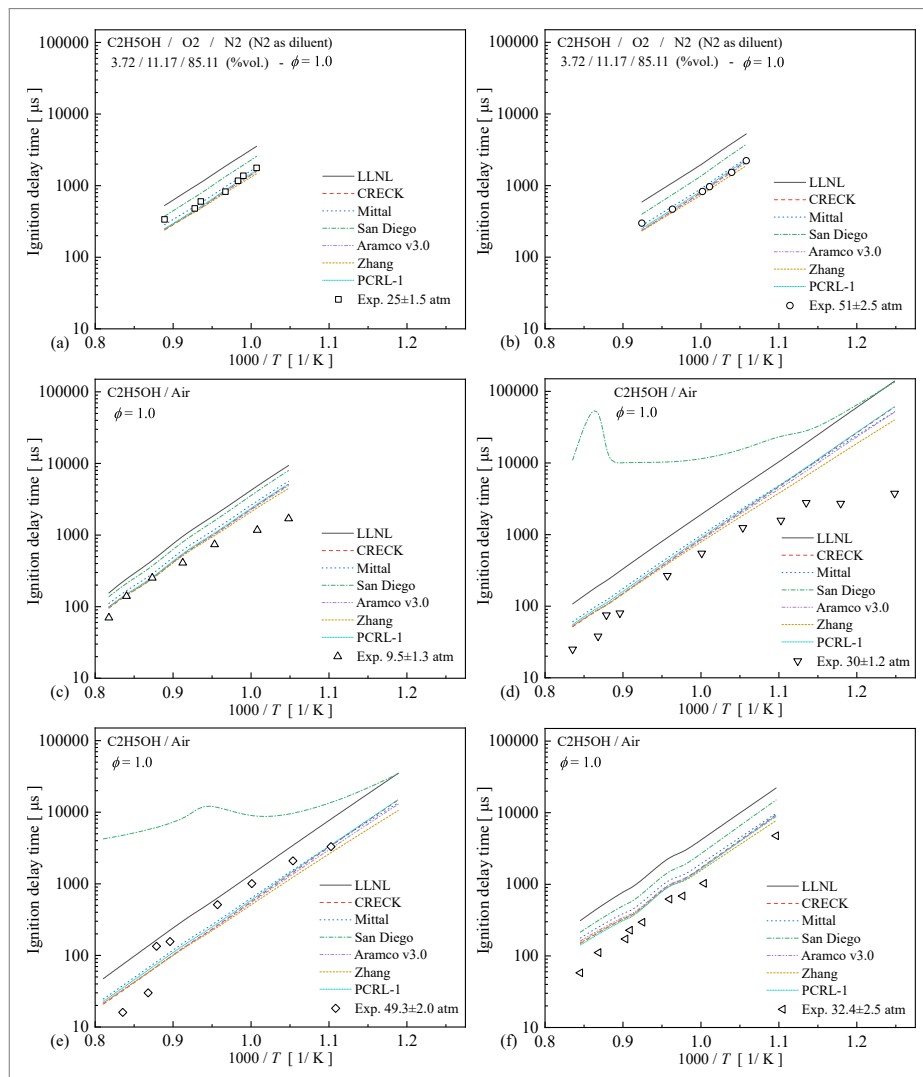


Figure 10 demonstrates that by increasing temperature, ignition delay times decrease in all conditions evaluated. At higher temperatures, the reactivity increases, resulting in shorter ignition delays. This trend was consistently observed in all kinetics models evaluated during this study. At lower temperatures, however, the slower oxidation pathways mediated by hydroperoxyl radicals are dominant, which promotes the formation of stable peroxides H_2O_2 , delaying ignition.

Among the kinetics models assessed in this work, the Creck, Aramco v3.0, Zhang, Mittal, and PCRL demonstrated superior performance in predicting ignition delay times in shock tube experiments. These models accurately represented the experimental data obtained by Mathieu et al. (2019b), as depicted in Figure 10 (a) and (b). However, some deviations occur when comparing the mechanisms to the experiments of L. R. Cancino et al. (2010) (i.e., Figure 10 (c), (d), (e), and (f)). Specifically, at a pressure of 9 ± 1.3 atm, as shown in Figure 10 (c), all kinetic models overpredicted IDT at temperatures higher than 1096 K. In addition, at lower temperatures, the mechanisms exhibited higher divergence from the experimental results. This discrepancy may be related to the limited knowledge of lower-temperature chemical kinetics, with some coefficients and pathways yet to be well-characterized.

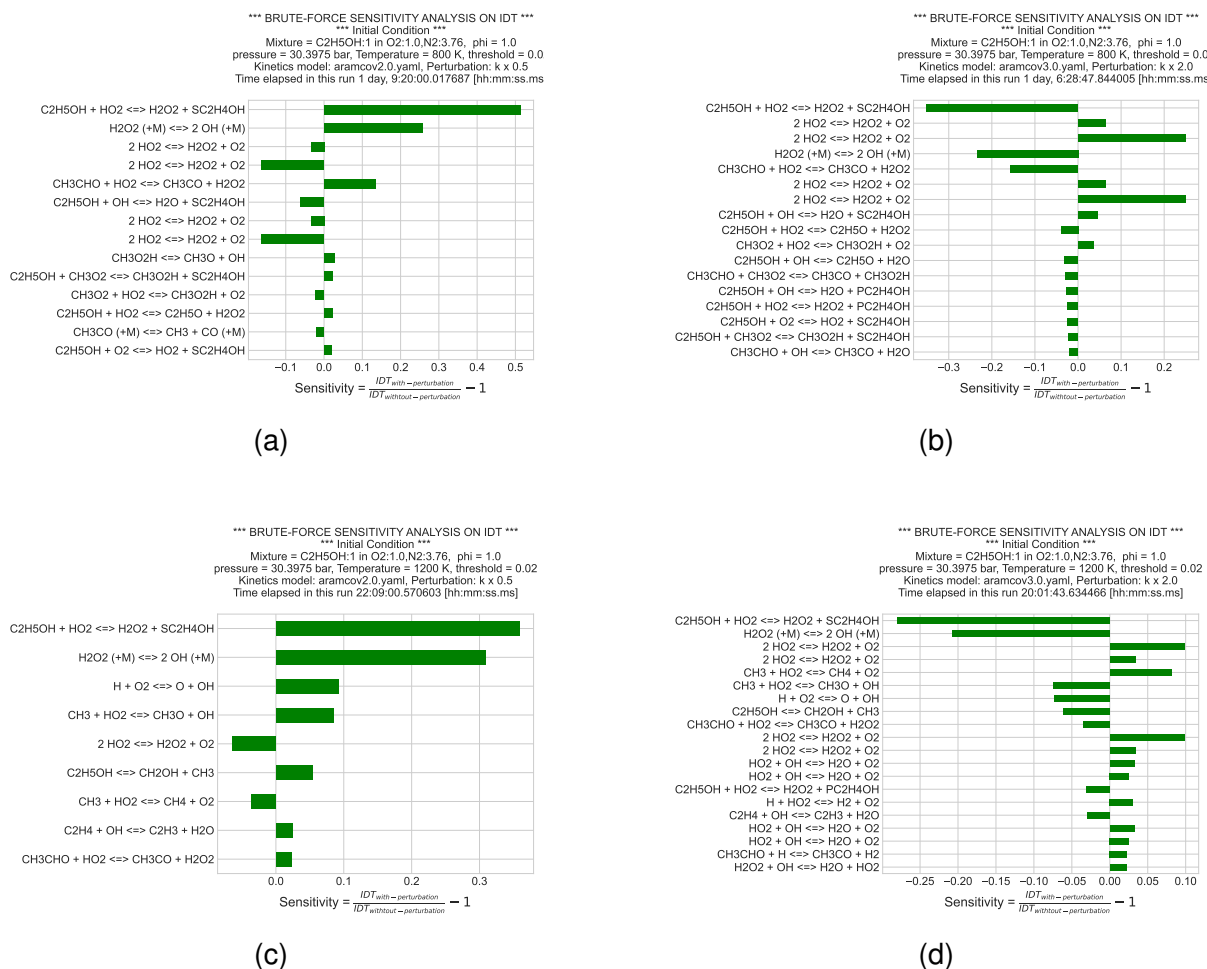
The experimental data showed a highly nonlinear reactivity increase at lower temperatures, whereas the models predicted a much lower IDT, displaying exponential behavior on the log scale.

Furthermore, according to Figure 10 (d) and (e), at $\varphi = 1.0$ and pressures higher than 30 atm, the calculated IDT from the San Diego mechanism oscillated within the experimental range. However, this trend was not observed at $\varphi = 0.3$, as shown in Figure 10 (f). Notably, at $p \sim 30$ atm, all mechanisms overpredicted the experimental data of L. R. Cancino et al. (2010), whereas at $p \sim 50$ atm, the IDT was underestimated, as indicated in Figure 10 (e), and the LLNL model demonstrated a better fit to the data.

To further investigate the key reactions responsible for discrepancies in IDT, a brute-force sensitivity analysis was applied. The simulations were performed at temperatures of 800 K and 1200 K, and a pressure of 30 atm. Figure 11, Figure 12, Figure 13, Figure 14, Figure 15, Figure 16, and Figure 17 highlights the key reactions with the greatest influence based on a threshold of 0.5% and 2.0% change (absolute) in IDT.

From the brute-force analysis, it is observed that hydroperoxyl radicals are present in the most sensitive reactions. Indeed, previous chapters have already established the influence of these radicals in deriving the low-temperature oxidation and ignition of hydrocarbons, as noted by Rawadieh et al. (2019). Primary alcohols such as ethanol demonstrate the same trend, as well-established in the works of Song Cheng et al. (2020), and Hashemi, Jakob M Christensen, and Glarborg (2018). The works of Changyoul Lee et al. (2012) and Heghes (2007), indeed highlight the crucial role of these radicals within these temperature ranges. Leonel Rincón Cancino (2009) further

Figure 11 – Brute-force sensitivity analysis results for ethanol/air ($\varphi = 1.0$) ignition delay using the Aramco mechanism. (a) $k \times 0.5$, $T = 800$ K, (b) $k \times 2.0$, $T = 800$ K, (c) $k \times 0.5$, $T = 1200$ K, (d) $k \times 2.0$, $T = 1200$ K.



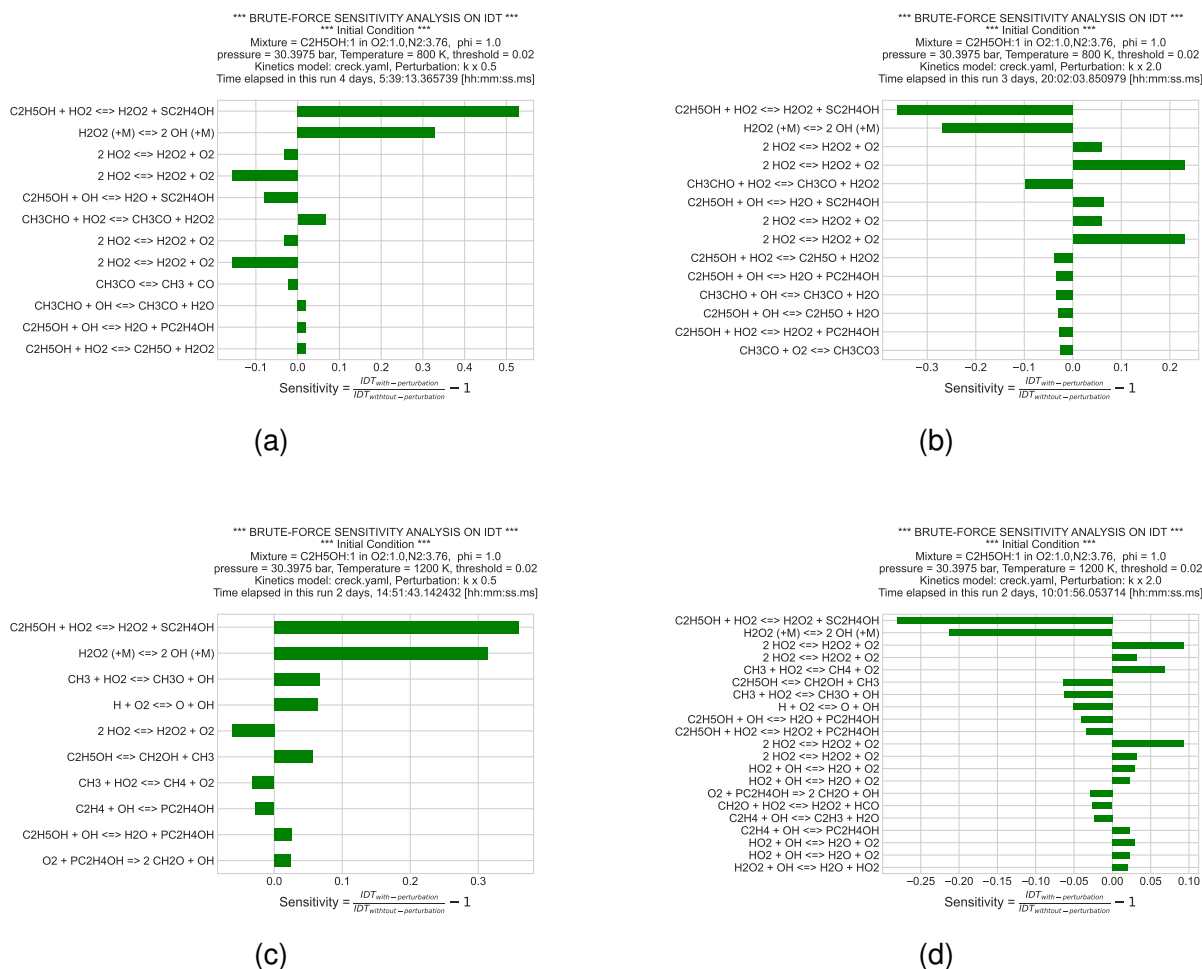
Source: Author, 2025

demonstrates the importance of $\text{HO}_2^\bullet$ radicals at high-pressure conditions. H-atom abstractions trap the hydroperoxyl radicals into hydrogen peroxide (H_2O_2), which are stable molecules at low temperatures (HEGHES, 2007). As temperature increases, H_2O_2 molecules dissociate to form two $\text{OH}^\bullet$ radicals (LEE, C. et al., 2012). The resulting $\text{OH}^\bullet$ radicals enhance ethanol reactivity and restore oxidation capacity. As a result, ignition delay times are sensitive to the kinetics of H-atom abstraction reactions by $\text{HO}_2^\bullet$ radicals over a wide temperature range (HEGHES, 2007).

The seven mechanisms studied herein encompass the chemistry of hydrogen abstraction by $\text{HO}_2^\bullet$ radicals. Also, as expected, these reactions are sensitive to ignition delay times in all cases.

Notably, six models include abstractions from the α , β , and hydroxyl sites. PCRL only includes H-abstractions from the hydroxyl site, which is sensitive to IDT, as demonstrated in Figure 16. Despite this absence of reactions, the model represents ethanol

Figure 12 – Brute-force sensitivity analysis results for ethanol/air ($\varphi = 1.0$) ignition delay using the Creck mechanism. (a) $k \times 0.5$, $T = 800$ K, (b) $k \times 2.0$, $T = 800$ K, (c) $k \times 0.5$, $T = 1200$ K, (d) $k \times 2.0$, $T = 1200$ K.

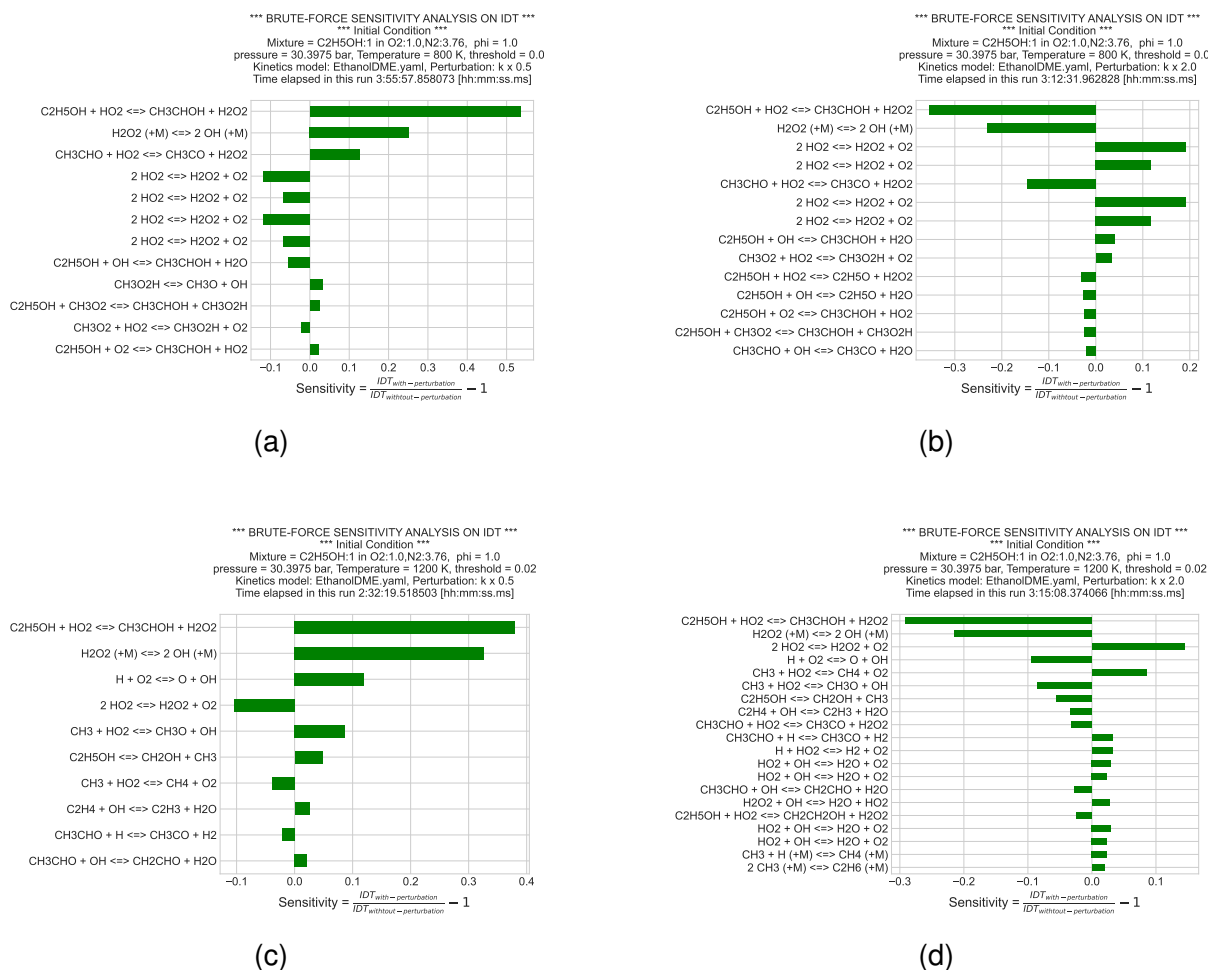


Source: Author, 2025

oxidation surprisingly well, as seen in Figure 10. However, it is worth mentioning that although PCRL shows good numerical performance, its chemical accuracy is limited. In this regard, it is important to note that the works of Zhao et al. (2019), Rotavera and Taatjes (2021), and Nghia (2020) indicate that the α and β channels are dominant, with the α being the most dominant of the two. According to Zhao et al. (2019), abstraction from the α site dominates not only in kinetics but also in thermodynamics. Such a statement is in agreement with Silva et al. (2009b) as well. Indeed, Nghia (2020) has demonstrated that at temperatures of 298 to 2000 K, abstractions of the hydroxyl site have only a minimal contribution. However, as temperature increases, the contribution of the α channel decreases.

To further understand the role of H-abstraction in the predictions of the mechanisms, Figure 18 and Table 9 compare the seven mechanisms and their respective parameters.

Figure 13 – Brute-force sensitivity analysis results for ethanol/air ($\varphi = 1.0$) ignition delay using the Zhang mechanism. (a) $k \times 0.5$, $T = 800$ K, (b) $k \times 2.0$, $T = 800$ K, (c) $k \times 0.5$, $T = 1200$ K, (d) $k \times 2.0$, $T = 1200$ K.



Source: Author, 2025

Table 9 – Arrhenius Parameters for Hydrogen Abstraction Reactions at α , β , and hydroxyl sites.

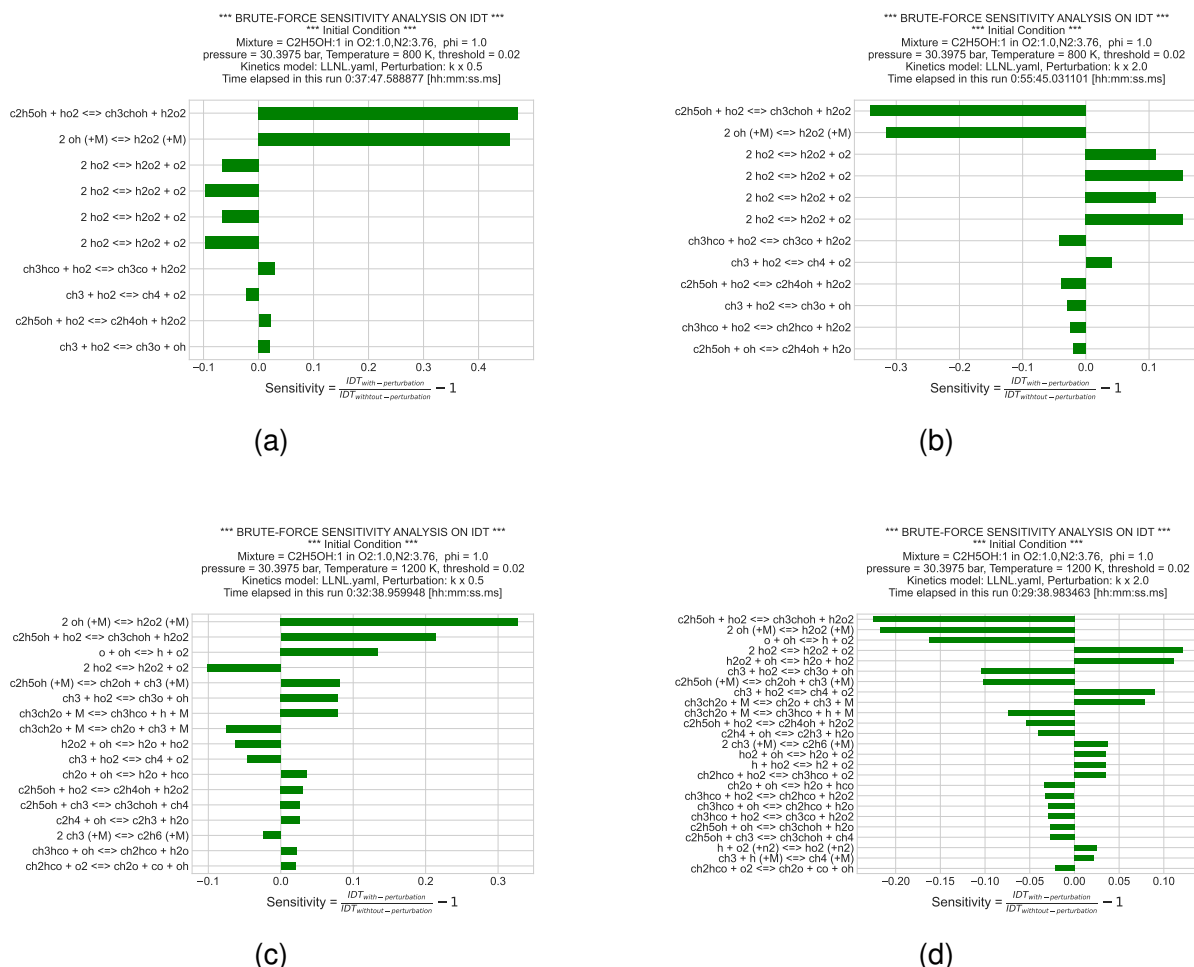
	H-abst. from the α site			H-abst. from the β site			H-abst. from the hydroxyl site		
	A	b	E_a	A	b	E_a	A	b	E_a
LLNL	8.20E+03	2.55	1.08E+04	1.23E+04	2.55	1.58E+04	2.50E+12	0.00	2.40E+04
Creck	2.45E-05	5.26	7.48E+03	3.99E-02	4.30	1.53E+04	6.47E-07	5.30	6.47E-07
Mittal	2.45E-05	5.26	7.48E+03	3.99E-02	4.30	1.53E+04	6.47E-07	5.30	6.47E-07
San Diego	8.20E+03	2.50	1.08E+04	2.43E-04	2.50	1.78E+04	3.80E+12	0.00	2.40E+04
Aramco	2.45E-05	5.26	7.48E+03	3.99E-02	4.30	1.53E+04	6.47E-07	5.30	1.05E+04
Zhang	2.10E-05	5.26	6.50E+03	3.99E-02	4.30	1.53E+04	6.47E-07	5.30	1.05E+04
PCRL	—	—	—	—	—	—	2.45E-05	5.26	7.48E+04
	—	—	—	—	—	—	3.99E-02	4.30	1.53E+04

Pre-exponential factor, A, in [mol, m, s]

Temperature dependency exponent, b, [-]

Activation energy, E_a , in [cal/mol]

Figure 14 – Brute-force sensitivity analysis results for ethanol/air ($\varphi = 1.0$) ignition delay using the LLNL mechanism. (a) $k \times 0.5$, $T = 800$ K, (b) $k \times 2.0$, $T = 800$ K, (c) $k \times 0.5$, $T = 1200$ K, (d) $k \times 2.0$, $T = 1200$ K.

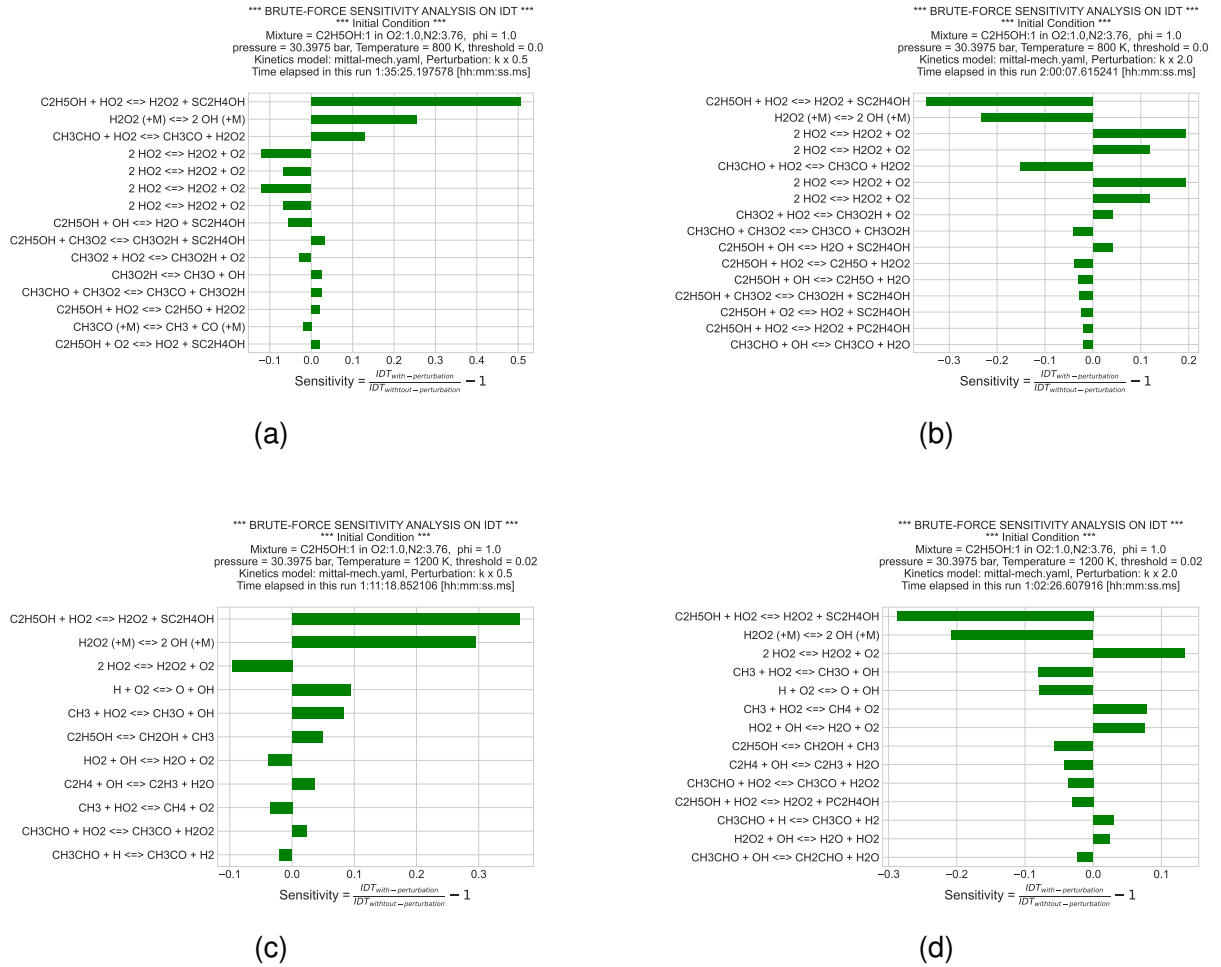


Source: Author, 2025

In Table 9, H-abstraction from the α site refers to the reaction $\text{C}_2\text{H}_5\text{OH} + \text{HO}_2^\bullet \rightleftharpoons \text{CH}_3\text{CH}^\bullet\text{OH} + \text{H}_2\text{O}_2$, some mechanisms may represent the $\text{CH}_3\text{CH}^\bullet\text{OH}$ species as $\text{SC}_2\text{H}_4\text{OH}$. The H-abstraction from the β site refers to the reaction $\text{C}_2\text{H}_5\text{OH} + \text{HO}_2^\bullet \rightleftharpoons \text{CH}_2^\bullet\text{CH}_2\text{OH} + \text{H}_2\text{O}_2$ and the H-abstraction from the hydroxyl site refers to the reaction $\text{C}_2\text{H}_5\text{OH} + \text{HO}_2^\bullet \rightleftharpoons \text{C}_2\text{H}_5\text{O}^\bullet + \text{H}_2\text{O}_2$. The rate constant plot regarding temperature can be seen in Figure 18. It is evident that in Figure 18 (a), San Diego and LLNL models underestimate the rate constants over the entire range evaluated, whereas the mechanisms of Mittal, Creck, Aramco and Zhang have very close constants at high temperatures. At lower temperatures, the mechanism of Zhang begins to slightly overestimate the constant. The effect of these variations correlates with what is demonstrated in Figure 10.

The calculated ignition delay times using the mechanisms of LLNL and San Diego are higher than the values obtained with the experimental results. The numer-

Figure 15 – Brute-force sensitivity analysis results for ethanol/air ($\phi = 1.0$) ignition delay using the Mittal mechanism. (a) $k \times 0.5$, $T = 800$ K, (b) $k \times 2.0$, $T = 800$ K, (c) $k \times 0.5$, $T = 1200$ K, (d) $k \times 2.0$, $T = 1200$ K.

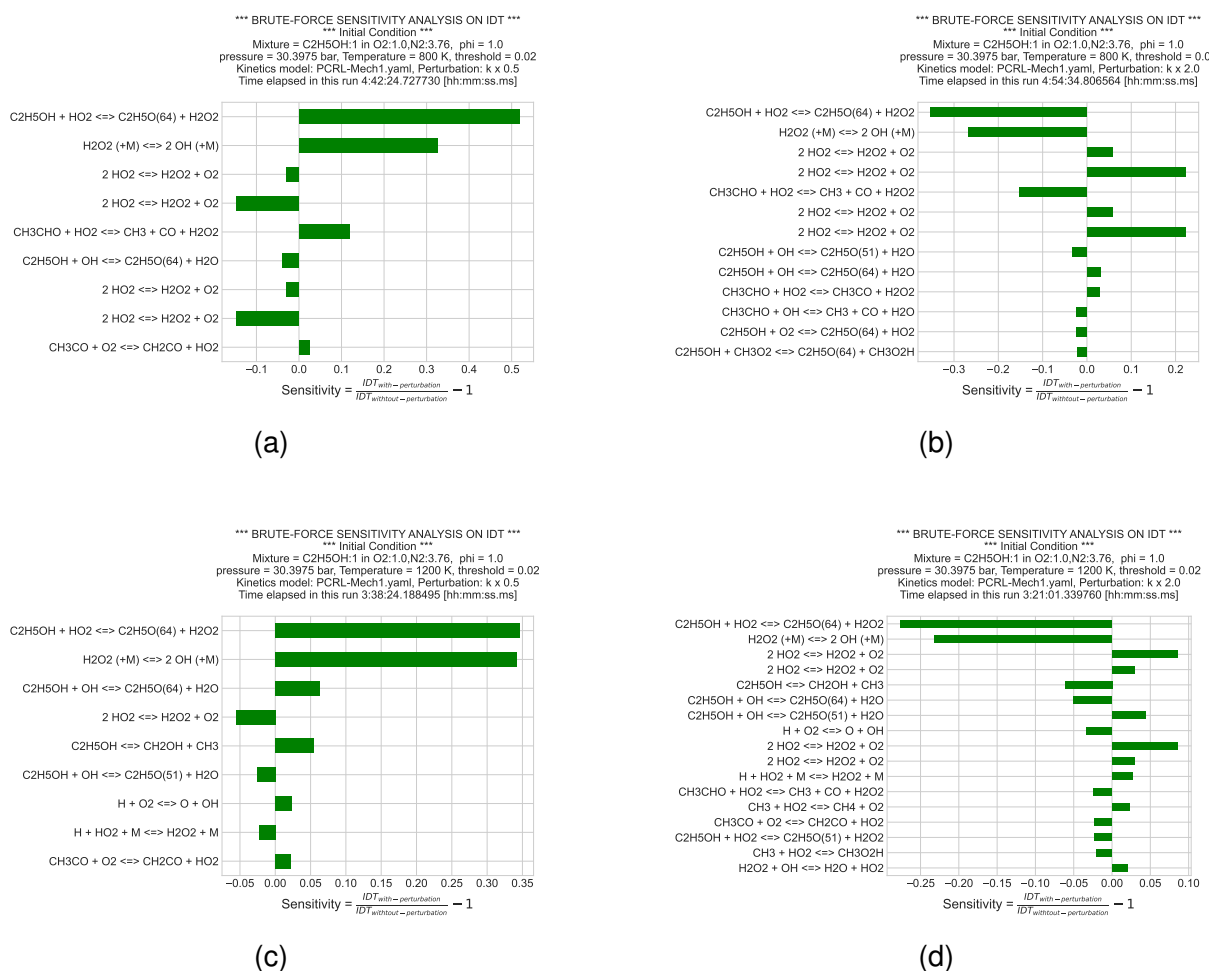


Source: Author, 2025

ical assessment of Mathieu et al. (2019b) indeed shows that LLNL is under-reactive compared to the Aramco v3.0, Creck, and Zhang mechanisms. The lack of reactivity in both models can possibly be explained by uncertainties in the Arrhenius parameters, which differ significantly from those in the other five mechanisms. The LLNL and San Diego mechanisms use higher activation energies ($E_a > 1.0\text{E}+04$ cal/mol) for the α -site H-abstraction reaction compared to recent theoretical calculations by Zhao et al. (2019), which recommend $E_a \sim 8.7\text{E}+03$ cal/mol. These discrepancies in Arrhenius parameters likely suppresses radical production at low temperatures, delaying ignition. Sensitivity analysis presented in Figure 14 and Figure 17 confirms that this reaction strongly influences IDTs under these conditions, supporting the hypothesis.

At higher temperatures, the deviation of IDTs from LLNL and San Diego, decrease, as depicted in Figure 10. This reflects the diminishing role of $\text{HO}_2^\bullet$ -mediated pathways. Under these conditions, ethanol oxidation is dominated by reactions with

Figure 16 – Brute-force sensitivity analysis results for ethanol/air ($\phi = 1.0$) ignition delay using the PCRL mechanism. (a) $k \times 0.5$, $T = 800$ K, (b) $k \times 2.0$, $T = 800$ K, (c) $k \times 0.5$, $T = 1200$ K, (d) $k \times 2.0$, $T = 1200$ K.



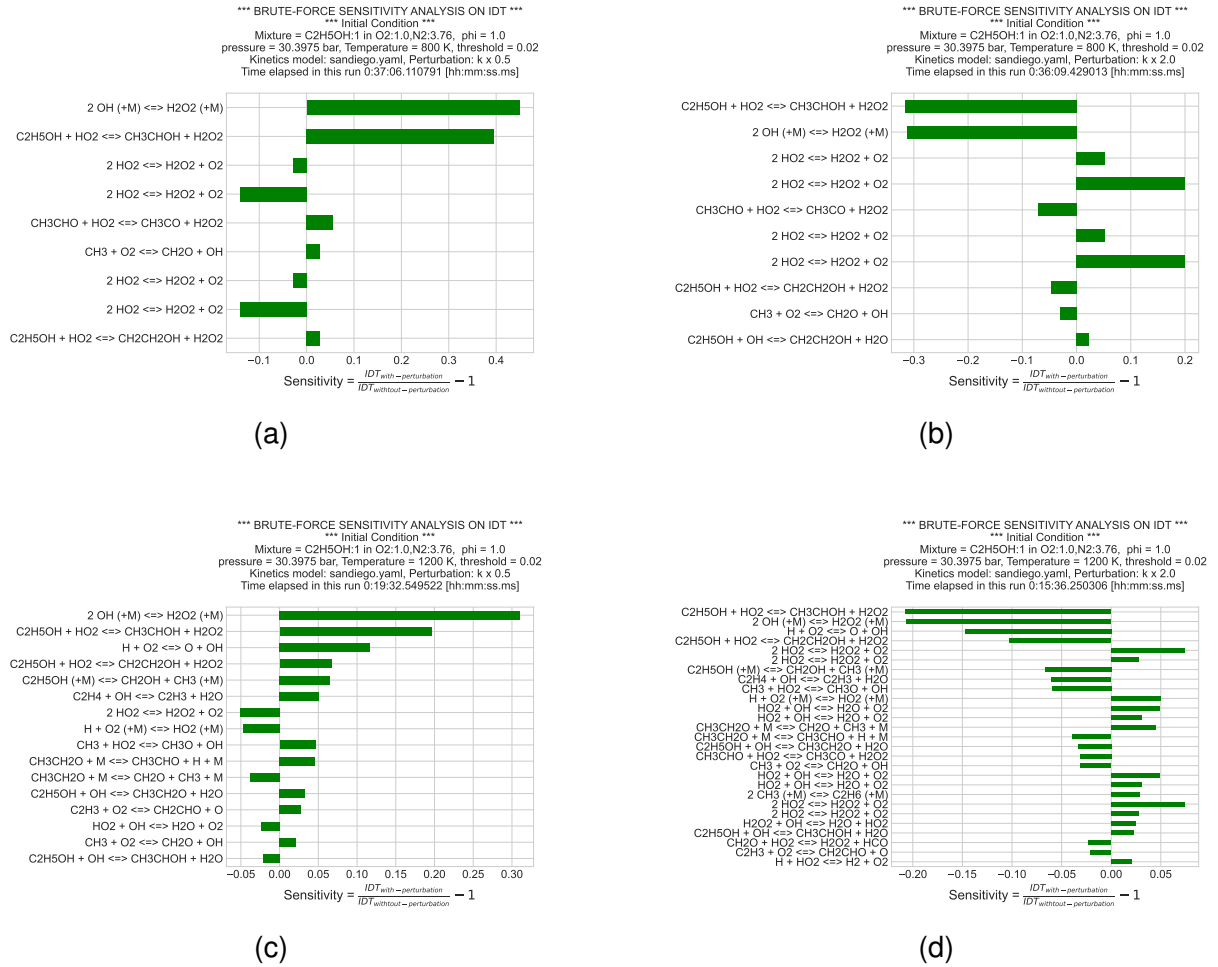
Source: Author, 2025

$OH^\bullet$ radicals, as seen in Figure 14 and Figure 17, which are less sensitive to uncertainties in HO_2 chemistry.

In Figure 18 (b), a different behavior is shown. In this case, there is a better agreement between the rate constants of six of the models (except PCRL) at higher temperatures. LLNL and San Diego slightly deviate only at lower temperatures. Important to note that the rate constants of the mechanisms of Zhang, Mittal, Creck and Aramco are exactly the same. This suggests that factors beyond the parameters of this specific reaction contributes to model divergence. For instance, differences in the treatment of secondary reactions—such as H_2O_2 decomposition, RO_2 isomerization, or third-body efficiencies in pressure-dependent steps—may play critical roles. This underscores the complexity of ethanol oxidation mechanisms, where global model performance depends on the interplay of multiple reactions.

Further, Figure 18 (c) shows that the PCRL mechanism overestimates the rate

Figure 17 – Brute-force sensitivity analysis results for ethanol/air ($\phi = 1.0$) ignition delay using the San Diego mechanism. (a) $k \times 0.5$, $T = 800$ K, (b) $k \times 2.0$, $T = 800$ K, (c) $k \times 0.5$, $T = 1200$ K, (d) $k \times 2.0$, $T = 1200$ K.

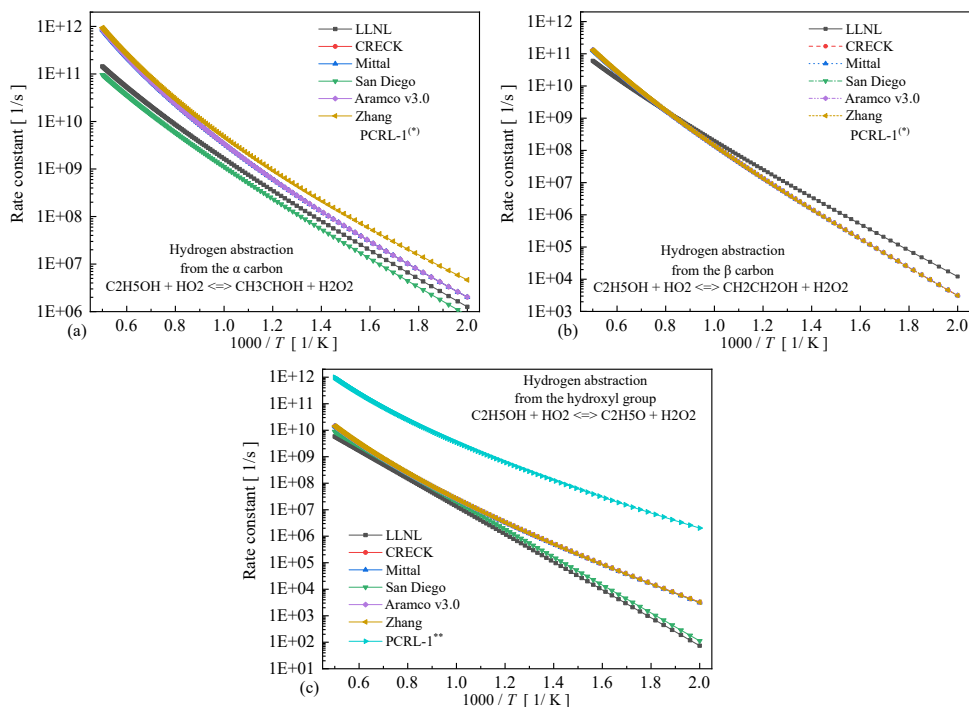


Source: Author, 2025

constant over the entire range of temperatures. On the contrary, LLNL and San Diego underestimate the rate. It can also be seen that Creck, Mittal, Aramco, and Zhang have rate constants that are very close to the ones of LLNL and San Diego at the high-temperature range, but at lower temperatures, they diverge. However, as already established, hydroxyl-site abstraction plays a negligible role in ethanol oxidation kinetics. Theoretical studies of Zhao et al. (2019) confirm that this pathway contributes less than 5% to the total H-abstraction, therefore, its impact on IDT is minimal. Indeed, the PCRL mechanism has good agreement with experimental data, whereas LLNL and San Diego have the biggest deviation among all seven models, even at higher temperatures, as previously seen in Figure 10.

Following, H-abstractions by $\text{HO}_2^\bullet$ compete with the termination reaction $\text{HO}_2^\bullet + \text{HO}_2^\bullet \rightleftharpoons \text{O}_2 + \text{H}_2\text{O}_2$ that strongly inhibits -ignition. This was already noted by the work of Pelucchi et al. (2017), and its influence is seen in the brute-force sensitivities

Figure 18 – Rate constant plots for all the kinetics models involving the hydrogen abstraction reactions at α , β , and hydroxyl sites.



in Figure 11, Figure 12, Figure 13, Figure 14, Figure 15, Figure 16, and Figure 17. The coefficients for these reactions are shown in Table 10 and Figure 19. Important to note that this is a duplicate reaction in all seven mechanisms. Due to its reversibility, it generates four distinct sensitivities (considering forward and reverse rates).

Figure 19 (a) demonstrates that the high-temperature rate constants increase with temperature, and are very close for all seven mechanisms, especially at low temperatures. With increasing temperature, it is possible to see that the Mechanisms of Zhang, LLNL, and Mittal slightly diverge from the other four, overestimating the rate constant. However, since $\text{HO}_2^\bullet$ -mediated pathways become negligible with increasing temperature, these inaccuracies have minimal effect. This explains why the Zhang and Mittal models, despite their deviations in $\text{HO}_2^\bullet$ chemistry, achieve better agreement with experimental IDTs than LLNL, as depicted in Figure 10. Their superior performance arises from accurate representation of high-temperature pathways (e.g., thermal decomposition, $\text{C}_2\text{H}_5\text{OH} + \text{OH}^\bullet$ reactions), which overshadow minor uncertainties in $\text{HO}_2^\bullet$ kinetics.

Conversely, Figure 19 (b) shows that the low-temperature reaction rates decrease with temperature. It is also possible to see that the difference between the models also increases when compared to high-temperature reaction rates. Also, this discrepancy intensifies with temperature. In this case, the mechanisms of Zhang, LLNL, and Mittal underestimate the rate constant, whereas the other four overestimate it. These deviations align with the uncertainty in low-temperature ethanol oxidation kinet-

ics highlighted in this work, where limited knowledge of pathways and coefficients lead to divergent IDT predictions.

The underestimation of $\text{HO}_2^\bullet + \text{HO}_2^\bullet$ rates by Zhang, LLNL, and Mittal, in theory, reduce H_2O_2 accumulation, delaying the release of $\text{OH}^\bullet$ radicals and resulting in overpredicted IDTs. Conversely, models overestimating this rate (Creck, Aramco) accumulate more H_2O_2 , partially mitigating the delay. However, no mechanism fully replicates the experimental nonlinearity (Figure 10). Additionally, it was seen that Mittal and Zhang's mechanisms have the same good agreement found in the Creck and Aramco mechanisms. Thus, the better performance to capture IDT, even at low temperatures, arises not from accurate $\text{HO}_2 + \text{HO}_2$, but as a result of precise α -site H-abstraction parameters, which sustain radical production despite H_2O_2 underestimation. Similarly, LLNL's improved agreement at $p \sim 50$ atm (Figure 10(e)) may be attributed to pressure-dependent third-body effects that stabilize HO_2 .

Table 10 – Arrhenius Parameters for the termination reaction $\text{HO}_2^\bullet + \text{HO}_2^\bullet \rightleftharpoons \text{O}_2 + \text{H}_2\text{O}_2$

	High temp dominance			Low temp dominance		
	A	b	E_a	A	b	E_a
LLNL	4.20E+14	0	1.1982E+04	1.30E+11	0	-1.629E+03
Creck	1.00E+14	0	1.1041E+04	1.90E+11	0	-1.409E+03
Mittal	3.66E+14	0	1.2000E+04	1.30E+11	0	-1.630E+03
San Diego	1.03E+14	0	1.1042E+04	1.94E+11	0	-1.409E+03
Aramco	1.00E+14	0	1.1041E+04	1.90E+11	0	-1.481E+03
Zhang	3.66E+14	0	1.2000E+04	1.30E+11	0	-1.630E+03
PCRL	1.00E+14	0	1.1041E+04	1.90E+11	0	-1.490E+03

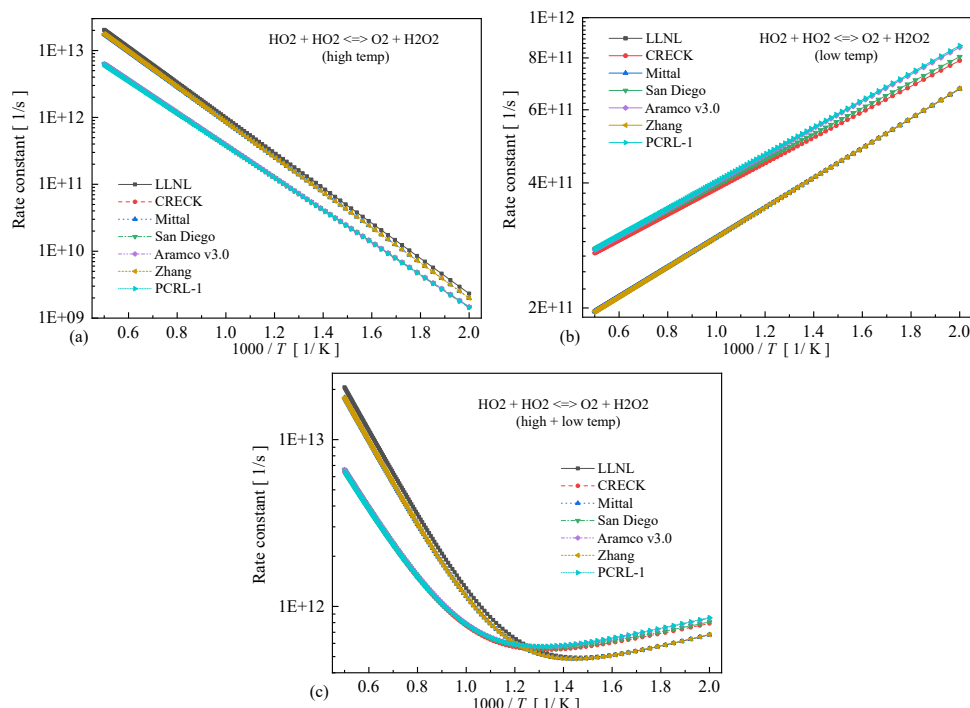
Pre-exponential factor, A, in [mol, m, s]

Temperature dependency exponent, b, [-]

Activation energy, E_a , in [cal/mol]

Additionally, given the previous statements, the decomposition of hydrogen peroxide is also expected to be sensitive to ignition delays, since it yields highly reactive $\text{OH}^\bullet$ radicals. In reality, this behavior has already been reported for ethanol. Indeed, as noted by Shrabanti Roy and Askari (2020), this reaction exhibits high sensitivity under high-pressure conditions. The Arrhenius parameters for the decomposition reaction $\text{H}_2\text{O}_2 (+ \text{M}) \rightleftharpoons \text{OH}^\bullet + \text{OH}^\bullet (+ \text{M})$ across different mechanisms are summarized in Table 11.

As already established in previous sections, and demonstrated in the sensitivity results in Figure 11, Figure 12, Figure 13, Figure 14, Figure 15, Figure 16, and Figure 17, the decomposition of hydrogen peroxide (H_2O_2) into hydroxyl ($\text{OH}^\bullet$) radicals plays a pivotal role in ethanol -ignition. The Creck, Aramco v3.0, Zhang, Mittal, and PCRL mechanisms exhibit identical high-pressure parameters, as seen in Table 11. This explains their consistent and accurate predictions of IDT in such conditions. These

Figure 19 – Arrhenius plot for the termination reaction $\text{HO}_2^\bullet + \text{HO}_2^\bullet \rightleftharpoons \text{O}_2 + \text{H}_2\text{O}_2$ Table 11 – Arrhenius Parameters for the decomposition reaction $\text{H}_2\text{O}_2 (+ \text{M}) \rightleftharpoons \text{OH}^\bullet + \text{OH}^\bullet (+ \text{M})$.

	High pressure			Low pressure		
	A	b	E_a	A	b	E_a
Mittal	2.00E+12	0.90	4.87E+04	1.86E+25	-2.3	4.87E+04
LLNL	1.24E+14	-0.37	0.000000	3.04E+30	-4.6	2.05E+03
San Diego	9.55E+13	-0.27	0.000000	2.76E+25	-3.2	0.000000
Creck	2.00E+12	0.90	4.87E+04	2.49E+24	-2.3	4.87E+04
Aramco v3.0	2.00E+12	0.90	4.87E+04	2.49E+24	-2.3	4.87E+04
PCRL	2.00E+12	0.90	4.87E+04	2.49E+24	-2.3	4.87E+04
Zhang	2.00E+12	0.90	4.87E+04	2.49E+24	-2.3	4.87E+04

Pre-exponential factor, A, in [mol, m, s]

Temperature dependency exponent, b, [-]

Activation energy, E_a , in [cal/mol]

models align well with shock tube experiments at elevated temperatures (e.g., (MATH-IEU et al., 2019b)), as shown in Figure 10 (a)–(b).

Notably, the activation energy of LLNL and San Diego mechanisms under high-pressure H_2O_2 decomposition is set to zero. While this may initially appear as a simplification, this treatment is common and intentional in pressure-dependent reactions modeled with the `fallOff` formulation. In such cases, the high-pressure limit reflects a regime in which the reaction becomes controlled by collisional stabilization rather than by the intrinsic energy barrier, resulting in a rate expression with minimal or no temperature dependence, i.e., $k = A \cdot T^b$. However, this leads to slower decomposition

of H_2O_2 at elevated temperatures, limiting the production of $\text{OH}^\bullet$ radicals and consequently delaying ignition. These discrepancies, combined with the sensitivity of other key reactions such as the H-abstraction pathways discussed earlier (whose kinetic parameters are detailed in Tables Table 9 and Figure 18), and the termination reaction shown in Figure 19 help to explain why the LLNL and San Diego models consistently overestimate ignition delay times (IDTs), as illustrated in Figure 10.

Moreover, as seen in Table 11, the Arrhenius parameters for low-pressure conditions vary significantly across mechanisms. Creck, Aramco v3.0, Zhang, Mittal, and PCRL preserve the temperature dependence of the reaction rate. In contrast, the LLNL mechanism adopts a much lower activation energy, and the San Diego mechanism simplifies further by setting it to zero. These choices strongly impact the predicted reactivity under low-to-intermediate pressure conditions. Since falloff reactions interpolate between low- and high-pressure rate limits, the accuracy of this transition relies heavily on the temperature dependence in both regimes. Neglecting the activation energy in the low-pressure limits, as in San Diego, can lead to underestimated radical production and thus longer IDTs, especially in conditions not strictly within the high-pressure limit.

Also, as previously established, H-abstractions will eventually lead to the formation of the important intermediate acetaldehyde, which further reacts with HO_2 and can contribute to discrepancies. Indeed, the works of Changyoul Lee et al. (2012) and Hashemi, Jakob M Christensen, and Glarborg (2018) already demonstrated that such reactions can be sensitive at higher pressures and intermediate temperatures. However, among the kinetic models being reviewed within this work, the LLNL mechanism does not include the acetaldehyde species, therefore, such a pathway is not included in the model. This absence can explain the deviations from the experimental results of Figure 10. It is important to note that the LLNL mechanism was last updated in 2004.

H-abstractions by $\text{OH}^\bullet$ radicals are expected to be important only at high temperatures. Further, according to Mathieu et al. (2019b), Shrabanti Roy and Askari (2020), and Rotavera and Taatjes (2021), another reaction that is important for ignition is the following chain-branching reaction: $\text{H}^\bullet + \text{O}_2 \rightleftharpoons \text{OH}^\bullet + \text{O}^\bullet$. For most all hydrocarbon fuels, this is the most important chain branching reaction in the combustion process. This reaction belongs to the well-known H_2 – O_2 chain cycle, and it is found to be sensitive at high temperatures, since it leads to the acceleration of chain branching efficiency and promotion of the total reaction rate. (ZHANG et al., 2012) The importance of this reaction will be discussed in the following section, since it is expected to affect flames as well.

The RMS uncertainties presented in Table 12 provide a quantification of the deviations between simulated and experimental IDT under the conditions used in this study.

The RMS results correlate with the observations discussed above. α and β H-

Table 12 – Statistical data on RMS (%) uncertainties in ethanol ignition delays

Mechanism	Experimental Conditions					
	Mathieu (a)	Mathieu (b)	Cancino (c)	Cancino (d)	Cancino (e)	Cancino (f)
LLNL	120.64	172.55	542.96	489.96	1369.48	695.23
Creck	9.45	6.48	239.95	210.94	491.79	183.58
Mittal	10.42	15.80	283.47	248.39	441.28	202.06
San Diego	56.23	64.25	422.57	1105.71	1517.72	395.85
Aramco v3.0	9.85	5.74	232.91	203.14	411.60	160.35
Zhang	15.21	13.02	199.94	171.90	311.40	121.84
PCRL-1	7.24	9.49	247.99	217.89	500.94	172.64

Note: (a)-(f) refer to experimental conditions from Mathieu et al. (2019a) and L. R. Cancino et al. (2010).
Source: Author, 2025

abstraction channels, for example, dominate ethanol oxidation, hence, mechanisms with accurate rate constants for these channels (Aramco, Mittal, Zhang, Creck) show lower RMS uncertainties, while those neglecting or underestimating them (LLNL, San Diego) exhibit higher deviations. LLNL and San Diego, in this case, have both higher pre-exponential factors (A) and higher activation energies for both channels (refer to Table 9), this leads to slower H-abstraction rates and a delayed ignition time, which was indeed observed in Figure 18 (a) and (b). The reduced radical production delays ignition, as seen in Figure 10.

PCRL, on the other hand, only includes hydroxyl-site abstraction, which contributes minimally at $T > 500$ K. However, it overestimates the hydroxyl rate constant (Figure 18 (c)), partially compensating for missing pathways. This results in moderate RMS uncertainties (172–501%) but limited chemical accuracy.

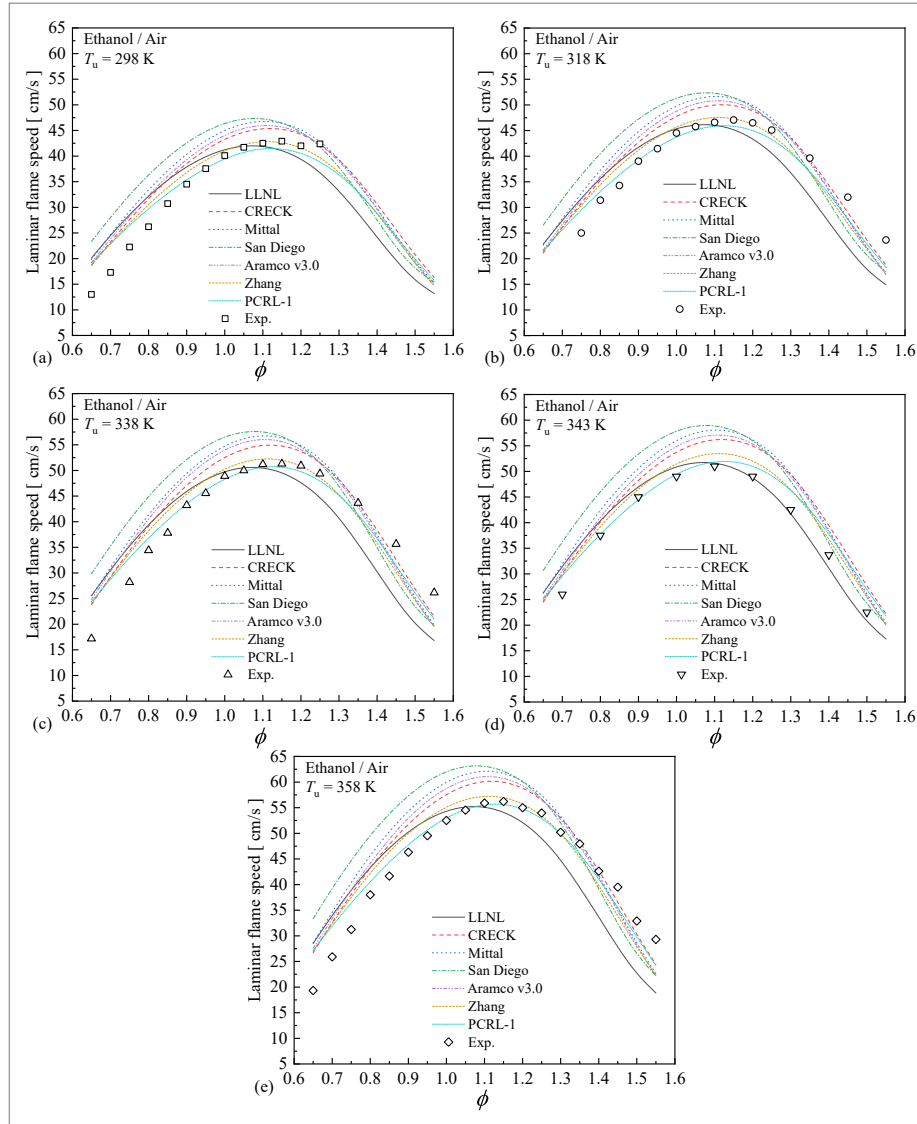
Overall, for ignition delay times, the Zhang mechanism demonstrates the lowest RMS uncertainties under the evaluated conditions (RMS = 15 – 311%), particularly at high pressures ($p > 30$ atm).

4.2 LAMINAR FLAME SPEED

The mechanisms are now compared in terms of LFS experiments. Figure 20 depicts the results obtained at pressure of 1 atm and different temperatures.

As shown, there are some notable relative differences between the simulations and the experimental data. The San Diego mechanism tends to overestimate laminar flame speeds at low equivalence ratios, across all temperatures evaluated. Similar trends are also observed in the works of Raida et al. (2021) and Katoch, Millán-Merino, and Kumar (2018). Firstly, it is essential to note the influence of the initial temperature on LFS results. In this case, laminar flame speed increases with increasing tempera-

Figure 20 – Comparison of ethanol laminar flame speeds for different mechanisms. (a), (b), (c) and (e) symbols represent the experimental results of A.A. Konnov, Meuwissen, and de Goey (2011b). (d) symbols represent the experimental results of Peter S. Veloo et al. (2010a)



Source: Author, 2025

ture. According to the findings in Lu et al. (2023b), at high temperatures, the system generates $H^\bullet$ or $OH^\bullet$ radicals, which are the key factors contributing to the increase in laminar flame speed.

Additionally, when compared to the experimental results of A.A. Konnov, Meuwissen, and de Goey (2011b), both the Aramco v3.0, Zhang, Mittal, and Creck, mechanisms also tend to overestimate laminar flame speeds at low equivalence ratios, while demonstrating reasonable agreement at high equivalence ratios, as seen in Figure 20 (a), (b), (c), and (e). Nevertheless, they overpredict LFS results at the fuel-rich side

when compared to the results of Peter S. Veloo et al. (2010a), as seen in Figure 20 (d). In contrast, the PCRL mechanism show accurate representation of the experimental data, although it also tend to overestimate the results of Peter S. Veloo et al. (2010a) at the rich side. Conversely, the LLNL mechanism exhibits a reasonable match with experimental data, especially the data from Peter S. Veloo et al. (2010a). However, regarding the experimental work of A.A. Konnov, Meuwissen, and de Goey (2011b), both mechanisms overestimate the flames at the fuel-lean side and underestimate it at the fuel-rich side.

In order to better understand the reduced ability of the mechanisms to predict the laminar flame speeds, a brute force sensitivity analysis on LFS was performed. Simulations were performed at a temperature of 358 K, at $\phi = 0.7$ and $\phi = 1.55$, and a pressure of 1 atm. Figure 21, Figure 22, Figure 23, Figure 24, Figure 25, Figure 26, Figure 27 show the most sensitive reactions in laminar flame speed calculations.

Figure 21 – Brute force sensitivity results for ethanol / air laminar flame speed using the Aramco mechanism at $T = 358$ K. (a) $k \times 0.5$, $\phi = 0.70$, (b) $k \times 2.0$, $\phi = 0.70$, (c) $k \times 0.5$, $\phi = 1.55$ (c) $k \times 2.0$, $\phi = 1.55$

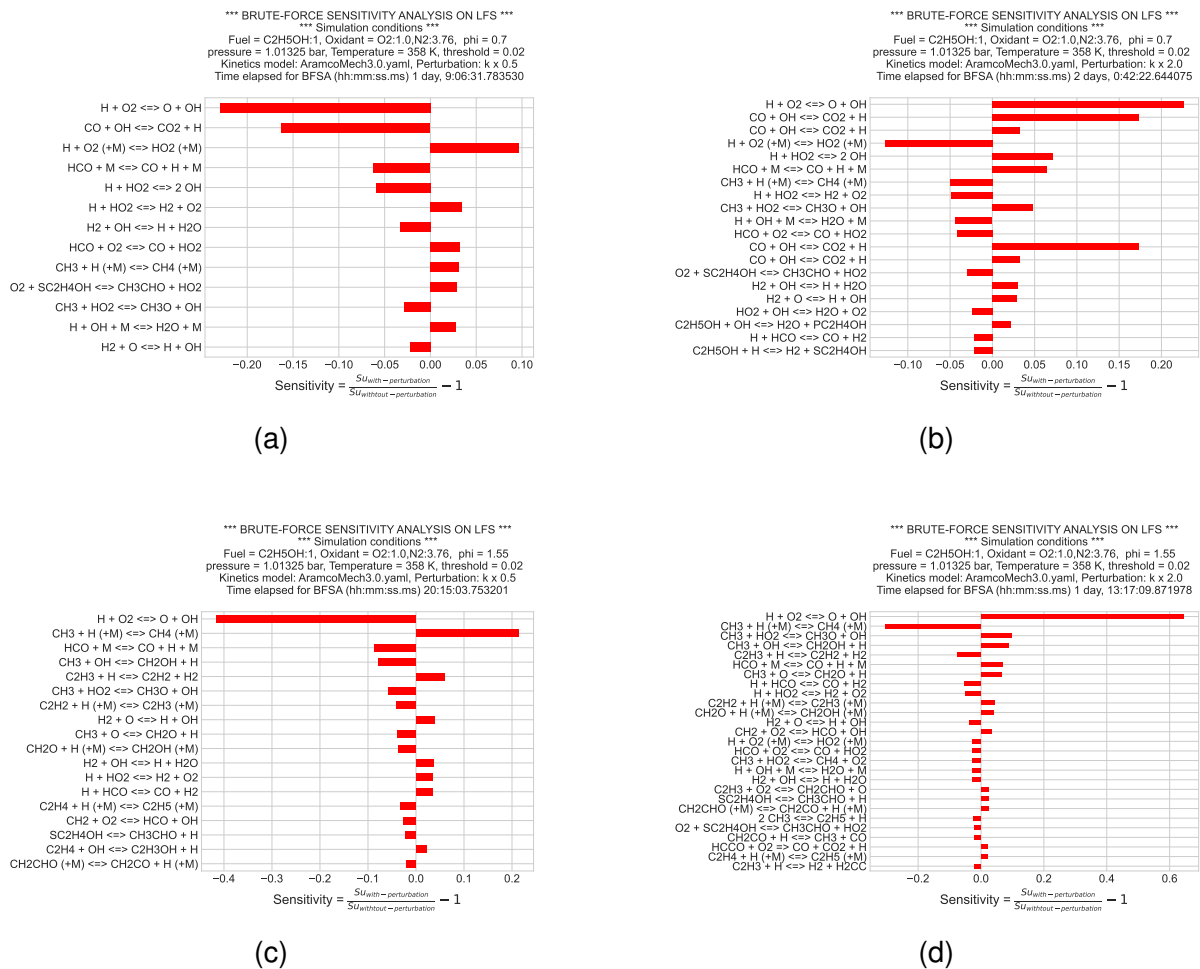
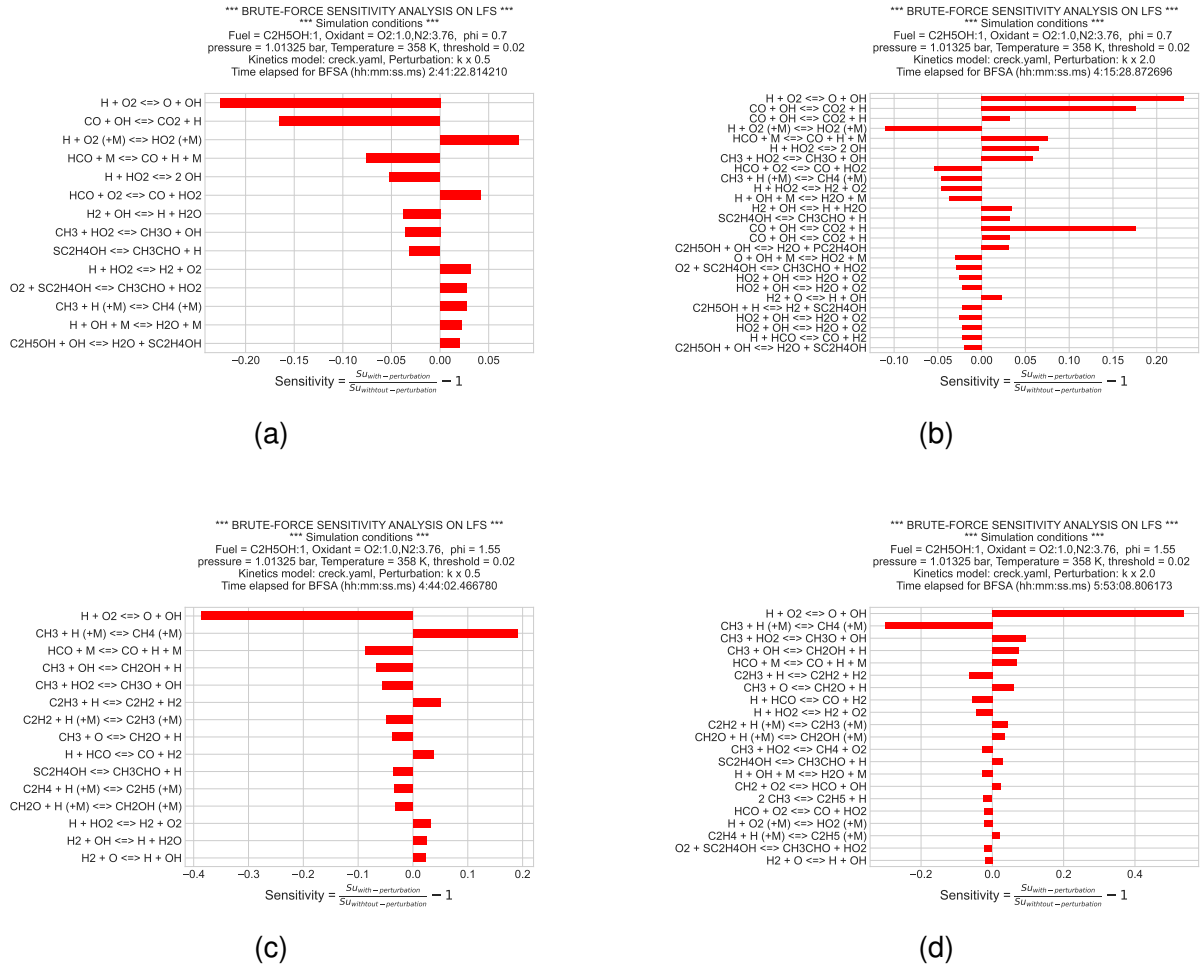


Figure 22 – Brute force sensitivity results for ethanol / air laminar flame speed using the Creck mechanism at $T = 358$ K. (a) $k \times 0.5$, $\varphi = 0.70$, (b) $k \times 2.0$, $\varphi = 0.70$, (c) $k \times 0.5$, $\varphi = 1.55$ (c) $k \times 2.0$, $\varphi = 1.55$



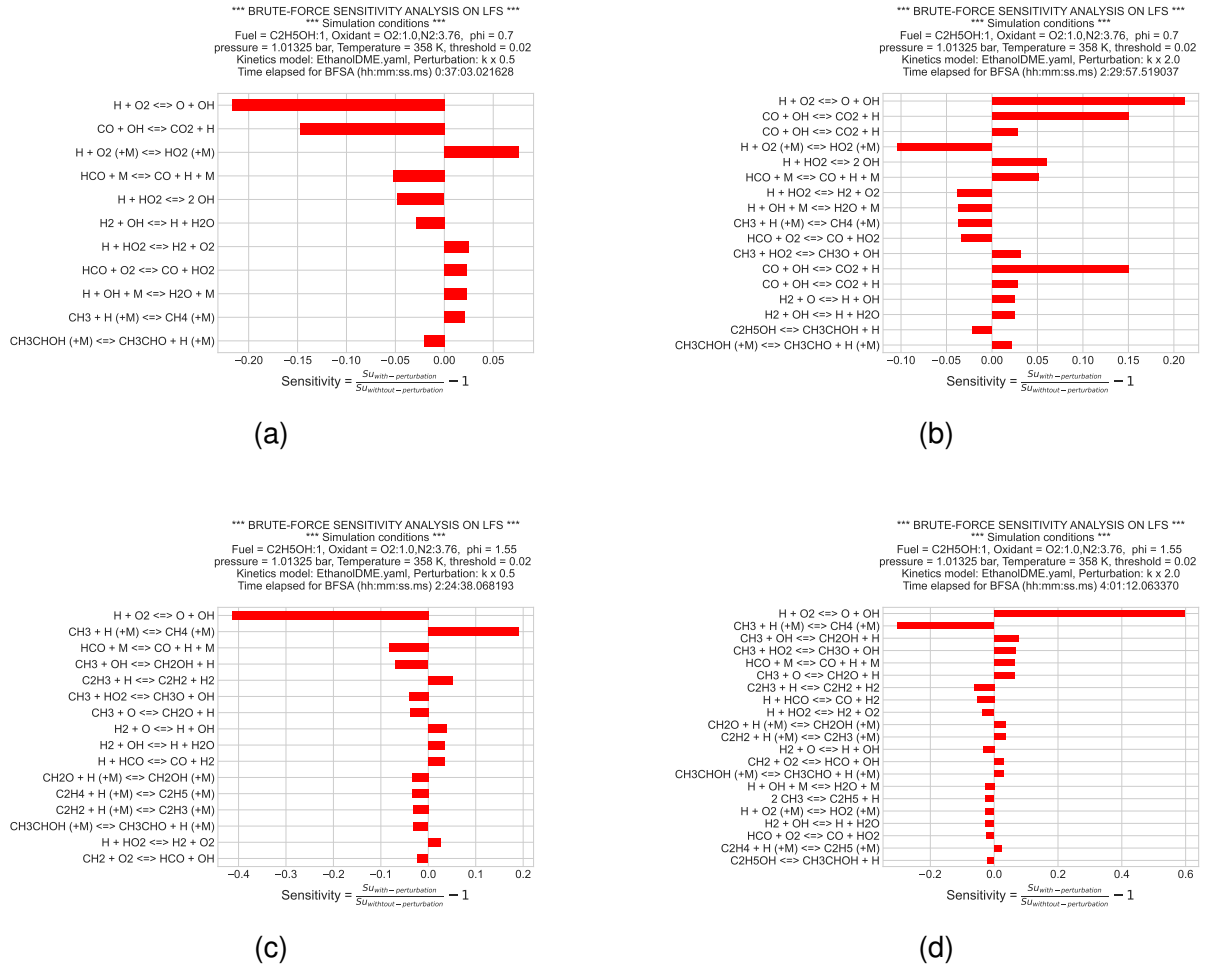
Source: Author, 2025

The magnitude of laminar flame speed is affected by chemical kinetics, thermodynamics, and transport properties of species (ZHENG et al., 2024). This study concentrates on the impact of chemical kinetics.

As expected, hydrogen oxidation reactions are the most sensitive in LFS calculations. Earlier sections have already established the importance of $\text{H}^\bullet$ and $\text{OH}^\bullet$ radicals to flames. In this regard, Xu et al. (2017) emphasizes the critical role of $\text{OH}^\bullet$ radicals in high-temperature flame combustion, serving as indicators of combustion intensity. Indeed, Aghsaee et al. (2015) defines $\text{OH}^\bullet$ radicals as responsible for 50% of ethanol depletion, ensuring their role in chemically reacting systems. Additionally, Lu et al. (2023a) underscores the importance of $\text{H}^\bullet$ radicals for flames. Hence, $\text{H}^\bullet$ and $\text{OH}^\bullet$ radicals are the main elements that increase the laminar flame speed.

The works of F N Egolfopoulos and C K Law (1990), Jinhua Wang et al. (2012), Al-Hamamre and Yamin (2013), Xu et al. (2017), and Ye et al. (2018b) highlight the

Figure 23 – Brute force sensitivity results for ethanol / air laminar flame speed using the Zhang mechanism at $T = 358$ K. (a) $k \times 0.5$, $\varphi = 0.70$, (b) $k \times 2.0$, $\varphi = 0.70$, (c) $k \times 0.5$, $\varphi = 1.55$ (c) $k \times 2.0$, $\varphi = 1.55$



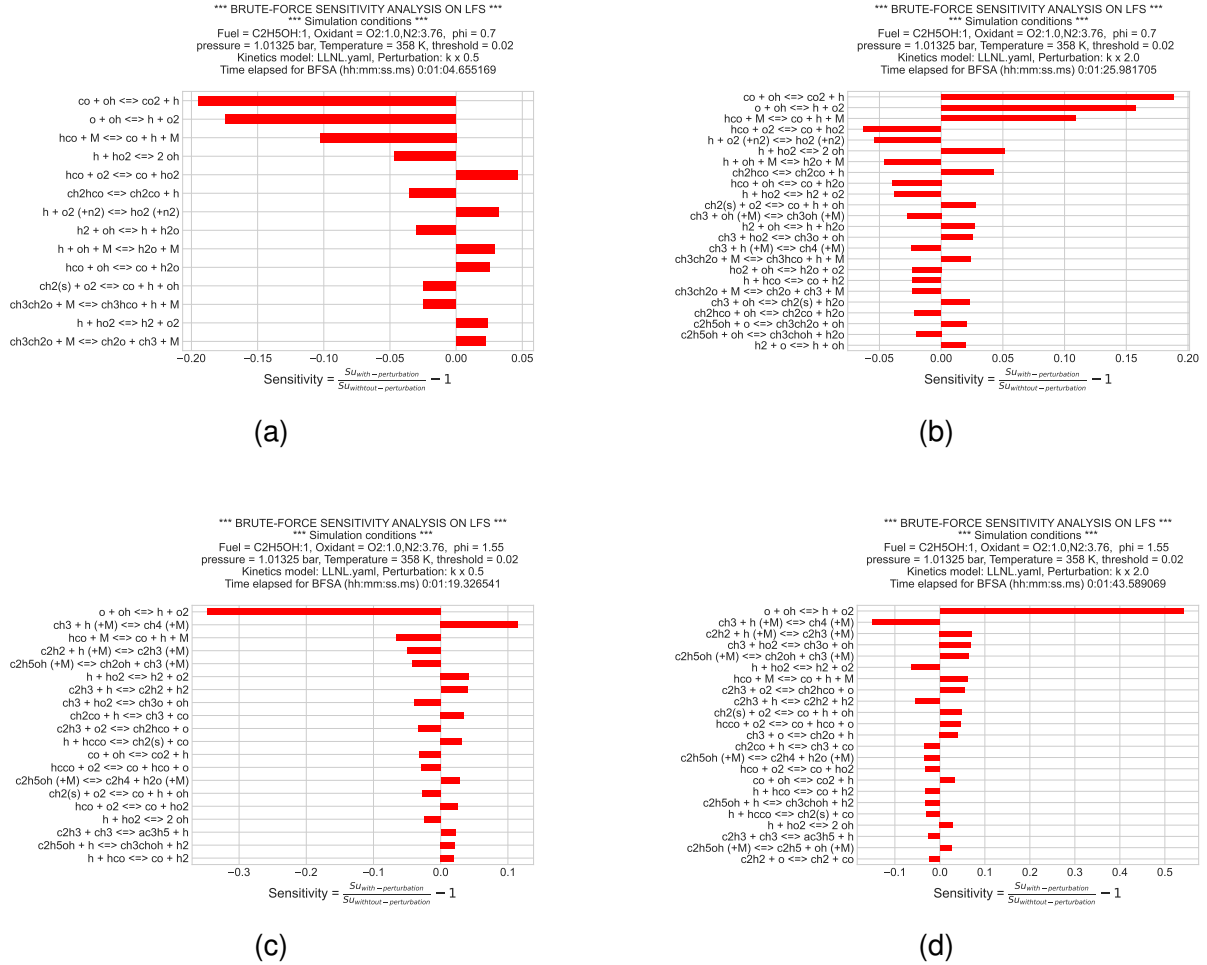
Source: Author, 2025

reaction $\text{H}^\bullet + \text{O}_2 \rightleftharpoons \text{O}^\bullet + \text{OH}^\bullet$ as very sensitive to flames. Aghsaee et al. (2015) corroborates this statement, describing $\text{OH}^\bullet$ formation as mainly dominated by this particular reaction. Indeed, as previously stated, this is most important elementary reaction in combustion systems, and it appears in the sensitive results for all mechanisms.

Earlier studies by Charles K Westbrook and Frederick L Dryer (1984) have already established that the the radical species pool is evolved among $\text{OH}^\bullet$, $\text{O}^\bullet$, and $\text{H}^\bullet$ by the following reactions:



Figure 24 – Brute force sensitivity results for ethanol / air laminar flame speed using the LLNL mechanism at $T = 358$ K. (a) $k \times 0.5$, $\varphi = 0.70$, (b) $k \times 2.0$, $\varphi = 0.70$, (c) $k \times 0.5$, $\varphi = 1.55$ (c) $k \times 2.0$, $\varphi = 1.55$



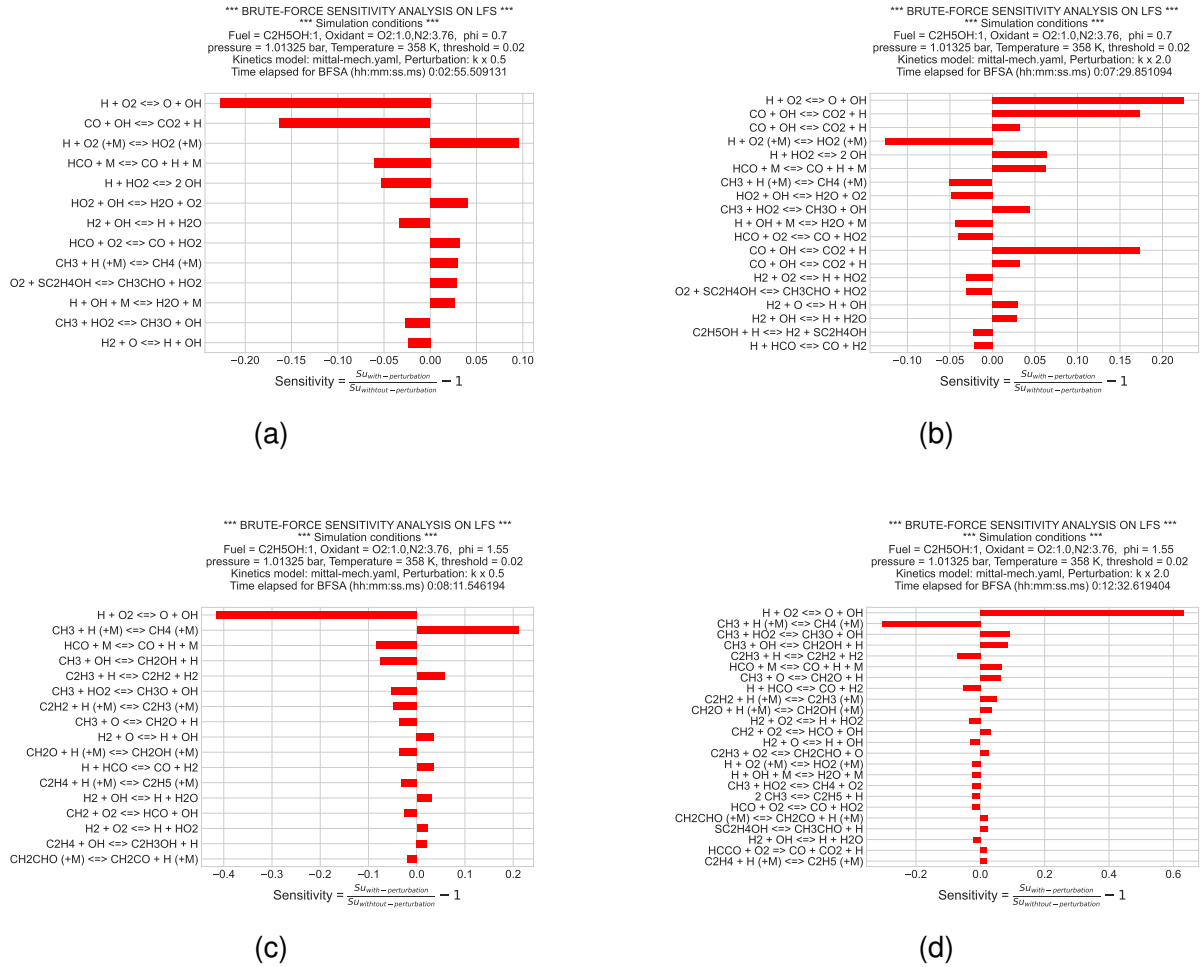
Source: Author, 2025



Notably, Equation (22) produces an $OH^\bullet$ radical by the consumption of an $H^\bullet$ radical with the presence of oxygen. Table 13 provides a comparison of the Arrhenius parameters for this reaction across the seven mechanisms. On the contrary, Equation (24) consumes an $OH^\bullet$ radical to increase the concentration of $H^\bullet$ radicals in the system. Additionally, a molecule of water is produced. Another main path for H_2 consumption is through Equation (23).

Interestingly, the San Diego mechanism exhibits the largest deviations in lean mixtures, consistently overpredicting LFS across all temperatures. This may be at-

Figure 25 – Brute force sensitivity results for ethanol / air laminar flame speed using the Mittal mechanism at $T = 358$ K. (a) $k \times 0.5$, $\varphi = 0.70$, (b) $k \times 2.0$, $\varphi = 0.70$, (c) $k \times 0.5$, $\varphi = 1.55$ (c) $k \times 2.0$, $\varphi = 1.55$

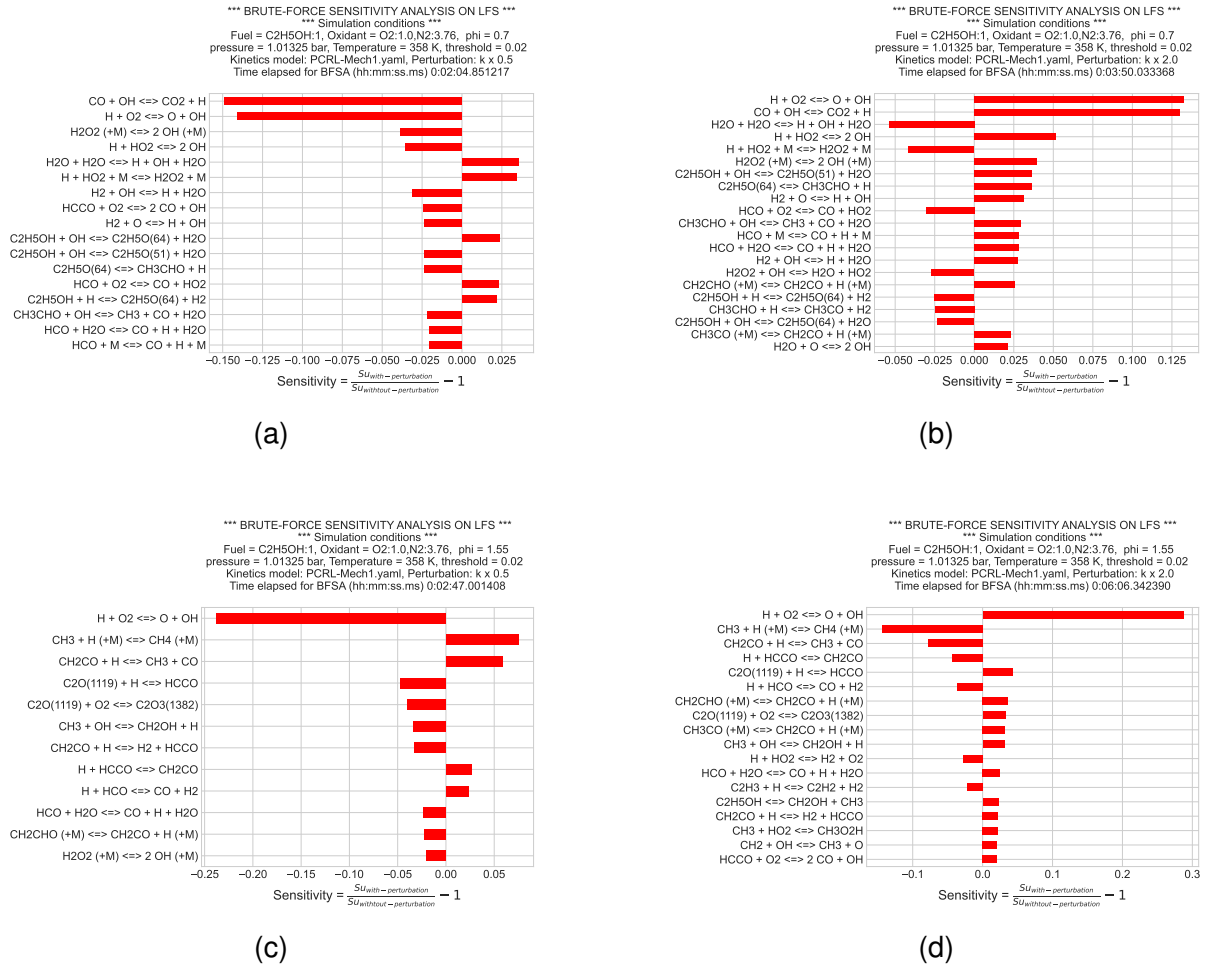


Source: Author, 2025

tributed to its unconventional parameterization of $H^\bullet + O_2 \rightleftharpoons OH^\bullet + O^\bullet$ reaction. It's high pre-exponential factor eventually leads to an increase in radical production. The negative temperature exponent b , further enhances reaction rates as temperatures rise, disproportionately increasing radical pools in lean conditions. Hence, by amplifying chain-branching, there is an excessive heat release which increases flame speeds, as observed in comparisons with experimental data. Creck, Aramco, Mittal, and Zhang share nearly identical coefficients, resulting in a moderate overestimation under lean conditions. PCRL, on the other hand, despite sharing parameters similar to those of the San Diego mechanism, still shows excellent agreement with experimental data. This may be attributed to other sensitive reactions, which are still to be discussed.

Following, the well known hydroperoxyl radical $HO_2^\bullet$, is formed primarily by $H^\bullet + O_2 + M \rightleftharpoons HO_2^\bullet + M$ (WESTBROOK, Charles K; DRYER, Frederick L, 1984). This radical is consumed by several reactions. One notable mention is reaction $HO_2^\bullet +$

Figure 26 – Brute force sensitivity results for ethanol / air laminar flame speed using the PCRL mechanism at $T = 358$ K. (a) $k \times 0.5$, $\varphi = 0.70$, (b) $k \times 2.0$, $\varphi = 0.70$, (c) $k \times 0.5$, $\varphi = 1.55$ (c) $k \times 2.0$, $\varphi = 1.55$

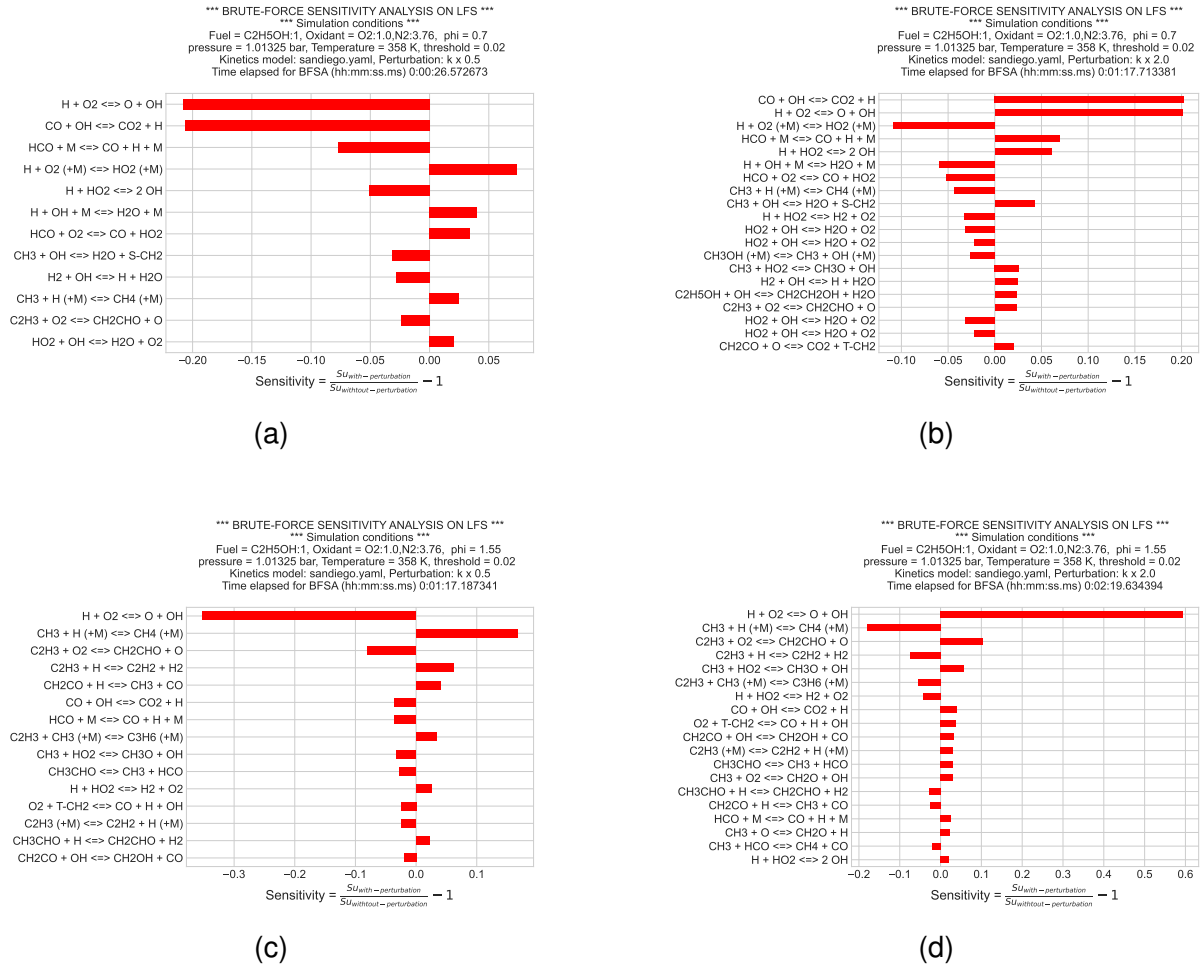


Source: Author, 2025

$\text{H}^\bullet \rightleftharpoons 2\text{OH}^\bullet$, which is one of the main OH-producing reactions (SUN et al., 2016). The sensitivity for this particular reaction was reported in the work of Hashemi, Jakob M Christensen, and Glarborg (2018). Table 13 also include the coefficients adopted by the models for this particular reaction.

According to Sun et al. (2016), in lean mixtures, where there is more oxygen than fuel (i.e., $\varphi < 1$) O_2 and H_2O are present in high concentrations, therefore, the chain branching Equation (22) and and the competitive three-body reaction $\text{H}^\bullet + \text{O}_2 + \text{M} \rightleftharpoons \text{HO}_2^\bullet + \text{M}$ are enhanced. In this case, $\text{OH}^\bullet$ concentration increases, whereas H concentration is decreased. This has been previously seen in the work of Beeckmann, Cai, and Pitsch (2014). The $\text{OH}^\bullet$ radicals generated participate in chain-terminating reactions. An example is the conversion of CO to CO_2 (QIU et al., 2021). Therefore, reaction $\text{CO} + \text{OH}^\bullet \rightleftharpoons \text{CO}_2 + \text{H}^\bullet$ is also indicated as sensitive to flames, specifically when the mixture is lean. This corroborates with the results of Figure 21, Figure 22,

Figure 27 – Brute force sensitivity results for ethanol / air laminar flame speed using the San Diego mechanism at $T = 358$ K. (a) $k \times 0.5$, $\varphi = 0.70$, (b) $k \times 2.0$, $\varphi = 0.70$, (c) $k \times 0.5$, $\varphi = 1.55$ (c) $k \times 2.0$, $\varphi = 1.55$



Source: Author, 2025

Figure 23, Figure 24, Figure 25, Figure 26, Figure 27 According to Jinhua Wang et al. (2012) and Ye et al. (2018a) this is the final reaction and is responsible for heat release. Heat release increases the temperature within the flame reaction zone, resulting in faster reaction rates that increase laminar flame speeds (ZHENG et al., 2024). However, it is crucial to note that CO_2 is a product that inhibits the combustion process (LU et al., 2023a). This reaction is less sensitive for rich mixtures due to the low oxygen content to convert CO to CO_2 (LIU, W.; KELLEY; LAW, Chung K., 2011). Table 14 provides a comparison of the Arrhenius plot for chain termination reactions across the seven mechanisms.

It can be seen that San Diego is the only mechanism that uses a single reaction with $A = 4.40E+06 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This difference, combined with was already noted for Table 13, may be the factors influencing the results presented in Figure 20. Both reactions appear in the sensitivity results presented in Figure 27. Notably, for PCRL,

Table 13 – Arrhenius Parameters for the chain branching reactions $\text{H}^\bullet + \text{O}_2 \rightleftharpoons \text{OH}^\bullet + \text{O}^\bullet$ and $\text{H}^\bullet + \text{HO}_2^\bullet \rightleftharpoons \text{OH}^\bullet + \text{OH}^\bullet$

Mechanism	$\text{H}^\bullet + \text{O}_2 \rightleftharpoons \text{OH}^\bullet + \text{O}^\bullet$			$\text{H}^\bullet + \text{HO}_2^\bullet \rightleftharpoons \text{OH}^\bullet + \text{OH}^\bullet$		
	A	b	E_a	A	b	E_a
LLNL	2.02E+14	-0.40	0.00E+00	1.50E+14	0	1.00E+03
Creck	1.14E+14	0.00	1.53E+04	7.07E+13	0	2.95E+02
Mittal	1.04E+14	0.00	1.53E+04	7.07E+13	0	2.95E+02
San Diego	3.52E+16	-0.70	1.71E+04	7.08E+13	0	2.95E+02
Aramco	1.04E+14	0.00	1.53E+04	7.07E+13	0	2.95E+02
Zhang	1.04E+14	0.00	1.53E+04	7.07E+13	0	2.95E+02
PCRL	2.65E+16	-0.67	1.70E+04	7.07E+13	0	2.95E+02

Pre-exponential factor, A, in [mol, m, s]

Temperature dependency exponent, b, [-]

Activation energy, E_a , in [cal/mol]Table 14 – Arrhenius Parameters for the chain-termination reaction $\text{CO} + \text{OH}^\bullet \rightleftharpoons \text{CO}_2 + \text{H}^\bullet$.

Mechanism	A	b	E_a
LLNL	9.42E+03	2.250	-2.35E+03
Creck	7.00E+04	2.053	-3.56E+02
Mittal	5.70E+12	-0.664	3.32E+02
	7.00E+04	2.053	-3.56E+02
San Diego	5.70E+12	-0.664	3.32E+02
	4.40E+06	1.500	-7.41E+02
Aramco v3.0	7.00E+04	2.053	-3.56E+02
	5.70E+12	-0.664	3.32E+02
Zhang	7.00E+04	2.053	-3.56E+02
	5.70E+12	-0.664	3.32E+02
PCRL	2.10E+05	1.900	-1.06E+03
	2.50E+05	1.880	-1.04E+03
	8.70E+05	1.730	-6.85E+02
	6.80E+06	1.480	4.80E+01
	2.30E+07	1.350	9.73E+02

Mechanisms with two coefficients indicate duplicate reactions.

In the PCRL mechanism, this reaction is pressure-dependent. Pressures used:

 1.348×10^2 , 1.349×10^3 , 1.348×10^4 , 1.350×10^6 , 1.350×10^7 kPa.

this reaction is pressure-dependent, which can explain why it is still good to represent experimental LFS data, despite having Arrhenius parameters similar to those from the San Diego for chain-branching (Table 13).

In contrast, in the fuel-rich state, where there is an excess of fuel (i.e., $\phi > 1$), Equation (22) remains important. It still is responsible to initiate the chain-branching process that generates $\text{OH}^\bullet$ and $\text{O}^\bullet$ radicals in the system. In this particular case, this reaction ensures that the limited oxygen is converted into radicals that help oxidize

the excess of fuel. Another reaction that become increasingly important to flames in fuel-rich mixtures, is the one producing methane. This trend was already noted in the work of Moah Christensen et al. (2015), and is demonstrated in Figure 21, Figure 22, Figure 23, Figure 24, Figure 25, Figure 26, Figure 27. The low and high-pressure Arrhenius parameters for this reaction can be seen in Table 15.

Table 15 – Arrhenius Parameters for the reaction $\text{CH}_3^\bullet (+ \text{M}) \rightleftharpoons \text{CH}_4 (+ \text{M})$.

Mechanism	High Pressure Limit			Low Pressure Limit		
	A	b	E_a	A	b	E_a
LLNL	2.14E+15	-0.40	0.00E+00	3.31E+30	-4.00	2.11E+03
Creck	1.27E+16	-0.63	3.83E+02	2.48E+33	-4.76	2.44E+03
Mittal	1.27E+16	-0.63	3.83E+02	2.48E+33	-4.76	2.44E+03
San Diego	1.35E+14	0.091	8.77E+01	1.59E+33	-4.76	2.43E+03
Aramco v3.0	1.27E+16	-0.63	3.83E+02	2.48E+33	-4.76	2.44E+03
Zhang	1.27E+16	-0.63	3.83E+02	2.48E+33	-4.76	2.44E+03
PCRL	1.27E+16	-0.63	3.83E+02	2.48E+33	-4.76	2.44E+03

Pre-exponential factor, A, in [mol, m, s]

Temperature dependency exponent, b, [-]

Activation energy, E_a , in [cal/mol]

Mechanisms such as Creck, Aramco, Mittal, PCRL, and Zhang adopt identical high-pressure parameters. In contrast, the San Diego mechanism employs a significantly lower pre-exponential factor and near-zero activation energy, affecting the production of methane. Hence, the accumulation of $\text{CH}_3^\bullet$ increases chain-branching and uncertainties in both lean and rich regimes. In contrast, The unusual $E_a = 0$ for LLNL at high pressures eliminates temperature dependency, allowing efficient CH_4 formation even at low temperatures. This suppresses $\text{CH}_3^\bullet$ radicals, reducing flame speeds and leading to underestimation in rich mixtures, as seen in Figure 20.

Additionally, a significant intermediate species that can influence flames is the $\text{HCO}^\bullet$, specifically in the propagating reaction $\text{HCO}^\bullet + \text{M} \rightleftharpoons \text{CO} + \text{H}^\bullet + \text{M}$. The work of Alviso et al. (2022) shows that such a reaction has nearly equal sensitivity coefficients for all equivalence ratios. This reaction is a source of $\text{H}^\bullet$ and CO , thus, enhances laminar flame speed by contributing to heat release and chain branching reactions (ZHENG et al., 2024). The sensitivity of this reaction can also be seen in the work of Hashemi, Jakob M Christensen, and Glarborg (2018). According to the authors, the decomposition of $\text{HCO}^\bullet$ indeed promotes the burning rate noticeably, although its reaction with $\text{H}^\bullet$, $\text{OH}^\bullet$, or O_2 can slow down the burning rate. Table 16 shows the third-body collision efficiencies adopted by the models for this reaction.

In fuel-lean flames, this reaction competes with $\text{HCO}^\bullet + \text{O}_2 \rightleftharpoons \text{CO} + \text{HO}_2^\bullet$. On the other hand, in rich mixtures, there is a competition with the terminating reaction $\text{HCO}^\bullet + \text{H}^\bullet \rightleftharpoons \text{CO} + \text{H}_2$ instead (VAN TREEK et al., 2019). The Arrhenius parameters

Table 16 – Third-body collision efficiencies for the propagation reaction $\text{HCO}^\bullet + \text{M} \rightleftharpoons \text{CO} + \text{H}^\bullet + \text{M}$.

Species	Mittal	LLNL	San Diego	CRECK	Aramco v3.0	PCRL	Zhang
H ₂	2.0	1.87	1.9	2.0	2.0	2.0	2.0
H ₂ O	6.0	5.00	12.0	6.0	6.0	0.0	6.0
CO	1.5	1.87	2.5	1.5	1.5	1.5	1.5
CO ₂	2.0	3.00	2.5	2.0	2.0	2.0	2.0
CH ₄	2.0	2.81	**	2.0	2.0	2.0	2.0
C ₂ H ₆	3.0	**	**	3.0	3.0	3.0	3.0

for both reactions are shown in Table 17.

Table 17 – Arrhenius Parameters for reactions $\text{HCO}^\bullet + \text{O}_2 \rightleftharpoons \text{CO} + \text{HO}_2^\bullet$ and $\text{HCO}^\bullet + \text{H}^\bullet \rightleftharpoons \text{CO} + \text{H}_2$

	$\text{HCO}^\bullet + \text{O}_2 \rightleftharpoons \text{CO} + \text{HO}_2^\bullet$			$\text{HCO}^\bullet + \text{H}^\bullet \rightleftharpoons \text{CO} + \text{H}_2$		
	A	b	E _a	A	b	E _a
LLNL	7.58E+12	0.00	4.10E+02	1.19E+13	0.00	0.00E+00
Creck	7.58E+12	0.00	4.10E+02	7.34E+13	0.00	0.00E+00
Mittal	7.58E+12	0.00	4.10E+02	7.34E+13	0.00	0.00E+00
San Diego	7.58E+12	0.00	4.10E+02	5.00E+13	0.00	0.00E+00
Aramco	7.58E+12	0.00	4.10E+02	7.34E+13	0.00	0.00E+00
Zhang	7.58E+12	0.00	4.10E+02	7.34E+13	0.00	0.00E+00
PCRL	6.90E+06	1.90	1.37E+03	7.07E+13	0.00	0.00E+00

Pre-exponential factor, A, in [mol, m, s]

Temperature dependency exponent, b, [-]

Activation energy, E_a, in [cal/mol]

When evaluating the lean side in Figure 20, it can be observed that PCRL, Zhang, Creck, Aramco and LLNL had a better representation of the experimental results, in this order. All models tend to overestimate the flame speeds when there is an excess of oxygen content (i.e., in lean mixtures). This behavior was already reported by A.A. Konnov, Meuwissen, and de Goey (2011b). The same behavior was noted for LLNL and San Diego mechanisms by Orbegoso and Junior (2011) and Beeckmann, Cai, and Pitsch (2014).

San Diego had the highest deviation in all cases. Interestingly, its Arrhenius parameters are very close to those of the PCRL model for chain branching reactions, as previously seen in Table 13. However, on the regard of the chain-terminating and propagating reactions, depicted in Table 14 and Table 16, respectively, this mechanism shows notable differences. For example, the value for activation energy is the double as those adopted by the other models for $\text{CO} + \text{OH}^\bullet \rightleftharpoons \text{CO}_2 + \text{H}^\bullet$ reaction. Also, the third-body collision efficiency of H₂O adopted by San Diego mechanism is 12, a value that is twice the value of 5 or 6 adopted by the other models. San Diego's mechanism

also omits the collision efficiency for methane. Further, it is important to note that PCRL uses 0 as a collision efficiency for H_2O .

Similarly, the mechanism of Lawrence Livermore (LLNL), which is also not very good in predicting flames, also adopted different activation energies for chain-branching $\text{H}^\bullet + \text{O}_2 \rightleftharpoons \text{OH}^\bullet + \text{O}^\bullet$ and $\text{H}^\bullet + \text{HO}_2^\bullet \rightleftharpoons 2\text{OH}^\bullet$ reactions. The same is found for chain-terminating reactions, as demonstrated in Table 14.

The rich side, on the other hand, are not well represented by the LLNL mechanism specifically, which underestimates the speeds at higher equivalence ratios. In this regard, Table 13 also shows that LLNL has different Arrhenius coefficients for both reactions. In addition the reaction producing methane demonstrated in Table 15 also include different Arrhenius coefficients. In this case, for high pressure conditions, this models adopted 0 as the value for activation energy, whereas for low pressure conditions, the coefficient A is slower when compared to those adopted by the other mechanisms.

It is evident that, as already discussed in earlier sections, the mechanisms of LLNL and San Diego have Arrhenius parameters that diverge from those found in the other models used in this study. Therefore, this explains the results obtained in Figure 20, where both mechanisms had a bigger deviation from experimental results at the rich side. Creck, Aramco and San Diego (and, consequently, Zhang and Mittal models) are referred to in the literature as developed only for high-temperature conditions, as emphasized by Masten, Hanson, and Craig T Bowman (1990) and Hong et al. (2011). This may result in a poor prediction of flames. Indeed, such behavior was also demonstrated in Figure 20.

In addition, in the PCRL mechanism, the reaction between acetaldehyde and the hydroperoxyl radical can also produce $\text{CO} + \text{H}_2\text{O}_2 + \text{CH}_3^\bullet$, which is indeed sensitive to flames. It is important to note that the remaining mechanisms do not include such a pathway.

Based on what was exposed in this section, reactions of the ethanol subset are not reported in the literature as exhibiting significant sensitivity to flames. The majority of reactions that appear in sensitivity analysis are mostly related to the $\text{H}_2 - \text{O}_2$ mechanism. This was already noted in the work of Hashemi, Jakob M Christensen, and Glarborg (2018).

The RMS uncertainties presented in Table 18 provide a quantification of the deviations between simulated and experimental LFS under the conditions used in this study.

The quantitative analysis of RMS percentage uncertainties between simulated and experimental laminar flame speeds (LFS) (Table 18) reveals critical patterns associated with the kinetic parameterizations of the evaluated mechanisms. The San Diego mechanism exhibits the largest deviations (22.72%–20.40%), consistent with its atypical Arrhenius parameter choices. The San Diego mechanism's overprediction of LFS

Table 18 – Statistical data on RMS (%) uncertainties in ethanol flame speeds

Mechanisms	Experimental Temperatures				
	298 K	318 K	338 K	343 K	358 K
LLNL	13.18	12.91	13.68	6.12	15.40
Creck	11.81	9.15	10.09	12.95	10.59
Mittal	16.86	9.15	14.38	15.28	14.92
San Diego	22.72	18.06	19.78	18.51	20.40
Aramco v3.0	16.86	13.91	14.97	15.35	15.25
Zhang	9.70	7.98	11.05	7.41	9.41
PCRL	9.09	6.24	7.01	7.30	7.12

in lean mixtures ($\varphi < 1$) arises from its parametrization of chain-branching (Table 13) which enhances radical pools, increasing LFS.

The LLNL mechanism, on the other hand, consistently underestimates LFS in rich mixtures. This is due to the unusual parametrization, as seen in Table 15. This allows an efficient conversion of $\text{CH}_3^\bullet$ in CH_4 , even in low temperatures, prematurely depleting the radical pool required to propagate the flame.

PCRL mechanism stands out as the most precise model to calculate flame speeds, with the slowest deviations among all (6.24%–9.49%). Even though it shares similar Arrhenius parameters with those from Aramco, Creck, Mittal, and Zhang, its multifactorial parameterization, which includes pressure dependence in the termination reaction $\text{CO} + \text{OH}^\bullet \rightleftharpoons \text{CO}_2 + \text{H}^\bullet$ (Table 14) explain its superiority. Under high-pressure conditions, the pathway with a positive activation energy dominates, promoting the efficient conversion of CO into CO_2 and reducing the excess of $\text{OH}^\bullet$ radicals. In contrast, at low pressures, the pathway with negative activation energy suppresses termination, preserving $\text{OH}^\bullet$ to sustain chain-branching reactions. This dynamic balance enables the PCRL mechanism to maintain high accuracy in both lean ($\varphi < 1$) and rich ($\varphi > 1$) mixtures.

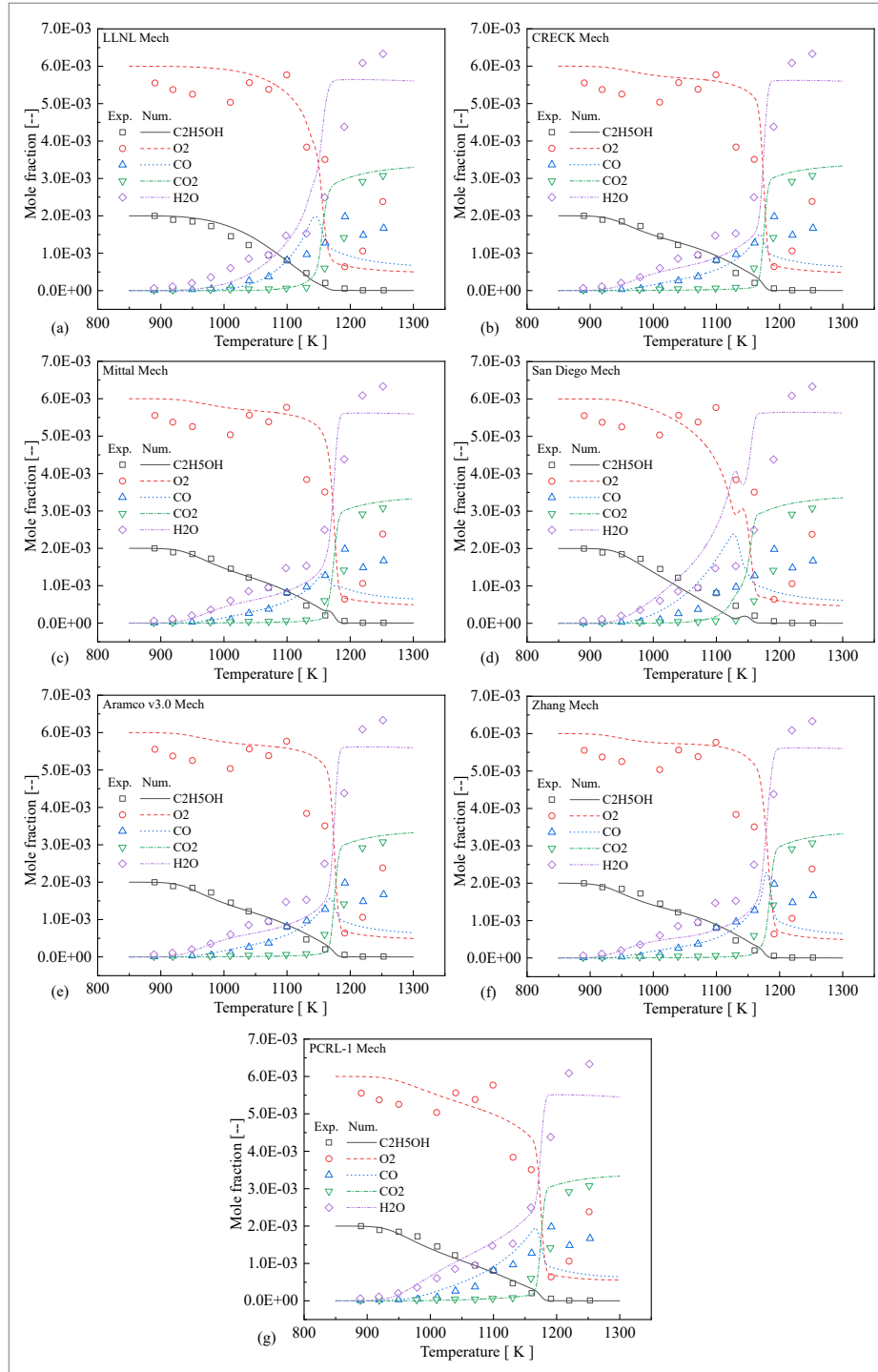
The following section delves into species concentration profiles, where it explores how the results of the JSR are affected by uncertainties in reactions and Arrhenius parameters.

4.3 SPECIES CONCENTRATION PROFILES

Lastly, the simulation results of mole fraction calculation from a jet-stirred reactor as a function of temperature are evaluated. Figure 28 shows the comparison of the mole fraction of ethanol oxidation compared with the results reported by Leplat et al. (2011b).

As it can be seen, the concentration of H_2O steadily rises in the temperature range of 950 to 1150 K, indicating the prevalence of high-temperature chemistry. In

Figure 28 – Comparison of mole fraction profiles under JSR conditions for different mechanisms with experimental data at pressure of 1 atm and equivalence ratio of 1.0. Symbols represent the experimental results of Leplat et al. (2011a)



Source: Author, 2025

contrast, the O₂ concentration decreases slightly between 900 and 1100 K. All the kinetics models can adequately represent the ethanol C₂H₅OH mass fraction (depletion)

along the temperature range evaluated. However, it can be noticed that, according to Figure 28 (a), the LLNL mechanism underestimates the ethanol reaction rate within the temperature range of approximately 980 K to 1080 K, while the San Diego mechanism exhibits a similar issue within the temperature range of approximately 960 K to 1150 K, as demonstrated in Figure 28(b). The Aramco3.0, Creck, Zhang, Mittal, and PCRL models, on the other hand, are nicely fit to the ethanol mass fractions (depletion) experimental data from (LEPLAT et al., 2011b). In addition, the seven mechanisms consistently show an overestimation of O_2 mass fractions, with PCRL Mech demonstrating a relatively lower deviation, as seen in Figure 28 (g). However, PCRL Mech tends to underestimate the mass fractions of O_2 within the temperature range of approximately 1040 to 1075 K, whereas the Creck, LLNL, Mittal, Zhang, and Aramco v3.0 overestimate the results at the same range. Similarly, according to Figure 28 (d), San Diego mechanism also underestimates the mass fractions over a slightly wider range, from around 1040 K to approximately 1155 K. It is important to note that, in all cases, the mechanisms tend to converge toward the experimental results as the temperature increases (> 1200 K). Unfortunately, there is a lack of sufficient experimental data above this temperature for further comparison.

The mole fractions of CO, however, show deviations from experimental results as the temperature increases, especially above 1150 K. At temperatures lower than this threshold, the Creck, Mittal, Zhang, and Aramco mechanisms exhibit a better fit to the experimental results, as observed in Figure 28 (b), Figure 28 (c), Figure 28 (e), and Figure 28 (f). On the other hand, the PCRL Mech tends to slightly overestimate the mole fractions at all evaluated temperatures in this study, as shown in Figure 28 (g). Further, among the five mechanisms evaluated, the San Diego mech exhibits a more significant overestimation of CO mole fractions when compared to the other mechanisms. Following, below 1150 K, all five mechanisms displayed accurate predictions of CO_2 mole fractions. However, at higher temperatures, the simulated mole fractions were consistently overestimated across all cases. Among them, the LLNL, Zhang, and Aramco v3.0 mechanisms exhibited only a minimal deviation.

Lastly, regarding H_2O mole fractions, the PCRL, Mittal and CRECK mechanisms demonstrated better agreement with the results of Leplat et al. (2011b), although slight deviations are still present. Overall, despite the deviations found, all mechanisms showed reasonable agreement with the experimental results.

To understand how the JSR or flow reactor results are affected by uncertainties in reactions and Arrhenius parameters from the seven models, it is essential to navigate through the steps of ethanol combustion chemistry. As discussed in the earlier sections, at high temperatures, the thermal decomposition of ethanol is supposed to proceed through three different channels, as demonstrated in Equation (1), Equation (2), and Equation (3) (HASHEMI; CHRISTENSEN, J. M.; GLARBORG, 2018). Equation (1)

is one of the channels responsible for water formation. Earlier studies by Park, Zhu, and Lin (2002) have indeed demonstrated that the reaction producing $C_2H_4 + H_2O$ is dominant at pressures below 10 atm, whereas at the high-pressure limit over 1500 K, formation of $CH_3^\bullet + CH_2OH$ dominates.

Table 19 and Table 20 present the differences between the Arrhenius coefficients for this particular reaction. It is important to note that LLNL and San Diego mechanisms treat this reaction as a Falloff reaction, whereas the other models treat it as a pressure-dependent reaction. Interestingly, LLNL and San Diego are not very good in predicting the water content, as demonstrated in Figure 28. Actually, water profiles are better reproduced by the PCRL mechanism. Despite this, predictions of Creck and Aramco can still be considered very accurate.

Table 19 – Arrhenius Parameters for the termination reaction $C_2H_5OH (+ M) \rightleftharpoons C_2H_4 + H_2O (+ M)$

	Low pressure			High pressure		
	A	b	E_a	A	b	E_a
LLNL	2.53E+83	-18.85	8.65E+04	2.79E+13	0.09	6.61E+04
San Diego	1.00E+17	0.00	5.40E+04	8.00E+13	0.00	6.50E+04

Pre-exponential factor, A, in [mol, m, s]

Temperature dependency exponent, b, [-]

Activation energy, E_a , in [cal/mol]

Table 20 – Arrhenius parameters for the decomposition reaction $C_2H_5OH \rightleftharpoons C_2H_4 + H_2O$.

p [atm]	A	b	E_a
1	5.23E+43	-8.90	8.15E+04
10	4.59E+32	-5.60	7.60E+04
100	3.84E+20	-2.06	6.94E+04

Pre-exponential factor, A, in [mol, m, s]

Temperature dependency exponent, b, [-]

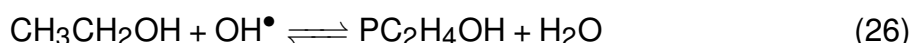
Activation energy, E_a , in [cal/mol]

Notably, LLNL mechanism has an extremely high A factor, which suggests an unusual parametrization, possibly made to compensate for other pathways and their respective reactions rates. San Diego, on the other hand, has no temperature dependence ($b = 0$), which can limit its accuracy in conditions beyond those used to validate this model. Both mechanisms are not very good in representing the water concentration, as seen in Figure 28 (a) and (d).

Despite sharing identical parametrization for this reaction, the Creck, Aramco, Zhang, Mittal, and PCRL mechanisms exhibit varying levels of accuracy in predicting species profiles. This discrepancy suggests that the PCRL mechanism likely benefits

from optimized adjustments in alternative reaction pathways or third-body efficiencies. Interestingly, none of these mechanisms incorporate the Arrhenius parameters derived experimentally by Pinzon Correa (2018). Implementing their reported reaction rate could enhance their predictive accuracy.

To further investigate the discrepancies in representing water formation, the mechanisms are still be investigated in regard of reactions that have water as a product. Hence, the following reactions will be delved (note that some mechanisms may have a different name for different species):



The Arrhenius parameters and the rate constants for these two reactions are presented in Table 21 and Figure 29 (a) and (b), respectively. As it can be seen, LLNL and San Diego models have different Arrhenius parameters in both cases. The remaining models share the same coefficients. The negative activation energies in Creck, Mittal, Aramco, Zhang, and PCRL mechanisms indicate a non-Arrhenius temperature dependence, likely compensating for pressure effects or multi-step pathways.

Table 21 – Arrhenius parameters for ethanol + OH[•] reactions: R1 = C₂H₅OH + OH[•] ⇌ CH₃CH[•]OH + H₂O[•]; R2 = C₂H₅OH + OH[•] ⇌ CH₂[•]CH₂OH + H₂O.

Mechanism	A	R1		E _a	R2		E _a
		b			b		
LLNL	4.64E+11	0.15	0.00E+00		1.74E+11	0.27	6.00E+02
CRECK	7.52E+04	2.49	-1.47E+03		3.76E+03	2.78	-1.81E+03
Mittal	7.52E+04	2.49	-1.47E+03		3.76E+03	2.78	-1.81E+03
San Diego	3.09E+10	0.50	-3.80E+02		1.81E+11	0.40	7.17E+02
Aramco	7.52E+04	2.49	-1.47E+03		3.76E+03	2.78	-1.81E+03
Zhang	7.52E+04	2.49	-1.47E+03		3.76E+03	2.78	-1.81E+03
PCRL	7.52E+04	2.49	-1.47E+03		3.76E+03	2.78	-1.81E+03

Pre-exponential factor, A, in [mol, m, s]

Temperature dependency exponent, b, [-]

Activation energy, E_a, in [cal/mol]

In Figure 29 (a) it is possible to note that the rate constant for LLNL and San Diego mechanisms is underestimated. The Arrhenius parameters for both models are very similar, thus, the curves are very close, especially at higher temperatures. The remaining models tend to overestimate the rate constant.

On the other hand, Figure 29 (b) demonstrates that the difference between the rate constant for LLNL and San Diego increases. In this case, San Diego mechanism

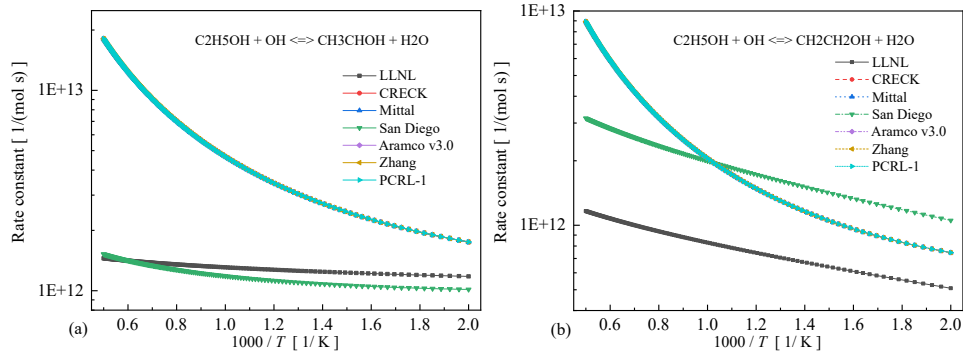


Figure 29 – Arrhenius plot for reactions $\text{C}_2\text{H}_5\text{OH} + \text{OH}^\bullet \rightleftharpoons \text{CH}_3\text{CH}^\bullet\text{OH} + \text{H}_2\text{O}$ and $\text{C}_2\text{H}_5\text{OH} + \text{OH}^\bullet \rightleftharpoons \text{CH}_2^\bullet\text{CH}_2\text{OH} + \text{H}_2\text{O}$

tends to overestimate the constant. The remaining models share common Arrhenius parameters and, therefore, the rate constant is the same. This uniformity suggests a shared source (e.g., the same literature or optimization dataset). Also, at lower temperatures, the rate constant for Aramco, Creck, Mittal, Zhang, and PCRL is close to the rate constant for San Diego, but the difference increases at higher temperatures.

In addition, the work of Mathieu et al. (2019b) highlights that water formation can be mainly attributed by $\text{H}_2 + \text{OH}^\bullet \rightleftharpoons \text{H}^\bullet + \text{H}_2\text{O}$ chain reaction. As in the majority of reactions, the mechanisms of Mittal, Creck, Aramco, and Zhang share the same coefficients. However, LLNL, San Diego and PCRL mechanisms have different Arrhenius parameters, as demonstrated in Table 22. Consequently, reaction rates will be distinguish.

Table 22 – Arrhenius Parameters for the chain reaction $\text{H}_2 + \text{OH}^\bullet \rightleftharpoons \text{H}^\bullet + \text{H}_2\text{O}$.

Mechanism	A	b	E_a
LLNL	2.14E+18	1.52	3.45E+03
Creck	4.38E+13	0.00	6.99E+03
Mittal	4.38E+13	0.00	6.99E+03
San Diego	1.17E+09	1.30	3.63E+03
Aramco v3.0	4.38E+13	0.00	6.99E+03
Zhang	4.38E+13	0.00	6.99E+03
PCRL	2.02E+08	1.51	3.43E+03

Pre-exponential factor, A, in [mol, m, s]

Temperature dependency exponent, b, [-]

Activation energy, E_a , in [cal/mol]

The consumption of ethanol is well reproduced by the majority of the models, a phenomenon clearly illustrated in Figure 28. However, it can be noticed that the LLNL mechanism underestimates the ethanol reaction rate within the temperature range of approximately 980 K to 1080 K, while the San Diego exhibits a similar issue within the temperature range of approximately 960 K to 1150 K. The remaining models are nicely fit to the ethanol mass fractions (depletion) experimental data.

However, a more nuanced examination reveals that the calculated water profiles exhibit slight deviations. These findings underscore the robustness of the models in capturing ethanol kinetics while also highlighting areas where further refinement may be warranted, particularly in the accurate prediction of water concentrations.

Going further on the chemistry of ethanol oxidation, at intermediate temperatures, H-abstraction reactions control ethanol oxidation. $\text{HO}_2^\bullet$ is the most dominant abstractor radical, as discussed in earlier sections. Abstraction of hydrogen yields the three known isomers of $\text{C}_2\text{H}_5\text{O}$ (i.e., α -hydroxyethyl ($\text{CH}_3\text{CH}^\bullet\text{OH}$)), β -hydroxyethyl ($\text{CH}_2^\bullet\text{CH}_2\text{OH}$), and ethoxy ($\text{CH}_3\text{CH}_2\text{O}^\bullet$), with $\text{CH}_3\text{CH}^\bullet\text{OH}$ being the most favored reaction product. Theoretical studies by (XI et al., 2021b) have already demonstrated that the reaction between α -hydroxyethyl and O_2 leads to the production of $\text{CH}_3\text{CHOO}^\bullet\text{OH}$, which can either generate a hydrogen-bond complex $\text{CH}_3\text{CHO}\cdots\text{HO}_2^\bullet$ that further dissociates to $\text{CH}_3\text{CHO} + \text{HO}_2^\bullet$, or undergo isomerization reactions to form $\text{C}^\bullet\text{H}_2\text{CH}(\text{OOH})\text{OH}$ and $\text{CH}_3\text{CH}(\text{O}^\bullet)\text{OOH}$, or a dissociation reaction to produce $\text{CH}_3\text{CH}(\text{O}^\bullet)\text{OOH} \longrightarrow \text{C}_2\text{H}_3\text{OH} + \text{HO}_2^\bullet$.

The acetaldehyde produced through this pathway loses one hydrogen atom to form the acetyl radical ($\text{CH}_3\text{CO}^\bullet$) (HASHEMI; CHRISTENSEN, J. M.; GLARBORG, 2018). The acetyl radical then dissociates to form CO and $\text{CH}_3^\bullet$ (HASHEMI; CHRISTENSEN, J. M.; GLARBORG, 2018). A vinoxy radical $\text{CH}_2\text{CHO}^\bullet$ is also produced in such pathway. Production of acetaldehyde + $\text{HO}_2^\bullet$ is more important at high temperatures and low pressures, while the other two reaction channels are more important at relatively low temperatures and high pressures. The other reaction channels are important at low temperatures and high pressures, and increase their importance at higher temperatures with elevated pressures (XI et al., 2021b). For a more complete information, please refer to Table 23. It is important to note that the Creck mechanism treats this as a pressure-dependent reaction. PCRL model, on the other hand, does not include this pathway.

Table 23 – Arrhenius Parameters for the reaction $\text{CH}_3\text{CO} (+ \text{M}) \rightleftharpoons \text{CH}_3^\bullet + \text{CO} (+ \text{M})$

Mechanism	High Pressure			Low Pressure		
	A	b	E_a	A	b	E_a
LLNL	3.00E+12	0.00	1.67E+04	1.20E+15	0.00	1.25E+04
Mittal	1.07E+12	0.63	1.69E+04	5.65E+18	-0.97	1.46E+04
San Diego	3.00E+12	0.00	1.67E+04	1.20E+15	0.00	1.25E+04
Aramco	1.07E+12	0.63	1.69E+04	5.65E+18	-0.97	1.46E+04
Zhang	1.07E+12	0.63	1.69E+04	5.65E+18	-0.97	1.46E+04

Pre-exponential factor, A, in [mol, m, s]

Temperature dependency exponent, b, [-]

Activation energy, E_a , in [cal/mol]

Conversely, at lower temperatures, the β -hydroxyethyl radical undergoes an O_2 addition reaction, and the subsequent Waddington reaction leads to formaldehyde (CH_2O) and OH. Hydrogen abstraction of the CH_2O molecule and subsequent reactions also led to the formation of CO and CO_2 . At higher temperatures, however, a β -scission reaction on $CH_2^{\bullet}CH_2OH$ occurs, and the stable intermediate ethylene (C_2H_4) is formed (LIU, B. et al., 2022). Another pathway to formation of CO is through the ethoxy radical, which first dissociates to CH_2O , and later gives carbon monoxide (HASHEMI; CHRISTENSEN, J. M.; GLARBORG, 2018).

Considerable amounts of CO are also produced via $HCO^{\bullet} (+ M) \rightleftharpoons CO + H^{\bullet} (+ M)$ reaction, whose Arrhenius parameters were already presented in Table 16. CO_2 is almost exclusively produced by the oxidation of CO by $OH^{\bullet}$. The reverse reaction $CO_2 + H^{\bullet} \rightleftharpoons CO + OH^{\bullet}$ is necessary to establish the water-gas equilibrium (HEGHES, 2007). The coefficients for this reaction can be seen in Table 14. Another pathway to production of CO_2 is through $HCCO^{\bullet} + O_2 \rightleftharpoons CO_2 + CO + H^{\bullet}$, although LLNL and PCRL mechanisms do not include such a reaction. The Arrhenius coefficients can be found in Table 24. Notably, in this case, San Diego is the only mechanism with different coefficients.

Table 24 – Arrhenius Parameters for reaction $HCCO^{\bullet} + O_2 \rightleftharpoons CO_2 + CO + H^{\bullet}$.

Mechanism	A	b	E_a
Creck	4.78E+12	-0.14	1.15E+03
Mittal	4.78E+12	-0.14	1.15E+03
San Diego	1.40E+07	1.70	1.00E+03
Aramco v3.0	4.78E+12	-0.14	1.15E+03
Zhang	4.78E+12	-0.14	1.15E+03

Pre-exponential factor, A, in [mol, m, s]
 Temperature dependency exponent, b, [-]
 Activation energy, E_a , in [cal/mol]

Oxidation of carbon monoxide can also occur through $CO + HO_2^{\bullet} \rightleftharpoons CO_2 + OH^{\bullet}$, although such as reaction is rarely as important as reaction $CO + OH^{\bullet} \rightleftharpoons CO_2 + H^{\bullet}$, as stated in the work of Charles K Westbrook and Frederick L Dryer (1984). However, at very high pressure conditions or in the initial stages of hydrocarbon oxidation, the high concentrations of $HO_2^{\bullet}$ radicals can make it competitive. The Arrhenius parameters for this particular reaction can be found in Table 25. As in the majority of reactions, LLNL and San Diego have both coefficients that differ from those found in the other models. Also, interestingly, coefficients adopted by PCRL mechanism are quite similar.

CO mass fractions are better reproduced by Creck, Aramco, Zhang, and Mittal models, while CO_2 profiles have a better fit with experimental data when LLNL, Creck, Aramco, Zhang, and Mittal mechanisms are used. This is well illustrated in Figure 28. The poor representation of carbon monoxide and carbon dioxide profiles by the PCRL

Table 25 – Arrhenius Parameters for reaction $\text{CO} + \text{HO}_2^\bullet \rightleftharpoons \text{CO}_2 + \text{OH}^\bullet$.

Mechanism	A	b	E_a
LLNL	5.80e+13	0.00	2.2934e+04
Creck	1.57e+05	2.18	1.7940e+04
Mittal	1.57e+05	2.18	1.7940e+04
San Diego	2.00e+13	0.00	2.2944e+04
Aramco	1.57e+05	2.18	1.7940e+04
Zhang	1.57e+05	2.18	1.7940e+04
PCRL	1.50e+14	0.00	2.3600e+04

Pre-exponential factor, A, in [mol, m, s]
Temperature dependency exponent, b, [-]
Activation energy, E_a , in [cal/mol]

mechanism can be explained by the absence of important pathways for production of both species, as established in earlier sections. The deviation of San Diego and LLNL models, on the other hand, is mainly attributed by divergence in the Arrhenius parameters.

The RMS uncertainties presented in Table 26 provide a quantification of the deviations between simulated and experimental oxidation of species in JSR under the conditions used in this study.

Table 26 – Statistical data on RMS uncertainties for ethanol oxidation species in JSR

Mechanism	$\text{C}_2\text{H}_5\text{OH}$	O_2	CO_2	H_2O	CO
San Diego	10.9	18.7	11.4	15.2	12.1
LLNL	11.2	17.3	11.1	15.5	11.7
Aramco	9.5	16.5	10.3	13.8	10.3
CRECK	9.2	16.5	10.3	13.8	10.6
Mittal	8.5	16.5	10.3	13.8	10.3
Zhang	9.9	16.5	10.1	14.2	10.1
PCRL	7.8	16.1	9.8	12.5	10.3

The quantitative evaluation of kinetic mechanisms for ethanol oxidation under JSR conditions revealed significant differences in their ability to reproduce experimental species concentration data. The PCRL mechanism emerged as the most accurate overall, exhibiting the lowest normalized root mean square uncertainty (RMS%) for ethanol (7.8%), coupled with competitive performance for carbon dioxide, oxygen, carbon monoxide and water. This balanced precision, particularly for the primary reactant species ($\text{C}_2\text{H}_5\text{OH}$), positions it as the preferred tool for studies of ignition kinetics and early-stage fuel decomposition. The Mittal and Zhang mechanism stands out as the second and third best options, with notable performance.

A common finding across all mechanisms is the systematically elevated uncertainties for O_2 , H_2O , CO, and CO_2 concentrations. This consistency suggests fundamental gaps in modeling the carbon oxidation pathway, particularly the conversion from

CO to CO₂, which consumes oxygen molecules. This result highlights the need for improvement in pollutant formation studies.

Based on the results obtained, combined with the previous results of IDT and LFS, the Zhang mechanism demonstrates to be the most consistent among all, even though it is not the most accurate in all cases. PCRL, despite its notable accuracy, is not very chemically precise, as established previously.

4.4 SUMMARY AND MECHANISM SELECTION GUIDE

Based on the results obtained from the present evaluation, Table 27 summarizes the identified performance gaps and the respective recommendations for mechanism improvement:

Table 27 – Identified performance gaps and recommendations for mechanism improvement

Target	Performance Gaps	Recommended Improvements
Ignition Delay	Poor low-temperature prediction	Refine α -site H-abstraction parameters
	Overestimation at high pressures	Improve H ₂ O ₂ decomposition kinetics
	Divergence in HO ₂ • chemistry	Update pressure-dependent reactions
Laminar Flame Speed	Overestimation in lean mixtures	Optimize $H^{\bullet} + O_2 \rightleftharpoons OH^{\bullet} + O^{\bullet}$ parameters
	Underestimation in rich mixtures	Improve CO/CO ₂ oxidation pathways
	Inaccurate chain-branching rates	Refine third-body efficiencies
Species Profiles	CO/CO ₂ prediction deviations	Enhance carbon oxidation pathways
	Water formation inaccuracies	Update ethanol decomposition channels
	Oxygen consumption rates	Include missing acetaldehyde pathways

Overall, the choice for the mechanisms must follow what is established in Table 28:

Table 28 – Performance assessment of ethanol combustion mechanisms

Mechanism	Ignition	Flame Speed	Species	Recommended Use
Zhang	Excellent	Good	Excellent	Multi-purpose applications
PCRL	Good	Excellent	Excellent	Flame speed studies
Aramco v3.0	Excellent	Fair	Good	Ignition delay studies
Creck	Excellent	Fair	Good	Ignition delay studies
Mittal	Excellent	Fair	Good	Ignition delay studies
LLNL	Poor	Fair	Fair	Limited applications
San Diego	Poor	Poor	Fair	Specific cases only

However, it is imperative to highlight that while the reactions delineated herein have consistently been attributed to disparities within the models, different temperatures, pressures, and equivalence ratios have the potential to include additional reactions that may affect the fidelity of the mechanisms. Hence, although it is not in the scope of this work, a reaction pathway analysis is of paramount importance.

5 CONCLUSIONS

In this work, the performance of 7 ethanol combustion mechanisms was investigated and evaluated according to different experiment types, in this case, ignition delay times in shock-tubes (IDT-ST), laminar burning velocities and concentration of species CO, CO₂, H₂O, C₂H₅OH, and O₂ in JSR.

For IDT-ST measurements, the Zhang mechanism demonstrated the best performance. LLNL and San Diego mechanisms were found to be less accurate in representing ignition, particularly due to underestimated H-abstraction rates and errors in H₂O₂ decomposition kinetics.

On the other hand, PCRL stands out as the best model for laminar burning velocity and species concentration profiles, even though in most cases it shares similar Arrhenius parameters with those from Aramco, Creck, Mittal, and Zhang. This is mostly related to its multifactorial parameterization, which includes pressure dependence in the termination reaction $\text{CO} + \text{OH}^\bullet \rightleftharpoons \text{CO}_2 + \text{H}^\bullet$. While PCRL's pressure-dependent treatment of termination reactions improves numerical accuracy, its omission of the dominant α -site H-abstraction pathway (critical for low-temperature ignition) limits its chemical fidelity in certain conditions.

Brute-force sensitivity analysis revealed some of the important steps regarding IDT and LFS. IDT sensitivity results identified HO₂-mediated pathways (e.g., C₂H₅OH + HO₂[•]) and H₂O₂ decomposition as dominant drivers of discrepancies at low temperatures. For flames, reactions related to the production/consumption of free radicals and heat release are responsible for uncertainties found.

Overall, PCRL, Zhang, and Mittal mechanisms were found to be the three best-performing mechanisms. Notably, most mechanisms could accurately predict the concentrations of C₂H₅OH. However, one of the most notable finding of this work was the fact that O₂, H₂O, CO₂ and CO were generally not described well by the mechanisms. The fact that both detailed and reduced mechanisms, such as the PCRL mechanism are not able to accurately predict the concentrations of oxygen and pollutants, highlights that there is fundamental gap in the understanding of carbon oxidation pathways, even in a fuel like ethanol, which has been the subject of several studies over the last decades.

The poor prediction of CO₂ and CO can be related not to a single reaction or rate constant, but to a complex chain of events which begins in the intermediate oxidation of ethanol and ends at the final step of the mechanism, where CO is finally converted to CO₂. Such a result cannot be considered merely a numerical discrepancy, but it should be taken into consideration due to its direct implication for the predictive simulation of pollutant formation. This finding highlights that to achieve an accurate prediction of emissions requires a fundamental revision of the kinetic pathways governing complete

carbon oxidation.

A notable contribution of this work is that it compiles the knowledge obtained over the years about ethanol combustion chemistry, emphasize the flaws of the mechanisms available in the literature and can further enable researchers to refine and develop more accurate models, thereby advancing our understanding of ethanol combustion processes. Future mechanisms should prioritize refining HO_2 -mediated low-temperature pathways and carbon oxidation kinetics, leveraging high-level theoretical calculations and shock-tube experiments at elevated pressures.

In summary, this research not only provides a guide to the selection of kinetic mechanisms for ethanol according to the desired application, but also indicates the knowledge gaps that prevent the truly predictive modeling of ethanol combustion, directing future efforts to where they are most needed.

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APPENDIX A – SUPPLEMENTARY INFORMATION

Figure A.1 – Pseudocode for calculation of the RMS results

```

BEGIN
// Initialize variables
SET sum_of_actual_values = 0

// Loop over all actual values to calculate the mean of
  actual values
FOR i FROM 1 TO N DO
  sum_of_actual_values = sum_of_actual_values +
    actual_value[i]
END FOR

SET mean_actual_value = sum_of_actual_values / N

// Calculate RMSE as a percentage
SET RMSE_percent = (RMSE / mean_actual_value) * 100

// Output the result
RETURN RMSE_percent
END

```

Table 29 – Experimental targets used in the validation of the Mittal mechanism

Parameter	IDT RCM	IDT ST	JSR	FR	LBV	BSF
Dilution	–	Ar / N ₂	N ₂	N/A	Ar	N ₂
Temperature [K]	825–985	800–1760	890–1250	800–1100	298–453	–
Pressure [bar]	10–50	2–40	1	1–12	1–8	0.05, 1.0
Equivalence ratio (φ)	0.3–1.0	0.5–2.0	0.25–2.0	0.3–1.4	0.6–1.8	0.75–1.25

Table 30 – Experimental targets used in the validation of the LLNL mechanism

Parameter	IDT RCM	IDT ST	JSR	FR	LBV	BSF
Dilution	–	Ar	N ₂ , H ₂	N ₂	Ar	N ₂ , O ₂
Temperature [K]	–	1100–1900	1056–1070	1100	300–453	300, 400
Pressure [bar]	–	1.8–4.5	1.0	1.0	1.0–2.0	1.0, 2.0
Equivalence ratio (φ)	–	0.25–2.0	1.0–2.0	1.0	0.55–1.8	0.5–1.8

Table 31 – Experimental targets used in the validation of the San Diego mechanism

Parameter	IDT RCM	IDT ST	JSR	FR	LBV	BSF
Dilution	–	Ar	–	–	–	O ₂ , N ₂
Temperature [K]	–	900-1400	–	–	298, 363, 428, 453	298-340
Pressure [bar]	–	1.0, 2.0, 3.5, 4.6	–	–	1.0	1.0
Equivalence ratio (φ)	–	0.25, 0.5, 1.0, 2.0	–	–	0.7-1.3	2.3

Table 32 – Experimental targets used in the validation of the Creck mechanism

Parameter	IDT RCM	IDT ST	JSR	FR	LBV	BSF
Dilution	–	Ar, N ₂	N ₂	N ₂	–	He, Ar
Temperature [K]	–	833-2500	800-1260	600-1400	295-600	300–2300
Pressure [bar]	–	0.66–263	1-10	1-60	1–10	0.026–0.051
Equivalence ratio (φ)	–	0.06–6.0	0.25–5.0	0.05–5.0	0.4–2.2	0.75–2.4

Table 33 – Experimental targets used in the validation of the Aramco mechanism

Parameter	IDT RCM	IDT ST	JSR	FR	LBV	BSF
Dilution	N ₂	Ar, N ₂	N ₂	N ₂	N ₂	–
Temperature [K]	645–961	990–1781	750–1250	1035–1125	295–399	–
Pressure [bar]	10–40	1–40	1–10	1	1–5	–
Equivalence ratio (φ)	0.5 1.0 2.0	0.5 1.0 2.0	0.3	0.6	0.4–1.4	0.4

Table 34 – Experimental targets used in the validation of the PCRL mechanism

Parameter	IDT RCM	IDT ST	JSR	FR	LBV	BSF
Dilution	N ₂ , Ar	N ₂ , Ar	–	–	N/A	N ₂ , O ₂
Temperature [K]	820-950	820-1450	850-1300	950	300-600	327
Pressure [bar]	25-40	3.3-80	1.0	3.	1-10	1.0
Equivalence ratio (φ)	0.5-1.0	0.3-2.0	–	–	0.6-1.4	–

Table 35 – Experimental targets used in the validation of the Zhang mechanism

Parameter	IDT RCM	IDT ST	JSR	FR	LBV	BSF
Dilution	O ₂ , N ₂	O ₂ , N ₂	O ₂ , N ₂	O ₂ , N ₂	O ₂ , N ₂	O ₂ , N ₂
Temperature (K)	650-1050	650-1250	850-1300	950	300-600	300-327
Pressure (bar)	20, 40	20, 40	10	3	1-10	1.0
Equivalence ratio (φ)	0.5, 1.0, 2.0	0.5, 1.0, 2.0	0.3	0.6	0.4-1.4	0.4