MOLECULES TO ENGINES: COMBUSTION CHEMISTRY OF ALCOHOLS AND THEIR APPLICATION TO ADVANCED ENGINES

by

SHAMEL SARFARAZ MERCHANT

M.S. Chemical Engineering Practice, Massachusetts Institute of Technology, 2011

B. Chemical Engineering, Institute of Chemical Technology, Mumbai, 2009

Submitted to the Department of Chemical Engineering in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering at the MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June 2015

© 2015 Massachusetts Institute of Technology. All rights reserved.

Signature of Author

Certified by

William H. Green
Hoyt C. Hottel Professor of Chemical Engineering

Accepted by

Richard D. Braatz
Edwin R. Gilliland Professor of Chemical Engineering
Chairman, Committee for Graduate Students
Abstract

**Molecules to Engines: Combustion Chemistry of Alcohols and their Application to Advanced Engines**

by

Shamel Sarfaraz Merchant

Submitted to the Department of Chemical Engineering on February 23rd, 2015, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering

A major challenge in energy is the identification of viable liquid fuels as alternatives to petroleum-based fuels. There are a wide variety of candidate fuels to select from and assessing each new fuel is far from trivial. Small variations in chemical structure can cause large changes in a fuel's performance. Simultaneously, engine designs are also changing rapidly. Accurately predicting how new fuels will perform in future engines are in many ways more valuable than knowing which fuels perform well in today’s engines. Predictive theoretical modeling is required to efficiently screen candidates.

The selection of a good candidate fuel requires the development of detailed kinetic models capable of accurately predicting fuel behavior over the entire range of engine operating conditions. Despite the fact that most literature models succeed to accurately predict primary combustion products and high temperature ignition delay, two areas require further scientific understanding: peroxy chemistry and polycyclic aromatic hydrocarbon (PAH) formation. The first section of this thesis describes significant contributions to both these areas. Peroxy chemistry is important for accurately predicting ignition in future engine designs based on the concept of low temperature combustion (LTC). This thesis provides a clear explanation of how peroxy chemistry affects low temperature ignition behavior. Simple analytical expressions are provided for the time constant for radical growth and first-stage ignition delay. To improve the understanding of PAH formation, ab initio calculations to indene and naphthalene from cyclopentadiene and cyclopentadienyl radical were performed. The calculated gas phase rate constants and thermochemistry were used to develop the first elementary micro-kinetic model for the formation of indene and
naphthalene from cyclopentadiene. The model is validated against cyclopentadiene pyrolysis data in flow reactors.

The second section of this thesis presents a combined computational-experimental approach to rapidly construct accurate combustion chemistry simulations for alcohol fuels. In this approach experiments and quantum chemical calculations are carried out in parallel, informing an evolving chemical kinetic model. This approach was used to understand and predictively model the combustion chemistry of iso-butanol and pentanol isomers. Detailed kinetic models for iso-butanol and pentanol isomers are presented which are validated against a large number of datasets spanning the entire range of operating conditions seen during real engine operation. We see that for many performance parameters, the model predictions are as accurate as experiment and help provide mechanistic insight into differing reactivity of a fuel's isomers. Lastly, we show how detailed kinetic model can be applied in multi-dimensional CFD simulations of a new type of engine, the reactivity controlled compression ignition engine (RCCI), in order to make predictions of how iso-butanol will affect the engine efficiency and emissions. This thesis covers the entire process of predictively accessing a fuel by taking a new fuel molecule, developing a detailed model, and evaluating it in a new engine design in order to make informed decisions.

Thesis Supervisor: William H. Green

Title: Hoyt C. Hottel Professor of Chemical Engineering
I dedicate this thesis to
my family. Mom, Dad, grandparents and my beloved brothers
for their constant support and unconditional love.
I love you all dearly.

I would also like to dedicate this thesis to
all the brave souls who were lost on July 11th 2006
in the Mumbai train tragedy.
Ajay Seveda you are dearly missed, my friend.
Acknowledgements

The journey of obtaining one's Ph.D. can be compared to traversing through a potential energy surface with many valley and hills. A graduate student learns to overcome failures and setbacks through perseverance and patience in order to ultimately reach an excited state of intellectual satisfaction. My journey would not have been possible without the support and mentorship of a great number of people.

My first note of gratitude goes to my advisor, Prof. William Green. You have been an excellent advisor and I feel lucky to have shared the journey of my Ph.D. under your mentorship. You have always been excited about my research and have been willing to answer all of my doubts and questions, regardless of how trivial they might be. Thank you for taking the time to read through my manuscripts and for pushing me to polish them to high standards. I have learnt so much about scientific publications under your tutelage. Your enthusiasm for life, science and community are a tremendous source of inspiration and will continue to be in the future. I am also grateful to my committee members, Prof. George Stephanopolous, Prof. Yury Roman and Prof. Bruce Tidor for being an instrumental part of my progress throughout my Ph.D. Your suggestions to keep the big picture in mind and to find the right balance between rigor and practicality have helped me tackle several scientific challenges. A special thank you to Prof. George Stephanopolous for believing in me 6 years ago and for admitting me into this department. I will always be in debt to you for that.

My thesis has greatly benefitted from numerous collaborators in the scientific community. If I have seen further it is by standing on the shoulders of these giants (including all my collaborators and advisor). Thank you to Prof. Stephen Klippenstein, Prof. Franklin Goldsmith and Prof. Michael Burke for meticulously checking every assumption and hypothesis that I made in the low temperature ignition work. Your thoughtful questions have helped to improve the propane work tremendously. I am greatly indebted to Dr. Aäron Vandeputte with whom I shared the journey of unraveling aromatic formation. Aäron's dedication and never-give-up spirit were crucial to successfully completing this project. The initial goal of the cyclopentadiene project was to fix benzene production in RMG. This
matured to finding toluene pathways, but along the way meandered, finally leading us to find pathways to polycyclic aromatics. Prof. Kevin Van Geem and his students Marko Djokic and Ruben De Bruycker have been a tremendous help for the butanol and pentanol pyrolysis work. I would like to express my sincerest gratitude to Kevin, for all the encouragement and wisdom that he has provided to me these past 5 years. The RCCI engine project would not have been possible without the help from Prof. Rolf Reitz and Hu Wang. Most of the engine design and simulation knowledge I have today is due to your coaching and willingness to answer all of my questions. The butanol project is a hallmark project in the kinetics community and a testament of the collaborative efforts of the CEFRC. I would like to thank all the members of the butanol team especially Dr. Nils Hansen, Dr. Bryan Weber, Dr, Genny Pang and Dr. Ivo Stranic for your helpful input and suggestions in developing the butanol mechanism.

Thank you to all of the RMG developers (both past and present) that I have had the pleasure of working with, including Dr. Michael Harper, Dr. Richard West, Dr. Greg Magoon, Dr. Josh Allen, Dr. Amrit Jalan, Dr. Caleb Class, Connie Gao, Nathan Yee, Dr. Beat Buesser, Dr. Aäron Vandeputte, Dr. Enoch Dames, Dr. Nick Vandewiele and Kehang Han. My thesis would not have been possible without your dedication to developing RMG to be a successful piece of software. Thank you for developing so many nice features and fixing bugs on my requests. This thesis would not have been possible without your contributions. Thank you to all Green group members. Your kind, helpful and fun nature has made coming to the office every day a pleasure. I would like to thank Dr. John Alecu and Dr. Josh Middaugh for the long senseless chats over coffee, Dr. Pepper or Quiznos subs • these are still some of my fondest memories in the group.

Life at MIT would have been much harder without the excellent administrative staff that supports the graduate community. Thank you to Gwen Wilcox, Alison Martin, Barbara Balkwill, Joel Danshaw and Suzanne Easterly for everything you have done. Every time I had a slip-up, I knew that I could come rushing to you for help.

Outside of lab, I am grateful to all my friends and family that have been there for me the past 5 years. Harshad Khadilkar, Somani Patnaik, Rutuparna Das, Radhika Marathe, Sivaraman Ramaswamy, Nihit Jain, Himanshu Dhamankar, Rathi Srinivas and Connie Gao • thank you for being there for me, for putting up with my tantrums and mood swings,
for dragging me out to events and outings, for always keeping me well-fed, and for introducing me to new aspects of life. Whenever I gave up, your encouragement kept me going. A special note of thank you to all the Desi junta - Vishnu Srest, Sagar Chakraborty, Sayalee Mahajan, Manish Shetty, Ankur Gupta, Parnika Agarwal, Krishna Kumar Selvam, Anasuya Mandal and Priyanka Raina. From organizing Sangam events, to recording Shuddh Bollywood Romance to the late night chai (tea) you have been an integral part of my life at MIT. Thank you to all my MIT ChemE friends – Tim Politano, Matt Glassman, Brandon Reizman, Mitchell Wang, Nicole Yang, Jonathan Glibert and Jonathan Harding, for all the fun times we have had at eating brunch, going out for dinner, frying things, making cryptic messages to send to Rathi, helping each other out at various stages during Ph. D. and job hunt. Leaving MIT is especially difficult since I know I will miss your company and I promise to cherish our memories forever. I would also like to thank my college friends – Akshay Bhat, Aniruddha Upadhye, Hrishikesh Munj, Saurabh Bhavsar, Akshay Mahajan and Adwaith Naimpally for their support and encouragement. It has been a sweet last decade knowing you guys and you rock!

Finally, I am deeply indebted to my family. You have been an endless source of support, love and motivation for me. This journey would have been much harder without all the sacrifices you have made that have brought me to this point. Thank you Mom, Dad, Nani Ma, Safir and Samer for always being there and for all your prayers.
Table of contents

1. Introduction ......................................................................................................... 25
   1.1 Predictive kinetic framework ............................................................................... 26
   1.2 Complexity of modeling fuels ............................................................................... 28
   1.3 Overview of thesis chapters ................................................................................... 29

2. Developing understanding for first stage ignition delay for alkane fuels ........31
   2.1 Introduction ............................................................................................................... 32
   2.2 Propane as an archetype for low temperature peroxy ignition pathways ............35
   2.3 Propane kinetic model ........................................................................................... 37
   2.4 Low temperature oxidation of propane ................................................................... 38
   2.5 Reduced model formulation for low temperature ignition ........................................ 46
      2.5.1 Analytic solution for stage-1A ....................................................................... 48
      2.5.2 Analytic solution for stage-1B ....................................................................... 53
      2.5.3 Predicting first-stage ignition ....................................................................... 55
      2.5.4 First stage ignition delay under adiabatic conditions ..................................... 57
      2.5.5 First stage ignition delay under isothermal conditions ................................... 61
   2.6 Predicting first stage ignition delay for longer chain alkane fuels ....................... 63
      2.6.1 Implications for chemistry of first-stage ignition ......................................... 69
      2.6.2 Overall activation energy of first-stage ignition for long chain alkanes ........... 71
2.7 Concluding remarks ...........................................................................................................72

2.8 Supplemental Material ........................................................................................................75

2.8.1 Derivation for explosive eigenvalue using reduced model for stage-1A .............76

2.8.2 Analytical solution for the explosive eigenvalue for stage-1A .........................83

2.8.3 Simplification of the explosive eigenvalue for stage-1B ..............................................86

2.8.4 Prediction for first stage ignition delay for propane under varying equivalence ratios and pressure ...............................................................................................................87

3. Developing detailed understanding for pyrolysis of cyclopentadiene to polycyclic aromatics .................................................................................................................91

3.1 Introduction ..........................................................................................................................91

3.2 Pyrolysis experimental procedure ....................................................................................93

3.3 Reaction mechanism generation .....................................................................................96

3.3.1 Quantum calculation and statistical mechanics .....................................................96

3.3.2 Master equation calculations .....................................................................................97

3.4 Results ..................................................................................................................................98

3.4.1 Co-pyrolysis of cyclopentadiene and ethene .....................................................98

3.4.2 Reactions paths towards indene and naphthalene .............................................99

3.4.3 Rate of production and sensitivity analysis .........................................................103

3.4.4 Model predictions and validation ........................................................................108

3.5 Conclusions ......................................................................................................................113

4. iso-Butanol pyrolysis and combustion .............................................................................115

4.1 Introduction .......................................................................................................................115

4.2 Pyrolysis experiment setup ............................................................................................117

4.3 Reactor models ................................................................................................................120

4.3.1 Pyrolysis ................................................................................................................120

4.3.2 Doped methane diffusion flame .............................................................................121

4.3.3 Jet-stirred reactor .....................................................................................................123
4.3.4 Laminar burning velocities .......................................................... 123
4.3.5 Opposed flow diffusion flame .................................................. 123
4.3.6 Shock tube experiments ............................................................. 124
4.4 Reaction mechanism generation .................................................. 124
  4.4.1 Automatic reaction mechanism generation and refinement .......... 124
  4.4.2 Unimolecular decomposition of iso-butanol .................................. 126
  4.4.3 Quantum calculation and statistical mechanics .......................... 127
4.5 Results ....................................................................................... 129
  4.5.1 Pyrolysis experiment ................................................................. 129
  4.5.2 Doped methane flame ............................................................... 135
  4.5.3 Jet-stirred reactor .................................................................. 141
  4.5.4 Opposed-flow diffusion flame .................................................. 152
  4.5.5 Laminar flame speeds .............................................................. 158
  4.5.6 Ignition delay time ................................................................. 162
4.6 Conclusion ................................................................................... 167

5. Extending alcohol mechanisms to n- and iso-pentanol ...................... 169
  5.1 Introduction ............................................................................... 170
  5.2 Experimental and the simulation method ...................................... 172
    5.2.1 The pyrolysis setup ................................................................. 172
    5.2.2 Reaction mechanism generation ............................................ 174
    5.2.3 Quantum calculations .......................................................... 175
  5.3 n-Pentanol results and discussion .............................................. 182
    5.3.1 Pyrolysis experiment ............................................................... 182
    5.3.2 Laminar flame speed experiment ............................................. 189
    5.3.3 Ignition delay experiment ....................................................... 192
  5.4 iso-Pentanol results and discussion ............................................ 198
5.4.1 Pyrolysis experiment .......................................................................................199
5.4.2 Jet Stirred Reactor...........................................................................................205
5.4.3 Ignition delay experiment................................................................................208
5.5 Conclusion ...........................................................................................................212

6. Investigating Reactivity Controlled Compression Ignition (RCCI) using iso-
butanol and di-tert-butyl-peroxide ........................................................................213
6.1 Need for a high efficiency and clean engine .......................................................213
6.2 Reactivity controlled compression ignition (RCCI) engine.................................214
6.3 Case Study: iso-Butanol + Peroxide in RCCI engine ..........................................216
   6.3.1 Single cylinder experiments ...........................................................................216
   6.3.2 Multi-Dimensional CFD ..............................................................................218
   6.3.3 Chemistry mechanism ..................................................................................220
   6.3.4 Results and discussion ................................................................................225
6.4 Conclusion ...........................................................................................................229

7. Recommendations for future work .....................................................................231
   7.1 Develop understanding for low temperature ignition .......................................231
   7.2 Developing kinetic models for higher PAHs .....................................................233
      7.2.1 Improving RMG thermochemistry estimation ..............................................233
      7.2.2 Developing rate rules for higher PAHs .........................................................234
      7.2.3 RMG speed up and memory issues ..............................................................234
   7.3 Alcohol modeling ..............................................................................................234
      7.3.1 Investigating decomposition kinetics for ketohydroperoxide ..................235
      7.3.2 Investigating the O₂ dependence for low temperature alcohol ignition ......236

8. Bibliography ............................................................................................................237
List of figures

Figure 2-1: Experimental measured overall (filled symbols) and first stage (open symbols) ignition delays in a rapid compression machine (RCM) for methylcyclohexane (MCH) [66] and dimethylether (DME) [67] at $P\approx 15$ bar, $\varphi(MCH) = 1$ and $\varphi(DME) = 0.75$. For low temperatures the measured first stage ignition delay is almost equal to the overall measured ignition delay. For higher temperatures the later stages of ignition contribute more to the overall ignition delay.

Figure 2-2: Schematic mechanism for the low temperature alkane oxidation and autoignition chemistry adapted from the work of Zádor et al. [19], including the Korkek reaction [42]. The pathways shown by a blue arrow lead to additional OH radicals (chain branching) while the pathways indicated by a red arrow lead to chain termination. Note that in some cases HOOQ'OOH may not be a true stationery point on the potential energy surface (e.g. for HOOQ'OOH where the radical site is on the carbon adjacent to the hydroperoxy group [48]).

Figure 2-3: Schematic of major reaction pathways during the first stage of propane ignition. Reactions shown in blue lead to formation of OH radicals while those in red consume OH radicals. The reactions shown by dotted lines divert radicals away from the main chain branching pathway and delay the first-stage ignition. During stage-1A, HO$_2$ radicals reacts with the fuel accelerating the chemistry, but later much of it recombines reducing the concentration of radicals. Note: For clarity some well-skipping pathways and reactions of HO$_2$ are omitted from the figure.

Figure 2-4: OH and HO$_2$ mole fraction profile (on semi-log scale) and temperature profile for isochoric (constant-volume) adiabatic simulation for a stoichiometric mixture of propane and air initially at $P_0 = 10$ bar and $T_0 = 650$K. $\tau_{overall}$ is the overall ignition delay of the fuel. $\tau_{stage-1}$ is the first-stage ignition delay of the fuel, the time when the temperature (or pressure) of the system makes a small jump prior to the main ignition event. The first-stage ignition delay can be further divided into two stages A and B that are characterized by different time constants for the exponential rise of the OH concentration. $\tau_{stage-1A}$ is the time when the early exponential rise in OH concentration ends.

Figure 2-5: Fraction of propane consumed by each reaction during stage-1A (0.1s) and stage-1B (0.39s). HO$_2$ reaction with the fuel is significant during stage-1A, but negligible during stage-1B.

Figure 2-6: Magnitudes of the rates of important reactions producing or consuming HO$_2$, for stoichiometric mixture of propane and air initially at $P_0 = 10$ bar and $T_0 = 650$K. The transition from stage-1A to stage-1B occurs when HO$_2$ recombination becomes comparable to other...
Figure 2-7: Evolution of key species during isochoric adiabatic reaction of stoichiometric mixture of propane:air at \( P_0 = 10 \) bar and \( T_0 = 650 \) K. It should be noted that OQ’OOH peaks shortly before \( T_{\text{stage-1}} \). The full scale values of H\(_2\)O\(_2\), CH\(_2\)O and OQ’OOH were chosen to be of twice the maximum value reached in the simulation.

Figure 2-8: Arrhenius plot for adiabatic isochoric stoichiometric mixture of propane in air initially at \( P_0 = 10 \) bar comparing \( T_{\text{OQ’OOH peak}} \) to \( T_{\text{stage-1}} \) (determined by inflection in temperature). The \( T_{\text{OQ’OOH peak}} \) is a good estimate of \( T_{\text{stage-1}} \).

Figure 2-9: a) Net rate of production for reactions involved in \( n \)-propyl (nR) peroxy cycle, for adiabatic isochoric simulations \( (P_0 = 10 \) bar, \( T = 650 \) K) of stoichiometric mixture of propane and air using the full propane model. The arrows indicate the time when the species come into quasi-steady state, most species are in quasi-steady state after \( t \sim 5 \) ms. b) Inset of plot 5a) - the rate of O\(_2\)Q’OOH \( \rightarrow \) OQ’OOH + OH and OQ’OOH \( \rightarrow \) OQ’O + OH are significantly different indicating OQ’OOH is not in quasi-steady state. For reference \( T_{\text{stage-1A}}, T_{\text{OQ’OOH}} \) and \( T_{\text{stage-1}} \) are \(-0.2, -0.44 \) and \(-0.56 \) s respectively.

Figure 2-10: Effect of temperature on \( \theta \) (equation (2-13)) at three different pressures for oxygen mole fraction of 0.2. As the temperature increases, the fraction of nRO\(_2\) that participates in the chain branching sequence approaches zero. The fraction of nRO\(_2\) that participates in the chain branching sequence is higher at higher pressures.

Figure 2-11: Comparison of the predicted and the simulated OH mole fraction profiles, for adiabatic isochoric simulations at \( P = 10 \) bar, \( T = 650 \) K and stoichiometric mixture of propane:air using the full model. The red line corresponds to the stage-1A prediction while the black line corresponds to the stage-1B prediction. The predictions are made using the equation \([\text{OH}] = C_{\text{OH,X}} \exp(\lambda_{1X}t)\) where \( \lambda_{1A} = 55.4 \) s\(^{-1}\) and \( \lambda_{1B} = 25.3 \) s\(^{-1}\).

Figure 2-12: Simulated OH loss terms \( \alpha \) and \( \beta \) as function of time for stoichiometric mixture of propane at \( T_0 = 650 \) K and \( P_0 = 10 \) bar under adiabatic conditions. The dashed grey line indicates the time when OQ’OOH peaks in the simulation.

Figure 2-13: Comparison of the first-stage ignition delays \( (\tau_{\text{OQ’OOH peak}}) \) obtained from 1) the time of the inflection point in the temperature profile from full model simulation, 2) the time of the OQ’OOH peak in the full model simulation 3) the time for \( \phi_{\text{II}} = 1 \) predicted from the solution to equations (2-30)-(2-35) and 4) the time for \( \phi_{\text{III}} = 1 \) predicted by equation (2-41) for adiabatic, isochoric simulations of stoichiometric mixtures of propane and air, \( P_0 = 10 \) bar.

Figure 2-14: Comparison of the \( \tau_{\text{OQ’OOH peak}} \) obtained from 1) the time numerical location of the OQ’OOH peak for the full model simulation, 2) the time at which criterion set by equation (2-26) is met using reaction fluxes obtained from simulations, 3) the time predicted by equation (2-43), all for an isothermal isochoric simulation of a stoichiometric mixture of propane and air.

Figure 2-15: Schematic of a long \( n \)-alkane fuel undergoing low temperature peroxy chemistry. As the carbon chain increases every site can be treated as an equivalent site. The blue arrows are OH formation reactions while the red arrows show loss of OH radicals. The dotted arrows are reactions that compete with low temperature branching reactions and delay the first stage ignition of the fuel.

Figure 2-16: Comparison of simulated full-model adiabatic isochoric overall ignition delays with the first stage ignition delay predicted by Eq. (2-54). for different \( n \)-alkanes with initial conditions \( P_0 = 10 \) bar and \( \phi = 1 \) in air. The parameters for equation (2-54) are tabulated in Table...
The value of $\gamma$ is uncertain for fuels larger than propane. Here, we plot results using $\gamma = 1$ and $\gamma = 0.7$.

**Figure 2-17:** Comparison of the predicted first stage ignition delay for constant volume adiabatic simulations using the full and reduced propane model, for $P_0 = 10$ bar, stoichiometric mixture of propane in air. The $\tau_{\text{stage-1}}$ was obtained using the first inflection in the temperature profile.

**Figure 2-18:** Predictions (dotted lines) for relative concentrations of species involved in first stage ignition (stage-1A) by eigen mode analysis for simulations at $P_0 = 10$ bar and $T_0 = 650$ K for a stoichiometric mixture of propane in air. The solid lines are obtained from full model simulations, the dotted lines are the ratio of the eigenvector elements $V_{\text{species}}/V_{\text{OQOOH}}$ corresponding to the positive eigenvalue in stage-1A.

**Figure 2-19:** Comparison of the net HO2 flux (from the full model simulation) and the approximation $2k_{\text{OQOOH decamp}}[\text{OQOOH}]$ for $P_0 = 10$ bar and $T_0 = 650$ K.

**Figure 2-20:** Comparison of the simulated adiabatic isochoric overall ignition delay with the predicted first stage ignition delay for various equivalence ratios of propane in air. All simulations are for $P_0 = 10$ bar. The overall ignition delay (solid line) is obtained from the full model simulations, while the predicted first stage ignition delay (dashed line) is obtained using equation (2-41).

**Figure 2-21:** Comparison of the simulated adiabatic isochoric overall ignition delay with the predicted first stage ignition delay for various pressure. All simulation are for stoichiometric mixture of of propane in air. The overall ignition delay (solid line) is obtained from the full model simulations, while the predicted first stage ignition delay (dashed line) is obtained using equation (2-41).

**Figure 3-1:** Illustration of the growth of soot particles from smaller molecules.

**Figure 3-2:** CBS-QB3 enthalpy diagram $H(0 \text{ K})$ (kJ mol$^{-1}$) for the C$_{10}$H$_{10}$ surface initiated by the recombination of two CPDyl radicals. All enthalpies are relative to the adduct 1a. The lowest entrance and exit channel are indicated in green. At low pressures, the chemically-activated reactions C$_5$H$_5$+C$_5$H$_5$ $\rightarrow$ C$_{10}$H$_{10}$ + H is significant. However in many systems C$_{10}$H$_9$ + R $\rightarrow$ C$_{10}$H$_9$ + RH is the dominant consumption pathway. The enthalpy does not include BAC corrections.

**Figure 3-3:** CBS-QB3 enthalpy diagram $H(0 \text{ K})$ (kJ mol$^{-1}$) on the C$_{10}$H$_5$ surface leading to the formation of naphthalene. All enthalpies are relative to component 2b which represents the dominant entrance channel. The barrier for the rate limiting step is indicated in red and was calculated using CCSD(T)-F12/cc-pVDZ. The lowest entrance and exit channel are indicated in green. The enthalpy does not include BAC corrections.

**Figure 3-4:** CBS-QB3 enthalpy diagram $H(0 \text{ K})$ (kJ mol$^{-1}$) on the C$_9$H$_9$ surface leading to the formation of indene. All enthalpies are relative to the entrance channel CPD + CPDyl. The barrier for the rate limiting step is indicated in red and was calculated using CCSD(T)-F12/cc-pVDZ. The enthalpy does not include BAC corrections.

**Figure 3-5:** Reaction used in most literature models to predict the rate of naphthalene formation.

**Figure 3-6:** Rate of production analysis on the C$_{10}$H$_{10}$ surface presented in Figure 2 for 30% CPD conversion at 1123 K, 1.7 bar and a dilution of 5 mol N$_2$/mol CPD. All rates are normalized by the rate obtained for the recombination of two CPDyl radicals, which is the entrance channel for this surface.
Figure 3-7: Computed RRKM rate coefficients for the recombination of two CPDyl radicals to form various products at 1500K in N₂. The corresponding PES is shown in Figure 3-2.

Figure 3-8: Normalized sensitivity coefficients for the pyrolysis of CPD (1.7 bar, 5 mol N₂/mol CPD, 1000 K). The top five reactions are shown for (a) indene and (b) naphthalene and that at 10% (darker) and 30% (lighter) CPD conversion.

Figure 3-9: Reaction selected to study the influence of the basis set for the reaction 4 \rightarrow 5 (see Figure 3-3).

Figure 3-10: Rate of production analysis for the formation of benzene at 1123 K, 1.7 bar and a residence time of 0.22 s. Normal values correspond with a dilution of 5 mol N₂/mol CPD. Bold values correspond with a dilution of 10 mol N₂/mol CPD and 1 mol ethene/mol CPD. All rates are normalized by the net production rate of benzene.

Figure 3-11: Main reaction path leading to the formation of fulvene. The β-scission reaction has a fairly high activation barrier (E = 39 kcal/mol), so below ~1100 K this pathway is not very important.

Figure 3-12: Model predictions of the main reaction products during the pyrolysis of CPD (1.7 bar, dilution of 5 mol N₂/mol CPD, F₀,Cpd = 27 mg/s). Current model predictions are indicated by full lines, prediction made with the model presented in ref. [103] are indicated with dashed lines.

Figure 3-13: Predicted indene (left) and naphthalene yield (right) in weight percentages as function of the CPD conversion (1.7 bar). Dashed lines and hollow data points correspond with a dilution of 5 mol N₂/mol CPD (F₀,Cpd = 27 mg/s), full lines and filled data points correspond with a dilution of 24 mol N₂/mol CPD (F₀,Cpd = 6 mg/s). The trends are due to variations in steady-state [CPDyl]/[CPD] with respect to the feed concentration.

Figure 3-14: Model predictions of the main reaction products during the co-pyrolysis of CPD and ethene (1.7 bar, dilution of 1 mol ethene / 1 mol CPD / 10 mol N₂, F₀,Cpd = 13.6 mg/s). Current model predictions are indicated by full lines, predictions made with the model presented in [103] are indicated with dashed lines.

Figure 4-1: GC×GC-FID chromatogram of the on-line sampled undiluted iso-butanol pyrolysis effluent at Tᵥ=1053 K and Fiso-butanol = 6.66 \times 10^{-2} g s⁻¹.

Figure 4-2: iso-Butanol conversion as a function of the average pyrolysis reactor temperature (symbols – experimental: • undiluted, ■ N₂ diluted: 3 mol N₂/mol iso-butanol, – simulated • undiluted and ■ diluted).

Figure 4-3: Comparison of the experimental (symbols) and simulated (lines) yields of the major products at diluted (3 mol N₂/mol iso-butanol) and undiluted pyrolysis conditions. A) methane, B) CO, C) ethene, D) propene, E) isobutene, F) propanal + prop-1-enol, G) water, H) formaldehyde (symbols – experimental, lines – model simulations).

Figure 4-4: Comparison of the experimental (symbols) and simulated (lines) yields of the minor products at diluted (3 mol N₂/mol iso-but) and undiluted conditions. A) hydrogen, B) CO₂, C) ethane, D) 1,3-cyclopentadiene, E) benzene, F) 1,3-butadiene (symbols – experimental, lines – model simulations).

Figure 4-5: Reaction pathway analysis of iso-butanol pyrolysis (undiluted) in a plug flow reactor operated at p = 1.7 bar and T = 1000 K for 70% conversion. Percentages are expressed relative to the total iso-pentanol consumption rate.
Figure 4-6: Experimental (symbols) and simulated (line) centerline mole fraction profiles of iso-butanol in doped methane diffusion flame [152]. The offset along the X axis is mostly due to uncertainty in the assumed temperature profile, see Van Geem et al. [162].

Figure 4-7: Predicted centerline rate of production for iso-butanol in doped methane flame.

Figure 4-8: Experimental (symbols) and simulated (line) centerline mole fraction of iso-butanol products in doped methane flame [152]. A) MW = 42 (mostly propene), B) MW = 44 (acetaldehyde + vinylalcohol), C) MW = 54 (1-butyne + 2-butyne + 1,3-butadiene + 1,2-butadiene), D) MW = 56 (mostly iso-butene) E) MW = 78 (mostly benzene) and F) MW = 58 (propanal + prop-1-enol+ prop-2-enol).

Figure 4-9: Simulated centerline rate of production for A) acetaldehyde, B) vinyl alcohol, C) iso-butene and D) 1-butyne in iso-butanol doped methane diffusion flame. For Figure 10 D at low temperatures, propargyl + CH₃ form 1-butyne which is attacked by H to form allene. However at high temperatures the reactions run in reverse.

Figure 4-10: Normalized sensitivity coefficients for the centerline iso-butanol concentration in the doped diffusion flame with respect to Lennard-Jones collision diameter σ for iso-butanol, nitrogen and methane.

Figure 4-11: Simulated (lines) and experimental (symbols) profiles of major species for jet stirred reactor experiment [157] for ϕ =0.5 and P=10 atm. (C2H4O is sum of acetaldehyde + vinyl alcohol).

Figure 4-12: Simulated rate of production for iso-butanol in the 10 atm jet stirred reactor [157] for equivalence ratios A) 0.5, B) 1 and C) 4.

Figure 4-13: Simulated (line) and experimental (symbols) profiles of iso-butene for jet stirred reactor experiment [157] for equivalence ratios A) 0.5, B) 1, C) 2 and D) 4.

Figure 4-14: Simulated rate of production for iso-butene in the 10 atm jet stirred reactor [157] for equivalence ratios A) 0.5, B) 1 and C) 4.

Figure 4-15: Sensitivity analysis for iso-butene production in jet stirred reactor [157] at 10 atm as function of temperature (700 – 1100 K) and equivalence ratios A) 0.5, B) 1 and C) 4.

Figure 4-16: Model comparison for all measured species in opposed flow diffusion flame of Grana et al. [153] (experimental –symbols and simulated • line).

Figure 4-17: Simulated rate of production for iso-butanol for opposed flow diffusion flame experiment[153].

Figure 4-18: Simulated rate of production for A) formaldehyde and B) acetaldehyde for opposed flow diffusion flame.

Figure 4-19: Simulated (line) and experimental (symbol) zero-strain laminar flame speed of iso-butanol air mixtures as a function of equivalence ratios (Experiment: 1 atm ○ Veloo et al. [149], △ Liu et al. [150] and 2 atm □ Liu et al. [150]).

Figure 4-20: Reaction sensitivity analysis for zero-strain laminar flame speed of iso-butanol in air mixtures. at P= 1 atm, T(unburnt) = 343 K and ϕ = 1.4.

Figure 4-21: Comparison of literature rate coefficients for C₂H₃+O₂=HCO+CH₂O (Knyazev et al.
Figure 4-22: Experimental [154] (shapes) and simulated (lines) autoignition delay for iso-butanol at high temperatures. The stated pressures are used for modeling the shock tube experiments.

Figure 4-23: Simulated rate of production of iso-butanol for adiabatic isochoric shock tube autoignition [154] at $P = 1$ atm, $T = 1400$ K and $\phi = 1$.

Figure 4-24: Experimental [155] (symbols) and simulated (lines) autoignition delay for iso-butanol at low temperature. The stated pressure correspond was used for modeling the RCM experiments. These simulations do not include the experimental heat losses, so the model vs data agreement is not as good at low temperature as it appears in this plot.

Figure 4-25: Simulated rate of production of iso-butanol during adiabatic isochoric autoignition ($P = 30$ atm, $T = 750$ K and $\phi = 1$). Hydrogen abstraction by HO$_2$ is the dominant consumption path during the pre-ignition period.

Figure 5-1: Experimental setup for pyrolysis experiment.

Figure 5-2: $n$-Pentanol conversion as a function of the average reactor temperature (symbols: experiment; lines: simulation; square: low dilution, 1 mol $n$-pentanol/1 mol N$_2$; circle: high dilution, 1 mol $n$-pentanol/4 mol N$_2$).

Figure 5-3: The major pyrolysis products at two dilution conditions as a function of temperature (symbols: experimental; lines: simulation results; black square: low dilution, 1 mol $n$-pentanol/1 mol N$_2$; red circle: high dilution, 1 mol $n$-pentanol/4 mol N$_2$).

Figure 5-4: Reaction pathway analysis for $n$-pentanol pyrolysis (1 mol $n$-pentanol : 4 mol N$_2$) in a plug flow reactor operated at $P = 1.7$ bar and $T = 1000$ K. Rates are expressed relative to the total $n$-pentanol consumption rate and the values for 10% conversion are written in normal font while those for 90% conversion are written in bold.

Figure 5-5: Soot precursors at two dilution conditions as a function of temperature (symbols: experimental; lines: simulation results; black square: low dilution, 1 mol $n$-pentanol/1 mol N$_2$; red circle: high dilution, 1 mol $n$-pentanol/4 mol N$_2$).

Figure 5-6: Predicted major formation pathways to benzene for $n$-pentanol pyrolysis in a plug flow reactor operated at $P = 1.7$ atm and $T = 1000$K (bold italics) and $T = 1100$K (normal text). Rates are expressed relative to the total benzene formation rate. All minor channels are not shown in the picture and in certain cases these channels can add up to a significant flux.

Figure 5-7: The comparison of the laminar flame speed of $n$-pentanol simulated with three mechanisms. Experimental data from ref. [16].

Figure 5-8: Sensitivity analysis of $n$-pentanol laminar flame speed for three models at $T_s = 433$ K, $P_s = 0.1$ MPa and $\phi = 1.4$.

Figure 5-9: Comparison of experimental [227] (shapes) and simulated (lines) autoignition delay for $n$-pentanol oxidation at high temperatures. The three mechanisms used are this work (solid line), Ref. [16] (dash line), and Ref. [228] (dash dot line). The stated pressures are used for modeling the shock tube experiments.

Figure 5-10: Reaction sensitivity analysis for OH radical production with three mechanisms at
1.0 bar, 1400K, and $\varphi = 1.0$ for 0.5% $n$-pentanol and 40% fuel conversion.

**Figure 5-11**: Reaction pathway analysis for $n$-pentanol oxidation ($\varphi = 1.0$) in an isothermal batch reactor simulation at $P = 1$ bar and $T = 1400$K. Rates are expressed relative to the total $n$-pentanol consumption rate. The values are at 40% conversion. (bold: RMG model; *italic*: NUI model; normal: Li model).

**Figure 5-12**: Experimental [224] (symbols) and simulated (lines) autoignition delay for $n$-pentanol at low temperature. The stated pressure correspond was used for modeling the RCM experiments. These simulations for all models do not include the experimental heat losses, so the model vs data agreement is not as good at low temperature as it appears in this plot. RMG model uses the NUI ketohydroperoxide decomposition rate.

**Figure 5-13**: Comparison of RMG and the NUI model [228] decomposition rate for a ketohydroperoxide formed during $n$-pentanol oxidation. RMG reverse rate coefficient is estimated using the thermochemistry obtained from Benson groups.

**Figure 5-14**: $iso$-Pentanol conversion as a function of the average pyrolysis reactor temperature (symbols – experimental: $\bullet$ N$_2$ diluted: 4 molN$_2$/mol iso-pentanol, – RMG model predictions).

**Figure 5-15**: Comparison of the experimental (symbols) and simulated (lines) yields of the major products at diluted (4 mol N$_2$/mol iso-pentanol). (symbols are experimental measurements, – RMG model predictions).

**Figure 5-16**: Comparison of the experimental (symbols) and simulated (lines) yields of alkenes formed at diluted (4 mol N$_2$/mol iso-pentanol). (symbols are experimental measurements, – RMG model predictions).

**Figure 5-17**: Reaction pathway analysis for $iso$-pentanol pyrolysis (1 mol $iso$-pentanol : 4 mol N$_2$) in a plug flow reactor operated at $P = 1.7$ bar and $T = 1000$ K. rates are expressed relative to the total $iso$-pentanol consumption rate for 80% conversion.

**Figure 5-18**: Comparison of the experimental (symbols) and simulated (lines) yields of soot precursors and smaller aromatics formed at diluted (4 mol N$_2$/mol iso-pentanol). (symbols are experimental measurements, – RMG model predictions).

**Figure 5-19**: Simulated (lines) and experimental (symbols) profiles of major species for jet stirred reactor experiment [231] for $\varphi =$1.0 and $P=10$ bar.

**Figure 5-20**: Simulated rate of production for $iso$-pentanol in the 10 atm jet stirred reactor for equivalence ratios A) 0.5, B) 1 and C) 2.

**Figure 5-21**: Comparison of experimental (shapes) and simulated (lines) autoignition delay for $iso$-pentanol oxidation at $P = 7$ bar. Experimental data below 1000 K measured by RCM and above 1000 K in ST [216]. The mechanisms used are RMG (solid line), Sarathy et al. model [233] (dash line). The stated pressures are used for modeling the shock tube experiments.

**Figure 5-22**: Comparison of experimental (shapes) and simulated (lines) autoignition delay for $iso$-pentanol oxidation at $P = 20$ bar. Experimental data below 1000 K measured by RCM and above 1000 K in ST [216]. The mechanisms used are RMG (solid line), Sarathy et al. model [233] (dash line). The stated pressures are used for modeling the shock tube experiments.

**Figure 5-23**: Sensitivity analysis of the $iso$-pentanol ignition delay for the RMG-generated model, $S \equiv \frac{\varphi}{k} \ln [OH]/\frac{\varphi}{k} \ln k$. Based on the model predictions at 800 K and 20 bar.
**Figure 6-1:** Cartoon representation of the RCCI engine concept. The low reactive fuel + air is injected through the intake port and high reactive fuel is injected directly into the cylinder.

**Figure 6-2:** Schematic of “single fuel” injection RCCI engine strategy.

**Figure 6-3:** FORTÉ computational sector mesh used for the heavy-duty Caterpillar engine.

**Figure 6-4:** Predicted ignition delay as a function of DTBP mole % in iso-Butanol + DTBP mixture. The simulations conditions are representative of a real RCCI engine operation.

**Figure 6-5:** Comparison of species profiles in constant volume adiabatic reactor between iso-Butanol and iso-Butanol with 5% DTBP mixture at \( P = 40 \text{ bar} \), \( T = 900 \text{ K} \) and \( q = 0.3 \) (Air). As seen from panel b) DTBP decomposes to give CH₃ radicals which get converted to OH radicals speeding up the reactivity.

**Figure 6-6:** Major decomposition pathway for DTBP (DTBP \( \rightarrow \) tC₃H₉O \( \rightarrow \) CH₃ \( \rightarrow \) CH₃O₂ \( \rightarrow \) CH₃O₂H \( \rightarrow \) OH).

**Figure 6-7:** Comparison between FORTÉ CFD modeling and experiments of iso-Butanol + DTBP RCCI in a Caterpillar engine (6 bar IMEP, 1300 RPM). The IVC temperature used in the simulation was 363 K.

**Figure 6-8:** Breakdown of the predicted UHC emissions, for the 6 bar IMEP iso-Butanol + DTBP RCCI case.

**Figure 6-9:** Predicted distribution of the oxygenate species, for the 6 bar IMEP iso-Butanol + DTBP RCCI case.

**Figure 7-1:** Comparison of RMG and Sarathy et al. [ref] decomposition rate for ketohydroperoxide. RMG reverse rate coefficient is estimated using the thermochemistry obtained from Benson groups.
List of tables

Table 2-1: Simplified reaction mechanism for low-temperature propane ignition.

Table 2-2: Arrhenius rate coefficient parameters for reactions required to calculate the first stage ignition delay using equation (2-54). The parameters come from the 10 atm PLOG fits for n-propyl pathway from Goldsmith et al. [48], from the detailed model of Healey et al. [74] for propane + OH and butane and the detailed model by Mehl et al. [87] for pentane and heptane.

Table 2-3: Critical temperature (T_{stage \cdot t_{max}}) calculated for stoichiometric mixture of fuel in air. The range in T_{stage \cdot t_{max}} corresponds to the y value 0 and 1 respectively. For propane the fate of OQ'O is well understood and y = 1.

Table 2-4: Overall activation energy (kcal/mol) for first stage ignition delay for different n-alkanes for stoichiometric mixture of fuel and air at P_0 = 10 bar.

Table 2-5: Comparison of the positive eigenvalue (\lambda_{1A}) obtained solving (S 44) numerically and the positive root of the cubic equation (S 57) for P_0 = 10 bar, stoichiometric mixture of propane in air.

Table 2-6: Comparison of important parameters used in predicting first stage ignition delay for propane under varying T_0, P_0 and equivalence ratio.

Table 3-1: Summary of the measured product yields at the reactor outlet, for 1.7 atm and a dilution of 1 mol CPD/ 1 mol ethene/ 10 mol N_2.

Table 3-2: Comparison between experiments for the pyrolysis of CPD and co-pyrolysis of CPD and ethene. The ethene yield for the co-pyrolysis of CPD and ethene was omitted and the remaining product yields were renormalized.

Table 4-1: Overview of experimental conditions for the pyrolysis of iso-butanol in the bench scale set-up.

Table 4-2: Species thermochemistry properties calculated using CBS-QB3 RRHO with 1-D hindered rotor corrections\textsuperscript{a}.

Table 4-3: Modified Arrhenius rate coefficients parameters, computed using conventional transition state theory at CBS-QB3 for important reactions involving iso-butanol\textsuperscript{a}. 
Table 4.4: Comparison of measured and predicted peak product concentration, rounded to the nearest ppm, in the 10 atm jet-stirred reactor of [157]. Italicized numbers represent measured values and bold numbers are the predicted values using the new mechanism.

Table 5.1: Experimental conditions for the pyrolysis of \textit{n-} and \textit{iso-} pentanol.

Table 5.2: Rate coefficients (mol\(^{-1}\) cm\(^3\) s\(^{-1}\)) for hydrogen abstraction reactions by H, CH\(_3\) and OH from \textit{n-}pentanol calculated using CBS-QB3 and the 1D-HR treatment for torsional modes.

Table 5.3: High-pressure limit rate coefficients (s\(^{-1}\)) for important $\beta$-scission reactions calculated using CBS-QB3 and the 1D-HR treatment for torsional modes.

Table 5.4: High-pressure limit rate coefficients for Fulvene + H going to Benzene + H reactions calculated using CBS-QB3 and the 1D-HR treatment for torsional modes.

Table 6.1: Stock 3401 SCOTEx Geometry.

Table 6.2: Engine operating conditions.

Table 6.3: Initial conditions used in the FORTE CFD simulation for the \textit{iso-}Butanol + DTBP RCCI run.

Table 6.4: Comparison of the experimental and FORTE CFD simulation predictions for the \textit{iso-}Butanol + DTBP RCCI run (6 bar IMEP, 1300 rpm).

Table 7.1: Comparison of CBS-QB3 and PM7 calculated enthalpy at 298 K for selected species.
Chapter 1

Introduction

Petroleum based liquid fuel accounts for over 95% of transportation energy in the United States and the rest of the world [1, 2]. Although the total reserves of oil are unknown, oil is a finite resource and even conservative estimates predict “peak oil” to be reached within the next fifty years [3]. On the other hand, world energy consumption is projected to increase at a rate of 1.4% up to 2040 [4], driven largely by the rising populations and living standards of countries like China and India. The environmental impact of these petroleum based fuels is also significant: the transportation sector accounts for over 30% of the CO₂ released in the atmosphere every year [5]. Experts believe an atmospheric CO₂ level reaching the critical 550 ppm mark will correspond to a 2°C rise in global temperature [6]. In response, many countries have passed new regulations mandating higher energy efficiency and decreased emissions. In 2011, the United States signed the CAFE agreement, requiring gas mileage to increase to 54.5 mpg and emissions to be cut by half for the entire fleet by 2025 [7]. Europe has passed regulations mandating a reduction in greenhouse emissions by at least 6% in 2020 compared to the 2010 baseline [8]. These pressing demands motivate the search for alternative sources of energy that not only meet energy demands affordably but also minimize environmental impact.

Over the past few decades, these concerns have led to two major thrusts in the energy field: identification of potential candidates for alternative fuels and the development of novel, efficient engine technologies. Hundreds of alternative fuel molecules such as alcohols, esters, ethers, and ketones have been identified as possible fuel candidates, which can be synthesized via chemical and biological routes often from non-fossil carbon such as
biomass [9-12]. Simultaneously, new engine technologies like the homogenous charge compression ignition (HCCI) [13], partial-premixed combustion compression ignition (PCCI) [14], reactivity controlled compression ignition (RCCI) [15] and other dilute low temperature combustion engines are being developed. Most of these new in-cylinder strategies focus on reducing the combustion temperature by operating under high dilution. These technologies promise a 25-50% increase in efficiency and significant reduction in emissions [16]. However, the development of any new engine technology takes a long time as it must undergo extensive testing in order to assess its performance over a broad range of operating conditions.

The advent of novel engine technologies along with a large pool of alternative fuels has led to a problem of “plenty”. Experimentally evaluating each of these alternative fuels is impractical. Testing a single fuel-engine combination requires design and construction of the prototype engine plus a significant amount of fuel to be produced and can cost millions of dollars. Several dozen new engines and fuels are currently under consideration and experimentally testing every combination will cost over a billion dollars. This estimate does not consider testing blends of different fuels or modification of the engines. It would be valuable to have a means to predict the performance of a fuel-engine combination, so that we can quickly focus our attention on the most promising candidates. Ideally, we want a screening tool where we can define the engine configuration, its operating conditions, select the fuel chemistry and be able to get reliable predictions of the engine performance and emissions. One of the critical elements of such a tool is a comprehensive chemical kinetic mechanism which can reliably describe fuel behavior under engine relevant conditions. The objectives of this thesis are to develop comprehensive models for alternative alcohol fuels, understand how fuel structure fundamentally changes ignition behavior, and validate models under relevant engine conditions. The insights from these models can be used not only as a selection tool but also act as a guide to contribute to better experimental design and interpretation. The approach taken to develop these models is described in the next section.

1.1 Predictive kinetic framework

Developing predictive kinetic models involves a hierarchical approach starting with determining the rate coefficients and equilibrium constants of elementary reactions,
expanding complex reaction networks, then incorporating physical and transport phenomena for application to macroscopic observations.

**Single reaction kinetics**

For fuel combustion it is important to first understand the kinetics and equilibrium of important elementary reactions (e.g. rate of dehydration of alcohols to give alkene). However, it is infeasible to measure all of these rates in a laboratory setting. To fill in the gaps in experimental rate coefficients, we must use theoretical methods to determine the kinetics and equilibria of a given reaction. These calculations typically use a variety of quantum chemistry methods (such as Density Functional Theory), statistical mechanics (e.g. calculating partition functions, densities of states, etc.) and reaction rate theory (e.g. Transition State Theory) to obtain accurate estimates.

**Reaction networks**

Fuel chemistry is rarely governed only by a single class of reaction. Often, complex reaction networks are needed to predict performance related observations like ignition delay, flame speeds and soot formation. These complex models involve hundreds of chemical species and thousands of chemical reactions. Such models can be constructed manually by an expert chemist but this process is often prone to error and driven by the biases of the model builder. Software tools such as automatic mechanism generation can help build detailed kinetic mechanisms systematically. These tools work by representing the fuel molecule as a chemical species, determining which reactions can occur, estimating the thermodynamic and kinetic parameters for those species and reactions, and enlarging the model until it accurately represents the underlying chemical phenomena. The Green Group at MIT has developed an open-source software package Reaction Mechanism Generator (RMG) which can generate these detailed mechanisms. RMG is used as a main tool in this thesis for developing detailed models for alcoholic alternative fuels.

**Macroscopic models**

For practical problems like engine design, a detailed description of the kinetics often needs to be coupled with other physical effects like mass, energy and momentum conservation equations to obtain macroscopic observables. This is used to validate kinetic
models against complex experimental observations. Coupling the kinetic model with these physical phenomena inside commercial engine simulator packages can be used to predict fuel performance in a real engine.

1.2 Complexity of modeling fuels

A number of predictive kinetic models for hydrocarbon fuels exist in the literature. In order for fuel models to accurately predict engine performance and emissions it must represent fuel behavior over a wide range of engine operating conditions. A typical internal combustion engine operates within the following conditions: \( T = 600 - 2500 \text{K}, P = 1 - 40 \text{bar} \) and equivalence ratios of 0.3 (lean in fuel) – 4 (rich in fuel) \([17]\). Current combustion models do a reasonable job of predicting primary decomposition products under pyrolytic conditions and high temperature oxidation. However, adaptation of these combustion models to new engines is not straightforward. Two areas where scientific understanding is still needed are peroxy chemistry and polycyclic aromatic formation.

Peroxy chemistry is important for predicting ignition behavior in low temperature combustion (LTC) conditions. In-cylinder technologies based on LTC are characterized by greater dilution, greater premixing and cooler in-cylinder gases (~ 750 K). In conventional diesel engines the apparent heat release is mainly due to the hot ignition, premixed burning and mixing-controlled combustion as shown by Dec et al.[18]. New diesel engines based on LTC, however show a distinct two stage heat release \([14, 19]\). The small early heat release is due to decomposition of the products formed due to peroxy chemistry \([14, 19]\), and significantly affects the temperature inside the cylinder. Most current kinetic models fail to predict chemistry at low temperatures with reasonable accuracy. Thus, future models which aim to simulate these engines need to include low temperature peroxy chemistry. The second chapter of this thesis will focus on the mechanistic understanding of low temperature peroxy chemistry with well-developed alkane models.

Another shortcoming of current fuel models is their inability to predict polycyclic aromatic hydrocarbons (PAH). The current state-of-art for predicting soot in engine simulations is to use empirical fitted model based on acetylene \([20]\). This approach relies on tuning the parameters of the model to match experiments and is not reliable for predicting the behavior of new fuels. The first step to have a predictive soot model is to understand
PAH formation. Models which can accurately predict smaller PAHs can be used to understand the sooting tendency of the fuel. Chapter 3 focuses on developing accurate chemistry to predict the formation of indene and naphthalene in kinetic models.

1.3 Overview of thesis chapters

Chapter 2

This chapter addresses the mechanistic understanding of low temperature auto-ignition in fuels. Most long chain alkane fuels are known to show two distinct stages of ignition; however, a clear explanation of what happens during this phenomenon is still not clearly explained in literature. In this study, a detailed numerical and analytical exploration of the first stage ignition delay for low temperature auto-ignition of propane is provided. Simple analytical approximations were derived for the time constant for radical population increase and first-stage ignition delay. These expressions clarify which rate coefficients control first-stage ignition and quantify how the ignition is influenced by mixture composition, temperature and pressure. The analysis is also extended to higher chain alkane fuels and is shown to provide reliable predictions of the first stage ignition delay.

Chapter 3

Cyclopentadiene is a known precursor to polycyclic aromatics like indene and naphthalene, however, most combustion models are unable to accurately predict their formation. In this chapter, ab initio calculations to indene and naphthalene from cyclopentadiene and cyclopentadienyl radical were explored. Geometries and frequencies of all stationary points are obtained using B3LYP/CBSB7 DFT model chemistry, while energies were obtained at CBS-QB3 level. For the rate determining step, we calculate the energies at RCCSD(T)-F12a/cc-pVDZ-F12 single-point calculations. The calculated rates and thermochemistry were incorporated into the RMG’s software database. Using RMG, we present the first elementary micro-kinetic model that captures the initial formation of indene and naphthalene from cyclopentadiene. The model is able to quantitatively describe the pyrolysis of pure cyclopentadiene and cyclopentadiene/ethene mixtures in a flow reactor.

Chapter 4
This chapter discusses the application of RMG to develop reaction mechanism for \textit{iso}-butanol pyrolysis and combustion that includes pressure dependent kinetics and proposes reaction pathways to soot precursors. \textit{iso}-Butanol is a potential candidate for gasoline alternative fuel, and has seen strong commercial interest in recent years. In order to understand its feasibility in current and future engines, detailed chemistry across a wide range of temperature, pressures, and equivalence ratios must be known. The proposed \textit{iso}-butanol model is validated against several experimental datasets.

\textbf{Chapter 5}

In this chapter we extend the butanol model to higher carbon pentanol fuel. Pentanols have a higher cetane number and can be blended into diesel fuels. Detailed mechanisms for \textit{n}\-pentanol and \textit{iso}\-pentanol pyrolysis and oxidation are developed. The model is validated across a wide range of engine relevant conditions. This work highlights the mature state of the RMG-database for modeling alcohol combustion as only a limited number of reaction rates had to be updated to predict the experimental data accurately.

\textbf{Chapter 6}

The goal of this thesis is to provide a methodology of how alternative fuels will perform in novel engines. In this chapter the detailed \textit{iso}-butanol model developed in Chapter 4 is applied in engine CFD simulations of the reactivity controlled compression ignition engine (RCCI) in order to make predictions of how butanol will affect the engine efficiency and emissions. This case study explores a single fuel RCCI engine strategy where \textit{iso}-butanol is the primary fuel and a small amount of \textit{di-tert-butyl} peroxide (cetane improver) is blended to give the highly reactive fuel.

\textbf{Chapter 7}

This chapter summarizes the thesis contributions and discusses future challenges to be addressed for predicting higher polycyclic aromatics and low combustion temperature ignition delays.
Chapter 2

*Developing understanding for first stage ignition delay for alkane fuels*

The low-temperature auto-ignition of fuels is a complex process, occurring in multiple stages with distinct chemical processes governing each stage. The conversion from alkyl radical to chain branching products, which occurs through successive O\(_2\) additions followed by thermal decomposition of the products, is at the core of the auto-ignition process. Our detailed understanding of this central process continues to evolve, with recent theoretical kinetics studies providing a particularly comprehensive description of the radical oxidation process for propane. In this chapter, we employ this improved description in a detailed numerical and analytical exploration of the first stage ignition delay for low-temperature auto-ignition of propane. The traditional first stage of ignition can be divided into two sub-stages. During the first sub-stage both OH and HO\(_2\) grow together, while during the second sub-stage only OH radicals carry the chain mechanism. The end of stage-1 ignition occurs when the temperature and the secondary chemistry has grown such that the net gain of OH radicals becomes equal to 1. We present simple analytical approximations for the time it takes to complete these two sub-stages. These expressions clarify which rate constants control first-stage ignition, and they quantify how the ignition is influenced by mixture composition, temperature and pressure. The analysis is also extended to longer alkane fuels and is shown to provide fairly reliable predictions of the first stage ignition delay.
2.1 Introduction

Low temperature (600-800 K) ignition delay is among the most important chemical properties of ground transportation fuels; it is the basis of the octane rating system for gasoline and the cetane rating system for diesel [21], and it is critical in new engine concepts like homogenous charge compression ignition (HCCI), premixed charge compression ignition (PCCI), and reactivity controlled compression ignition (RCCI) [22, 23]. Low-temperature auto-ignition is also a highly complex phenomenon; it exhibits non-Arrhenius (sometimes even non-monotonic) temperature behavior, and it has strong sensitivities to modest changes in fuel structure and pressure. Models aimed at a complete description of the ignition process, typically involve hundreds of species and thousands of reactions, thereby complicating the analysis and obscuring the essential chemistry.

To facilitate understanding, several prior authors have attempted to identify the rate-controlling processes. These analyses have proven helpful in clarifying which reactions are most important; we note in particular significant papers in this vein by Gibson et al. [24], Keck and Hu (1988) [25], Griffiths [26], Westbrook [27], Peters et al. [28], Kazakov et al. [29], Zhao and Law (2013) [30], and Beeckman et al. [31]. Many of the recent studies like [29] base their analysis on the Curran et al. n-heptane model, first published in 1998 [32]. Other recent studies [29, 30] base their analysis on skeletal models for n-heptane [28, 33].

However, as demonstrated by Kazakov et al. [29], different conclusions regarding the controlling chemistry can be drawn using different models that employ different rate coefficients and thermochemistry, especially when they involve simplifications in generating the skeletal scheme. Therefore, it would appear valuable to use a detailed model that is as fundamentally sound as possible in order to draw reliable conclusions regarding the controlling chemistry for low-temperature oxidation.

Since the time of development of the models employed in previous studies, our fundamental understanding of low-temperature oxidation processes has significantly improved. For example, due to limited understanding at the time of their study, several critical reactions were not included in the detailed model of Curran et al. (1998), and subsequent model studies have each retained some of these shortcomings. Three important examples include (i) the concerted reactions of the type \( \text{RO}_2 \rightarrow \text{HO}_2 + \text{alkene} \), where \( \text{RO}_2 \) is a alkylperoxy radical [34-37], (ii) molecular elimination of carboxylic acids and aldehydes
from ketohydroperoxides [38-43], and (iii) the interception of vibrationally excited free radicals by O₂ [44, 45]. The thermochemistry and elementary rate coefficients for many peroxy radicals have also been significantly revised during the last few years [46-55]. Also, there have been tremendous methodological advances for computing the pressure-dependence of rate-coefficients [56-59], but few large mechanisms consider pressure-dependence in a consistent way. Only a small fraction of the many reactions in these mechanisms have been measured experimentally or computed theoretically, so most rate coefficients are approximated from rough estimates; this crude approach is particularly true for peroxide chemistry, where the multiplicity of possible isomers and pathways is commonly replaced with a single lumped irreversible pathway and an empirically adjusted rate coefficient [32, 60, 61].

For propane, the number of intermediates is small enough to permit detailed exploration (e.g. five distinct isomers on the C₃H₇O₂ potential energy surface (PES), and five distinct isomers on the C₃H₇O₄ PES), and mechanisms for propane oxidation have been developed in which all of the reactions are represented by reversible elementary rate coefficients, e.g. by Healy et al. [62]. A recent study of Hughes et al. [63] presented a global uncertainty analysis for low temperature autoignition of propane, which highlighted a number of the key reaction and species. Goldsmith et al. [48] performed high-level quantum calculations on most of the species and reactions involved in the low-temperature ignition of propane, and made predictions of the pressure-dependent rate coefficients. A follow-up study explored the global uncertainty in the predicted rate coefficients for the n-propyl + O₂ reaction [64]. Here we use a comprehensive detailed propane mechanism drawn from the prior studies, which provide a secure basis for analysis.

As has been discussed in the literature [27, 28], ignition chemistry depends dramatically on both the temperature and the pressure of the initial state, with remarkably different species and reactions being important at 650 K, 800 K, and 1100 K. The chemistry of low-temperature ignition goes through several distinct stages, which are driven largely by the temperature changes during the process. It is often possible to experimentally discern two distinct stages in the ignition process [65]. The end of the first stage is marked by a small increase in temperature (e.g. ΔT of 10-100 K), followed by a second induction period before the more violent “hot” or “explosive” ignition. When the ignition is initiated at
low temperature, the first stage is typically much longer in duration than the second stage, see for example the experimental data in Figure 2-1. Consequently, accurate prediction of the final ignition delay time for those conditions requires accurate prediction of the first-stage ignition delay.

Although detailed kinetic models have been developed for the low-temperature oxidation of a many fuels, our understanding of low-temperature ignition chemistry is far from complete. Simple changes to the fuel structure can have significant impact on ignition delay, and these effects are not reproduced in all models. Our goal in the present work is to elucidate the chemistry occurring during the first stage of ignition. Rather than merely catalogue all the reactions, however, we aim to simplify the process first by identifying the most important reactions and second by quantifying the effects of these reactions on the first-stage ignition delay in a manner that is both illuminating and practical for combustion chemists and engineers alike. To that end, we present simple algebraic formulae for estimating the duration of the first stage ignition in propane, and we demonstrate how these formulae can be extended to cover larger, more complex fuels.
2.2 Propane as an archetype for low temperature peroxy ignition pathways

Low temperature ignition of alkanes is governed by a complex set of reactions that involve alkylperoxy radicals. Zádor et al. [19] recently presented a thorough review of this topic, and only a brief summary is provided here. Figure 2-2 shows a schematic mechanism for low temperature alkane oxidation and auto-ignition chemistry, adapted from [19]. The alkyl radical, R, reacts with molecular oxygen to form an energetically excited adduct, RO$_2^*$, which can undergo collisional stabilization, isomerization, or decomposition into bimolecular products.

At low temperatures and normal or high pressures, the R + O$_2$ reaction leads primarily to RO$_2$. The RO$_2$ radical under these conditions will mainly undergo isomerization to form hydroperoxyalkyl radical, QOOH. However as the temperature is increased the branching ratio to QOOH decreases with a significant fraction of RO$_2$ radicals instead converted to HO$_2$ + alkene, which is often effectively terminating because HO$_2$ is largely
non-reactive at low to moderate temperatures. Higher temperatures also cause the $R + O_2 \rightleftharpoons RO_2$ equilibrium to shift towards the reactants. Consequently, the production of RO$_2$ and QOOH effectively ceases and the energetically excited adduct, RO$_2^+$, either returns back to R + O$_2$ or decomposes to alkene + HO$_2$. The cumulative effect is the negative temperature coefficient (NTC) regime, where the ignition delay actually increases with increasing temperature.

All of the above reactions are at best chain propagating. For a radical driven auto-ignition to occur, however, the total number of radicals must increase. Two pathways can lead to chain branching. In the first pathway, RO$_2$ abstracts an H atom from the parent fuel molecule (RH), leading to formation of alkylhydroperoxide, ROOH, which decomposes to an alkyloxy radical (RO) and OH. This pathway is thought to be the main source of radicals at very low temperatures and high densities – e.g. in oxidation of liquid hydrocarbons [68].

The second chain-branching pathway involves QOOH. In the gas-phase the unimolecular isomerization reaction $RO_2 \rightleftharpoons QOOH$ is often faster than the bimolecular reaction $RO_2 + RH \rightarrow ROOH + R$. The QOOH radical can then undergo addition with a second O$_2$ molecule to form a hydroperoxyalkylperoxy radical, O$_2$QOOH, which rapidly decomposes to a ketohydroperoxide (OQ’OOH) and OH at most conditions. As in the alkylhydroperoxide, the O–O bond in the ketohydroperoxide is quite weak (typically ~ 40 kcal/mol), and this species often decomposes to form ketoalkyloxy radical (OQ’O) + OH. Consequently, the reaction sequence $R + 2O_2 \rightarrow RO_2 + O_2 \rightarrow QOOH + O_2 \rightarrow O_2QOOH \rightarrow OQ’OOH + OH \rightarrow OQ’O + 2OH$ is chain branching, since three radicals are formed (OQ’O + 2OH) for every one radical consumed (R).

For chain branching to be fast, the concentration of QOOH needs to be sufficiently high. However, at low temperatures, the $RO_2 \rightleftharpoons QOOH$ equilibrium favors RO$_2$, while at high temperatures the $R + O_2 \rightleftharpoons RO_2$ equilibrium favors R + O$_2$, so there is a limited temperature regime in which QOOH concentrations will be sufficiently high. QOOH is formed by intramolecular H transfer reaction from a peroxy radical. Although there may be several possible intramolecular H transfer reactions for a given RO$_2$, the energetically most favorable reactions involve either a six- or seven-membered ring, so the most relevant QOOH radicals are those with the HOO- group in the gamma or delta position, relative to the radical site. $\pi$-Propyl is the smallest alkyl radical that has the key six-member ring
transition state (e.g. to form the $\gamma$-QOOH, 3-hydroperoxypropyl from $\pi$-propylperoxy). As a result the $\pi$-propyl radical exhibits all the key features of ignition of larger alkyl radicals, such as second $O_2$ addition, and propane is considered as a combustion archetype [48, 55, 69].

\[
\begin{align*}
RH + OH \rightarrow & R + H_2O \quad \text{R' + alkene} \\
& + O_2 \rightarrow ROOH \rightarrow RO + OH \\
& \downarrow \quad \text{chain branching} \\
& \rightarrow HO_2 + alkene \\
& + O_2 \rightarrow OH + O-heterocycle \\
& \downarrow \quad \text{QOOH} \\
& \downarrow \quad \text{chain branching} \\
& \rightarrow HO_2 + Q'O'OOH \\
& \rightarrow OH + Q'O'OOH \\
& \rightarrow Q'O + OH \quad \text{chain branching} \\
& \rightarrow \text{cyclic peroxide} \\
& \rightarrow \text{acid + carbonyl}
\end{align*}
\]

**Figure 2-2**: Schematic mechanism for the low temperature alkane oxidation and autoignition chemistry adapted from the work of Zádor et al. [19], including the Korcek reaction [42]. The pathways shown by a blue arrow lead to additional OH radicals (chain branching) while the pathways indicated by a red arrow lead to chain termination. Note that in some cases HOOQ'O'OH may not be a true stationery point on the potential energy surface (e.g. for HOOQ'O'OH where the radical site is on the carbon adjacent to the hydroperoxy group [48]).

### 2.3 Propane kinetic model

The chemical kinetic mechanism that is used in this study is a combination of several previously published mechanisms. The core of the mechanism is based upon the high-level ab initio calculations for $C_3H_7 + O_2$, $C_3H_7O_2 + O_2$, and $C_3H_6O_3$ decomposition kinetics of Goldsmith et al [48]. The hydrogen/oxygen sub-mechanism was taken from Burke et al. [70]. The rest of the mechanism was taken from Dooley et al [71], which itself was the union of four previous mechanisms: the CH$_2$O/CH$_3$OH mechanism of Li et al. [72]; the CH$_3$OCH$_3$ mechanism of Zhao et al. [73]; the C$_1$-C$_4$ mechanism of Healy et al.[74]; and the methyl-ester mechanism of Fisher et al. [75]. The Korcek reaction was included in the full model with the rate coefficient adopted from calculations by Jalan et al. [42], however in line with the conclusion from Goldsmith et al.[43] OH + OQ'O is the only significant product channel.
from OQ’OOH decomposition above 600 K. The fraction of nR + O2 + O2 that directly proceeds to OH + OQ’OOH via a non-Boltzmann kinetic sequence was calculated by Burke et al. [45] to be less than 1% at similar conditions to those investigated here (10 atm and T < 800 K). Thus, those sequences were not included in the full model.

The full model is provided in supporting information. All model simulations presented in this work are performed using Chemkin Pro [76].

**2.4 Low temperature oxidation of propane**

A detailed schematic for the initial stage of the oxidation of propane is presented in Figure 2-3. The oxidation is initiated by hydrogen abstractions by O2. The resulting nR (nC3H7) and iR (iC3H7) radicals will react with the oxygen leading to their respective peroxy radicals (nRO2 and iRO2). The nRO2 can undergo a facile isomerization via a six-membered ring transition state to a QOOH radical which will go on to react with a second oxygen molecule to form an O2QOOH radical. This radical will decompose to one OH and ketohydroperoxide, OQ’OOH, which itself decomposes to a second OH and OQ’O radical. The OQ’O radical decomposes to CH2O and vinoxy, CH2CHO, which reacts with a third O2 molecule to form CO, CH2O and a third OH radical. This overall sequence starting with nRO2 thus releases three reactive OH radicals. By contrast, iRO2 cannot undergo a six-membered isomerization and instead mostly decomposes to give C3H6 + HO2.

The main chain-branching mechanism is the cyclic pathway, shown in black. Reactions that produce OH are shown in blue, and pathways that consume OH are shown in red. Pathways that divert flux away from the central chain-branching mechanism, such as the formation of iC3H7 from C3H8, the formation of C3H6 + HO2 from nRO2, reactions of OH and nRO2 with XH (e.g. CH2O and HO2), and the Korcek pathway from OQ’OOH, are each shown with a dotted line. Whether or not the system is explosive (supercritical) depends on whether the OH production is larger than the OH consumption, i.e. is there net positive feedback, such that an initially small concentration of radicals is exponentially amplified. Note that to a good approximation both of these rates are linear in OH concentrations during the early stages of ignition. For propane, over the temperature range from 500 K to 700 K two of the steps in the positive feedback in Figure 2-3 are particularly lossy, they are labeled as a and B. We define these two important ratios as follows:
The values of the branching ratios $\alpha$ and $\beta$ depend on the temperature, pressure and the composition of the reactive system. If there are no losses, 3 OH radicals are later generated for each OH entering the cycle. Considering the losses of OH characterized by $\alpha$ and $\beta$, the gain ($f_{\text{OH}}$) in OH is defined as:

$$f_{\text{OH}} = 3\alpha\beta$$

There is positive feedback and the OH concentration grows rapidly if $f_{\text{OH}} > 1$, while values lower than 1 indicate that the OH concentration will diminish with time.

Figure 2-3: Schematic of major reaction pathways during the first stage of propane ignition. Reactions shown in blue lead to formation of OH radicals while those in red consume OH radicals. The reactions shown by dotted lines divert radicals away from the main chain branching pathway and delay the first-stage ignition. During stage-1A, HO$_2$ radicals reacts with the fuel accelerating the chemistry, but later much of it recombines reducing the concentration of radicals. Note: For clarity some well-skipping pathways and reactions of HO$_2$ are omitted from the figure.
Figure 2-4: OH and HO\textsubscript{2} mole fraction profile (on semi-log scale) and temperature profile for isochoric (constant-volume) adiabatic simulation for a stoichiometric mixture of propane and air initially at \( P_0 = 10 \) bar and \( T_0 = 650 \) K. \( \tau_{\text{overall}} \) is the overall ignition delay of the fuel. \( \tau_{\text{stage-1}} \) is the first-stage ignition delay of the fuel, the time when the temperature (or pressure) of the system makes a small jump prior to the main ignition event. The first-stage ignition delay can be further divided into two stages A and B that are characterized by different time constants for the exponential rise of the OH concentration. \( \tau_{\text{stage-1A}} \) is the time when the early exponential rise in OH concentration ends.

Figure 2-4 shows the simulated temperature evolution and OH concentration for an isochoric (constant-volume), adiabatic system containing a stoichiometric mixture of propane and air (at a representative low-temperature condition of \( \phi = 1 \), \( P_0 = 10 \) bar, and \( T_0 = 650 \) K). As seen in Figure 2-4, the temperature increases in two stages, with a small rise at \( 0.56 \) s and a much larger rise at \( 0.78 \) s. Though not readily apparent from the temperature profile, the OH and HO\textsubscript{2} profiles demonstrate that the first stage itself can be divided into two stages, denoted 1A and 1B.

The first noticeable time scale \( \tau_{\text{stage-1A}} \) (see Figure 2-4) corresponds to a distinct change in the slope of the OH rise (\( d\ln[\text{OH}] / dt \)) and in slope of HO\textsubscript{2} rise. \( \tau_{\text{stage-1A}} \) marks the end of stage-1A and the beginning of stage-1B. This time scale is usually not observed experimentally, since there is little or no change in the temperature and the OH concentrations are still too low to be detected. Both in stage-1A and 1B an exponential build-up of radicals is observed. The different exponential rise rate observed between stage-1A and 1B is mainly due to reactions involving HO\textsubscript{2} radicals. At early times (on the order of
10's and 100's of milliseconds), essentially every HO$_2$ formed reacts with the fuel. Since OH and HO$_2$ are formed in comparable amounts, they each contribute to fuel consumption. In this period, the HO$_2$ concentration is about 5 orders of magnitudes higher than OH (see Figure 2-4). Consequently, even though the rate coefficients for fuel + OH are orders of magnitude larger than the rate coefficients for fuel + HO$_2$ at these conditions, HO$_2$ nonetheless is responsible for a significant percentage of the total fuel consumption in stage-1A, as illustrated by the red bars in Figure 2-5.

The concentration of HO$_2$ radicals continues to build until the rate of the recombination reaction, HO$_2$ + HO$_2$ → H$_2$O$_2$ + O$_2$, becomes one of the dominant HO$_2$ consumption channels (see Figure 2-6). This happens at around ~0.2 s for the conditions presented in Figure 2-4 and just precedes the observed kink in the OH concentration profile which indicates the start of stage-1B. At this point the exponential growth rate of HO$_2$ concentration decreases significantly and the fuel + HO$_2$ reactions become relatively unimportant (see Figure 2-5). Similar behavior will be observed for all fuels that produce significant amounts of HO$_2$ (e.g. propane, iso-butane, alcohols).

**Figure 2-5:** Fraction of propane consumed by each reaction during stage-1A (0.1s) and stage-1B (0.39s). HO$_2$ reaction with the fuel is significant during stage-1A, but negligible during stage-1B.
Stage-1B ends at time $t_{\text{stage-1}}$, which is called the first-stage ignition delay of the fuel. The first-stage ignition delay may be experimentally observed if there is a detectable change in the temperature (or pressure) of the system followed by a second induction time prior to the main ignition event. $t_{\text{stage-1}}$ is generally defined as the time when there is the first point of inflection in $\dot{T}(t)$. The last important time scale (Figure 2-4) is the overall ignition delay of the fuel, $t_{\text{overall}}$. $t_{\text{overall}}$ is observed experimentally when there is a sudden, dramatic change in the thermodynamic state of the system. Although the ignition event is relatively unambiguous, several different diagnostic techniques are used to measure $t_{\text{overall}}$ in practice, and these methods do not always agree precisely [77, 78]. Here we have defined the overall ignition delay as the time required for the first derivative of the temperature to reach its global maximum.
Figure 2-7: Evolution of key species during isochoric adiabatic reaction of stoichiometric mixture of propane-air at $P_o=10$ bar and $T_0=650$ K. It should be noted that OQ'OHH peaks shortly before $\tau_{\text{stage-1}}$. The full scale values of H$_2$O$_2$, CH$_2$O and OQ'OHH were chosen to be of twice the maximum value reached in the simulation.

Figure 2-7 summarizes the evolution of four key closed-shell species at the conditions of Figure 2-4. The oxidation process begins with an exponential rise in the concentration of ketohydroperoxide (OQ'OHH). As the temperature gradually increases, the concentration of OQ'OHH reaches a maximum ($\tau_{\text{OQ'OHHpeak}}$). It can be seen from Figure 2-7 that this maximum occurs shortly before the first-stage ignition delay $\tau_{\text{stage-1}}$. Both the first-stage ignition delay and overall ignition delay can also be identified from the concentration profiles of the intermediates. For example, the H$_2$O$_2$ concentration profile shows a clear kink around $\tau_{\text{stage-1}}$ while its concentration drops toward zero at $\tau_{\text{overall}}$.

The peak in the OQ'OHH concentration (Figure 2-7) can be attributed to decrease in both $a$ and $b$ components of the gain. First, the reaction cycle illustrated in Figure 2-3 is net exothermic and this leads to a rise in the temperature of the system. As the temperature increases, the rate coefficient for nRO$_2$ $\rightarrow$ alkene $+$ HO$_2$ increases and the equilibrium constants for nR $+$ O$_2$ $\rightleftarrows$ nRO$_2$ and QOOH $+$ O$_2$ $\rightleftarrows$ O$_3$QOOH shift back towards the reactants, thereby decreasing the ratio $b$ (given by (2-2)). So every time an OQ'OHH decomposes a smaller fraction of the OH radicals created will return back to the cycle to form new OQ'OHH. The
second contributing factor to the peak in OQ'OOH is the loss of nRO₂ and OH radicals to
the growing secondary products. Prior to \( \tau_{\text{stage-1A}} \) (stage-1A), the concentration of products is
sufficiently low that secondary reactions such as OH + products and nRO₂ + products are
negligible. Under these conditions there are more OH radicals being produced than
consumed (i.e. OH gain factor \( f_{OH} > 1 \)), thereby propagating the chain branching cycle, e.g.
the sequence of black and blue lines in Figure 2-3. However eventually, the product
concentrations are no longer negligible, and any reaction of OH or nRO₂ with these
products diverts the active radicals away from the chain branching pathway, thereby
reducing the gain of the feedback system. The most important products in this context are
CH₂O and H₂O₂ for diverting OH and CH₂O and HO₂ for diverting nRO₂, these pathways
are illustrated by the dotted lines in Figure 2-3.

By \( \tau_{\text{OQ'OOHpeak}} \) the gain \( f_{OH} \) has decreased close to unity, hence additional losses will
result in the cycle no longer being able to sustain itself. Beyond \( t > \tau_{\text{OQ'OOHpeak}} \) the OQ'OOH
concentration that has built-up during the initial stages of the oxidation decreases,
primarily decomposing via pathways that create two OH radicals (see Figure 2-3). The
release of these radicals in the system causes a sudden jump in the temperature (and
pressure), signaling the first-stage ignition, \( \tau_{\text{stage-1}} \). At the same time the CH₂O
ccentration, which is a side product of the OQ'OOH decomposition, is also seen to spike
(see Figure 2-7). For this sequence, \( \tau_{\text{OQ'OOHpeak}} \) is a fairly reliable approximation for \( \tau_{\text{stage-1}} \).
This correlation is illustrated in Figure 2-8, where the solid line is the overall ignition
delay, the dashed line is the first-stage ignition delay (as determined by the inflection point
in the temperature), and the dashed-dotted line is the time of the peak OQ’OOH. Note that
the peak in OQ’OOH is an excellent predictor of the first-stage ignition delay, even well
into the NTC regime, at which point the first-stage ignition delay is no longer a reliable
predictor for the overall ignition delay anyway.
Before we can derive analytical expressions that describe the low temperature combustion of propane, it is important to know whether or not quasi-steady state assumptions can be made for the system presented in Figure 2-7. Therefore, the net rate of reaction for the main oxidation reactions of nR (nC₃H₇) are shown in Figure 2-9. The net rate of reaction is defined as the flux for the forward reaction minus the reverse flux. Figure 2-9 illustrates that most rates of production quickly converge to the corresponding rates of destruction. First, at t ~ 5x10⁻⁵ s, the net rates for nRO₂ → QOOH (dashed blue) and O₂ + QOOH → O₂QOOH (solid blue) converge. This indicates that the net accumulation of QOOH is very small compared to its throughput and QOOH is in quasi-steady state beyond this time. Next, at t ~ 5x10⁻³ s, the net rates for O₂ + QOOH → O₂QOOH (solid blue) converges with that for O₂QOOH → OQ’OOH + OH (dashed green) signaling O₂QOOH comes in quasi steady state. The net rate for OQ’OOH → OQ’O + OH and OQ’O → CH₂CHO + CH₂O converge t~ 2x10⁻³ s, this reaction is not shown in the plot. Other reactions not shown in the plot is the net rate of formation (RH + O₂OH/HO₂ → nR + HO₂/H₂O/H₂O₂) and consumption of nR which converge within microseconds, indicating nR to be the first species to reach quasi-steady state. Figure 2-9 shows that nRO₂ is close to quasi steady state while OQ’OOH is not in quasi steady state during first stage of ignition.
Figure 2.9: a) Net rate of production for reactions involved in \( \text{n-propyl (nR)} \) peroxy cycle, for adiabatic isochoric simulations \( (P_0 = 10 \text{ bar}, \ T = 650 \text{ K}) \) of stoichiometric mixture of propane and air using the full propane model. The arrows indicate the time when the species come into quasi-steady state, most species are in quasi-steady state after \( t \sim 5 \) ms. b) Inset of plot 5a) the rate of \( \text{O}_2 \text{QOOH} \rightarrow \text{OQ}'\text{OOH} + \text{OH} \) and \( \text{OQ}'\text{OOH} \rightarrow \text{OQ'O} + \text{OH} \) are significantly different indicating \( \text{OQ}'\text{OOH} \) is not in quasi-steady state. For reference \( t_{\text{stage-1A}}, t_{\text{OQ}'\text{OOH}} \text{ and } t_{\text{stage-1}} \) are \(-0.2, -0.44 \) and \(-0.56 \) s respectively.

2.5 Reduced model formulation for low temperature ignition

The objective of this paper is not to provide a new propane mechanism; rather, it is to elucidate analytically what reactions in the larger mechanism are responsible for the low-temperature, first-stage ignition delay. Based upon the preceding analysis, we begin with a simple model that consists of only the most important reactions prior to first-stage ignition (the predicted ignition delay for the reduced and full model are within a factor of 2, see supplemental material for the comparison). This reduced model includes reactions for: fuel + \( \text{O}_2 \) initiation, fuel + radical, \( \text{O}_2 + \text{R}, \text{O}_2 + \text{QOOH}, \text{QO'O} \text{OH} \) decomposition, and other important sources and sinks of \( \text{OH} \) from secondary chemistry of key species, including hydrogen abstraction from \( \text{HO}_2, \text{H}_2\text{O}_2 \) and \( \text{CH}_2\text{O} \). The \( \text{H}_2\text{O}_2 \) generation loop and the secondary chain branching loop (involving the alkoxy radical), which were found to be important in previous studies \([79, 80]\), also are included. During the prelude to ignition some reactions will rapidly equilibrate, and the corresponding reverse rate coefficients are
included. For other reactions, the reverse reaction is negligible, and only the forward rate coefficient is required. The complete list of reactions in the reduced model is provided in Table 2-1.

Table 2-1: Simplified reaction mechanism for low-temperature propane ignition.

<table>
<thead>
<tr>
<th>Label</th>
<th>Reaction</th>
<th>Rate coefficient</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>RH + O₂ → nR + HO₂</td>
<td>k₁</td>
<td>[62]</td>
</tr>
<tr>
<td>R2</td>
<td>RH + O₂ → iR + HO₂</td>
<td>k₂</td>
<td>[62]</td>
</tr>
<tr>
<td>R3</td>
<td>RH + OH → nR + H₂O</td>
<td>k₃</td>
<td>[62]</td>
</tr>
<tr>
<td>R4</td>
<td>RH + OH → iR + H₂O</td>
<td>k₄</td>
<td>[62]</td>
</tr>
<tr>
<td>R5</td>
<td>RH + HO₂ → nR + H₂O₂</td>
<td>k₅</td>
<td>[81]</td>
</tr>
<tr>
<td>R6</td>
<td>RH + HO₂ → iR + H₂O₂</td>
<td>k₆</td>
<td>[81]</td>
</tr>
<tr>
<td>R7</td>
<td>nR + O₂ ⇌ nRO₂</td>
<td>k₇, k₇</td>
<td>[48]</td>
</tr>
<tr>
<td>R8</td>
<td>iR + O₂ ⇌ iRO₂</td>
<td>k₈, k₈</td>
<td>[48]</td>
</tr>
<tr>
<td>R9</td>
<td>nR + O₂ ⇌ QOOH</td>
<td>k₉, k₉</td>
<td>[48]</td>
</tr>
<tr>
<td>R10</td>
<td>nR + O₂ → C₃H₆ + HO₂</td>
<td>k₁₀</td>
<td>[48]</td>
</tr>
<tr>
<td>R11</td>
<td>iR + O₂ → C₃H₆ + HO₂</td>
<td>k₁₁</td>
<td>[48]</td>
</tr>
<tr>
<td>R12</td>
<td>nRO₂ → C₃H₆ + HO₂</td>
<td>k₁₂</td>
<td>[48]</td>
</tr>
<tr>
<td>R13</td>
<td>iRO₂ → C₃H₆ + HO₂</td>
<td>k₁₃</td>
<td>[48]</td>
</tr>
<tr>
<td>R14</td>
<td>nRO₂ ⇌ QOOH</td>
<td>k₁₄, k₁₄</td>
<td>[48]</td>
</tr>
<tr>
<td>R15</td>
<td>QOOH + O₂ ⇌ O₂QOOH</td>
<td>k₁₅, k₁₅</td>
<td>[48]</td>
</tr>
<tr>
<td>R16</td>
<td>O₂QOOH → OQ′OOH + OH</td>
<td>k₁₆</td>
<td>[48]</td>
</tr>
<tr>
<td>R17</td>
<td>OQ′OOH → OQ′O + OH</td>
<td>k₁₇</td>
<td>[48]</td>
</tr>
<tr>
<td>R18</td>
<td>OQ′O → CH₂CHO + CH₂O</td>
<td>k₁₈</td>
<td>[48]</td>
</tr>
<tr>
<td>R19</td>
<td>CH₂CHO + O₂ → CH₂O + CO + OH</td>
<td>k₁₉</td>
<td>[82]</td>
</tr>
<tr>
<td>R20</td>
<td>CH₂O + OH → HCO + H₂O</td>
<td>k₂₀</td>
<td>[83]</td>
</tr>
</tbody>
</table>
The mechanism listed in Table 2-1 represents a system of non-linear ordinary differential equations that consists of 20 species and 27 reactions (plus equations for the thermodynamic state variables). The original full model and reduced model are provided in the Supplemental Materials.

2.5.1 Analytic solution for stage-1A

The extent to which the growth in radical concentration is exponential depends upon the comparative rates of production for radicals versus their loss to other channels. If decomposition to produce OH radicals exceeds OH losses (e.g. R4, R20 and R23), then there will be explosive growth.

During stage-1A the concentration of products is negligible, and the fuel and O₂ concentration remain essentially constant. These two assumptions effectively linearize the system of equations. For a system of linear ordinary differential equations, the solution is a sum of exponentials, and after an initial incubation period the eigenmode with the largest positive exponent ($\lambda$) will dominate all the other modes. This incubation period is expected to be on the order of the larger of the two quantities: 1) the induction period where the initiation reactions contribute non-negligibly to the production of radicals and 2) $\sim 1/(\lambda - \lambda_1)$ where $\lambda_1$ is the second largest eigenvalue. We expect that to a good approximation, after the incubation period, all species (except for fuel, O₂, N₂) will grow approximately exponentially with a single growth rate defined by the positive eigenvalue, e.g.
\[ [\text{OH}] \approx C_{\text{OH}} \exp(\lambda t) \]

\[ [\text{OQ'OOG}] \approx C_{\text{OQ'OOG}} \exp(\lambda t) \]

\[ [\text{HO}_2] \approx C_{\text{HO}_2} \exp(\lambda t) \]

The ratios of the pre-exponential factors, \( C_{\lambda} \), and the exponent \( \lambda \) can be evaluated numerically by diagonalizing the rate coefficient matrix (for details see Supplemental Materials). These parameters depend upon the initial concentrations, \([\text{RH}]_0\) and \([\text{O}_2]_0\), and upon the rate coefficients evaluated at the initial conditions, \( T_0 \) and \( P_0 \). To simplify the analysis, we note that after the initial induction period, several of the species will be in a quasi-steady state, including \( n\text{R} \), \( i\text{R} \), \( \text{QOOH} \), \( \text{O}_2\text{QOOH} \), \( \text{OQ'O} \), \( \text{OH} \), and \( \text{CH}_2\text{CHO} \). It is also assumed that the vast majority of \( \text{QOOH} \) is formed via isomerization from \( n\text{RO}_2 \), while the chemically activated production of \( \text{QOOH} \) from \( n\text{R} + \text{O}_2 \) is negligible [48]. This leads to the following equations (see Supplemental Material for how these equations were obtained):

\[ [n\text{R}] = \frac{(k_1[\text{O}_2] + k_3[\text{OH}] + k_5[\text{HO}_2])[\text{RH}] + k_7[n\text{RO}_2] + k_9[\text{QOOH}]}{(k_7 + k_9 + k_{10})[\text{O}_2]} \]  

\[ [i\text{R}] = \frac{(k_3[\text{O}_2] + k_4[\text{OH}] + k_6[\text{HO}_2])[\text{RH}] + k_8[i\text{RO}_2]}{(k_6 + k_{11})[\text{O}_2]} \]

\[ [\text{QOOH}] = \frac{k_9[n\text{R}][\text{O}_2] + k_{14}[n\text{RO}_2] + k_{15}[\text{O}_2\text{QOOH}]}{k_{-9} + k_{-14} + k_{15}[\text{O}_2]} \]

\[ [\text{O}_2\text{QOOH}] = \frac{k_{15}}{k_{-15} + k_{16}}[\text{O}_2][\text{QOOH}] \]

\[ [\text{OQ'O}] = \frac{k_{17}[\text{OO'OOG}]}{k_{18}} \]

\[ [\text{OH}] = \frac{k_{16}[\text{O}_2\text{QOOH}] + k_{17}[\text{OO'OOG}] + k_{19}[\text{CH}_2\text{CHO}][\text{O}_2] + 2k_{23}[\text{H}_2\text{O}_2]}{(k_3 + k_4)[\text{RH}] + k_{20}[\text{CH}_2\text{O}] + k_{23}[\text{H}_2\text{O}_2]} \]

\[ [\text{CH}_2\text{CHO}] = \frac{k_{21}[\text{OO'O}]}{k_{10}[\text{O}_2]} \]

Three dimensionless parameters are introduced that will prove helpful in evaluating the differential equations:
\[
\alpha = \frac{k_3}{k_3 + k_4} \quad (2-11)
\]

\[
\beta = \frac{\theta k_{14}}{\theta k_{14} + k_{12}} \quad (2-12)
\]

\[
\theta = \frac{k_{16}[O_2 \text{QOOH}]}{k_{14}[n\text{RO}_2]} = \frac{k_{15}k_{16}}{k_{-15} + k_{16}} \cdot \frac{[O_2]}{k_{-14} + k_{-15} + k_{16}} \quad (2-13)
\]

In equation (2-11) above, \( \alpha \) is defined as the fraction of OH radicals consumed that form \( nR \) (\( nC_3H_7 \)) under the assumption that during stage-1A the OH radicals will predominantly react by abstracting hydrogen from the parent fuel. However, \( \alpha \) can be more generally interpreted as the fraction of OH radicals that reacts to form radicals that have the potential for chain branching. \( \beta \) is the fraction of \( n\text{RO}_2 \) radicals that react to form \( \text{OQ'OOH} \) via the sequence R14, R15 and R16 relative to the loss of \( n\text{RO}_2 \) due to concerted \( \text{HO}_2 \) elimination. \( \theta \) in equation (2-13) is defined as the fraction of QOOH formed which goes on to form \( \text{OQ'OOH} \) (ratio of flux through \( \text{O}_2\text{QOOH} \rightarrow \text{OQ’OOH} + \text{OH} \) over the flux for \( n\text{RO}_2 \rightarrow \text{QOOH} \)). \( \theta \) can be interpreted as a correction factor for cases where \( n\text{RO}_2 \rightarrow \text{QOOH} \) is not the rate limiting step. It is constrained to be between 0 and 1 and it decreases with increasing temperature and decreasing pressure as illustrated in Figure 2-10. At low temperatures and high oxygen partial pressures, \( \theta \) is close to 1 indicating that the reaction \( n\text{RO}_2 \rightarrow \text{QOOH} \) is the rate limiting step. As the temperature increases, \( \theta \) starts to decrease primarily because of strong temperature dependence of \( k_{-15} \) (\( \text{O}_2\text{QOOH} \rightarrow \text{QOOH} + \text{O}_2 \)) which begins to significantly compete with \( \text{O}_2\text{QOOH} \rightarrow \text{OQ’OOH} + \text{OH} \). This shift in the \( \text{O}_2\text{QOOH} \Rightarrow \text{QOOH} + \text{O}_2 \) equilibrium can also be achieved by lowering the pressure at fixed stoichiometry: at 600 K in air \( \theta \) drops from 1 at 100 bar to 0.3 at 1 bar.
Using equations (2-4)-(2-13), it is possible to decouple the differential equations for nRO₂, iRO₂, OQ'OOH, and HO₂ from the remaining species. This leads to the following set of equations:

\[
\begin{bmatrix}
\frac{d[nRO₂]}{dt} \\
\frac{d[iRO₂]}{dt} \\
\frac{d[HO₂]}{dt} \\
\frac{d[OQ'OOH]}{dt}
\end{bmatrix} =
\begin{bmatrix}
\theta k_{i+} & (1-\alpha) + \frac{(1-\beta)}{\beta} & 0 & k_i[RH]_b & 2\alpha k_i \\
(1-\alpha)\theta k_{i+} & -k_i & k_i[RH]_b & 2(1-\alpha)k_i & 0 \\
(1-\beta)\theta k_{i+} & -k_i & -k_i & 0 & 0 \\
\theta k_{i+} & 0 & 0 & -k_i & 0 \\
\end{bmatrix}
\begin{bmatrix}
[nRO₂] \\
[iRO₂] \\
[HO₂] \\
[OQ'OOH]
\end{bmatrix}
\]

This system of equations can be written as

\[
\frac{dC}{dt} = MC + R 
\]

which has an exact solution given by (see Supplemental material for complete details)

\[
C = V \exp(\Lambda t) V^{-1} C_0 + V(\exp(\Lambda t) - I) \Lambda^{-1} V^{-1} R 
\]
where \( V \) and \( A \) are the eigenvector and eigenvalue matrices of \( M \) (i.e. \( M = V \Lambda V^{-1} \)). From this set of four linear ordinary differential equations, we obtain four eigenvalues. For \( P_0 = 10 \) bar and \( T_0 = 650 \) K, the two real eigenvalues are \( \lambda_{1A} = 55.4 \text{ s}^{-1} \) and \( \lambda_{2A} = -39.4 \text{ s}^{-1} \); the remaining eigenvalues \( \lambda_{3A} \) and \( \lambda_{4A} \) are complex with a negative real component \((-542 \pm 42j) \text{ s}^{-1}\). (Note that, while the values above are obtained through a numerical solution of equations (2-14) - (2-16), an analytical solution is possible under an additional simplifying approximation as shown in the supplemental material but this introduces significant error.). The positive real eigenvalue can be interpreted as the rise rate (inverse of the time constant) during stage-1A. It is perhaps worth noting that the smallest time constant of decay for the other eigenmodes is \( \sim 1/94.8 \) s or 0.011 s; and the induction time during which initiation reactions contribute non-negligibly to production of radicals is on the order of \( \sim 0.01 \) s. Thus, after a brief incubation time much shorter than the relevant ignition time scales, the concentration of the various species in this stage can hence be written as:

\[
[X] \approx C_x A \exp(\lambda_{1A} t) \tag{2-17}
\]

This exponential growth should continue until one of the following events occurs and introduces nonlinearities to the system:

1. One of the species builds up to such a high concentration that its second-order reactions between itself and other minor species (i.e. not \( \text{C}_3\text{H}_8 \) and \( \text{O}_2 \)) become significant.
2. Concentrations of the fuel or \( \text{O}_2 \) are no longer sufficiently close to their initial concentrations.
3. The net heat release alters the temperature (and pressure) enough to affect the kinetics through rate constants and/or equilibrium constants. Effects due to temperature are expected to be dominant over effects due to pressure rise. Note that while the linear approximation holds, we expect the temperature to follow \( T = T_0 + C_T \exp(\lambda t) \).

For all the cases studied, stage-1A ends when the concentration of \( \text{HO}_2 \) increases to the point where the self-recombination reaction, \( \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \) dominates the \( \text{HO}_2 \) disappearance. This time can be estimated by the following approximation:
\[
\frac{d[\text{HO}_2]}{dt} \approx \lambda_{1A} C_{\text{HO}_2-A} \exp(\lambda_{1A} \tau_{\text{stage-1A}}) - 2k_{24} \left( C_{\text{HO}_2-A} \exp(\lambda_{1A} \tau_{\text{stage-1A}}) \right)^2 = 0 \quad (2-18)
\]

Solving equation (2-18) for \( \tau_{\text{stage-1A}} \) yields

\[
\tau_{\text{stage-1A}} \approx \frac{1}{\lambda_{1A}} \ln \left( \frac{\lambda_{1A}}{2k_{24} C_{\text{HO}_2-A}} \right) \quad (2-19)
\]

The pre-exponential factor for \( \text{HO}_2 \) \( (C_{\text{HO}_2-A}) \), can be determined using the eigenvector, eigenvalues, vector \( R \) and the initial conditions of the system, the exact equation is provided in the supplemental materials (S 53).

2.5.2 Analytic solution for stage-1B

The transition from stage-1A to stage-1B occurs when the self-reaction \( \text{HO}_2 + \text{HO}_2 \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \) becomes the major \( \text{HO}_2 \) consumption channel and slows the growth rate of \( \text{HO}_2 \).

In this stage, hydrogen abstractions by \( \text{HO}_2 \) from the parent fuel are much less important than those by \( \text{OH} \) and it can be assumed that \( \text{HO}_2 \) no longer contributes significantly to the production of propyl radicals. This observation implies that the differential equation for \( \text{HO}_2 \) can be decoupled from those for \( n\text{RO}_2 \) and \( \text{OQ'OOH} \), and yields the following set of differential equations for stage-1B:

\[
\begin{bmatrix}
\frac{d[n\text{RO}_2]}{dt} \\
\frac{d[\text{OQ'OOH}]}{dt} \\
\frac{d[n\text{RO}_2]}{dt} \\
\frac{d[\text{OQ'OOH}]}{dt}
\end{bmatrix}
= \begin{bmatrix}
(1-\alpha) + \frac{(1-\beta) \theta k_{14}}{\beta} & 2\alpha k_{17} \\
\theta k_{14} & -k_{17}
\end{bmatrix}
\begin{bmatrix}
[n\text{RO}_2] \\
[\text{OQ'OOH}]
\end{bmatrix}
\quad (2-20)
\]

The eigenvalues for this system are:

\[
\lambda_{1B} = \frac{k_{17}}{2} \left(-\left(1 + \frac{(1-\alpha \beta) \theta k_{14}}{\beta k_{17}}\right) + \sqrt{4 \left(3\alpha \beta - 1\right) \theta k_{14} k_{17} + \left(1 + \frac{(1-\alpha \beta) \theta k_{14}}{\beta k_{17}}\right)^2}\right) \quad (2-21)
\]
\[ \lambda_{2B} = \frac{k_{17}}{2} \left( -\left(1 + \frac{(1-\alpha\beta)}{\beta k_{17}}\right) \right) - \sqrt{4 \left( \frac{(3\alpha\beta - 1)\theta k_{14}}{\beta k_{17}} \right) + \left(1 + \frac{(1-\alpha\beta)}{\beta k_{17}}\right)^2} \]  \hspace{1cm} (2-22)

The second eigenvalue is negative under all conditions (with a value of \(-505.2 \text{ s}^{-1}\) for \(P_0 = 10 \text{ bar}\) and \(T_0 = 650 \text{ K}\)) such that its time constant for decay is small compared to the relevant ignition time scales. For \(P_0 = 10 \text{ bar}\) and \(T_0 = 650 \text{ K}\), the positive eigenvalue is \(\lambda_{4B} = 25.3 \text{ s}^{-1}\). Using this linearized model the \(\text{OH}\) concentration during stage-1B (\(t > \tau_{\text{stage-1A}}\)) is given by:

\[ [\text{OH}] = C_{OHB} \exp(\lambda_{4B}t) \]  \hspace{1cm} (2-23)

Where the pre-exponential factor is given as

\[ C_{OHB} = C_{OHA} \exp\left(\left(\lambda_{4A} - \lambda_{4B}\right)\tau_{\text{stage-1A}}\right) \]  \hspace{1cm} (2-24)

Using the above equations we can plot the predicted rise of \(\text{OH}\) radicals for stage-1B in propane ignition. Figure 2-11 provides a comparison between the predicted and simulated \(\text{OH}\) mole fraction during stage-1A and stage-1B for an adiabatic, isochoric system at \(P_0 = 10 \text{ bar}\) and \(T_0 = 650 \text{ K}\) using the full propane oxidation model. It can be seen that both the rise rate in stage-1A and the initial rise rate of stage-1B are reproduced well. At later times in stage-1B the rise rate decreases due to loss of \(\text{OH}\) and \(n\text{RO}_2\) radicals to secondary reactions. End of stage-1B will occur when the rise rate has decreased to zero therefore the initial rise rate in stage-1B (\(\lambda_{4B}\)) represents an upper bound and the expressions based on this rise rate give a lower bound on the predicted first stage ignition delay.
100,

simulation using full model

10-2 predicted using OH=COH,a exp(IAt)

10--
predicted using OH=COHb exp(XBt)

10-1

0

0

10.

10

101

0.1 0.2 0.3 0.4 0.5 0.6 0.7

0.8

Time (sec)

Figure 2-11: Comparison of the predicted and the simulated OH mole fraction profiles, for adiabatic isochoric simulations at \( P = 10 \) bar, \( T = 650 \) K and stoichiometric mixture of propane: air using the full model. The red line corresponds to the stage-1A prediction while the black line corresponds to the stage-1B prediction. The predictions are made using the equation \([OH] = C_{OH,0} \exp(A_{1A}t)\) where \( A_{1A} = 55.4 \) s\(^{-1}\) and \( A_{1B} = 25.3 \) s\(^{-1}\).

2.5.3 Predicting first-stage ignition

Similar to stage-1A, stage-1B will end when secondary reactions become important and interfere with the chain mechanism presented in Figure 2-3 or when the temperature rises enough to significantly alter the kinetics. The end of this stage may be experimentally observed if there is a large enough change in temperature (or pressure) of the system. The kink in the temperature profile is correlated with the depletion of OQ'OOH, which had built-up in the initial stages of the ignition. For straight-chain alkanes as shown in Figure 2-8 (for propane) and also by Musculus et al. [14] (for heptane), there is only a small delay between the peak in OQ'OOH and the point of inflection in \( T(t) \). A reasonable approximation is, hence to equate the first-stage ignition delay with the peak in OQ'OOH.

The OQ'OOH concentration will peak when the rise rate has decreased to zero:

\[
\lambda_{1B}(C, T) = 0
\]

(2-25)

where \( \lambda_{1B} \) here is both a function of the temperature and the composition of the system, the former due to rate coefficients and equilibrium constants and latter due to secondary reactions. The rise rate \( \lambda_{1B} \) (equation (2-21)) will be zero when the following condition is satisfied:
\[ f_{\text{OH}} = 3\alpha\beta = 1 \]  

(2-26)

In other words, OQ’OOH peaks when the three OH radicals that are generated by the decomposition of O₂QOOH, are insufficient to overcome losses in order to maintain the radical chain mechanism. Both \( \alpha \) and \( \beta \) depend on the temperature, i.e. through the rate coefficients, and also on the composition of the mixture. As the concentrations of the secondary products grow, additional loss channels (primarily due to hydrogen abstractions from CH₂O and H₂O₂) will influence the OH balance of the chain mechanism. In that case \( \alpha \) and \( \beta \) can be represented as:

\[
\alpha = \frac{k_3}{k_3 + k_4 + k_{20} \frac{[\text{CH}_2\text{O}]}{[\text{RH}]} + k_{23} \frac{[\text{H}_2\text{O}_2]}{[\text{RH}]}}
\]  

(2-27)

\[
\beta = \frac{\theta k_{14}}{\theta k_{14} + k_{12} + k_{26} [\text{CH}_2\text{O}] + k_{27} [\text{HO}_2]} \]  

(2-28)

The evolution of \( \alpha \) and \( \beta \) during the various stages of the ignition for the adiabatic case at 650 K and 10 bar using the full model is shown in Figure 2-12. It can be seen that \( \alpha \) starts from a value of around 0.5 and hardly decreases while the value of \( \beta \) drops from an initial value of 0.84 to 0.66 at the end of stage 1B. As the relative decrease in \( \beta \) is much larger than that in \( \alpha \), the variation in \( \beta \) will have a larger influence on the OH balance of the chain mechanism. The OH loss due to hydrogen abstraction from the secondary products is partially compensated by the additional production of OH radicals from the decomposition of hydroperoxides (ROO + HO₂ → ROOH + O₂ → RO + OH + O₂). The inclusion of this cycle makes the system very complex and for sake of simplicity here we assume that \( \alpha \approx 0.5 \) throughout the simulation under all conditions, yielding equation (2-29) at the end of stage 1. In the following sections it is demonstrated how equation (2-29) can be used to predict first stage ignition delay under adiabatic conditions.

\[
\frac{\theta k_{14}}{\theta k_{14} + k_{12} + k_{26} [\text{CH}_2\text{O}] + k_{27} [\text{HO}_2]} = \frac{2}{3}
\]  

(2-29)
2.5.4 First stage ignition delay under adiabatic conditions

Under adiabatic conditions, the time at which OQ’OOH peaks is determined by both the temperature increase of the system and the loss of nRO2 (active RO2) radicals to the growing secondary chemistry. At higher temperatures nRO2 radicals are more likely to react by the higher barrier HO2 elimination channel which yields HO2 and propene reducing β and thereby reducing the gain term \( f_{\text{OH}} \).

The temperature rise can be modeled by assuming overall reactions for the chain mechanism presented in Figure 2-3. As OH is the main fuel abstractor in stage-1B, this can be achieved by introducing two global reactions:

\[
\begin{align*}
\text{C}_3\text{H}_8 + \text{OH} + \text{O}_2 & \rightarrow \text{C}_3\text{H}_6 + \text{H}_2\text{O} + \text{HO}_2 \\
\text{C}_3\text{H}_8 + \text{OH} + 3 \text{O}_2 & \rightarrow \text{CO} + 2 \text{CH}_2\text{O} + \text{H}_2\text{O} + 3 \text{OH}
\end{align*}
\]

(R1) (R2)

R1 corresponds to the sum of the hydrogen abstraction from the secondary carbon atom in propane and the decomposition of nRO2 into C3H6 + HO2. R2 is the overall reaction for the chain mechanism presented in Figure 2-3 and starts with the hydrogen abstraction by OH.
from the primary carbon atom. Reaction enthalpies (at 298 K) for R1 and R2 amount to -153.5 kJ \text{ mol}^{-1} \text{ and } -399 \text{ kJ \text{ mol}^{-1}}, respectively [86]. As the rate coefficients for hydrogen abstractions by OH from the primary and secondary site in propane are almost identical, the effective heat released per mole of propane consumed amounts to approximately -275 kJ \text{ mol}^{-1} (Most of the heat is released later in stage-1 since this is an exponential process).

In stage-1B, the fuel conversion \(X\) and temperature are correlated:

\[
dT = -\frac{\Delta H_{\text{eff}}}{c_v C_{\text{tot}}} d[RH] = \frac{\Delta H_{\text{eff}} X_{0,RH}}{c_v} dX
\]

with \(\Delta H_{\text{eff}}\) the effective reaction enthalpy, \(c_v\) the average molar specific heat capacity of the system and \(X_{0,RH}\) the initial fuel mole fraction. Integrating the above equation will give

\[
T - T_0 = \frac{\Delta H_{\text{eff}} X_{0,RH}}{c_v} X
\]

where \(T_0\) is the initial temperature of the system. Assuming that formaldehyde and \(OQ'OOH\) have the stage-1B exponential behavior and \(HO_2\) is in quasi-steady state (see supplemental material), yields:

\[
[\text{CH}_2\text{O}] = C_{\text{CH}_2\text{O,B}} \exp(\lambda_{1h}t) = \frac{C_{\text{CH}_2\text{O,B}}[\text{OQ'OOH}]}{C_{\text{OQ'OOH,LB}}}
\]

\[
[\text{HO}_2] = \sqrt{\frac{k_{12}}{k_{24}}[\text{OQ'OOH}]}
\]

Since both the ketohydroperoxide and the fuel conversion are assumed to be exponentially increasing at the same rate, equation (2-32) and (2-33) can also be expressed in terms of fuel conversion

\[
[\text{CH}_2\text{O}] = C_{\text{CH}_2\text{O,B}} \exp(\lambda_{1h}t) = \frac{C_{\text{CH}_2\text{O,B}} X}{X_{0,B}}
\]
where the fuel conversion is given by \( X = X_{0,B} \exp(A_{1B} \theta) \). The pre-exponential factor \( X_{0,B} \) is given by

\[
X_{0,B} = X_{0,A} \exp\left( (\lambda_{1A} - \lambda_{1B}) \tau_{\text{stage-1A}} \right) \tag{2-36}
\]

Where \( X_{0,A} \) is obtained from full model simulations, for \( T_0 = 650 \) K and \( P_0 = 10 \) bar \( X_{0,A} \) was \( \sim 4E-8 \). The value of \( X_{0,A} \) will vary by an order of magnitude, depending on conditions. Sensitivity analysis shows that the exact value has little impact on the predictions; hence we keep it fixed for all the conditions studied. The pre-exponential factor for \( \text{CH}_2\text{O} \) and \( \text{OQ'OOH} \), \( C_{X,B} \) is given by

\[
C_{X,B} = C_{X,A} \exp\left( (\lambda_{1A} - \lambda_{1B}) \tau_{\text{stage-1A}} \right) \tag{2-37}
\]

As stated in the previous section the criterion to determine the end of stage-1 is given by (2-29). Substituting for \([\text{CH}_2\text{O}]\) and \([\text{HO}_2]\) using equation (2-34) and (2-35) in (2-29), we reduce it to a function of conversion and temperature.

\[
\frac{\theta k_{14}}{\theta k_{14} + k_{12} + k_{26} \frac{C_{\text{CH}_2\text{O},0}}{X_{0,B}} + k_{27} \frac{k_{17} C_{\text{Q'OOH},B}}{k_{24} X_{0,B}}} = \frac{2}{3} \tag{2-38}
\]

Substituting for conversion with (2-31), we reduce the above equation to be only a function of temperature. This can be solved for \( T_{\text{stage-1}} \), which is also the cross over temperature described by Peters et al. [28] (or alternatively fuel conversion at end of stage-1 \( X_{\text{stage-1}} \)).

### 2.5.4.1 Critical temperature for the autocatalytic QOOH cycle

It is interesting to note that if the secondary chemistry is ignored (set \( k_{26}[^{1}\text{CH}_2\text{O}] \) and \( k_{27}[\text{HO}_2] = 0 \), equation (2-29) simplifies to an equation giving a specific temperature \( T_{\text{stage-1,max}} \), at which the system becomes subcritical:
\[
\frac{\theta(T_{\text{stage-1,max}}, P_0, [O_2]_0)k_{14}(T_{\text{stage-1,max}}, P_0)}{\theta(T_{\text{stage-1,max}}, P_0, [O_2]_0)k_{14}(T_{\text{stage-1,max}}, P_0) + k_{12}(T_{\text{stage-1,max}}, P_0)} = \frac{2}{3} \] (2-39)

In that case, \(T_{\text{stage-1,max}}\) is independent of the initial temperature \(T_0\) of the system. At this temperature, the loss of radicals due to concerted \(\text{HO}_2\) elimination alone becomes large enough to decrease the value of \(\beta\) to 0.66. \(T_{\text{stage-1,max}}\) also represents the maximum possible temperature to which the system can rise before \(\text{O}_3\text{O}_2\text{H}\) peaks. For propane in air at \(P = 10\text{ bar}\), \(T_{\text{stage-1,max}} = 690\text{ K}\). Above the critical temperature the autocatalytic cycle does not operate; positive feedback leading to ignition must come from other cycles (e.g. \(\text{H}_2\text{O}_2\)). Since the temperature is exponentially rising the temperature of the system at any time can be given by integrating equation (2-30) to give:

\[
T - T_0 = \frac{\Delta H_{\text{eff}} x_{0,\text{RH}}}{c_V} (X_B - X_A) \] (2-40)

And the time required for the temperature to reach the \(T_{\text{stage-1,max}}\) will be given by

\[
\tau_{\text{O}_3\text{O}_2\text{Hpeak}} \approx \frac{1}{\lambda_{1B}(T_0)} \ln \left( \frac{T_{\text{stage-1,max}} - T_0}{\Delta H_{\text{eff}} x_{0,\text{RH}}}{c_V} X_A \right) + \tau_{\text{stage-1A}} \] (2-41)

where \(\lambda_{1B}\) is the rise rate at start of stage-1B given by equation (2-21). Figure 2-13 provides a comparison of the \(\tau_{\text{O}_3\text{O}_2\text{Hpeak}}\) obtained from the full model simulations and predicted using (2-41) for adiabatic isochoric conditions. The time delay for peak \(\text{O}_3\text{O}_2\text{H}\) as predicted by (2-41) is longer than that computed by the full model simulations; however they are within 30% over the temperature range investigated. Equation (2-41) provides a practical way to estimate first stage ignition delays for \(T_0 < T_{\text{stage-1,max}}\) (\(\approx 690\text{ K}\) for mixtures of propane: air at \(P_0 = 10\text{bar}\)) and to understand how they depend on initial temperature, stoichiometry and mixture heat capacity. The dependence on rate coefficients and thermochemistry is manifested in \(\tau_{\text{stage-1A}}, \lambda_{1B}, \Delta H_{\text{eff}}\) and \(T_{\text{stage-1,max}}\). The first stage ignition delay as estimated by equation (2-41) is an analytical expression depending on 10 rate coefficients, while the full model is a stiff system of differential equations involving 630 rate coefficients.
2.5.5 First stage ignition delay under isothermal conditions

Under isothermal conditions, the criticality of the system will be completely determined by the concentrations of CH2O and H2O2. Substituting (2-32) and (2-33) in (2-29) and solving for the OQ’OOH concentration yields:

\[
\begin{align*}
[\text{OQ'OOH}]_{\text{peak}} &= \frac{C_{\text{OQ'OOH}}}{k_{28}C_{\text{CH}_2\text{O},B}} \left((3\alpha-1)\theta k_{14} - k_{17}\right) + \frac{k_{24}^2 C_{\text{OQ'OOH}}}{k_{28}^2 C_{\text{CH}_2\text{O},B}} \left(\frac{k_{12}^2 k_{17}}{2 k_{24}} + \frac{k_{28}^2 C_{\text{CH}_2\text{O},B}}{C_{\text{OQ'OOH}}} \left((3\alpha-1)\theta k_{14} - k_{17}\right) + \frac{k_{28}^2 k_{17}^2}{4k_{24}^2}\right) \\
&\quad \text{(2-42)}
\end{align*}
\]

The first-stage ignition delay under isothermal conditions is then approximated by:
\[
\tau_{\text{OOHpeak}} \approx \frac{1}{\lambda_{1B}(T_0)} \ln \left( \frac{[\text{OOH}]_{\text{peak}}}{C_{\text{OOH}}_{1B}} \right) + \tau_{\text{stage-1A}} \tag{2-43}
\]

where \(\lambda_{1B}(T_0)\) is the rise rate at start of stage-1B. Figure 2-14 gives a comparison between various estimates for \(\tau_{\text{OOHpeak}}\) obtained from 1) the time at which \(\text{OOH}\) peaks in the full model simulation, 2) the time at which the simulated OH multiplication factor is equal to 1, where \(f_{\text{OH}}\) is defined as:

\[
f_{\text{OH}} = 3\alpha \left( 1 + \frac{\sum k_{\text{ROOH} \rightarrow \text{RO} + \text{OH}}[\text{ROOH}]}{3(k_{\text{O}_2\text{QOOH} \rightarrow \text{QOOH} + \text{OH}}[\text{O}_2\text{QOOH}])] \beta \right) \tag{2-44}
\]

3) the time when the system becomes subcritical using the time predicted by equation (2-43). The predictions are within a factor of 2 for the entire low temperature regime and the accuracy increases as we approach the negative temperature coefficient (NTC) region.

**Figure 2-14**: Comparison of the \(\tau_{\text{OOHpeak}}\) obtained from 1) the time numerical location of the \(\text{OOH}\) peak for the full model simulation, 2) the time at which criterion set by equation (2-26) is met using reaction fluxes obtained from simulations, 3) the time predicted by equation (2-43), all for an isothermal isochoric simulation of a stoichiometric mixture of propane and air.
2.6 Predicting first stage ignition delay for longer chain alkane fuels

The framework developed for interpreting propane ignition can be extended to larger n-alkane fuels. For longer straight chain fuels (e.g. butane, pentane etc.), all sites on the carbon chain can participate in the peroxy chemistry cycle \((R + 2O_2 \rightarrow \text{intermediates} \rightarrow OQ'OOH)\) to produce OH radicals. This change in reactivity is due to the availability of at least two hydrogen atoms on the \(\gamma\)-C for every alkyl radical site, which can participate in the facile six-membered isomerization transition states that permit the peroxy chemistry cycle to occur. Figure 2-15 provides a schematic of a generalized fuel molecule undergoing peroxy chemistry. As the length of the carbon chain increases, one reaches a limit where effectively every site on the fuel can be treated as an equivalent site; a single-site assumption can be used to estimate the first-stage ignition delay. For straight-chain and branched fuels \(\beta\)-scission of the alkyl radical can occur to form alkenes and smaller radicals. However, for \(T < 800\) K this was seen as an insignificant loss channel for \(P > 10\) bar.

![Figure 2-15](image-url): Schematic of a long n-alkane fuel undergoing low temperature peroxy chemistry. As the carbon chain increases every site can be treated as an equivalent site. The blue arrows are OH formation...
reactions while the red arrows show loss of OH radicals. The dotted arrows are reactions that compete with low temperature branching reactions and delay the first stage ignition of the fuel.

For long chain fuels the OH radicals can abstract hydrogen from the fuel and also secondary products with carbonyl groups (that tend not to contribute to chain branching, these secondary products are labeled as “aldehyde” in the equations below). In this case, since all hydrogen abstractions by OH from the fuel lead into potential chain branching sequences for all alkyl radical sites, the generalized fraction of OH consumption reactions that can lead to chain branching, $a$, can be represented as:

$$
a = \frac{\text{fuel} + \text{OH} \rightarrow \sum R_i + \text{H}_2\text{O}}{\text{total consumption rate of OH}} = \frac{\sum k_{\text{RH-OH} \rightarrow \text{R} + \text{H}_2\text{O}}[\text{RH}]}{k_{\text{RH-OH} \rightarrow \text{R} + \text{H}_2\text{O}}[\text{RH}] + \sum k_{\text{aldehyde-OH} \rightarrow \text{aldehyde}} + \sum k_{\text{HO}_2\cdot \text{OH} + \text{HO}_2\cdot \text{H}_2\text{O}}[\text{H}_2\text{O}]} \quad (2-45)
$$

In long straight chain alkanes all $n$ sites are assumed equivalent, which reduces $a$ to:

$$
a = \frac{k_{\text{RH-OH} \rightarrow \text{R} + \text{H}_2\text{O}}[\text{RH}]}{k_{\text{RH-OH} \rightarrow \text{R} + \text{H}_2\text{O}}[\text{RH}] + \sum k_{\text{aldehyde-OH} \rightarrow \text{aldehyde}} + \sum k_{\text{HO}_2\cdot \text{OH} + \text{HO}_2\cdot \text{H}_2\text{O}}[\text{H}_2\text{O}]} \quad (2-46)
$$

$\beta$ for long chain alkanes is given by:

$$
\beta = \frac{\text{net rate of RO} \rightarrow \text{QOOH}}{\text{total consumption of RO}} = \frac{\sum \theta k_{\text{RO} \rightarrow \text{QOOH}}}{\sum \theta k_{\text{RO} \rightarrow \text{QOOH}} + k_{\text{RO} \rightarrow \text{aldehyde}} + \sum k_{\text{RO} \rightarrow \text{aldehyde}} + \sum k_{\text{RO} \rightarrow \text{HO}_2}[\text{HO}_2]} \quad (2-47)
$$

We simplify the above expression by assuming all $n$ sites to be equivalent to the secondary RO$_2$ radical going to secondary $\gamma$-QOOH radical, which reduces $\beta$ to:

$$
\beta = \frac{\theta k_{\text{RO} \rightarrow \text{QOOH}}}{\theta k_{\text{RO} \rightarrow \text{QOOH}} + k_{\text{RO} \rightarrow \text{aldehyde}} + \sum k_{\text{RO} \rightarrow \text{aldehyde}} + \sum k_{\text{RO} \rightarrow \text{HO}_2}[\text{HO}_2]} \quad (2-48)
$$

where expression for $\theta$ is given by equation (2-49).

$$
\theta = \frac{k_{\text{QOOH-O}_2 \rightarrow \text{O}_2 + \text{QOOH}} + k_{\text{QOOH-O}_2 \rightarrow \text{O}_2 + \text{QOOH}}}{k_{\text{QOOH-O}_2 \rightarrow \text{QOOH}} + k_{\text{QOOH-O}_2 \rightarrow \text{QOOH}}} \quad (2-49)
$$
For long straight chain alkanes the carbonyl radical formed by decomposition of the OQ'O radical can either react with an additional O₂ to give OH radical or decompose to give radical + stable product. However we found that current detailed mechanisms have no systematic treatment for this species. To account for this we define an additional ratio

\[
\gamma = \frac{\text{rate of Carbonyl + O}_2 \rightarrow OH + \text{Side Product}}{\text{total consumption rate of Carbonyl}}
\]  \hspace{1cm} (2-50)

The value of \(\gamma\) is uncertain and ranges from 0 to 1. The gain in OH for the cycle shown in Figure 2-15 can be defined as follows

\[
f_{OH} = (2 + \gamma) \alpha \beta
\]  \hspace{1cm} (2-51)

The concentration of HO₂ to OH for long straight chain alkanes is often so low that HO₂ does not contribute significantly to fuel consumption. The two sub-stages are therefore not observed distinctly \((\lambda_{λ1} \approx \lambda_{λ2})\) in long chain alkanes. The generalized differential equation over a single site for the first stage ignition can then be written as:

\[
\begin{bmatrix}
\frac{d[RO_2]}{dt} \\
\frac{d[OQ'OHH]}{dt}
\end{bmatrix} =
\begin{bmatrix}
-\left((1-\alpha) + \left(\frac{1-\beta}{\beta}\right)k_{i4}\right)\theta k_{i4} & (1+\gamma)\alpha k_{i7} \\
\theta k_{i4} & -k_{i7}
\end{bmatrix}
\begin{bmatrix}
[RO_2] \\
[OQ'OHH]
\end{bmatrix}
\]  \hspace{1cm} (2-52)

In the above equation, \(\theta\), \(k_{14}\) and \(k_{17}\) correspond to the parameters for the secondary RO₂ radical. The positive eigenvalue for the above system of equation is given by:

\[
\lambda_{1,\beta} = \frac{k_{i7}}{2} \left(1 + \frac{(1-\alpha \beta)\theta k_{i4}}{\beta k_{i7}}\right) + \sqrt{4\left((2+\gamma)\alpha \beta - 1\right)\theta k_{i4} + \left(1 + \frac{(1-\alpha \beta)\theta k_{i4}}{\beta k_{i7}}\right)^2}
\]  \hspace{1cm} (2-53)

It is worth noting that in contrast to propane where approximately 50% of the OH radicals are lost to the i-propyl channel, for large n-alkanes the loss of OH radicals is effectively only due to secondary chemistry (i.e reactions with aldehydes, alkenes, cyclic ethers). Thus, within the single site assumption in the initial stages of the ignition where intermediates and secondary products have relatively small concentrations, the value of \(\alpha\) will be close to unity.
The time for first stage ignition delay is given approximately by the following expression:

\[ \tau_{QO'OOHpeak} \approx \frac{1}{\lambda_{1B}(T_0)} \ln \left( \frac{T_{stage-1,max} - T_0}{\Delta H_{eff} x_{O,RH} X_{0,B}} \right) \]  

(2-54)

where \( \lambda_{1B} \) is given by equation (2-53), the \( \beta \) and \( \theta \) needed to evaluate \( \lambda_{1B} \) given by expressions (2-12) and (2-13) respectively. Table 2-2 gives the rate coefficients for the respective alkanes needed to evaluate \( \lambda_{1B} \). The value for \( \alpha \) is assumed to be 1 for long alkanes. The critical temperature \( T_{stage-1,max} \) for long chain alkanes is obtained by solving:

\[ \theta \left( T_{stage-1,max}, P_0, [O_2]_0 \right) k_{14} \left( T_{stage-1,max}, P_0 \right) \frac{T}{\theta \left( T_{stage-1,max}, P_0, [O_2]_0 \right) k_{14} \left( T_{stage-1,max}, P_0 \right) + k_{12} \left( T_{stage-1,max}, P_0 \right)} = \frac{1}{2 + \gamma} \]  

(2-55)

Table 2-3 gives the calculated critical temperatures for \( \gamma = 0 \) and \( \gamma = 1 \) for various alkanes. Since the fate of OQ’O is uncertain in the current chemical mechanisms, we assume the value of \( \gamma = 1 \) for the rest of the section. More research is needed to identify the proper value of \( \gamma \) for various alkanes. The fuel conversion at the end of the incubation period \( (X_{0,B}) \), was kept fixed for all alkanes at the value obtained for full model simulations of propane \( \approx 3E-7 \). Sensitivity analysis shows that this term does not have a large effect on the predicted ignition.

The rate coefficients in Table 2-2 come from the chemical kinetic mechanism we will be using to compare our predictions. However this table highlights significant discrepancies between these literature mechanisms. For example the OQ’OOH \( \rightarrow \) OQ’O + OH rate is faster for heptane than for pentane, butane and propane. Also the RO2 \( \rightarrow \) alkene + HO2 rate has a very non-Arrhenius behavior probably because it comes from a pressure dependent calculation, but the form should be different for different size.

Figure 2-16 provides a comparison of the overall ignition delay for the full model simulations of propane, \( n \) butane (Healy et al. [74]), \( n \) pentane (Mehl et al. [87]) and \( n \) heptane (Mehl et al. [87]) with that predicted for the first stage ignition delay using (2-54). The predicted ignition delay \( (T < 700K) \) is within a factor of 2-3 of the full model simulation.
for most fuels. The value of $\alpha$ will not be unity as the secondary products grow in as the reaction proceeds. Notably, even decreasing the value of $\alpha$ to 0.9 (10% loss of OH radicals to secondary chemistry, which was the typical loss seen from full model simulations) or $\gamma$ to 0.7 markedly improves the agreement between the predicted and simulated ignition delays as shown by the dashed-dotted lines in Figure 2.16. The good agreement suggests that the approximations (e.g. lumping of all the different type of carbon sites in the molecule to a single site) used to calculate $\tau_{Q^{1}OOH_{peak}}$ are reasonably accurate.

Table 2-2: Arrhenius rate coefficient parameters for reactions required to calculate the first stage ignition delay using equation (2.54). The parameters come from the 10 atm PLOG fits for $n$-propyl pathway from Goldsmith et al. [48], from the detailed model of Healey et al. [74] for propane + OH and butane and the detailed model by Mehl et al. [87] for pentane and heptane.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Fuel</th>
<th>A</th>
<th>n</th>
<th>$E_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RH + OH → R + H$_2$O</td>
<td>Heptane</td>
<td>4.9E+06</td>
<td>2.0</td>
<td>-0.59</td>
</tr>
<tr>
<td></td>
<td>Pentane</td>
<td>9.3E+07</td>
<td>1.61</td>
<td>-0.035</td>
</tr>
<tr>
<td></td>
<td>Butane</td>
<td>9.3E+07</td>
<td>1.61</td>
<td>-0.035</td>
</tr>
<tr>
<td></td>
<td>Propane</td>
<td>1.0E+10</td>
<td>0.97</td>
<td>1.59</td>
</tr>
<tr>
<td>$RO_2 \equiv QOOH^a$</td>
<td>Heptane</td>
<td>2.5E+10</td>
<td>0.0</td>
<td>20.5</td>
</tr>
<tr>
<td></td>
<td>Pentane</td>
<td>2.5E+10</td>
<td>0.0</td>
<td>20.8</td>
</tr>
<tr>
<td></td>
<td>Butane</td>
<td>3.8E+10</td>
<td>0.0</td>
<td>24.4</td>
</tr>
<tr>
<td></td>
<td>Propane</td>
<td>1.01</td>
<td>3.38</td>
<td>18.9</td>
</tr>
<tr>
<td>$RO_2 \rightarrow$ alkene + HO$_2$</td>
<td>Heptane</td>
<td>20.0E+42</td>
<td>-9.4</td>
<td>42.5</td>
</tr>
<tr>
<td></td>
<td>Pentane</td>
<td>20.0E+42</td>
<td>-9.4</td>
<td>42.5</td>
</tr>
<tr>
<td></td>
<td>Butane</td>
<td>20.0E+42</td>
<td>-9.4</td>
<td>42.5</td>
</tr>
<tr>
<td>Reaction</td>
<td>Species</td>
<td>k (10^12)</td>
<td>( A )</td>
<td>( E_a )</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>---------</td>
<td>-----------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>( \text{QOOH} + \text{O}_2 \rightleftharpoons \text{O}_2\text{QOOH}^a )</td>
<td>Propane</td>
<td>2.6E+16</td>
<td>-1.2</td>
<td>32.8</td>
</tr>
<tr>
<td></td>
<td>Heptane</td>
<td>7.5E+12</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>Pentane</td>
<td>7.5E+12</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>Butane</td>
<td>4.5E+12</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>Propane</td>
<td>2.2E+27</td>
<td>-4.8</td>
<td>4.0</td>
</tr>
<tr>
<td>( \text{O}_2\text{QOOH} \rightarrow \text{OQ}'\text{OOH} + \text{OH} )</td>
<td>Heptane</td>
<td>1.2E+10</td>
<td>0.0</td>
<td>17.5</td>
</tr>
<tr>
<td></td>
<td>Pentane</td>
<td>1.2E+10</td>
<td>0.0</td>
<td>17.5</td>
</tr>
<tr>
<td></td>
<td>Butane</td>
<td>2E+11</td>
<td>0.0</td>
<td>26.4</td>
</tr>
<tr>
<td></td>
<td>Propane</td>
<td>4.5E+11</td>
<td>-0.5</td>
<td>18.4</td>
</tr>
<tr>
<td>( \text{OQ}'\text{OOH} \rightarrow \text{OQ}'\text{O} + \text{OH} )</td>
<td>Heptane</td>
<td>1.0E+16</td>
<td>0.0</td>
<td>39.0</td>
</tr>
<tr>
<td></td>
<td>Pentane</td>
<td>1.5E+16</td>
<td>0.0</td>
<td>42.0</td>
</tr>
<tr>
<td></td>
<td>Butane</td>
<td>1.5E+16</td>
<td>0.0</td>
<td>41.6</td>
</tr>
<tr>
<td></td>
<td>Propane</td>
<td>5.2E+43</td>
<td>-8.7</td>
<td>51.5</td>
</tr>
</tbody>
</table>

*Note: (a) The reverse rate coefficients were obtained from the respective thermodynamic parameters of the species and are provided in a separate file.
2.6.1 Implications for chemistry of first-stage ignition

In this section we analyze how different chemical kinetic parameters and mixture composition affect first stage ignition delay. Since the time for first stage ignition is inversely proportional to the rise rate, parameters that affect the eigenvalue necessarily affect the first-stage ignition delay. The rise rate \( \lambda_{IB} \) for long straight chain alkanes is given by equation (2-53), and for \( \gamma = 1 \) this equation reduces to equation (2-21). As discussed previously, \( \lambda_{IB} \) is a function of \( \alpha \) the fraction of OH radicals that participates in the chain-branching process by producing viable alkyl radicals, and \( \theta \), which is the fraction of \( RO_2 \) radicals that can go on to participate in the peroxy cycle. The third parameter, \( \theta \), is the ratio of flux through \( O_3QOOH \rightarrow QOOH + OH \) over the flux for \( RO_2 \rightarrow QOOH \). The rise rate is independent of the fuel concentration \( [RH] \), however the fuel concentration will affect the initial condition of the system via the \( RH + O_2 \) reaction which forms the initial radical pool. Changing the fuel concentration also proportionally affects the amount of heat released in the system. However, as seen from equation (2-54) the first stage ignition delay has only a logarithmic dependence on the net heat of reaction. Hence increasing the fuel concentration modestly decreases the first stage ignition delay. The oxygen dependence of
the first stage ignition delay is via RH+O₂, similar to the fuel dependence discussed above and more significantly via 0. As discussed in section 2.5.1, 0 for propane tends to 1 for T < 600 K and P > 10 bar and the rise rate will become independent of the oxygen concentration. Under these conditions the reaction nRO₂ → QOOH is the rate limiting step. However for T > 650 K and low pressures, 0 is no longer 1 and the rise rate is a function of 0.5. As the temperature is increased or pressure is decreased (i.e. oxygen concentration is decreased) a larger fraction of O₂QOOH will dissociate back to O₂ and QOOH. An increase in temperature also increases the reverse rate of RO₂ → QOOH and consequently the reaction O₂QOOH → OQ'OOH + OH becomes rate limiting. The parameter 0 can be approximated by:

\[
\theta \approx \frac{K_{16}xO_2P}{K_{34} + K_{15}xO_2P}
\]

(2-56)

where xo₂ is the mole fraction of oxygen.

The parameter 0 also affects the T_{stage1,max} through 0. As the pressure is increased a smaller fraction of RO₂ radicals are lost via RO₂ → alkene + HO₂ causing the critical temperature (T_{stage1,max}) to increase. Table 2-3 gives T_{stage1,max} as function of pressure for various straight chain alkanes. Both of these effects lead to first stage ignition delay having a modest dependence on the oxygen concentration at higher temperatures (the supplemental material provides predictions for propane first stage ignition delays under varying equivalence ratios and pressures).

<table>
<thead>
<tr>
<th>Fuel</th>
<th>P₀ = 1 bar</th>
<th>P₀ = 10 bar</th>
<th>P₀ = 50 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane</td>
<td>650</td>
<td>690</td>
<td>760</td>
</tr>
<tr>
<td>Butane</td>
<td>680 · 710</td>
<td>710 · 750</td>
<td>740 · 810</td>
</tr>
<tr>
<td>Pentane</td>
<td>760 · 800</td>
<td>860 · 930</td>
<td>930 · 1030</td>
</tr>
<tr>
<td>Heptane</td>
<td>790 · 830</td>
<td>890 · 950</td>
<td>970 · 1070</td>
</tr>
</tbody>
</table>

Table 2-3: Critical temperature (T_{stage1,max}) calculated for stoichometric mixture of fuel in air. The range in T_{stage1,max} corresponds to the y value 0 and 1 respectively. For propane the fate of OQ'O is well understood and y = 1.
2.6.2 Overall activation energy of first-stage ignition for long chain alkanes

It has often been observed that the low-temperature portion of a measured ignition delay for long-chain fuels can be well represented by an Arrhenius expression. Using the expression derived above (2-54), we can determine the overall activation energy. For long straight-chain alkanes, as a first approximation, during pre-ignition we can assume $a \approx 1$ (this was verified using full model simulations for $n$-alkanes). For $T < 600$ K and $P > 10$ bar it is reasonable to further approximate $\beta \approx 1$ (alkene + HO$_2$ is negligible) and $\theta \approx 1$ (the back reaction of RO$_2 = \text{QOOH}$ is insignificant compared to the rate at which QOOH reacts away to O$_2$QOOH), which greatly simplifies (2-54) as follows (See supplemental material for details):

$$\tau_{\text{OQ'OOHpeak}} \propto \frac{1}{\sqrt{2k_{14}k_{17}}}$$

such that the ignition delay can be expressed as an Arrhenius expression

$$\ln\left(\tau_{\text{OQ'OOHpeak}}\right) = -\left(\ln A_{\text{eff}} - \frac{E_{\text{eff}}}{T}\right)$$

where

$$E_{\text{eff}} \approx \frac{1}{2}(E_{14} + E_{17})$$

$$\ln A_{\text{eff}} \approx \frac{1}{2}\ln\left(2A_{14}A_{17}\right)$$

The above equation has an important implication that the overall activation energy $E_{\text{eff}}$ for the first stage ignition delay $\tau_{\text{OQ'OOHpeak}}$ is dependent not only on the activation energy of the isomerization between RO$_2$ (secondary carbon) and QOOH (radical on the secondary carbon), as stated by Zhao and Law [30], but also on the activation energy of the ketohydroperoxide decomposition. Zhao and Law [30], obtained their correlation by simply comparing their fitted $E_{\text{eff}}$ with the activation energy of different reactions in their mechanism. Since the decomposition of ketohydroperoxide controls the release of OH radicals it is reasonable to expect this term to affect the activation energy of the ignition. Table 2-4 provides the overall activation energy $E_{\text{eff}}$ for the first stage ignition delay
for different fuels in the temperature range of 550 – 650 K as obtained via Arrhenius expressions fitted to full model simulations, equation (2-59) and $E_{\text{eff}} = E_{a, \text{RO}_2=\text{QOOH}}$. Clearly, equation (2-59) provides a better prediction of the overall activation energy than does $E_{a, \text{RO}_2=\text{QOOH}}$.

$\tau_{\text{QOOHpeak}}$ for different fuels in the temperature range of 550 – 650 K as obtained via Arrhenius expressions fitted to full model simulations, equation (2-59) and $E_{\text{eff}} = E_{a, \text{RO}_2=\text{QOOH}}$. Clearly, equation (2-59) provides a better prediction of the overall activation energy than does $E_{a, \text{RO}_2=\text{QOOH}}$.

Table 2-4: Overall activation energy (kcal/mol) for first stage ignition delay for different n-alkanes for stoichiometric mixture of fuel and air at $P_0 = 10$ bar.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Activation Energy (Full model)</th>
<th>Activation Energy Eq (49)</th>
<th>$E_a (\text{RO}_2=\text{QOOH})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butane</td>
<td>35.0</td>
<td>32.6</td>
<td>24.4</td>
</tr>
<tr>
<td>Pentane</td>
<td>33.9</td>
<td>31.0</td>
<td>20.8</td>
</tr>
<tr>
<td>Heptane</td>
<td>28.6</td>
<td>29.3</td>
<td>20.5</td>
</tr>
</tbody>
</table>

*Note: The overall activation energy from the full model is obtained by linear least square fit of the simulated full model first stage ignition delay to the temperature ($\ln(\tau_{\text{QOOHpeak}}) = A + E/RT$). The temperature range was limited to $T < 650$ K.

2.7 Concluding remarks

Using a detailed propane model we analyze the controlling chemistry for the first-stage ignition of propane. The analysis demonstrates that low-temperature auto-ignition of straight-chain alkanes is a multi-stage process. The experimentally observed first-stage ignition can be divided into two stages. In stage-1A, both OH and HO$_2$ radicals abstract hydrogen atoms from the fuel, and the resulting alkyl radicals initiate a peroxo radical cycle, which leads to chain branching via the thermal decomposition of ketohydroperoxides. This process causes OH and HO$_2$ concentration to rise exponentially and continues until the concentration of HO$_2$ is sufficiently large that the recombination reaction, HO$_2$ + HO$_2$ $\rightarrow$ H$_2$O$_2$ + O$_2$, becomes competitive with the rate of HO$_2$ formation. Once this occurs, which marks the beginning of stage-1B, the [OH]/[HO$_2$] ratio rises sharply and the vast majority of fuel consumption occurs through OH. Fuels that do not produce a significant amount of HO$_2$ (e.g. long straight-chain alkanes) will not show this “multistage” phenomenon so distinctly, but instead stage-1A and stage-1B will be observed as a single stage driven by
OH radicals. Several phenomena occur as the first stage ends. First, oxidation products such as aldehydes, alkenes and \( \text{H}_2\text{O}_2 \) accumulate, diverting some of the OH radicals from chain branching pathways. An increasing fraction of the \( \text{nRO}_2 \) radicals also get consumed by the growing secondary chemistry (\( \text{CH}_2\text{O} \) and \( \text{HO}_2 \)). Most importantly the increase in temperature of the system speeds up the loss due to the concerted elimination of \( \text{RO}_2 \) to alkene + \( \text{HO}_2 \). This diversion of the OH and \( \text{nRO}_2 \) radicals reduces the gain of the autocatalytic cycle to \( < 1 \). The combination of these effects causes the ketohydroperoxide concentration to first rise exponentially, then peak and drop rapidly leading to the point of inflection in the temperature profile, that has often been used to mark the end of first stage ignition. The peak in ketohydroperoxide concentration, which occurs when gain \( \approx 1 \), is used as a convenient chemical marker for the end of first stage ignition.

The analysis also clarifies which species are in quasi steady-state. From these approximations, analytical expressions for first stage ignition delay were derived. Furthermore, from the dependence of \( \tau_{\text{QOOHpeak}} \) on important rate coefficients and mixture composition, the following observations can be made:

1. The first stage ignition delay is nearly independent of the fuel and oxygen concentration for low temperatures \( (T< 650K) \) and high pressure \( (P > 50 \text{ bar}) \).
2. The first stage ignition delay however will have a weak \( [\text{O}_2] \) dependence for lower pressures and higher temperatures \( (T > 650 \text{ K}) \).
3. The overall activation energy of first-stage ignition delay is dependent on the activation energy of isomerization of \( \text{RO}_2 \) to \( \text{QOOH} \) and the activation energy of the decomposition of the ketohydroperoxide. For large alkanes at high oxygen partial pressures and low temperatures \( < 650 \text{ K} \), the global activation energy for the ignition delay time can be estimated through the following equation:

\[
E_{\text{eff}} \approx \frac{1}{2} \left( E_{\text{ROO-QOOH}} + E_{\text{QOOHdecmp}} \right)
\]

4. The first-stage ignition delay is determined by the competition between pathways that go on to chain branch versus those that go onto chain terminate. The major branch points are
   a. Fuel + \( \text{OH} \) selectivity towards fuel radicals with different reactivity e.g. \( \text{n-propyl} \) vs \( \text{iso-propyl} \) radicals. We denote this branching ratio by \( \alpha \). For
propane only n-propyl radicals contribute to chain branching and $\alpha \sim 0.5$. For longer n-alkanes all alkyl radicals can contribute to radical generation and we use a value of $\alpha \sim 1$.

b. Peroxy radical (RO$_2$) that are lost by decomposition to alkene + HO$_2$ and by reaction with oxidation products (e.g. HO$_3$, H$_2$O$_2$, carbonyl compounds). This decomposition is often the major loss term and it increases with increasing temperature leading to longer ignition delays. We denote this branching ratio by $\beta$. The value of $\beta$ is a strong function of temperature for all alkanes.

c. What fraction of the carbonyl (acyl-methyl) radicals formed by ketohydroperoxide decomposition go on to form OH or otherwise initiate new autocatalytic cycles. We denote this branching ratio by $\gamma$. For propane, which forms formyl-methyl (vinoxy) radicals, there is a consensus that $\gamma \sim 1$, but for longer n-alkanes the value of $\gamma$ is unclear, different literature models give different values.

5. Above a critical fuel specific temperature ($T_{stage-1,max}$) the QOOH cycle is ineffective at creating additional radicals ($\text{gain} \cdot f_{\text{OH}} = (2 + \gamma) \alpha \beta \approx 1$).

The results obtained from the present simple model for the first stage of propane ignition were extended to longer straight chain fuels under the approximation of a single effective (average) site. This simplifying assumption gives reasonable agreement of the predicted $\tau_{stage-1}$ with the numerical solutions of large reaction mechanisms.
2.8 Supplemental Material

The reduced model provided in Table 2-1 provides reasonable predictions of the first stage ignition delay for propane as illustrated in Figure 2-17.

![Graph showing comparison of predicted first stage ignition delay for propane model](image)

**Figure 2-17:** Comparison of the predicted first stage ignition delay for constant volume adiabatic simulations using the full and reduced propane model, for $P_0 = 10$ bar, stoichometric mixture of propane in air. The $\tau_{\text{stage-1}}$ was obtained using the first inflection in the temperature profile.
2.8.1 Derivation for explosive eigenvalue using reduced model for stage-1A

The following set of ODE’s can be constructed from the reduced model

\[
\frac{d[nR]}{dt} = k_1[RH][O_2] + k_3[RH][OH] + k_5[RH][HO_2] - k_6[nR][O_2] + k_7[nR][O] + k_9[QOOH] - k_{10}[nR][O_2] \tag{S 1}
\]

\[
\frac{d[iR]}{dt} = k_2[RH][O_2] + k_4[RH][OH] + k_6[RH][HO_2] - k_8[iR][O_2] + k_9[iRO_2] - k_{11}[iR][O_2] \tag{S 2}
\]

\[
\frac{d[nRO_2]}{dt} = k_2[nR][O_2] - k_7[nRO_2] - k_{12}[nRO_2] - k_{14}[nRO_2] + k_{-14}[QOOH] \tag{S 3}
\]

\[
\frac{d[iRO_2]}{dt} = k_8[iR][O_2] - k_8[iRO_2] - k_{14}[iRO_2] \tag{S 4}
\]

\[
\frac{d[QOOH]}{dt} = k_4[nR][O_2] - k_{10}[nR][O_2] + k_{14}[nRO_2] - k_{14}[QOOH] - k_{15}[QOOH][O_2] + k_{-15}[O_2QOOH] \tag{S 5}
\]

\[
\frac{d[O_2QOOH]}{dt} = k_{15}[QOOH][O_2] - k_{15}[O_2QOOH] - k_{16}[O_2QOOH] \tag{S 6}
\]

\[
\frac{d[OQ'OOH]}{dt} = k_{16}[O_2QOOH] - k_{17}[OQ'OOH] \tag{S 7}
\]

\[
\frac{d[OQ'O]}{dt} = k_{17}[OQ'OOH] - k_{18}[OQ'O] \tag{S 8}
\]
\[ \frac{d[\text{CH}_2\text{CHO}]}{dt} = k_{18}[\text{OQ'O}] - k_{19}[\text{CH}_2\text{CHO}][\text{O}_2] \] (S 9)

\[ \frac{d[\text{OH}]}{dt} = -k_1[\text{RH}][\text{OH}] - k_2[\text{RH}][\text{OH}] + k_{16}[\text{O}_2\text{QOOH}] + k_{17}[\text{OQ'OOH}] + k_{19}[\text{CH}_2\text{CHO}][\text{O}_2] \]
\[ + 2k_{25}[\text{H}_2\text{O}_2] \] (S 10)

\[ \frac{d[\text{HO}_2]}{dt} = k_1[\text{RH}][\text{O}_2] + k_2[\text{RH}][\text{O}_2] - k_5[\text{RH}][\text{HO}_2] - k_6[\text{RH}][\text{HO}_2] + k_{10}[\text{nR}][\text{O}_2] + k_{11}[\text{iR}][\text{O}_2] \]
\[ + k_{12}[\text{nRO}_2] + k_{13}[\text{iRO}_2] + k_{21}[\text{CH}_2\text{O}][\text{O}_2] + k_{22}[\text{HCO}][\text{O}_2] + k_{23}[\text{H}_2\text{O}_2][\text{OH}] - 2k_{24}[\text{HO}_2] \] (S 11)

\[ \frac{d[\text{CH}_2\text{O}]}{dt} = k_{18}[\text{OQ'O}] + k_{19}[\text{CH}_2\text{CHO}][\text{O}_2] - k_{20}[\text{CH}_2\text{O}][\text{OH}] - k_{21}[\text{CH}_2\text{O}][\text{O}_2] \] (S 12)

After the induction period, several radical species will be in QSS including nR, iR, OH, QOOH, O_2QOOH, OQ'O and CH_2CHO

\[ [\text{nR}] = \frac{(k_1[\text{O}_2] + k_3[\text{OH}] + k_5[\text{HO}_2])[\text{RH}] + k_2[\text{nRO}_2] + k_9[\text{QOOH}]}{\left(k_7 + k_9 + k_{10}\right)[\text{O}_2]} \] (S 13)

\[ [\text{iR}] = \frac{(k_2[\text{O}_2] + k_4[\text{OH}] + k_6[\text{HO}_2])[\text{RH}] + k_8[\text{iRO}_2]}{\left(k_8 + k_{11}\right)[\text{O}_2]} \] (S 14)

\[ [\text{QOOH}] = \frac{k_9[\text{nR}][\text{O}_2] + k_{14}[\text{nRO}_2] + k_{15}[\text{O}_2\text{QOOH}]}{k_{19} + k_{14} + k_{15}[\text{O}_2]} \] (S 15)

\[ [\text{O}_2\text{QOOH}] = \frac{k_{15}}{k_{15} + k_{16}}[\text{O}_2][\text{QOOH}] \] (S 16)

\[ [\text{OQ'O}] = \frac{k_{17}[\text{OQ'OOH}]}{k_{18}} \] (S 17)

\[ [\text{OH}] = \frac{k_{16}[\text{O}_2\text{QOOH}] + k_{17}[\text{OQ'OOH}] + k_{19}[\text{CH}_2\text{CHO}][\text{O}_2] + 2k_{25}[\text{H}_2\text{O}_2]}{(k_3 + k_4)[\text{RH}] + k_{20}[\text{CH}_2\text{O}] + k_{25}[\text{H}_2\text{O}_2]} \] (S 18)
We make the following simplifications:

1) For pressures greater than one atmosphere, the vast majority of QOOH is formed via isomerization from RO₂, such that the chemically activated production of QOOH from R + O₂ is sufficiently small that its contribution can be considered negligible.

2) Similarly the contributions of reaction 10 and 11 are also negligible, as confirmed by flux analysis with the complete model.

3) For temperatures less than 800 K (those considered here) the decomposition of H₂O₂ to OH is not significant during stage-I and can be neglected.

Applying these simplifications to (S 13)-(S 19):

\[
[\text{CH}_2\text{CHO}] = \frac{k_{18}[\text{Q'O}] }{k_{19}[\text{O}_2]} \tag{S 19}
\]

Substituting for O₂QOOH (S 23) in (S 22) and solving gives
Substituting for QOOH (S 22) in (S 23) and solving gives:

\[
[\text{QOOH}] = \frac{k_{14} [\text{nRO}_2]}{k_{-14} + \frac{k_{15} k_{16}}{k_{-15} + k_{16}} [O_2]}
\]  
(S 28)

Substituting for CH$_2$CHO (S 24) and (S 26) in the expression (S 25) for OH:

\[
[\text{OH}] = \frac{k_{16} [\text{O}_2 \text{QOOH}] + 2k_{17} [\text{Q'OOH}]}{(k_3 + k_4) [\text{RH}]} + k_{20} [\text{CH}_2\text{O}] + k_{23} [\text{H}_2\text{O}_2]
\]  
(S 29)

Initially during stage-1 the concentrations of intermediates and products is sufficiently small that their contributions to OH consumption can be neglected. However this assumption breaks down as the fuel is consumed, which leads to the production of secondary products.

\[
[\text{OH}] = \frac{k_{16} [\text{O}_2 \text{QOOH}] + 2k_{17} [\text{Q'OOH}]}{(k_3 + k_4) [\text{RH}]}
\]  
(S 30)

We can simplify the notation by introducing three non-dimensional parameters:

\[
\alpha = \frac{k_3}{k_3 + k_4}
\]  
(S 31)

\[
\beta = \frac{\theta k_{12}}{\theta k_{14} + k_{12}}
\]  
(S 32)

\[
\theta = \frac{k_{15} k_{16}}{k_{-15} + k_{16}} [O_2]
\]  
(S 33)

Using (S 27) in ODE for Q'OOH (S 7):
\[
\frac{d[OQ'OOH]}{dt} = k_{14}[nRO_2] - k_{17}[OQ'OOH]
\]  
(S 34)

Using (S 20), (S 28) and (S 30) in (S 3):

\[
\frac{d[nRO_2]}{dt} = \alpha (k_{16}[O_2QOOh] + 2k_{17}[OQ'OOH]) + (k_i[O_2] + k_s[H_2O])[RH] - k_{12}[nRO_2] - k_{14}[nRO_2]
\]  
(S 35)

Using (S 27) in (S 35) and simplifying:

\[
\frac{d[nRO_2]}{dt} = 2\alpha k_{17}[OQ'OOH] + (k_i[O_2] + k_s[H_2O])[RH] + ((\alpha - 1)k_i[O_2] - k_{13})[nRO_2]
\]  
(S 36)

Using (S 14) and (S 30) in (S 4):

\[
\frac{d[iRO_2]}{dt} = (1 - \alpha)(k_{16}[O_2QOOh] + 2k_{17}[OQ'OOH]) + (k_i[O_2] + k_s[H_2O])[RH] - k_{13}[iRO_2]
\]  
(S 37)

Using (S 27) in (S 37) and simplifying:

\[
\frac{d[iRO_2]}{dt} = (1 - \alpha)(\theta[nRO_2] + 2k_{17}[OQ'OOH]) + (k_i[O_2] + k_s[H_2O])[RH] - k_{13}[iRO_2]
\]  
(S 38)

The ODE for HO_2 after ignoring contributions from R10 and R11 is given by:

\[
\frac{d[HO_2]}{dt} = k_i[RH][O_2] + k_s[RH][O_2] - k_i[HO_2][H_2O] - k_s[HO_2][H_2O]
\]  
(S 39)

At early times the concentration of secondary product (CH₂O, H₂O₂) can be considered negligibly small. The HO_2 concentration is also sufficiently small that the rate of its self-reaction can be neglected, which allows for simplification of (S 39) to:

\[
\frac{d[HO_2]}{dt} = k_i[RH][O_2] + k_s[RH][O_2] - k_i[HO_2][H_2O] + k_{12}[nRO_2] + k_{13}[iRO_2]
\]  
(S 40)

We can also neglect the consumption terms for CH₂O simplifying (S 12) to:

\[
\frac{d[CH₂O]}{dt} = k_{14}[OQ'O] + k_{19}[CH₂CHO][O_2]
\]  
(S 41)
The above equation can be simplified using (S 24) and (S 26) to (S 42), which is valid during early times when the concentration of CH₂O has not grown significantly

\[ \frac{d[CH₂O]}{dt} \approx 2k_{17}[OQ'OOH] \]  

(S 42)

During stage-1 the concentration of the fuel and oxygen remains nearly constant such that

\[ [RH][O₂] = [RH]₀[O₂]₀ \]  

(S 43)

Since \( \alpha, \beta \) and \( \theta \) are approximately constants, equations (S 34), (S 36), (S 38) and (S 40) are linear ODE’s which can be solved using eigenvalue analysis

The system of linear ODE’s can be written in terms of a concentration vector \( C \), coefficient matrix \( M \) and source term \( R \).

\[ \frac{dC}{dt} = MC + R \]  

(S 45)

For which \( M \) can decomposed into an eigenvector matrix, \( V \) and eigenvalue matrix, \( \Lambda \) as

\[ M = V \Lambda V^{-1} \]

\[ \frac{dC}{dt} = V \Lambda V^{-1} C + R \]  

(S 46)

Transforming variables from the concentration vector to the eigenvectors, \( Z = V^{-1} C \) diagonalizes the equation

\[ \frac{dZ}{dt} = \Lambda Z + E \]  

(S 47)

where \( E = V^{-1} R \)
Another change of variables to \( \Lambda Y = \Lambda Z + E \) further simplifies the equation to

\[
\frac{dY}{dt} = \Lambda Y
\]  

(S 48)

This has a general solution of the form

\[
Y = \exp(\Lambda t)Y_0
\]  

(S 49)

Substituting for \( C \) we get back

\[
C = V\exp(\Lambda t)Y_0 - V\Lambda^{-1}V^{-1}R
\]  

(S 50)

where the value of \( Y_0 \) can be obtained from \( R \) and the true initial conditions \( C_0(t = 0) \)

\[
Y_0 = V^{-1}C_0 + \Lambda^{-1}V^{-1}R
\]  

(S 51)

Hence if the complete eigenvectors and the true initial conditions \( C_0(t = 0) \) are used, then the numerical solutions to the above can be found exactly (without any further approximations).

Since only one of the eigenvalues \( (\lambda_i) \) has a positive real number, after a brief induction period of time \( C \) can be approximated as

\[
C_i \approx y_{0,i}V_{i,1}\exp(\lambda_i t) \quad \text{where we assume } real(\lambda_i) > 0
\]  

(S 52)

The initial conditions for \( HO_2 \), \( RO_2 \) and \( OQ'OOH \) in stage-1A is given by

\[
C_{i,0,1} \approx y_{0,i}V_{i,1}
\]  

(S 53)

Initial conditions for all other species will just be linear combinations of \( HO_2 \), \( RO_2 \) and \( OQ'OOH \).

If desired we can take the ratio of concentrations to eliminate the initial condition

\[
\frac{C_{i,1}}{C_i} \approx \frac{V_{i,1,1}}{V_{i,1}}
\]  

(S 54)
Figure 2-18 compares the ratio of concentrations obtained from the eigenvectors (S 54) and the full model simulation.

![Figure 2-18](image)

**Figure 2-18:** Predictions (dotted lines) for relative concentrations of species involved in first stage ignition (stage-1A) by eigen mode analysis for simulations at \( P_0 = 10 \text{ bar} \) and \( T_0 = 650.0 \text{ K} \) for a stoichiometric mixture of propane in air. The solid lines are obtained from full model simulations, the dotted lines are the ratio of the eigenvector elements \( V_{\text{specie}}/V_{\text{OOOHO}} \) corresponding to the positive eigenvalue in stage-1A.

### 2.8.2 Analytical solution for the explosive eigenvalue for stage-1A

An analytical solution to the system of linear ODE’s, equation (S 44), can be achieved if the quartic system is reduced to a cubic equation by making the following assumption for HO2

\[
\frac{d[\text{HO}_2]}{dt} = 2k_{11}[\text{OOOHO}] - \frac{d[\text{nRO}_2]}{dt} - \frac{d[\text{iRO}_2]}{dt} \approx 2k_{17}[\text{OOQOHO}] \tag{S 55}
\]

The left hand side of the above expression comes from rearranging (S 40) using (S 37) and (S 38).
Figure 2-19 gives the comparison of the net HO₂ flux and the flux estimated by the approximation made in (S 55). As seen from Figure 2-19 the approximation provides a satisfactory reproduction of the net HO₂ flux until the HO₂ self-reaction becomes a significant contributor to HO₂ consumption near the end of stage 1A.

Figure 2-19: Comparison of the net HO₂ flux (from the full model simulation) and the approximation $2k_{\text{OQ'OOH decom}}[\text{OQ'OOG]}$ for $P_0 = 10$ bar and $T_0 = 650$ K.

This approximation effectively decouples iRO₂ from the system of differential equations (S 44), reducing it to a cubic system.

\[
\begin{align*}
\begin{bmatrix}
\frac{d[n\text{RO}_2]}{dt} \\
\frac{d[\text{HO}_2]}{dt} \\
\frac{d[\text{OQ'OOG}]}{dt}
\end{bmatrix}
&=
\begin{bmatrix}
-(1-\alpha) + \frac{(1-\beta)}{\beta} \theta k_{i4} & k_{i2}[\text{RH}]_0 & 2\alpha k_{i7} \\
0 & 0 & 2k_{i7} \\
\theta k_{i4} & 0 & -k_{i7}
\end{bmatrix}
\begin{bmatrix}
[n\text{RO}_2] \\
[\text{HO}_2] \\
[\text{OQ'OOG}]
\end{bmatrix}
\begin{bmatrix}
k_{i2}[\text{RH}]_b[\text{O}_2]_b \\
(k_i + k_j)[\text{RH}]_b[\text{O}_2]_b \\
0
\end{bmatrix}
\end{align*}
\] (S 56)

The eigenvalues are roots of the following cubic characteristic equation

\[
\lambda^3 + \left(1-\alpha + \frac{(1-\beta)}{\beta} \theta k_{i4} + k_{i7}\right) \lambda^2 + \left(1-3\alpha + \frac{(1-\beta)}{\beta} \theta k_{i4} k_{i7}\right) \lambda - 2\theta k_{i4} k_{i7} k_{i5}[\text{RH}] = 0
\] (S 57)
The characteristic equation is a general cubic of the form \( x^3 + bx^2 + cx + d = 0 \) and will have three roots.

\[
\lambda_1 = -\frac{b}{3} + \frac{\sqrt[3]{-2b^3 + 3\sqrt{3}4b^3d - b^2c^2 - 18bcd + 4c^3 + 27d^2 + 9bc - 27d}}{3\sqrt[6]{2}} - \frac{\sqrt[3]{2}(3c - b^2)}{3\sqrt[6]{2}(-2b^3 + 3\sqrt{3}4b^3d - b^2c^2 - 18bcd + 4c^3 + 27d^2 + 9bc - 27d)}
\]

\[
\lambda_2 = -\frac{b}{3} - \frac{(1 - i\sqrt{3})\sqrt[3]{-2b^3 + 3\sqrt{3}4b^3d - b^2c^2 - 18bcd + 4c^3 + 27d^2 + 9bc - 27d}}{6\sqrt[6]{2}} + \frac{(1 + i\sqrt{3})(3c - b^2)}{3 \times 2\sqrt[6]{2}(-2b^3 + 3\sqrt{3}4b^3d - b^2c^2 - 18bcd + 4c^3 + 27d^2 + 9bc - 27d)}
\]

\[
\lambda_3 = -\frac{b}{3} - \frac{(1 + i\sqrt{3})\sqrt[3]{-2b^3 + 3\sqrt{3}4b^3d - b^2c^2 - 18bcd + 4c^3 + 27d^2 + 9bc - 27d}}{6\sqrt[6]{2}} + \frac{(1 - i\sqrt{3})(3c - b^2)}{3 \times 2\sqrt[6]{2}(-2b^3 + 3\sqrt{3}4b^3d - b^2c^2 - 18bcd + 4c^3 + 27d^2 + 9bc - 27d)}
\]

where

\[
b = \left(1 - \alpha\right) + \left(\frac{1 - \beta}{\beta}\right)\theta k_{14} + k_{17}
\]

\[
c = \left(1 - 3\alpha\right) + \left(\frac{1 - \beta}{\beta}\right)\theta k_{13}k_{17}
\]

\[
d = -2\theta k_{14}k_{17}k_{5}[RH]
\]
Table 2-5: Comparison of the positive eigenvalue (\(\lambda_{1A}\)) obtained solving (S 44) numerically and the positive root of the cubic equation (S 57) for \(P_0 = 10\) bar, stoichiometric mixture of propane in air.

<table>
<thead>
<tr>
<th>(T_0) (K)</th>
<th>(\lambda_{1A}) (Numerical)</th>
<th>(\lambda_{1A}) (Cubic approx.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>0.7</td>
<td>0.9</td>
</tr>
<tr>
<td>600</td>
<td>8.5</td>
<td>9.8</td>
</tr>
<tr>
<td>650</td>
<td>55.4</td>
<td>61.0</td>
</tr>
</tbody>
</table>

2.8.3 **Simplification of the explosive eigenvalue for stage \(1B\)**

The expression for the explosive eigenvalue for a general fuel is given by:

\[
\lambda_n = \frac{k_{17}}{2} \left( -\left(1 + \frac{(1-\alpha\beta)\theta k_{14}}{\beta k_{17}}\right) + \sqrt{4\left(3\alpha\beta - 1\right)\theta k_{14}} + \left(1 + \frac{(1-\alpha)\theta k_{14}}{\beta k_{17}}\right)^2 \right)
\]  

(S 61)

Substituting for \(\beta\) using equation (S 32)

\[
\lambda_n = \frac{k_{17}}{2} \left( -\left(1 + \frac{(1-\alpha)\theta k_{14} + k_{12}}{k_{17}}\right) + \sqrt{4\left(2\alpha\theta k_{14} + (\alpha - 1)\theta k_{14} - k_{17}\right)} + \left(1 + \frac{(1-\alpha)\theta k_{14} + k_{12}}{k_{17}}\right)^2 \right)
\]  

(S 62)

For \(\alpha = 1\) we get

\[
\lambda_n = \frac{k_{17}}{2} \left( -\left(1 + \frac{k_{12}}{k_{17}}\right) + \sqrt{4\left(2\theta k_{14} - k_{17}\right)} + \left(1 + \frac{k_{12}}{k_{17}}\right)^2 \right)
\]  

(S 63)
For low temperatures \((T < 600 \text{ K}, P > 10 \text{ bar})\) the loss of \(\text{RO}_2\) radicals to alkene + \(\text{HO}_2\) is less than the production of \(\text{RO}_2\) radicals

\[
4 \left( \frac{2\theta k_{14} - k_{12}}{k_{17}} \right) > \left( 1 + \frac{k_{12}}{k_{17}} \right)^2 \quad \text{(S 64)}
\]

\[
2\theta k_{14} \gg k_{12} \quad \text{(S 65)}
\]

This reduces the expression of the explosive eigenvalue to

\[
\lambda_{i_B} \approx \frac{k_{17}}{2} \left( -1 + \sqrt{\frac{4\theta k_{14}}{k_{17}}} \right) \quad \text{(S 66)}
\]

For high pressures and low temperature \(\theta \to 1\), which yields

\[
\lambda_{i_B} \approx \frac{k_{17}}{2} \left( -1 + \sqrt{\frac{2k_{14}}{k_{17}}} \right) \quad \text{(S 67)}
\]

Rearranging yields

\[
\lambda_{i_B} \approx -\frac{k_{17}}{2} + \sqrt{2k_{14}k_{17}} \quad \text{(S 68)}
\]

Ignoring \(-k_{17}/2\) simplifies the above equation to (this approximation has significant error and not recommended to be used above the limited temperature and pressure range)

\[
\lambda_{i_B} \approx \sqrt{2k_{14}k_{17}} \quad \text{(S 69)}
\]

### 2.8.4 Prediction for first stage ignition delay for propane under varying equivalence ratios and pressure

87
Figure 2-20 provides the comparison of first stage ignition delay for propane under varying equivalence ratios in air for $P_0 = 10$ bar. The first stage ignition delay does not change significantly with fuel concentration.

Figure 2-20: Comparison of the simulated adiabatic isochoric overall ignition delay with the predicted first stage ignition delay for various equivalence ratios of propane in air. All simulations are for $P_0 = 10$ bar. The overall ignition delay (solid line) is obtained from the full model simulations, while the predicted first stage ignition delay (dashed line) is obtained using equation (2-41).

Figure 2-21 provides the comparison of first stage ignition delay for propane under varying pressure for $\varphi = 1$. The first stage ignition delay is a function of pressure (or oxygen concentration) as the temperature is increased ($T > 650$ K).
Figure 2.21: Comparison of the simulated adiabatic isochoric overall ignition delay with the predicted first stage ignition delay for various pressure. All simulation are for stoichometric mixture of of propane in air. The overall ignition delay (solid line) is obtained from the full model simulations, while the predicted first stage ignition delay (dashed line) is obtained using equation (2.41).
Table 2-6: Comparison of important parameters used in predicting first stage ignition delay for propane under varying $T_0$, $P_0$ and equivalence ratio.

<table>
<thead>
<tr>
<th></th>
<th>$T_0 = 600$ K</th>
<th>$T_0 = 650$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi = 1$</td>
<td>$P_0 = 10$ bar</td>
<td>$P_0 = 50$ bar</td>
</tr>
<tr>
<td>$\alpha(T_0)$</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>$\beta(T_0)$</td>
<td>0.94</td>
<td>0.95</td>
</tr>
<tr>
<td>$\theta(T_0)$</td>
<td>0.75</td>
<td>0.93</td>
</tr>
<tr>
<td>$\Lambda_{1A}(T_0)$ (s$^{-1}$)</td>
<td>8.5</td>
<td>13.1</td>
</tr>
<tr>
<td>$\Lambda_{1B}(T_0)$ (s$^{-1}$)</td>
<td>3.0</td>
<td>3.2</td>
</tr>
<tr>
<td>$\tau_{\text{stage1-A}}$ (s)</td>
<td>1.2</td>
<td>0.7</td>
</tr>
<tr>
<td>$\tau_{\text{QOOHpeak}}$ (s)</td>
<td>3.2</td>
<td>1.8</td>
</tr>
<tr>
<td>$T_{\text{stage1-max}}$ (K)</td>
<td>690</td>
<td>760</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$T_0 = 600$ K</th>
<th>$T_0 = 650$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi = 0.5$</td>
<td>$P_0 = 10$ bar</td>
<td>$P_0 = 50$ bar</td>
</tr>
<tr>
<td>$\alpha(T_0)$</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>$\beta(T_0)$</td>
<td>0.94</td>
<td>0.95</td>
</tr>
<tr>
<td>$\theta(T_0)$</td>
<td>0.75</td>
<td>0.93</td>
</tr>
<tr>
<td>$\Lambda_{1A}(T_0)$ (s$^{-1}$)</td>
<td>7.0</td>
<td>11.4</td>
</tr>
<tr>
<td>$\Lambda_{1B}(T_0)$ (s$^{-1}$)</td>
<td>3.0</td>
<td>3.2</td>
</tr>
<tr>
<td>$\tau_{\text{stage1-A}}$ (s)</td>
<td>1.5</td>
<td>0.8</td>
</tr>
<tr>
<td>$\tau_{\text{QOOHpeak}}$ (s)</td>
<td>4.0</td>
<td>2.1</td>
</tr>
<tr>
<td>$T_{\text{stage1-max}}$ (K)</td>
<td>690</td>
<td>760</td>
</tr>
</tbody>
</table>
Chapter 3


developing detailed understanding for pyrolysis of cyclopentadiene to polycyclic aromatics

In this chapter a combined experimental and theoretical study is presented which aims at understanding the growth of polycyclic aromatic hydrocarbons. The collaboration with Laboratory of Chemical Technology (Univ. of Ghent) helped provide new speciation data on the co-pyrolysis of cyclopentadiene with ethene. Using an automated reaction mechanism generator we present the first elementary-step micro-kinetic model that captures the initial formation of indene and naphthalene from cyclopentadiene. The model is able to qualitatively reproduce the product yields observed during pyrolysis of pure cyclopentadiene and cyclopentadiene/ethene mixtures in a flow reactor.

3.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of more than 100 chemicals that can be produced from various anthropogenic sources, such as the incomplete combustion of heating fuels, oil refining processes and the combustion of diesel fuels. Many PAHs are known to be carcinogenic or mutagenic and important precursors to soot [see Figure 3-1], which has been linked to human morbidity and global warming [88-91]. Increasing energy demand and more stringent emission norms have spurred research into various new technologies that reduce PAH emissions. Despite the attention that these PAHs have
attracted, some questions related to their formation remain unanswered, i.e. what are the key reactions responsible for the growth of PAHs and what are the main PAH precursors. Combustion researchers have developed extensive kinetic models that capture most of the underlying chemistry but, despite their success for predicting auto-ignition and flames speeds, the success rates of the current models drops sharply in the prediction of aromatics and soot particles. In this work we focus on the development of a detailed model that is able to predict the formation of naphthalene and indene from cyclopentadiene (CPD). The general applicability of the model is illustrated for a broad set of experimental data.

In order to obtain bond dissociation energies, the decomposition of CPD under pyrolytic conditions was studied by Szwarc [92]. Besides resonance stabilized cyclopentadienyl (CPDyl) radicals, the author found a whole decomposition spectra containing H2, CH4, C2 hydrocarbons and various aromatics. It was only many years later that the questions raised by this experiment could be answered when scientist started unraveling the reaction mechanism leadings to the formation of the first aromatic ring, i.e. benzene [93-95]. Miller and Melius proposed a mechanism involving the recombination of two propargyl radicals (C3H) [94]. This mechanism has proven to account for a large amount of the benzene observed under flame conditions. However, in 1972 Spielman and Cramers proposed a potential role of cyclopentadienic intermediates in the formation of the initial aromatics [96]. The important role of CPD and its radical in the formation of aromatics was further validated by studying the pyrolysis and hydrogenolysis of phenol [97-99]. Melius et al. [100] were the first to come up with a detailed mechanism that could account for the formation of naphthalene, initiated by the self-recombination of two CPDyl radicals. The high-temperature reactions of CPD were studied in a shock-tube by Roy et al. [101, 102]. Those authors report rate coefficients for the C–H bond scission and the reaction between CPD and a H radical. More recently, Djokic et al. studied the thermal decomposition of CPD in a flow reactor under various dilutions [103]. Using online GC×GC-FID/(TOF-MS) the authors were able to identify and quantify minor species such as anthracene, phenanthrene and fluorene with a high level of accuracy.

Various pathways to naphthalene have also been theoretically studied, such as the reactions of (i) phenyl with vinylacetylene [104, 105], (ii) benzene with 1-benzyne [106], and (iii) the self-reaction of CPDyl radicals [100, 107]. A recent study shows that the formation
of indene can be initiated by addition of CPDyl to CPD [108], although other pathways (i.e. CPDyl with acetylene and benzyl with allene) have been documented [109]. Till this date not a single experiment could corroborate to what extent all these mechanisms contribute to the formation of PAHs and detailed elementary-step mechanisms are still lacking. Moreover, the complexity of the components involved and the huge variety of reactions that PAHs can undergo make this problem almost impossible to tackle without the assistance of advanced computer algorithms. Automated kinetic model generators, such as the Reaction Mechanism Generator (RMG) offer a helpful tool to study these complex systems [110].

Figure 3-1: Illustration of the growth of soot particles from smaller molecules.

3.2 Pyrolysis experimental procedure

The pyrolysis experiments described here were conducted by Marco Djokic at the Laboratory for Chemical Technology (LCT), University of Ghent. The bench scale set-up used for the current study has been described in detail in previous papers [103, 111]. It consists of three main sections: a feed section, reactor section and analysis section. Prior to the pyrolysis dicyclopentadiene (Sigma Aldrich 99+% purity) is heated to liquid form (307 K) and fed to an evaporator kept at 473 K. This is 20 K above the boiling point of dicyclopentadiene and sufficient to convert all dicyclopentadiene to cyclopentadiene as shown by Kim et al. [112]. The co-reactant ethene is mixed with N₂ and heated to the same temperature. Both the evaporator and subsequent mixer are electrically heated and filled
with quartz beads, assuring a constant feed and uniform mixing. For the experiments presented in this work a 1:1 molar ratio of CPD to ethene was used. The dilution was set to 1 mol CPD / 10 mol N₂, while the temperature was varied between 873 to 1163 K. Flow rates were chosen in order to obtain CPD conversions ranging from a few percent up to 96%, which corresponds with a residence time between 300 to 400 ms.

A product analysis is obtained using two gas chromatographs: (a) a refinery gas analyzer (RGA) and (b) a GC x GC equipped with both a flame ionization detector (FID) and time of flight mass-spectrometer (TOF-MS). The latter allows both qualitative and quantitative analysis of the entire product stream. The RGA detects all permanent gases such as N₂ and H₂, but also helps with an additional analysis of the C₅-C₄ cut. Response factors of all permanent gasses (H₂, CH₄) and light hydrocarbons (C₁-C₄) were determined by means of a gaseous calibration mixture (Air Liquide, Belgium). The response factors of all C₅+ hydrocarbons were estimated using the carbon number concept, relative to methane. For each studied temperature at least two repetitions were performed in order to calculate the experimental error, which was less than 10% standard deviation, with naphthalene (7% standard deviation) being the highest. All component weight fractions were normalized to 100 wt% in order to enable straightforward interpretations of the results, as well as comparisons with the modeling results. Table 3-1 gives the summary of the operating conditions and the yield of major products observed during the experiment. It was expected that the addition of ethene as a co-reactant would lead to an increase in the yields of C₇ products, however the net observed yield of C₇H₁₀ isomers was less than 0.3 wt%, and maximum yield of toluene was less than 0.9 wt% at the highest temperature.
Table 3-1: Summary of the measured product yields at the reactor outlet, for 1.7 atm and a dilution of 1 mol CPD/1 mol ethene/10 mol N₂.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>873</th>
<th>973</th>
<th>1023</th>
<th>1073</th>
<th>1123</th>
<th>1163</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CPD flow rate (g/h)</td>
<td>49</td>
<td>49</td>
<td>49</td>
<td>49</td>
<td>49</td>
<td>49</td>
</tr>
<tr>
<td>Ethene flow rate (g/h)</td>
<td>21</td>
<td>21</td>
<td>21</td>
<td>21</td>
<td>21</td>
<td>21</td>
</tr>
<tr>
<td>N₂ flow rate (g/h)</td>
<td>206</td>
<td>206</td>
<td>206</td>
<td>206</td>
<td>206</td>
<td>206</td>
</tr>
<tr>
<td>CPD Conversion (%)</td>
<td>1.2</td>
<td>5.0</td>
<td>15.5</td>
<td>39.5</td>
<td>81.8</td>
<td>95.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Yield (wt%)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Permanent gases</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>0.00</td>
<td>0.02</td>
<td>0.09</td>
<td>0.20</td>
<td>0.78</td>
<td>1.19</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.00</td>
<td>0.11</td>
<td>0.36</td>
<td>1.09</td>
<td>2.56</td>
<td>2.56</td>
</tr>
<tr>
<td><strong>Alkenes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethene</td>
<td>29.92</td>
<td>29.50</td>
<td>29.11</td>
<td>28.32</td>
<td>27.09</td>
<td>15.24</td>
</tr>
<tr>
<td>Cyclopentene</td>
<td>0.16</td>
<td>0.42</td>
<td>0.56</td>
<td>0.29</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Cyclopentadiene</td>
<td>69.16</td>
<td>66.47</td>
<td>59.15</td>
<td>42.35</td>
<td>12.65</td>
<td>2.87</td>
</tr>
<tr>
<td><strong>Aromatics</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>0.01</td>
<td>0.21</td>
<td>1.16</td>
<td>2.70</td>
<td>4.50</td>
<td>5.57</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.02</td>
<td>0.03</td>
<td>0.18</td>
<td>0.42</td>
<td>0.65</td>
<td>0.87</td>
</tr>
<tr>
<td>Styrene</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.16</td>
<td>0.04</td>
<td>0.18</td>
</tr>
<tr>
<td>Indene</td>
<td>0.03</td>
<td>0.56</td>
<td>2.04</td>
<td>4.69</td>
<td>5.09</td>
<td>2.56</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0.05</td>
<td>0.40</td>
<td>2.33</td>
<td>6.99</td>
<td>13.83</td>
<td>15.72</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>0.00</td>
<td>0.00</td>
<td>0.02</td>
<td>0.43</td>
<td>3.59</td>
<td>7.50</td>
</tr>
<tr>
<td>Anthracene</td>
<td>0.00</td>
<td>0.00</td>
<td>0.03</td>
<td>0.36</td>
<td>3.15</td>
<td>4.53</td>
</tr>
<tr>
<td>Total PAH</td>
<td>0.51</td>
<td>2.76</td>
<td>9.10</td>
<td>26.13</td>
<td>54.75</td>
<td>76.66</td>
</tr>
</tbody>
</table>
3.3 Reaction mechanism generation

The reaction mechanism is generated using the automatic reaction mechanism generator (RMG) [110]. Given the initial conditions, RMG will automatically generate all possible species and reactions from a database of reaction families and libraries. It then uses a flux-based algorithm to select the most important pathways to include in the model. This process is iterated until all the important species and reactions are found for a given user tolerance. Details describing the model generation in RMG can be found here [113].

3.3.1 Quantum calculation and statistical mechanics

Parameters requiring refinement are identified through sensitivity analysis of the RMG prediction and by comparison to experiment. These important parameters are not “fitted” to the data: rather the individual reactions are subjected to an increased level of theoretical analysis or direct experimental measurement. The resulting, more accurate parameters are then added to the RMG database of chemistry rate rules to improve future model predictions for both the current fuel molecule and other similar molecules.

Thermodynamics and kinetics of sensitive species and reactions were calculated using quantum chemistry calculations at the CBS-QB3 [114, 115] level using Gaussian 03 [116]. Bond additivity corrections were added to the calculated enthalpies of formation in order to improve the agreement between the CBS-QB3 calculated results and experimental enthalpies. These empirical corrections were taken from the work of Sabbe et al. [117] and amount to -0.89, 0.84, -1.78 and -3.97 kJ mol⁻¹ for a C–H, C–C, C=C and C≡C bond, respectively. The calculated CBS-QB3 enthalpy of formation of CPDyl was decreased by 4 kJ mol⁻¹, to match the experimental bond dissociation energy by 344 kJ mol⁻¹ [102]. Rate coefficients were calculated within the high pressure limit according to

\[ k_\infty(T) = \kappa(T) \frac{k_B T}{h} \frac{q_z}{\prod_{i=1}^{\nu} q_{\text{reactant}-i}} e^{\frac{\Delta E_0}{RT}} \]  

with \( k_\infty \) the high-pressure limit rate coefficient, \( k_B \) Boltzmann’s constant, \( T \) the temperature, \( h \) Planck’s constant, \( q \) the partition function per volume, \( \Delta E_0 \) the zero-point energy corrected energy barrier and \( R \) the universal gas constant. The tunneling coefficient \( \kappa(T) \) was calculated using the Eckart method [19]. Internal rotations of key components
were treated as 1D-HR hindered rotors according to the formalism described in [20]. Due to discrepancies between theoretical results reported in literature, in this work we opted to recalculate the C\textsubscript{10}H\textsubscript{10} (CPDyl + CPDyl) and C\textsubscript{10}H\textsubscript{11} (CPDyl + CPD) surface leading to the formation of naphthalene and indene + CH\textsubscript{3}, respectively. Barriers for the most sensitive reactions were calculated using RCCSD(T)-F12a method using a double zeta basis set (cc-vdz) on geometries obtained with the B3LYP/6-311G(2d,d,p) functional method. The RCCSD(T)-F12 calculations were performed using Molpro [118].

3.3.2 Master equation calculations

Potential energy surfaces for C\textsubscript{10}H\textsubscript{9}, C\textsubscript{10}H\textsubscript{10} (naphthalene+H+H) and C\textsubscript{10}H\textsubscript{11} (indene+CH\textsubscript{3}) were modeled using a one-dimensional master equation, with the rotational degree of freedom as active. Microcanonical rate coefficients were computed using the conventional RRKM theory [119-121] including Eckart tunneling [122]. The density of states was computed via inverse Laplace transform of the partition function using the method of steepest descents [123-125]. Collisions were modeled using the conventional exponential down expression with single parameter $\langle \Delta E_{\text{down}} \rangle$ for the average energy transferred in a collision. A temperature dependent formulation was used for the average downward energy transferred per collision,

$$
\langle \Delta E_{\text{down}} \rangle = \langle \Delta E_{\text{down}} \rangle_{300} \left( \frac{T}{300 \text{ K}} \right)^{n} \text{cm}^{-1}
$$

With $\langle \Delta E_{\text{down}} \rangle_{300} = 295$ cm\textsuperscript{-1}, and $n = 0.7$ for N\textsubscript{2}. These values were adopted based on azulene energy collision parameters [126]. The collision frequency was computed by assuming a Lennard-Jones potential between the bath gas and the species of interest. Lennard-Jones parameters were estimated by first estimating the critical temperature and pressure using a group additivity method devised by Joback [127] and then using the equations for a Lennard-Jones gas [128] implemented by Harper et al. in RMG [113]. Phenomenological rate coefficients were computed from the conventional master equation model using the modified strong collision approximation [129]. All of the master equation calculations were performed using the open source CANTHERM software package [130].
3.4 Results

3.4.1 Co-pyrolysis of cyclopentadiene and ethene

The aim of the experiments presented in this work is to study the effect of temperature on the CPD and ethene conversion and on the product distribution. By working under similar reaction conditions as Djokic et al. [103] for the pyrolysis of CPD, the effect of ethene on the product distribution can be studied. An overview of the conducted experiments is given in Table 3-1. Both the reaction conditions (reactor temperature, flow rates and corresponding conversion) and the measured yields of the most important products are presented.

The co-pyrolysis of CPD and ethene produces a very complex product spectrum with a strongly varying composition depending on the temperature. At 873 K only a small number of pyrolysis products can be detected, such as indene, naphthalene, benzene, and cyclopentene. In contrast to the data obtained at 873 K the reactor effluent at 1123 K is significantly more complex, containing on the order of a hundred different compounds, however only 10% of the ethene has reacted. At the most severe conditions, 96% of CPD is converted yielding almost 77 wt% of PAHs with a carbon number up to C_{21}. At 1163 K, roughly 50% of the ethene fed to the reactor reacted. In Table 3-2 the product yields at 1073 and 1123 K for pure CPD and the renormalized (ethene treated as a diluent) yields for co-pyrolysis of CPD and ethene are compared. For both data sets similar residence times are obtained, since the molar feed rate to the reactor is the same. At 1073 K the CPD conversion drops from 61.7% for the pure pyrolysis to 39.5% for the co-pyrolysis with ethene. The lower CPD conversion is predominantly caused by a dilution effect. Since the main decomposition channels of CPD are bimolecular in nature, i.e. addition/recombination reactions involving CPDyl radicals, the CPD conversion decreases with a higher dilution. Up to 1073 K, ethene hardly reacts with the CPD decomposition products. At 1123 K, similar conversions are obtained for both experiments (81.8 and 83.8 % respectively) despite the lower initial CPD concentration. This illustrates that at these higher temperatures ethene will start influencing the CPD decomposition. The main effects of adding ethene above 1073 K are a higher benzene yield while the indene and naphthalene yield decrease in favor of larger polycyclic aromatics.
Table 3-2: Comparison between experiments for the pyrolysis of CPD and co-pyrolysis of CPD and ethene. The ethene yield for the co-pyrolysis of CPD and ethene was omitted and the remaining product yields were renormalized.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>This work</th>
<th>Djokic et al.[103]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (K)</td>
<td>1073</td>
<td>1123</td>
</tr>
<tr>
<td>$F_{\text{CPD}}$ (g/h)</td>
<td>49</td>
<td>97</td>
</tr>
<tr>
<td>$F_{\text{Ethene}}$ (g/h)</td>
<td>21</td>
<td>0</td>
</tr>
<tr>
<td>$F_{\text{N}_2}$ (g/h)</td>
<td>206</td>
<td>191</td>
</tr>
<tr>
<td>CPD Conversion (%)</td>
<td>39.5</td>
<td>61.7</td>
</tr>
<tr>
<td>Ethene Conversion (%)</td>
<td>5.6</td>
<td>-</td>
</tr>
<tr>
<td>Yield (g product/ 100 g CPD in feed)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Permanent gases</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2$</td>
<td>0.28</td>
<td>0.82</td>
</tr>
<tr>
<td>$\text{CH}_4$</td>
<td>1.52</td>
<td>2.7</td>
</tr>
<tr>
<td>Alkenes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethene</td>
<td>-</td>
<td>0.7</td>
</tr>
<tr>
<td>Cyclopentene</td>
<td>0.40</td>
<td>0.59</td>
</tr>
<tr>
<td>Aromatics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>3.77</td>
<td>4.08</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.59</td>
<td>0.69</td>
</tr>
<tr>
<td>Styrene</td>
<td>0.22</td>
<td>0.72</td>
</tr>
<tr>
<td>Indene</td>
<td>6.54</td>
<td>10.68</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>9.75</td>
<td>17.31</td>
</tr>
<tr>
<td>Total PAHs</td>
<td>36.45</td>
<td>47.1</td>
</tr>
</tbody>
</table>

3.4.2 Reactions paths towards indene and naphthalene

The dominant reaction channel leading to the formation of naphthalene is presented in Figure 3-2 and Figure 3-3. When two CPDyl radicals recombine, six bicyclopentadienyl isomers (1a to 1f) can be formed. These isomers can easily interconvert due to the relatively low barriers for the sigmatropic H shifts in these components. The CBS-QB3 method predicts barriers that are in the range of 90-120 kJ mol$^{-1}$. This agrees well with other values reported in literature [131]. This easy scrambling of hydrogen atoms is typical for cyclic conjugated systems, such as cyclopentadiene and cycloheptatriene. The isomers with co-
planar conjugated rings (1c, 1d, and 1e) are significantly more stable than other isomers. The conjugated system will weaken any adjacent C–H bonds and 1c and 1d can hence easily lose a hydrogen atom to form C_{10}H_{9} radicals, i.e. 2a to 2c. The C–H bond dissociation energies (BDE) of 1a to 1f range between 300 and 330 kJ mol\(^{-1}\) much weaker than typical C–H bond. The loss of a hydrogen atom can occur by hydrogen abstraction reactions or, at lower pressures, chemically activated C–H bond scission reactions. The energetically most favorable exit channel from the C_{10}H_{10} surface to the C_{10}H_{9}+H surface involves the formation of 2b. However, H atom scrambling in species 2b is fast and leads to the formation of its isomers 2a and 2c [see Figure 3-3]. Species 2a can undergo a 1,3-cycloaddition leading to species 4. β-scission of this component leads to the spirane-type species 5. This component then reacts via a 1,3-cycloaddition and β-scission to species 7, which yields naphthalene (9) by β-scission of a C–H bond. The results presented in Figure 3-2 and Figure 3-3 are in good agreement with Kislov and Mebel [132] who studied both surfaces at the G3(MP2,CC)/B3LYP level of theory. Since those authors did not include all the sigmatropic hydrogen shifts for the C_{10}H_{10} surface, models using their rates tend to under predict the build-up of C_{10}H_{10} isomers and the amount of naphthalene that forms through this path via H abstraction from C_{10}H_{10} species.
Figure 3.2: CBS-QB3 enthalpy diagram $H(0 \text{ K})$ (kJ mol$^{-1}$) for the $\text{C}_{10}\text{H}_{10}$ surface initiated by the recombination of two CPDyl radicals. All enthalpies are relative to the adduct $1a$. The lowest entrance and exit channel are indicated in green. At low pressures, the chemically-activated reactions $\text{C}_{5}\text{H}_{5} + \text{C}_{5}\text{H}_{5}$ → $\text{C}_{10}\text{H}_{6} + \text{H}$ is significant. However, in many systems $\text{C}_{10}\text{H}_{9} + \text{R} \rightarrow \text{C}_{10}\text{H}_{9} + \text{RH}$ is the dominant consumption pathway. The enthalpy does not include BAC corrections.

Figure 3.3: CBS-QB3 enthalpy diagram $H(0 \text{ K})$ (kJ mol$^{-1}$) on the $\text{C}_{16}\text{H}_{9}$ surface leading to the formation of naphthalene. All enthalpies are relative to component $2b$ which represents the dominant entrance channel. The barrier for the rate limiting step is indicated in red and was calculated using CCSD(T)-F12/cc-pVDZ. The lowest entrance and exit channel are indicated in green. The enthalpy does not include BAC corrections.
The main reaction path from CPD leading to the formation of indene is shown in Figure 3-4. CPDyl adds to CPD forming species 10a, which undergoes a fast H shift to 10b. β-scission in this component gives 11b which mainly decomposes by an intra-molecular hydrogen abstraction reaction to 12. The 1,5-addition in this component leads to the formation of 13a which can undergo a hydrogen transfer and β-scission leading to indene (14b). An alternative exit channel on the C₉H₇ surface leads to the formation of benzene and butadienyl. However, the bottleneck reaction for this channel (15 → 16) has a transition state whose energy is 30 kJ mol⁻¹ higher than any other reaction leading to the formation of indene. Based on these results we do not expect any significant amounts of benzene and butadiene to be formed through this channel, unless at elevated temperatures. The CPD + CPDyl surface has also been studied previously by Cavallotti et al.[108]. Despite the good agreement with their energy surface, the channel specific rate constants (at CCSD(T)/CBS level of theory and RRKM/ME) predicted by those authors are approximately one order of magnitude larger than those calculated in this present work. In agreement with Cavallotti et al.[108] we found that a pathway to naphthalene initiated by the addition of CPDyl to CPD is too highly activated to contribute to the formation of naphthalene.

![Figure 3-4: CBS-QB3 enthalpy diagram \(H(0 \text{ K})\) (kJ mol⁻¹) on the C₉H₇ surface leading to the formation of indene. All enthalpies are relative to the entrance channel CPD + CPDyl. The barrier for the rate limiting step is indicated in red and was calculated using CCSD(T)-F12/cc-pVDZ. The enthalpy does not include BAC corrections.](attachment:image)
3.4.3 Rate of production and sensitivity analysis

A rate of production analysis using high-pressure limit rate coefficients on the C_{10}H_{10} surface (Figure 3-2) is shown in Figure 3-6. This ROP analysis shows that 94.3% of the incoming flux reacts in some way by sigmatropic hydrogen shifts. At the studied conditions only 3.7% of the of the reactive flux will leave the C_{10}H_{10} surface by forming product 2a, which is the exit channel with the highest energy. Despite 2b being more stable than 2c, both exit channels contribute almost equally to the observed flux towards the C_{10}H_{9} surface. The loss of a hydrogen atom can occur by both C–H bond scission reactions and hydrogen abstraction reactions. Under the studied conditions, approximately 90% of the flux towards the C_{10}H_{9} surface is caused by hydrogen abstraction reactions. Pressure will hence have a large effect on the formation of naphthalene as at low pressures the contribution of bimolecular hydrogen abstraction reactions will diminish, hampering the leap to the C_{10}H_{9} surface. The rate coefficients for hydrogen abstraction reactions from species 1a to 1f (see Figure 3-2) were obtained from group additivity models, while the rate coefficients for C–H scission in 1a to 1f were estimated by RMG from reactions involving structurally similar species. Most of the current models that account for the formation of naphthalene from CPDyl generally assume the following one step reaction:

\[ \cdot + \cdot \rightarrow \text{Product} + 2 \cdot \]

Figure 3-5: Reaction used in most literature models to predict the rate of naphthalene formation.

Murakami et al. [133] studied this reaction behind reflected shocks using atomic resonance absorption spectroscopy and reported a rate coefficient of \( 3.3 \times 10^{17} \exp(-135 \text{ kJ mol}^{-1} / R T) \text{ cm}^{3} \text{ mol}^{-1} \text{ s}^{-1} \). Those authors however assumed a very simple reaction scheme and, for example, did not account for hydrogen abstraction reactions, which are important in order to grasp the effect of pressure on the naphthalene yield. As a results, the reported rate coefficient was found to lead to an excess of naphthalene in many related systems [134] which caused other authors to question the CPDyl + CPDyl route to naphthalene [135]. In order to validate this pathway, an RRKM analysis was performed on the C_{10}H_{10} surface, which is presented in Figure 3-2. The resulting rate coefficients at 1500 K can be found in
Figure 3-7 as function of the pressure. It is seen that at high pressures ($P > 10$ bar) the recombination reaction of the two CPDyl radicals results in the formation of 1a and well-skipping reactions are negligible. Around 3 bar and below, well-skipping reactions become important and 1c becomes the dominant product. This is also the most stable species on the C$_{10}$H$_{10}$ surface. This shows that, at low pressures, the hot intermediate formed after recombination of two CPDyl radicals will only slowly stabilize, allowing the weakly bound hydrogen atoms to freely move around in the molecule. Well-skipping reactions to the C$_{10}$H$_{9}$ surface were found to be minor channels for $P = 10^{-3}$ to 10 bar and at 1500 K contribute less than 1%.

![Chemical reaction diagram]

**Figure 3-6:** Rate of production analysis on the C$_{10}$H$_{10}$ surface presented in Figure 2 for 30% CPD conversion at 1123 K, 1.7 bar and a dilution of 5 mol N$_2$/mol CPD. All rates are normalized by the rate obtained for the recombination of two CPDyl radicals, which is the entrance channel for this surface.
Figure 3-7: Computed RRKM rate coefficients for the recombination of two CPDyl radicals to form various products at 1500K in N₂. The corresponding PES is shown in Figure 3-2.

The five most sensitive reactions for the formation of indene and naphthalene are shown in Figure 3-8.

Figure 3-8: Normalized sensitivity coefficients for the pyrolysis of CPD (1.7 bar, 5 mol N₂/ mol CPD, 1000 K). The top five reactions are shown for (a) indene and (b) naphthalene and that at 10% (darker) and 30% (lighter) CPD conversion.
The formation of naphthalene is very sensitive to the rate coefficient for reaction 4 → 5 (the rate-limiting step in Figure 3·3, and the second reaction Figure 3·8 (b)). The barrier for this reaction was calculated at the CCSD(T)-F12a/vdz level of theory. A double zeta basis set had to be used due to computational limitations. In order to get an estimate of the error introduced by the rather limited basis set, we studied the influence of the basis set on a similar system (Figure 3·9) and found that shifting from a double to a triple zeta basis set (i.e. CCSD(T)-F12a/cc-pVDZ to CCSD(T)-F12a/cc-pVTZ) only alters the calculated barrier by 0.5 kJ mol⁻¹. We therefore expect the CCSD(T)-F12 calculations are converged with respect to the basis set to within 4 kJ mol⁻¹. However, we note that there are other sources of uncertainty in the rate coefficient calculation including vibrational anharmonicity, imperfect geometries and harmonic frequencies.

The indene yield is very sensitive to the rate coefficient for the β-scission reaction 10b → 11b. Just as in the case for naphthalene the barrier for this reaction was obtained using CCSD(T)-F12a/vdz. As expected, both products are sensitive to the rate of cyclopentadiene dissociation which is the main radical initiation reaction in this system: for that important rate coefficient we use the value suggested by Roy et al.[102] As the entrance channels towards indene and naphthalene are respectively first and second order in the CPDyl concentration, a faster C–H scission to form CPDyl will have a more pronounced effect on the naphthalene concentration than on indene. This is reflected in the sensitivity coefficients shown in Figure 3·8.

![Figure 3·9: Reaction selected to study the influence of the basis set for the reaction 4 → 5 (see Figure 3·3).](image)

A rate of production analysis at 1123 K for the main reaction paths leading to the formation of benzene is shown in Figure 8. In this figure the various reaction paths leading to benzene are studied both for the CPD pyrolysis and co-pyrolysis of CPD with ethene. At 1123 K, the net production rate of benzene is a factor 3.4 higher for the co-pyrolysis with ethene. Figure 3·10 shows that during the pyrolysis of CPD, most benzene (88.8%) is formed by β-scission of a C–H bond in 1,3-cyclohexadienyl. 1,3-cyclohexadienyl is
predominantly formed by various isomerization reactions on a C₆H₇ surface involving various unsaturated species having a 5-membered ring.

**Figure 3-10**: Rate of production analysis for the formation of benzene at 1123 K, 1.7 bar and a residence time of 0.22 s. Normal values correspond with a dilution of 5 mol N₂/mol CPD. Bold values correspond with a dilution of 10 mol N₂/mol CPD and 1 mol ethene/mol CPD. All rates are normalized by the net production rate of benzene.

11.2% of the benzene is formed by β-scission in species 16 (see Figure 3-4). This channel however becomes negligible during the co-pyrolysis with ethene. Ethene increases the formation of benzene through the C₆H₇ surface due to (a) a higher fulvene concentration and (b) recombination reactions between ethyl and CPDyl leading to products that can easily dissociate to a C₆H₇ species and CH₃. Fulvene is mainly formed through the following reaction sequence, initiated by addition of CPDyl to ethylene (see Figure 3-11):
3.4.4 Model predictions and validation

The generated model is first validated by comparison with recent experimental data of Djokic et al. [103]. In that work, the pyrolysis of CPD was studied using the same laminar flow reactor as used throughout this work. This data set distinguishes itself from other data sets presented in literature by the higher dicyclopentadiene purity used and the lower dilution, which enhances the detectability of the major products. In Figure 3-12, experimental and simulated concentration profiles are shown. It can be seen that the model is ~ 30 K slower in predicting the CPD conversion which in turn is also reflected in profiles of other species like indene and naphthalene. The Djokic model on the other hand slightly overpredicts the conversion of CPD. Sensitivity analysis on the CPD conversion shows that the thermochemistry of CPD and CPDyl radical significantly affects the conversion. Given the uncertainty in the thermochemistry of CPD and CPDyl the level of agreement between the measured conversion and the current model predictions are considered reasonable. The model modestly underestimates the methane and benzene yields even after allowing for the ~30 K temperature shift. It is observed that the indene yield reaches a plateau around 1100 K. This is caused by the temperature dependence of the rate coefficients. At higher temperatures, more CPDyl radicals are formed and the second-order reaction path to naphthalene dominates the CPD consumption, reducing the yield of indene. In the current model the naphthalene yield continues to increase with temperature, but experimentally naphthalene yield plateaus and instead larger PAHs are formed. Most of these larger PAH are not included in the present kinetic model, so naphthalene is an accumulating final product in the model. Future work, will address the issue of growth to higher PAHs beyond naphthalene.
Figure 3-12: Model predictions of the main reaction products during the pyrolysis of CPD (1.7 bar, dilution of 5 mol N₂/mol CPD, \( F_{0,CPD} = 27 \) mg/s). Current model predictions are indicated by full lines, prediction made with the model presented in ref. [103] are indicated with dashed lines.

In Figure 3-13 the indene and naphthalene yields are shown for the low and high dilution experiments presented in [103]. It can be seen that the model qualitatively reproduces the dependence of the yield on the dilution. In particular at lower conversions the agreement is very good. The model overpredicts the naphthalene and indene yield at higher conversion as it does not include reactions that account for the conversion of indene and naphthalene to larger PAHs. As observed experimentally, the selectivity to indene increases with a lower dilution while the opposite is true for naphthalene. The reason behind this is that at higher dilutions radical recombination reactions are hampered, leading to a larger \([\text{CPDyl}]/[\text{CPD}]\) ratio. This will predominately enhance the formation of naphthalene, at the expense of indene.
Figure 3-13: Predicted indene (left) and naphthalene yield (right) in weight percentages as function of the CPD conversion (1.7 bar). Dashed lines and hollow data points correspond with a dilution of 5 mol N₂/mol CPD (F₀,CPD = 27 mg/s), full lines and filled data points correspond with a dilution of 24 mol N₂/mol CPD (F₀,CPD = 6 mg/s). The trends are due to variations in steady-state [CPDyl]/[CPD] with respect to the feed concentration.
In Figure 3-14 the model predictions are compared with the experimental data obtained for the co-pyrolysis of CPD and ethene. As observed for the pyrolysis of CPD (see Figure 3-12), CPD starts reacting around 950 K while the co-product ethene is unreactive up to 1073 K. Up to this temperature the weight fraction of ethene in the product stream remains approximately 30 wt%. The model predicts that from 1073 K on, ethene will react with CPDyl and form fulvene and CH₃. The fulvene formed will react with the hydrogen radicals to form benzene. The rate coefficients for these reactions were obtained from
Sharma et al. [95]. The model overpredicts 1,3-butadiene concentration at high temperatures. Butadiene is primarily formed by recombination of vinyl radicals. In reality the vinyl radicals react with indene and naphthalene to form higher polycyclic aromatics, however since the RMG mechanism was restricted to C_{11} species during its generation reactions leading to heavier species were omitted from the model.

The model by Djokic et al. [103] that was able to reproduce the pyrolysis of CPD does not perform well for the CPD + ethene data. It overestimates the conversion at lower temperatures and hence overpredicts the indene, benzene and naphthalene yield. We suspect that this is mainly caused by the fact that the network of Djokic et al. contains some non-elementary reactions that are not well understood and were assigned incorrect rate coefficients, e.g. the recombination of two CPDyl radicals leading to naphthalene and two hydrogen radicals (Figure 3-5). The rate coefficient for this reaction was estimated [103] to be $2.0 \times 10^{12} \exp(-25 \text{kJ mol}^{-1}/R\bar{T})$ (cm$^3$/mole-s) and –at low temperatures– gives rise to excessive amounts of hydrogen radicals, which speeds up the pyrolysis of CPD and all the chemistry.

This shows that the newly identified reaction sequence for naphthalene formation has very different kinetic consequences than the simple single-step reaction used in many models. In the single-step model, two unreactive cyclopentadienyl radicals are being converted to two very reactive H atoms, and the number of radicals is unchanged, so overall this reaction accelerates the chemistry. But in the multistep scheme we propose, two C$_5$H$_5$ radicals plus another radical R. are being consumed to produce a single H atom: net 2 radicals are consumed every time a naphthalene molecule formed, so this process slows the overall chemistry. The present experiment on a mixture of cyclopentadiene and ethene clarifies this important difference: models built on the single-step reaction predict a lot of H atom formation even at relatively low temperature, and some of these H atoms will react with ethene, ultimately forming a lot of benzene at low temperature. But with the multi-step reaction scheme proposed here based on detailed quantum chemistry calculations, there is not much reactivity at low temperature, relatively few H atoms are released, the ethene remains rather inert, and less benzene is predicted to be formed. This is in much better concord with the experimental result.
3.5 Conclusions

This chapter presents a study that aims at better understanding the formation of the first aromatics in various pyrolytic processes. The co-pyrolysis of CPD and ethene was studied both experimentally and theoretically. The experimental data shows that CPD mainly decomposes to indene and naphthalene in agreement with other studies [103, 112, 136]. CPD starts decomposing around 950 K, while ethene is mostly unreactive up to 1073 K. Compared to the pure pyrolysis of CPD, ethene tends to (a) increase the benzene yields and (b) lower the naphthalene and indene yields in favor of larger polycyclic aromatic hydrocarbons.

The theoretical results show that the formation of indene and naphthalene, observed during the pyrolysis and combustion of various hydrocarbons, can be explained by reaction paths involving CPD or CPDyl. The formation of indene is primarily initiated by the addition of CPD to CPDyl and follows a complicated series of isomerizations. The rate-limiting step is the opening of a 5-membered ring in C_{10}H_{11}. The formed product later closes to form the fused 6-membered ring structure, and ultimately a methyl group is lost by beta-scission to form indene (C_9H_8). Naphthalene (C_{10}H_8) is formed by recombination of two cyclopentadienyl radicals. However, in the temperature and pressure range of this study the important reaction sequence forming naphthalene is not the simple single-step C_5H_5 + C_5H_5 -> C_{10}H_8 + H + H, but instead the following sequence:

\[
\begin{align*}
\text{(1)} & \quad \overset{\cdot}{\text{C}}_5\text{H}_5 + \overset{\cdot}{\text{C}}_5\text{H}_5 & \leftrightarrow & \overset{\cdot}{\text{C}}_{10}\text{H}_{15} \\
\text{(2)} & \quad \overset{\cdot}{\text{C}}_5\text{H}_5 + R & \leftrightarrow & \overset{\cdot}{\text{C}}_5\text{H}_5 + \overset{\cdot}{\text{C}}_5\text{H}_5 + RH \\
\text{(3)} & \quad \overset{\cdot}{\text{C}}_5\text{H}_5 + \overset{\cdot}{\text{C}}_5\text{H}_5 & \leftrightarrow & \overset{\cdot}{\text{C}}_{10}\text{H}_{15} + H' \\
\text{(Net)} & \quad \overset{\cdot}{\text{C}}_5\text{H}_5 + \overset{\cdot}{\text{C}}_5\text{H}_5 + R & \leftrightarrow & \overset{\cdot}{\text{C}}_{10}\text{H}_{15} + H' + RH
\end{align*}
\]

At the conditions studied here, the third step, isomerization of a C_{10}H_9 species with two separated 5-membered rings into a form with fused six-membered rings is rate-limiting. In general our results are in concord with calculations by Kislov and Mebel [132]. However, we
identified additional deeper wells on the C₁₀H₁₀ potential energy surface, that shift the equilibrium of step 1 more to the right and allow the C₁₀H₁₀ species to live longer than predicted from the truncated potential energy surface computed by Kislov and Mebel [132]. This longer lifetime and higher concentration of C₁₀H₁₀ makes the second step relatively fast and leads to a higher net production rate of naphthalene.

Using RMG, an automated reaction network generator, a kinetic model could be developed that captures this chemistry and allows us to make predictions over a wide range of reaction conditions. The model succeeds to fairly accurately predict the conversion of CPD and ethene, and the formation of the main products: benzene, methane, H₂, indene and naphthalene up to 1100 K. The minor product cyclopentene is underpredicted by an order of magnitude. The model also does not include species heavier than C₁₁, so it does not capture the growth of PAHs which become major product above ~1100 K. In concord with the experimental data, the model indicates that the naphthalene/indene ratio increases with dilution due to changes in [CPDyl]/[CPD]. The benzene yield observed during the co-pyrolysis of CPD and ethene is partly due to reactions involving fulvene. The importance of having a single-event model that captures all underlying chemistry is highlighted in this work: older networks that use estimated and fitted parameters that work well for literature datasets but fail to reproduce the new data. The importance of having a single-event model that captures all underlying chemistry is highlighted in this work. Under the studied reaction conditions, we show that the naphthalene yield cannot be modeled by a simple single-step mechanism C₅H₅ + C₅H₅ → C₁₀H₈ + H + H [103, 133]. Only when all intermediate C₁₀H₁₀ and C₁₀H₉ species are accurately accounted for, the experimentally observed naphthalene yield can be qualitatively reproduced.

It is concluded that the formation of the first PAHs is a complex process that involves many intermediates and reactions. The growth to larger PAHs, such as anthracene and phenanthrene, would require even more intermediates and reactions and might prove too complex to study manually. Automated network generators, such as RMG, are hence indispensable in order to unravel the important steps in the growth of PAHs. Future work should try to address the growth to tri- and tetracyclic PAHs.
Chapter 4

**iso-Butanol pyrolysis and combustion**

The Combustion Energy Frontier Research Center (CEFRC)[43] is a DOE established center for developing detailed understanding for the next-generation fuels. The CEFRC consists of 15 principal investigators from 8 academic institutes in the United States. One of their initial thrust was to develop comprehensive understanding of alcoholic fuels. The efforts at MIT were directed at developing detailed kinetic models and validating them against the large amount of experimental data generated by the other groups. This chapter is a summary of the *iso*-butanol kinetic model developed as part of that effort. A major part of this chapter has been adapted from references [137, 138].

4.1 Introduction

The demand for a clean, renewable biofuel increases as new benchmarks are legislated amid increased pressure to reduce the world’s dependence on fossil fuels for energy and chemicals. Biobutanol is in pole position to become a major game changer in the 21st century [139]. It is considered an advanced biofuel - superior to ethanol in almost every way - and convertible to jet fuel and biogasoline [140]. Not only are the fuel properties of butanol better than ethanol, butanol is also considered a ‘greener’ fuel than ethanol [141]. One of the remaining unanswered questions is which of the four butanol isomers (*n*-butanol, *sec*-butanol, *iso*-butanol, and *tert*-butanol) should be favored in the coming decades.
Although today the butanol isomers are largely produced from petrochemicals, all isomers, apart from tertiary butanol, can be developed independently in renewable forms [142] to be marketed as biobutanol at competitive prices to oil based fuels. \(n\text{-}\)Butanol was initially considered to be the logical favorite to replace ethanol because of its mature production technology via the well-known acetone-butanol-ethanol process by anaerobic fermentation of sugar substrates using solventogenic clostridia [143]. However, this technology is handicapped in competitiveness by high energy cost due to low concentrations of butanol produced and significant volumes of water processed, even with new clostridia strains [140]. That is why in recent years \(iso\text{-}\)butanol has gradually become favored by industry. One of the main advantages of the \(iso\text{-}\)butanol technology is that it can be produced at adapted ethanol plants from corn and other grains or sugarcane and even from cellulose, as demonstrated by among others Gevo Inc.[100, 144]. With diminishing subsidies on conventional fermentation ethanol, producers looking for higher margin derivatives are potential candidates for switching to \(iso\text{-}\)butanol. Looking at the fuel properties of both isomers the differences are relatively small with the exception of \(iso\text{-}\)butanol having a higher octane rating (motor octane number of 89) compared to \(n\text{-}\)butanol (motor octane number of 78), this gives it a slightly higher value as gasoline blend stock.

The strong interest from industry in butanol as a potential replacement for ethanol in combustion engines has resulted in many recent combustion studies of the different butanol isomers. Only a brief summary, focusing on \(iso\text{-}\)butanol, is presented in this work. \(iso\text{-}\)Butanol has received considerable attention from the engine community with studies performed in spark-ignition engines [145, 146] and in compression–ignition engines [147, 148]. These studies are essential for assessing the feasibility and performance of \(iso\text{-}\)butanol in practical systems and are complementary with more fundamental combustion science research. The latter include experimental studies on premixed laminar flame propagation [149, 150], premixed laminar flame structure [151], non-premixed laminar diffusion flame structure [150, 152, 153], shock tube and rapid compression machine ignition delay [154-156], spray chamber combustion [61], and jet-stirred reactor oxidation chemistry[157].

All this recent experimental work has certainly helped the development and validation of detailed chemical kinetic models for \(iso\text{-}\)butanol, such as those presented by [150, 153, 158-160]. These fundamental kinetic models have the ambition to be predictive in
nature with the ultimate goal of advancing design and optimization of practical engine systems through coupling with computational fluid dynamic (CFD) models. However, despite the recent leaps in butanol kinetic modeling, a comprehensive model for iso-butanol pyrolysis and combustion - valid at the temperature and pressure ranges found in practical engines - is still lacking. Moreover the experimental dataset for iso-butanol is far from complete. For example, although pyrolysis reactions are an essential part of any combustion mechanism [161], prior to this work accurate pyrolysis data for iso-butanol have not been available. These pyrolysis reactions play an important role in areas of fuel rich conditions in internal combustion engines, e.g. in case of incomplete mixing.

The goal of the present study is to develop a detailed kinetic mechanism for iso-butanol pyrolysis and combustion building on the mechanisms developed for other isomers in earlier work [113, 162]. This study differentiates itself from other iso-butanol chemical kinetic model studies by consistently including pressure dependent kinetics, with most rate coefficients from high-pressure limit rate rules built into the open source mechanism generator RMG [110]. Most rate rules originate from literature but for the most important reactions in our system new rate rules have been determined from quantum calculations. The mechanism is tested against a large number of new and recently published data including - pyrolysis product profiles in plug flow reactor, jet-stirred reactor mole fraction profiles, opposed flow diffusion flame mole fraction profiles, laminar flame speeds at different pressures and autoignition delays in rapid-compression machine and high-pressure shock tube experiments. Furthermore, this study attempts to guide future iso-butanol pyrolysis and combustion chemistry research by elucidating those reactions that are the most significant and uncertain for the experimental conditions that have been studied.

4.2 Pyrolysis experiment setup

The experimental setup has been described in detail elsewhere. [111, 113, 162, 163] and therefore only a brief description based Djokic et al. [111] and Pyl et al. [163] will be given here. It consists of three parts: the feed section, the furnace/reactor section and the analysis section. Iso-Butanol (Acros Organics, Belgium, purity 99.5%+, used as obtained) is pumped towards an evaporator kept at 523 K using a peristaltic pump (Heidolph, Germany). The mass flow rate of the feed is calibrated using an electronic balance. The
diluent, N₂ (Air Liquide, Belgium, purity 99.999%), is heated separately to the same temperature. Both the evaporators/heaters and the subsequent mixer are electrically heated and filled with quartz beads, enabling a smooth evaporation of the feed and uniform mixing of the feed and diluent. The flow rate of the latter is controlled by a coriolis mass flow controller (Bronkhorst, The Netherlands). Typical experimental conditions for low and high conversion and diluted and undiluted iso-butanol are provided in Table 4-1. The overall residence time varies between 1.1 s and 0.57 s. The residence time between the diluted and undiluted conditions at higher temperatures is different by ~0.18 s because of a difference in molar flow rate due to the decomposition of iso-butanol into predominantly species with lower molecular weight. Due to this increase in residence time, the conversion for the diluted experiments is higher for an identical temperature profile in the plug flow reactor.

Table 4-1: Overview of experimental conditions for the pyrolysis of iso-butanol in the bench scale set-up.

<table>
<thead>
<tr>
<th></th>
<th>Diluted</th>
<th>Undiluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_{inl} (K)</td>
<td>550 – 660</td>
<td>550 – 660</td>
</tr>
<tr>
<td>T_{avg} (K)</td>
<td>913 – 1093</td>
<td>913 – 1093</td>
</tr>
<tr>
<td>Outlet pressure (10⁵ Pa)</td>
<td>1.72</td>
<td>1.72</td>
</tr>
<tr>
<td>Hydrocarbon flow rate (g s⁻¹)</td>
<td>1.666 x10⁻²</td>
<td>6.666 x10⁻²</td>
</tr>
<tr>
<td>Nitrogen flow rate (g s⁻¹)</td>
<td>1.889 x10⁻²</td>
<td>0</td>
</tr>
<tr>
<td>Conversion (%)</td>
<td>15 – 98</td>
<td>15 – 94</td>
</tr>
</tbody>
</table>

The reactor is a 1.475 m long, 6 mm internal diameter tube, made of Incoloy 800HT (Ni, 30-35; Cr, 19-23; and Fe, >39.5 wt %). Prior to its use in these experiments, the reactor tube was passivated to suppress potential catalytic activity of the wall. Control experiments with a second reactor having a two times larger surface to volume ratio showed that the influence of the wall on conversion and product selectivity was negligible. The reactor is placed vertically in an electrically heated rectangular furnace. In all experiments discussed
in this work, the reactor is operated nearly isothermally, i.e. with a steep temperature increase at the inlet and a steep temperature drop at the reactor outlet. Eight thermocouples along the reactor monitor the process gas temperature at different positions. The pressure in the reactor is controlled by a downstream back pressure regulator. Two manometers, positioned at the inlet and outlet of the reactor, record the coil inlet pressure (CIP) and the coil outlet pressure (COP), respectively. The pressure drop over the reactor was found to be negligible. During a typical 6-hour operation the pressure drop did not increase noticeably since the amount of coke deposited on the reactor inner wall was found to be marginal. Even under the most severe conditions ($T > 1073$ K) no significant pressure drop was observed, with the pressure remaining constant in the coil at 1.7 bar. No entrained coke particles were collected.

The analysis section of the pyrolysis setup is similar to the one discussed previously [164, 165]. More than one hundred different components are observed and identified using the on-line comprehensive 2D gas chromatograph (GC×GC) equipped with a flame ionization detector (FID) and a Time-of-Flight Mass Spectrometer (TOF-MS). Figure 4-1 shows part of the GC×GC chromatogram during one of the iso-butanol experiments. The settings and the characteristics of the GC×GC can be found elsewhere [163]. The increased separation power of GC×GC makes it very suitable for analyzing complex effluents containing oxygenates. The 1st dimension separation is based on volatility, the 2nd on polarity. Major products formed during the cracking of iso-butanol include hydrogen, CO, methane, formaldehyde, ethene, propene, iso-butene, propenal, butene-ol and ethanol. Minor products, such as methanol, iso-butanal, ketene, acetaldehyde, acetone, 1 and 2-butenes, and 1,3-butadiene are also found in the effluent. At higher conversions significant amounts of 1,3-cyclopentadiene, benzene, toluene, xylenes, and ethylbenzene, and even traces of naphthalene, methylnaphthalene and biphenyl are detected. Peak identification and integration of the FID chromatogram is performed by a commercial integration package, GC-Image (Zoex Corp.), using the information obtained from GC×GC TOF-MS analysis. For each studied condition, at least 3 repeat analyses were performed. For all runs the mass balances were within the range of 95-105%. Deviations are attributed to uncertainties in the mass flow rates of iso-butanol and the internal standard (N₂). Subsequently, the component weight fractions were normalized to 100 wt%, in order to enable straightforward interpretation of the observed trends. After normalization of the
total mass balance, elemental balances (C, H, O) were verified. The estimated uncertainty of the measured product yields is 5% rel in line with previous work [111, 164]. Uncertainty is lower for components with higher mole fractions.

![GC×GC-FID chromatogram](image)

**Figure 4-1**: GC×GC-FID chromatogram of the on-line sampled undiluted iso-butanol pyrolysis effluent at $T_{avg}=1053$ K and $F_{iso\text{-butanol}} = 6.66 \times 10^{-2}$ g s$^{-1}$.

### 4.3 Reactor models

#### 4.3.1 Pyrolysis

For simulating the pyrolysis experiments in the pyrolysis set-up, the reaction network was implemented in Chemkin-Pro [76]. The laminar flow reactor was simulated first using Chemkin’s cylindrical shear flow option to investigate the importance of radial temperature and concentration gradients for this set-up. In line with the model results obtained for the three other butanol isomers [113, 162] and mixtures of butanol [165], minor radial concentration and temperature non-uniformities are computed, indicating that the assumption of using a plug flow reactor model for this reactor is indeed valid [166]. Based on the characteristic times and non-dimensional numbers [167] [168] [169] pertinent to our
tubular flow reactor the validity of the plug flow treatment of tubular reactor data has been further verified and these results show that the plug flow treatment is valid. Hence, we have employed the Chemkin-Pro plug flow reactor (PFR) module for modeling the tubular reactor. The PFR module was supplied with the measured temperature and pressure profile, and the reactor dimensions used were those discussed in Section 4.2. The default absolute and relative tolerances were sufficient for convergence.

4.3.2 Doped methane diffusion flame

The doped methane flame data of McEnally and Pfefferle [152] were simulated using the reactor model constructed and utilized by Sharma et al. [95], however significant changes have been made in the computational method used for solving the problem. The Sharma et al. [95] solver could not handle the stiff system presented by the butanol model which has been overcome in the current solver. Only a brief description of the reactor model is given in this work; please see [95] for a more detailed explanation.

The doped methane flame was modeled as a steady-state system, using an axisymmetric geometry. In general, solving this problem requires solving for the temperature, axial and radial velocities, and species concentration profiles as a function of r and z. Bennett et al. [170] solved this problem for an undoped methane diffusion flame using the same reactor geometry as McEnally and Pfefferle [152]. Additionally McEnally and Pfefferle have demonstrated that for the small amount of dopant used, the centerline temperature profile exhibits no significant change between the undoped- and doped-flame, within the experimental uncertainty of 65 K for the gas temperature [171]. Hence, we used the temperature profile obtained in the numerical solution of the undoped methane flame as the temperature profile for the doped-methane flame. Furthermore, since the temperature profile was not greatly affected, we assumed the velocity profiles would not be affected significantly either. With the temperature and velocity profiles known, the reactor model only needs to solve for the species concentration profiles in the doped methane flame.

The form of the species conservation equation is given in equation below

$$\rho v_r \frac{\partial Y_r}{\partial z} + \rho v_z \frac{\partial Y_z}{\partial r} = \gamma_i MW_i - \frac{1}{r} \frac{\partial}{\partial r} (r \rho v_r Y_i) - \frac{\partial}{\partial z} (\rho v_z Y_i)$$  (4-1)
\(\rho\) is the total density, \(v_z\) is the axial velocity, \(Y_i\) is the mass fraction of species \(i\), \(v_r\) is the radial velocity, \(y_i\) is the molar rate of production of species \(i\), \(MW_i\) is the molecular weight of species \(i\), and the radial and axial diffusive flux terms are given in Equations (4-2) and (4-3), respectively. \(D_i\) is the mixture-averaged diffusion coefficient for species \(i\).

\[v_{r,i}Y_i = -D_i(Y_i) \frac{\partial Y_i}{\partial r}\]  \hspace{1cm} (4-2)

\[v_{z,i}Y_i = -D_i(Y_i) \frac{\partial Y_i}{\partial z}\]  \hspace{1cm} (4-3)

As the Peclet number on the centerline exceeds 70 we neglect the axial diffusion term and solve the species conservation equation using methods of lines. Moving the radial convective term from the left-hand side of Equation (4-3) to the right-hand side isolates all \(r\)-dependent terms to the right-hand side of the equation, resulting in Equation (4-4).

\[\rho v_z \frac{\partial Y_i}{\partial z} = y_i MW - \rho v_r \frac{\partial Y_i}{\partial r} - \frac{1}{r} \frac{\partial}{\partial r} (r \rho v_{r,i} Y_i)\]  \hspace{1cm} (4-4)

Using second-order centered finite differences to approximate the diffusion term and first-order upwind differences to approximate the radial convection term of Equation (4-4) reduces the overall problem from a partial differential equation to a first-order ordinary differential equation initial-value problem (ODE-IVP). This problem was solved using a modified form of Strang splitting [172] which reduces errors for some stiff problems [173]. The reaction terms were integrated using the \(\alpha\)-QSS (quasi steady state) method [174]; the convection terms were integrated using the variable-order Adams-Bashforth method as implemented by CVODE [175]; and the diffusion terms were integrated using a second-order backward differentiation formula (BDF) method. Thermodynamic properties, transport coefficients and kinetic rates were evaluated using Cantera [176].

The \(z=0\) initial boundary conditions for the doped methane flame is all species mole fractions are zero except for the species \(\text{CH}_4\), \(\text{N}_2\), \(\text{O}_2\), \(\text{Ar}\), and \(\text{iso-butanol}\). There are two boundary conditions in the \(r\)-direction for each species. Since the geometry of the problem is assumed to be axisymmetric, \(dC_i/dr = 0\) at \(r = 0\) for all species. The other boundary condition we impose in the \(r\)-direction is zero species flux \((dC_i/dr = 0)\) at the edge of the
reactor model, 54-mm from the center of the burner; the burner has an outer diameter of 6.35-mm

4.3.3 Jet-stirred reactor

The mechanism was validated against the jet-stirred reactor (JSR) data measured by Togbé et al. [157]. The reactor was simulated using the Perfectly Stirred Reactor (PSR) module in Chemkin-Pro [76]. The reactor is solved as an isothermal system with volume of 30.5 cm$^3$. The JSR is solved for feed mole fraction of $iso$-butanol 0.1% (0.15% for $\varphi=4$), the equivalence ratios simulated are 0.5, 1, 2 and 4 with N$_2$ as bath gas. The pressure for all simulations is 10 atm spanning temperature range of 700 to 1250 K with a residence time of 0.7s. The absolute and relative tolerance of the solver was set to $1 \times 10^{-6}$ and $1 \times 10^{-8}$ respectively; the absolute and relative tolerance for pseudo time stepping was also set to $1 \times 10^{-16}$ and $1 \times 10^{-8}$ respectively.

4.3.4 Laminar burning velocities

This study also reports the premixed laminar flame velocities as measured (and extrapolated to zero strain) by Veloo and Egolfopoulos [149] and Liu et al. [150]. Here these velocities were simulated using the PREMIX laminar flame code module in Chemkin-Pro [153]. The final temperature profile was set at the adiabatic flame temperature and unburnt gas temperature was set to 343 K and 353 K for measurements by Veloo and Liu et al. respectively. The measurements by Veloo and Egolfopoulos were only at atmospheric pressure, while Liu et al. measured the flame speed at 1 atm and 2 atm.

The PREMIX flame code was solved with initial grid points of 200 adaptable to maximum of 1500. The simulations accounted for thermal diffusion (i.e. Soret effect) and used mixture averaged diffusivities. The adaptive grid control based on solution curvature and gradient were reduced to 0.2 in order to obtain converged results. The absolute and relative tolerances of the solver are set to $1 \times 10^{-6}$ and $1 \times 10^{-3}$.

4.3.5 Opposed flow diffusion flame

The mechanism was also validated against the opposed-flow diffusion data of Grana et al. [153] using the Premixed Opposed-flow flame module in Chemkin-MFC[177]. The energy equation is solved in the simulation with the experimental temperature profile
provided as an initial guess to the solver. The default settings of the Chemkin solver are used for the simulation i.e. cylindrical coordinates, windward differencing scheme, thermal diffusion and mixture averaged transport properties. The absolute and relative tolerances of the solver are set to \(1 \times 10^{-9}\) and \(1 \times 10^{-4}\). The adaptive grid control based on solution gradient and curvature were both set to 0.5. Lowering the gradient and curvature setting did not have any noticeable effect on the solution.

The simulated conditions for fuel inlet stream are inlet velocity of 24.8 cm/s and inlet temperature of 353K with an initial mole fraction of 0.14 for iso-butanol and 0.86 for \(N_2\). The oxidizer stream has an inlet velocity of 25 cm/s and temperature of 298K with mole fractions of 0.21 and 0.79 for \(O_2\) and \(N_2\) respectively.

### 4.3.6 Shock tube experiments

The shock tube experiments [154] were modeled in Chemkin-Pro[153], using the Closed Homogenous Batch reactor module. The reactor was solved as an adiabatic system with constant volume. The default absolute and relative tolerances were used for the simulations, including the one where the time-dependent sensitivities were calculated. The ignition delay was calculated as the time required to reach half of maximum OH concentration, and was found to be reasonably close to other metrics used in literature (i.e. the time of steepest rise in pressure and the time at which the product \([C_2H][O]\) reaches its maximum).

### 4.4 Reaction mechanism generation

#### 4.4.1 Automatic reaction mechanism generation and refinement

The chemical kinetic model is constructed using the automated “Reaction Mechanism Generator” (RMG) software package [110], originally developed by Jing Song [178]. RMG uses a rate based [179] algorithm, that constructs a valid reaction network at given conditions and user defined tolerances. RMG estimates the high pressure kinetics using over 40 RMG-defined reaction templates (e.g. H-abstraction, radical recombination, \(\beta\)-scissions), the fall-off effects are estimated using Modified Strong Collision (MSC) approach of Chang et al. [129] or Reservoir State method (RS) developed by Green and Bhatti[180]. The pressure dependent kinetics for this mechanism have been estimated by Modified
Strong Collision. It was found after extensive analysis that MSC provides more robust estimates than RS when considered over the entire temperature and pressure range. The RS estimates were found to be much poorer than MSC when compared to Chemically Significant Eigenvalue (CSE) analysis [181] when a well in the pressure dependent network was shallow. In these cases the rates from RS at low pressure or high temperatures were unphysically orders of magnitudes different from the CSE value and would lead to extreme stiffness in the kinetic equations. (As discussed in literature, RS is quite accurate for deep wells and at low temperatures [56, 180])

The thermochemistry of most species in the mechanism are estimated using Benson’s group additivity scheme[182]. The transport properties like Lennard-Jones parameters for species are estimated using empirical correlations based on species critical properties i.e. temperature and pressure, which are estimated using a group-additivity scheme[183]. Whenever the user has better knowledge of reaction rate expressions and species thermochemistry or transport properties, these can be supplied externally to RMG in the form of a library and will be used instead of RMG estimates. This is advantageous as the uncertainty associated with the rate coefficient estimated by RMG (from functional group analogy) can be greater than an order of magnitude especially in cases where no closely analogous literature rate is available. A RMG simulation can be seeded with an entire reaction mechanism which will then be expanded using the rate based algorithm until it satisfies the termination criterion for the simulation; in this manner a previous model can be expanded for different starting species and initial conditions.

The current iso-butanol mechanism is made by using the previous butanol model that has been developed for n-butanol, sec-butanol and tert-butanol [113, 184], as its seed mechanism. Briefly the seed consists of thermochemistry parameters and rate coefficients from previous butanol model (281 species and 3600 reactions) for n, sec- and tert-butanol isomers. The small molecule chemistry in the seed originated from GRI-Mech 3.0 [185] and the Marinov ethanol mechanism [186] with updates as mentioned in references [113] and [184]. The conditions for the RMG simulation used to grow the mechanism are:

- **iso-Butanol Pyrolysis**: The simulation was run at a pressure of 1.5 atm over a temperature range of 900 to 1200 K (in steps of 100 K) for initial mass fraction of
1 for iso-butanol and diluted case with mass fraction of 0.33 for iso-butanol and 0.67 N₂. The termination criterion was 99 % conversion of fuel in all cases.

- iso-Butanol Oxidation: These simulations were run at pressures of 1 and 10 bars over a temperature range of 700-2000 K (in steps of 200 K) for equivalence ratio \( \phi \) of 0.5, 1, 2, and 4. These conditions cover most of the operating regime of the experiments discussed below.

The following additional updates have been made to the model reported in [184].

### 4.4.2 Unimolecular decomposition of iso-butanol

The pressure dependent network for unimolecular decomposition of iso-butanol was solved by Zhou et al. [187]. That study provides high level ab-initio analysis of three dominant decomposition pathways for iso-butanol.

\[
\begin{align*}
(CH_3)_2CHCH_2OH & \rightarrow (CH_3)_2CH + .CH_2OH \\
(CH_3)_2CHCH_2OH & \rightarrow CH_3CH.CH_2OH + .CH_3 \\
(CH_3)_2CHCH_2OH & \rightarrow (CH_3)_2C=CH_2 + H_2O
\end{align*}
\]

Zhou et al. treated the radical forming channels with variable-reaction-coordinate transition state theory on a PES derived from at CASPT2(2e,2o)/cc-pVDZ calculations while the dehydration channel was treated as simple transition state theory at CCSD(T) level of theory with Eckart tunneling[188] and 1-d hindered rotor corrections. They assumed \( < \Delta E_d > \text{ cm}^{-1} = 200 \left( T/298 \text{ K} \right)^{0.85} \) when computing the \( k(T,P) \). Recently the rate of dehydration of iso-butanol was measured by Rosado-Reyes et al. [138] and is within a factor of 2 of the ab-initio calculations by Zhou et al. The experiments also determined, in agreement with the calculations that this reaction system is not significantly pressure dependent up to 1250 K at 1.5 bar. The current model uses the calculated values by Zhou et al.
4.4.3 Quantum calculation and statistical mechanics

The sensitivity analysis over different experiments identified key species and reactions. For these important species the enthalpy of formation, the entropy at 298 K and the heat capacity at the following temperatures 300, 400, 500, 600, 800, 1000 and 1500 K were calculated. These parameters were then fit to a NASA polynomial form for use in the CHEMKIN input file. CBS-QB3 calculations [115, 189, 190] were done using the Gaussian03 suite[116] to obtain electronic energies. The vibrational frequencies are calculated using B3LYP/CBSB7 method and are uniformly scaled by factor of 0.99 [191]. The RRHO with 1-d hindered rotor correction for every heavy atom-heavy atom dihedral was implemented. The 1-d hindered rotor potentials were done at B3LYP/CBSB7 using a step size of 10° and relaxing all other degree of freedom. The resulting energies were fit to a Fourier series as a function of dihedral angle $\phi$. The reduced moment of inertia of the equilibrium geometry was computed and resulting one-dimensional Schrodinger equation was solved for the lowest 200 energy levels. These energies were used to compute the partition function and desired thermodynamic quantities. For the heats of formation, the Bond Additivity Corrections (BAC) to CBS-QB3 as proposed by Petersson et al. [192] were applied. The reported (forward) rate coefficients are from ab-initio calculations. The BAC does not affect these rate coefficients but will affect the reverse rates used in the model due to change in equilibrium constant $K_{eq}$.

The high pressure limit rate coefficients were calculated using the transition state theory as given by the following equation

$$k = \kappa(T) \frac{k_b T}{hC^o} \exp \left( \frac{G^{TS} - \sum G^i}{RT} \right)$$

(4-5)

Where $k$ is the reaction rate coefficient, $k_b$ is Boltzmann's constant, $T$ is temperature, $h$ is Planck's constant, $R$ is the universal gas constant; $C^o$ is the standard state concentration ($C^o=P^o/RT$). $G^i$ is the free energy of species $i$ at concentration $C^o$. $\kappa(T)$ is the asymmetric Eckart tunneling [188] correction and was calculated using the formalism presented by Johnston and Heicklen [193] with their eq. 15 corrected by Garrett and Truhlar [194]. All these calculations are performed using an in house code CANTHERM [195]. Table 4-2 gives the list of species and their calculated thermochemistry and Table 4-3
reports the list of reactions and their fitted modified Arrhenius parameters. The CBS-QB3 method has an uncertainty of 2-3 kcal/mol in the barrier height [196] and the 1-d hindered rotor approximation has an uncertainty of factor of ~2 (only when there is no strong coupling between the torsions and other degrees of freedom) in the A factor [48]. In absence of any hindered rotor model (i.e. harmonic oscillator assumption) the uncertainty in the A factor is greater than an order of magnitude [197]. It is important to note for iso-butanol + HO₂ the rates reported in Table 4-3 are in the exothermic direction and the important endothermic direction is additionally sensitive to uncertainties in thermochemistry of iso-butanol and the corresponding radical.

Table 4-2: Species thermochemistry properties calculated using CBS-QB3 RRHO with 1-D hindered rotor corrections:

<table>
<thead>
<tr>
<th>species</th>
<th>Hf,298</th>
<th>S298</th>
<th>Cp300</th>
<th>Cp400</th>
<th>Cp500</th>
<th>Cp600</th>
<th>Cp800</th>
<th>Cp1000</th>
<th>Cp1500</th>
</tr>
</thead>
<tbody>
<tr>
<td>iBuOH</td>
<td>-68.34</td>
<td>83.38</td>
<td>27.21</td>
<td>33.74</td>
<td>39.68</td>
<td>44.72</td>
<td>52.64</td>
<td>58.55</td>
<td>67.90</td>
</tr>
<tr>
<td>(CH₃)₂CHCHOH</td>
<td>-24.24</td>
<td>84.93</td>
<td>27.12</td>
<td>33.12</td>
<td>38.42</td>
<td>42.88</td>
<td>49.87</td>
<td>55.11</td>
<td>63.43</td>
</tr>
<tr>
<td>(CH₃)₂CCH₂OH</td>
<td>-22.94</td>
<td>84.64</td>
<td>27.11</td>
<td>32.27</td>
<td>37.18</td>
<td>41.54</td>
<td>48.70</td>
<td>54.18</td>
<td>62.91</td>
</tr>
<tr>
<td>CH₂CH(CH₃)CH₂OH</td>
<td>-18.28</td>
<td>86.11</td>
<td>28.03</td>
<td>33.68</td>
<td>38.81</td>
<td>43.16</td>
<td>49.99</td>
<td>55.12</td>
<td>63.33</td>
</tr>
<tr>
<td>(CH₃)₂CHCH₂O</td>
<td>-15.78</td>
<td>80.19</td>
<td>26.32</td>
<td>32.81</td>
<td>38.45</td>
<td>43.15</td>
<td>50.50</td>
<td>55.97</td>
<td>64.52</td>
</tr>
</tbody>
</table>

* Enthalpy has units of kcal mol⁻¹; entropy and heat capacity have units of cal mol⁻¹K⁻¹

Table 4-3: Modified Arrhenius rate coefficients parameters, computed using conventional transition state theory at CBS-QB3 for important reactions involving iso-butanol:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A</th>
<th>n</th>
<th>Eₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>iBuOH + H = (CH₃)₂CHCHOH + H₂</td>
<td>5.2E+03</td>
<td>3.04</td>
<td>2.5</td>
</tr>
<tr>
<td>iBuOH + H = (CH₃)₂CCH₂OH + H₂</td>
<td>5.8E+03</td>
<td>3.02</td>
<td>3.5</td>
</tr>
<tr>
<td>iBuOH + H = CH₂CH(CH₃)CH₂OH + H₂</td>
<td>6.2E+03</td>
<td>3.2</td>
<td>7.1</td>
</tr>
<tr>
<td>iBuOH + H = (CH3)₂CHCH₂O + H₂</td>
<td>2.9E-1</td>
<td>4.14</td>
<td>4.8</td>
</tr>
<tr>
<td>iBuOH + CH₃ = (CH₃)₂CHCHOH + CH₄</td>
<td>2.5E-3</td>
<td>4.44</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>Reaction</td>
<td>Rate Coefficient</td>
<td>correction</td>
</tr>
<tr>
<td>---</td>
<td>--------------------------------------------------------------------------</td>
<td>------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>6</td>
<td>iBuOH + CH₃ = (CH₃)₂CCH₂OH + CH₄</td>
<td>1.5E-02</td>
<td>4.47</td>
</tr>
<tr>
<td>7</td>
<td>iBuOH + CH₃ = CH₂CH(CH₃)CH₂OH + CH₃</td>
<td>9.6E-05</td>
<td>4.94</td>
</tr>
<tr>
<td>8</td>
<td>iBuOH + CH₃ = (CH₃)₂CHCH₂O + CH₄</td>
<td>5.7E-4</td>
<td>4.35</td>
</tr>
<tr>
<td>9</td>
<td>iBuOH + C₂H₃ = (CH₃)₂CHCHOH + C₂H₄</td>
<td>5.19E-02</td>
<td>3.9</td>
</tr>
<tr>
<td>10</td>
<td>iBuOH + C₂H₃ = (CH₃)₂CCH₂OH + C₂H₄</td>
<td>2.69E-02</td>
<td>3.9</td>
</tr>
<tr>
<td>11</td>
<td>iBuOH + C₂H₃ = CH₂CH(CH₃)CH₂OH + C₄</td>
<td>1.10E-03</td>
<td>4.55</td>
</tr>
<tr>
<td>12</td>
<td>(CH₃)₂CHCHOH + H₂O₂ = iBuOH + HO₂</td>
<td>5.69E+01</td>
<td>3.04</td>
</tr>
<tr>
<td>13</td>
<td>(CH₃)₂CCH₂OH + H₂O₂ = iBuOH + HO₂</td>
<td>2.91E+00</td>
<td>3.31</td>
</tr>
<tr>
<td>14</td>
<td>CH₂CH(CH₃)CH₂OH + H₂O₂ = iBuOH + HO₂</td>
<td>3.01E+00</td>
<td>3.28</td>
</tr>
</tbody>
</table>

n The rate coefficient expression is \( k = A(T/K)^n \exp(-E_a/RT) \)

4.5 Results

4.5.1 Pyrolysis experiment

Figure 4-2 reports the conversion of iso-butanol at diluted and undiluted conditions and shows that the predicted iso-butanol conversion versus the average process gas temperature properly matches the experimental measurements. Slightly higher conversions are observed experimentally than simulated, but deviations are less than the uncertainty on the measured conversions. The temperature range that has been studied in the pyrolysis experiments covers almost the complete conversion range for iso-butanol, and hence, the average process gas temperature in the hot zone of the reactor is a good measure for the cracking severity for the present set of pyrolysis experiments.
Figure 4-2: *iso*-Butanol conversion as a function of the average pyrolysis reactor temperature (symbols – experimental: ● undiluted. ■ N₂ diluted: 3 mol N₂/mol *iso*-butanol, – simulated · · undiluted and · · diluted).

Figure 4-3 reports the yields of some of the major species obtained from the pyrolysis of *iso*-butanol. Methane, CO, alkenes as well as major oxygenated species such as formaldehyde and water are properly predicted by the kinetic model. Enols cannot be detected by the analytical techniques employed in this work because surface-catalyzed reactions rapidly convert enols into the corresponding aldehydes (or ketones) [198]. In order to compare the measured and simulated concentrations the enol and aldehyde concentrations from the simulations have been summed and these have been matched against the measured values, see for example Figure 4-3 F. The presented mechanism simulates the trend for propanal well, although the maximum in the yield is underestimated by the kinetic model.
Figure 4-3: Comparison of the experimental (symbols) and simulated (lines) yields of the major products at diluted (3 mol N₂/mol iso-butanol) and undiluted pyrolysis conditions. A) methane, B) CO, C) ethene, D) propene, E) isobutene, F) propanal + prop-1-enol, G) water, H) formaldehyde (symbols – experimental, lines – model simulations).
A good agreement is also observed for the yields of the minor species such as hydrogen, ethane, CO₂, acetone, 1,3-butadiene and benzene reported in Figure 4-4. The effect of the dilution is most pronounced for ethane in line with earlier work [199]. The yield of 1,3-cyclopentadiene is correctly estimated using the present model. The latter can be important for the simulation of soot formation, where the cyclopentadienyl radical plays an essential role. [136, 200, 201].
Figure 4-4: Comparison of the experimental (symbols) and simulated (lines) yields of the minor products at diluted (3 mol N₂/mol isobut) and undiluted conditions. A) hydrogen, B) CO₂, C) ethane, D) 1,3-cyclopentadiene, E) benzene, F) 1,3-butadiene (symbols – experimental, lines – model simulations).
To gain further insight in the reaction mechanism and the role of certain kinetic parameters, a rate of production analysis is carried out for the pyrolysis experiments. Figure 4-5 shows the schematic picture of the main iso-butanol decomposition pathways. Hydrogen abstraction reactions by methyl and hydrogen are predominantly responsible for the conversion of iso-butanol producing at the same time methane and hydrogen. The 1-hydroxy-2-methylpropyl radical (alpha) primarily beta-scission to give prop-1-enol + CH₃ radical. For iso-butanol the beta-scission of the 3-hydroxy-2-methylpropyl (gamma) radical gives propene + CH₂OH radical. The radical pathway starting from the 2-hydroxy-1,1-dimethylethyl (beta) radical is the major route to iso-butene formation. The main route towards ethene is the beta scission of the n-propyl radical that originates almost entirely from propene. The direct dehydration of iso-butanol and hydrogen abstractions by OH radicals accounts for the significant amounts of water measured. The formation of formaldehyde and methanol is related to the formation of the CH₂OH radical from iso-butanol and the decomposition of ketene that is formed from acetone. Methanol and formaldehyde are the main intermediates towards CO and CO₂ in agreement with previous work [162, 165].

Figure 4-5: Reaction pathway analysis of iso-butanol pyrolysis (undiluted) in a plug flow reactor operated at $P = 1.7$ bar and $T = 1000$ K for 70% conversion. Percentages are expressed relative to the total iso-pentanol consumption rate.
Aromatics are partly formed by a series of addition reactions such as the addition of the vinyl radical to 1,3-butadiene [202] leading to benzene. Other important pathways are the reactions of cyclopentadienyl radical with methyl and ethyl radicals. These pathways will be discussed in greater detail in the following pentanol chapter. Naphthalene and indene is formed via the recombination pathways involving the cyclopentadienyl radical and 1,3-cyclopentadiene as discussed in the previous chapter.

4.5.2 Doped methane flame

The model was validated against doped methane flame data of McEnally and Pfefferle [152] using the flame solver discussed in Section 4.3.2. Figure 4-6 gives the simulated and experimental centerline iso-butanol profile. Experimentally it is seen that iso-butanol concentration drops to zero ~ 26 mm while the simulated profile reaches zero concentration ~ 29 mm, the 3 mm difference is within the uncertainty caused due to the experimental uncertainty of the measured gas temperature ~ 65K.

![Figure 4-6: Experimental (symbols) and simulated (line) centerline mole fraction profiles of iso-butanol in doped methane diffusion flame [152]. The offset along the X axis is mostly due to uncertainty in the assumed temperature profile, see Van Geem et al. [162].](image-url)
4.5.2.1 Butanol flux analysis

Figure 4-7 gives the rate of production for the dopant iso-butanol. The main route of decomposition of iso-butanol is the C-C bond fission to give iso-propyl and hydroxymethyl radical. The iso-propyl radical undergoes β scission to give propene and H radical while hydroxymethyl radical undergoes β scission to give formaldehyde and H radical. The other significant pathways for iso-butanol decomposition are C-C bond fission to give 1-(hydroxymethyl)ethyl + methyl radical, hydrogen atom abstraction by methyl radical to give 2-hydroxy-1,1-dimethylethyl radical and dehydration of iso-butanol to iso-butene. The intermediates 1-(hydroxymethyl)ethyl and 2-hydroxy-1,1-dimethylethyl radicals undergo β scission to give propene and iso-butene respectively.

![Graph showing the rate of production for iso-butanol in doped methane flame.](image)

**Figure 4-7:** Predicted centerline rate of production for iso-butanol in doped methane flame.

4.5.2.2 Butanol product centerline profiles and flux analysis

The centerline profiles of a few of the products of iso-butanol decomposition are given in Figure 4-8: the species corresponding to each molecular weight are $M_w = 42$ (propene + ketene), $M_w = 44$ (acetaldehyde + vinyl alcohol), $M_w = 54$ (1,2-butadiene + 1,3-butadiene + 1-butyne + 2-butyne) and $M_w = 56$ (iso-butene). The model is able to predict profiles of all species well within the uncertainty reported by McEnally and Pfefferle [152] (factor of 2 uncertainty in measured mole fractions) with exception of $M_w = 54$. 

136
As seen from Figure 4-8 the predicted peak concentration for propene (M_w = 42) is a factor of 1.75 greater than the experimental measured profile. Propene is the major product formed from iso-butanol decomposition as seen from flux analysis of iso-butanol discussed in previous section. Flux analysis shows the major consumption channel is a well skipping path of propene reacting with H atom to give ethene and methyl radical.

**Figure 4-8**: Experimental (symbols) and simulated (line) centerline mole fraction of iso-butanol products in doped methane flame [152]. A) MW = 42 (mostly propene), B) MW = 44 (acetaldehyde + vinylalcohol), C) MW = 54 (1-butyne + 2-butyne + 1,3-butadiene + 1,2-butadiene), D) MW = 56 (mostly iso-butene) E) MW = 78 (mostly benzene) and F) MW = 58 (propanal + prop-1-enol + prop-2-enol).
The flux analysis for acetaldehyde and vinyl alcohol are shown in Figure 4-9 A and B. The main route to vinyl alcohol is the well skipping reaction of ethene + OH, the rate coefficient for which is estimated by RMG. Acetaldehyde is formed primarily by tautomerization of vinyl alcohol and the well skipping reaction of ethene and hydroxyl radical to give acetaldehyde and H atom. The tautomerization rate coefficient was calculated by da Silva [203] \( k = 8.59 \times 10^{11} \ T^{-0.318} \ \exp\left[-55900(\text{cal/mol})/RT\right] \) and the rate coefficient for the chemically-activated well skipping path is estimated using RMG. The primary decomposition path of acetaldehyde is C-C bond fission to give CH₃ + HCO radical.

Flux analysis for \textit{iso}-butene is given in Figure 4-9 C. The major routes for \textit{iso}-butene formation are β scission of 2-hydroxy-1,1-dimethylethyl radical to give \textit{iso}-butene + OH and dehydration of \textit{iso}-butanol to \textit{iso}-butene. Unlike \textit{sec}- and \textit{tert}-butanol [113] where the butenes were formed almost exclusively by dehydration reaction, in \textit{iso}-butanol the bond scission channel is the major channel in this temperature range (about 1300 K). The \textit{iso}-butene is consumed primarily by CH₃ and H atom. The rate coefficients for the H atom abstraction from \textit{iso}-butene come from CBS-QB3 calculations.

Species corresponding to \( M_w = 54 \) (1,2-butadiene + 1,3-butadiene + 1-butyne + 2-butyne) are under predicted by a factor of 3 by the current mechanism. Figure 4-8 D gives the flux diagram for 1-butyne (predicted to be the major species with \( M_w = 54 \)). According to the model the major route for formation of 1-butyne is recombination of propargyl + CH₃ radicals to \(~ 29 \) mm downstream from the burner. Further downstream the well skipping reaction of allene + CH₃ to give 1-butyne + H atom becomes dominant. The current mechanism save from the exceptions mentioned above predicts the centerline concentration of all other species including aromatics such as benzene (Figure 4-8 E) reasonably well.
Vinyl alcohol

iso-Butene

\[
\begin{align*}
\text{CH}_2\text{CHOH} + \text{H} &= \text{C}_2\text{H}_4 + \text{OH} \\
\text{CH}_3 + \text{HCO} &= \text{CH}_2\text{CHOH} \\
\text{CH}_2\text{CHOH} &= \text{CH}_3\text{CHO} \\
\end{align*}
\]
4.5.2.3 Sensitivity analysis to Lennard-Jones parameters

Normalized sensitivity coefficients were computed with respect to the Lennard-Jones \( o \) and \( e \) parameters for a few key species as shown in Figure 4-10. The normalized sensitivity coefficient was calculated by numerical differentiation where the Lennard-Jones parameters were varied by \( \pm 10\% \) from the nominal value. The centerline concentration profiles of most species were found to be sensitive to the collision diameter (\( a \) parameter) of \( \text{N}_2 \) and \( \text{CH}_3 \) since they have the highest mole fraction in the flame. The value of these parameters were obtained from Burke et al. [70] and GRI-Mech 3.0 [185] mechanism respectively. The predicted species concentration profiles are also sensitive to the collision diameter of the dopant \( \text{iso-butanol} \). The value of \( a_{\text{OH}} \) used in this study is 5.667 Å and was computed using the group additivity scheme described in reference [113]. It is ~ 10\% larger than the value in reference [204].
**Figure 4-10:** Normalized sensitivity coefficients for the centerline iso-butanol concentration in the doped diffusion flame with respect to Lennard-Jones collision diameter $o$ for iso-butanol, nitrogen and methane.

### 4.5.3 Jet-stirred reactor

The mechanism was also validated against the jet-stirred reactor data (JSR) of Togbé et al. [157]. For all the figures for this section “C2H4O” is the summation of acetaldehyde and its tautomer vinyl alcohol as these species were indistinguishable with the analytic equipment used in the experiment. Figure 4-11 gives the model prediction for major species for $\varphi = 0.5$. As seen from Figure 4-11 the iso-butanol consumption is not predicted accurately by the current model. The conversion is overpredicted for $T < 850$ K and underpredicted (by $\sim 5\%$) as temperature is increased beyond $900$ K. Figure 4-12 gives the flux analysis for the consumption of iso-butanol for all the experiments. For all three equivalence ratios, the three most dominant iso-butanol consumption reactions at temperatures $< 1000$ K are hydrogen abstractions by OH forming the 1-hydroxy-2-methylpropyl, 2-hydroxy-1,1-dimethylethyl radical and 3-hydroxy-2-methylpropyl radicals. The rate coefficients for these reactions come from analogies to $n$-butanol and have a high uncertainty associated with them and by adjusting these rate constants a better agreement between the predicted conversion can be achieved. However, for purpose of this study (testing the predictive power of the model) the rate constants are not adjusted. In the lean and stoichiometric cases for temperatures $> 1100$ K hydrogen abstraction by O atom...
forming 1-hydroxy-2-methylpropyl also becomes significant. In the rich case at high temperature the C-C bond fission to give iso-propyl and hydroxymethyl radical is the dominant pathway.

**Figure 4-11**: Simulated (lines) and experimental (symbols) profiles of major species for jet stirred reactor experiment [157] for $\phi = 0.5$ and $P = 10$ atm. (C2H4O is sum of acetaldehyde + vinyl alcohol).
Jet-stirred reactor at 10 atm, $\phi = 0.5$

Jet-stirred reactor at 10 atm, $\phi = 1$
The model predictions for the concentration of CO, CO₂, H₂O, H₂, methane, ethene, formaldehyde, acetaldehyde + vinyl alcohol and acetylene are within a factor of two of the experimental data across the entire temperature range for all the equivalence ratios considered in the experiment.

iso-Butene concentration is under predicted for all the equivalence ratios as seen in Figure 4-13, with the discrepancy increasing as we move from rich to lean conditions. At 0.5 the peak concentration is under predicted by a factor of 6. Studies by Sarathy et al. [159] and Moss et al. [160] also under predict the peak concentration of iso-butene increasingly for rich to lean conditions. Figure 4-14 and Figure 4-15 give the flux and sensitivity analysis respectively, for iso-butene formation for all the experiments. The predicted major pathway for formation of iso-butene for all three equivalence ratios over the complete range of JSR temperatures is the β-scission of the 2-hydroxy-1,1-dimethylethyl radical to give isobutene and hydroxyl radical. In the lean case the model predicts most of
the 2-hydroxy-1,1-dimethylethyl adds molecular oxygen instead of undergoing β-scission to form iso-butene while for rich case most of the 2-hydroxy-1,1-dimethylethyl undergoes β-scission. Other pathways that contribute to production of iso-butene are the chemically activated pathway 2-methylprop-2-enol + H atom to iso-butene + OH and the β-scission of 1,1-dimethylpropyl radical (formed primarily by H addition to iso-pentene) to give iso-butene + CH₃. The rate expressions for the above reactions come from RMG estimates. The predominant decomposition pathway of iso-butene is abstraction of primary hydrogen by hydroxyl radical for lean and stoichiometric conditions while for the rich conditions the hydrogen abstraction by H atom is the dominant reaction especially at higher temperatures. The rate expression for abstraction by hydroxyl radical comes from Dooley et al. [71] while abstraction by H atom is by quantum calculation.

![Graphs showing mole fraction of iso-butene for different equivalence ratios](image)

**Figure 4-13:** Simulated (line) and experimental (symbols) profiles of iso-butene for jet stirred reactor experiment [157] for equivalence ratios A) 0.5, B) 1, C) 2 and D) 4.
Jet-stirred reactor at 10 atm, $\phi = 0.5$

Jet-stirred reactor at 10 atm, $\phi = 1$
Figure 4-14: Simulated rate of production for iso-butene in the 10 atm jet stirred reactor [157] for equivalence ratios A) 0.5, B) 1 and C) 4.

Figure 4-15 A – C give the sensitivity analysis for iso-butene concentration at three different temperatures (800, 900 and 1100 K) for equivalence ratio $\phi = 0.5$ (lean), $\phi = 1$ and $\phi = 4$ (rich). As seen from Figure 4-15 A the reactions which are most sensitive to iso-butene concentration are the hydrogen abstraction from the alpha and beta sites of iso-butanol by hydroxyl radical to form 1-hydroxy-2-methylpropyl and 2-hydroxy-1,1-dimethylpropyl radical. Other reactions which are sensitive are the H abstraction from iso-butene by hydroxyl, and several small molecule reactions e.g. H+O$_2$=O+OH, HO$_2$+O=O$_2$+OH, HO$_2$+OH=H$_2$O+O$_2$, HO$_2$+CH$_3$=OH+CH$_3$O, HO$_2$+CH$_3$=O$_2$+CH$_4$. The rate coefficients for reactions for the H$_2$/O$_2$ sub-mechanism come from the updated mechanism by Burke et al. [70] as stated previously, and the rate coefficients for HO$_2$+CH$_3$ reactions come from the ab-initio quantum calculations by Jasper et al. [205].
Sensitivity of iso-butene at 10 atm, $\phi = 0.5$

![Graph a](image1)

Sensitivity of iso-butene at 10 atm, $\phi = 1$

![Graph b](image2)
Figure 4-15: Sensitivity analysis for iso-butene production in jet stirred reactor [157] at 10 atm as function of temperature (700 – 1100 K) and equivalence ratios A) 0.5, B) 1 and C) 4.

At lower temperature the hydrogen abstraction from iso-butanol by HO2 radical becomes important, the kinetics of which come from our CBS-QB3 RRHO quantum calculations. The system has strongly coupled internal rotors which are not treated accurately by current methods (uncertainty in the rate coefficients is an order of magnitude), so we recommend this reaction for future studies as discussed in Section 4.4.3. The sensitivity analysis for rich condition, \( \phi = 4 \) gives similar results to that for lean conditions except that the hydrogen abstraction from the beta site of iso-butanol by hydroxyl radical has the highest sensitivity coefficient and hydrogen abstraction from iso-butene by hydrogen atom becomes important as temperature is increased.

A summary of the model predictions at different equivalence ratio is given in Table 4-4 where the peak experiment and simulation value for each species are compared for the entire dataset. Our model predicts the peak concentration of most species within a factor of 2 across all equivalence ratios, with the exception of the unsaturated aldehydes 2-propenal and 2-methylpropenal which are underpredicted significantly. The jet stirred reactor experiments measure \( \sim 20 \) ppm for both unsaturated aldehydes while the model predicts \( \sim 10 \) ppm for 2-methylpropenal and less than 2 ppm for 2-propenal for all equivalence ratios. Sensitivity analysis indicates the important reactions for formation of the unsaturated
aldehydes are hydrogen abstractions by OH and HO₂ radicals from the corresponding saturated aldehydes and have a high uncertainty.
Table 4-4: Comparison of measured and predicted peak product concentration, rounded to the nearest ppm, in the 10 atm jet-stirred reactor of [157]. Italicized numbers represent measured values and bold numbers are the predicted values using the new mechanism.

<table>
<thead>
<tr>
<th></th>
<th>$\varphi = 0.5$</th>
<th>$\varphi = 1.0$</th>
<th>$\varphi = 2.0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde</td>
<td>134</td>
<td>126</td>
<td>124</td>
</tr>
<tr>
<td></td>
<td>132</td>
<td>135</td>
<td>139</td>
</tr>
<tr>
<td>Methane</td>
<td>103</td>
<td>210</td>
<td>622</td>
</tr>
<tr>
<td></td>
<td>175</td>
<td>256</td>
<td>467</td>
</tr>
<tr>
<td>Acetaldehyde + Vinyl alcohol</td>
<td>47</td>
<td>37</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>33</td>
<td>29</td>
</tr>
<tr>
<td>Ethene</td>
<td>124</td>
<td>199</td>
<td>418</td>
</tr>
<tr>
<td></td>
<td>103</td>
<td>187</td>
<td>302</td>
</tr>
<tr>
<td>Propene</td>
<td>203</td>
<td>219</td>
<td>228</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>172</td>
<td>159</td>
</tr>
<tr>
<td>Acetone</td>
<td>65</td>
<td>46</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>33</td>
<td>35</td>
</tr>
<tr>
<td>Propanal*</td>
<td>22</td>
<td>30</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>16.7</td>
<td>22.5</td>
<td>33</td>
</tr>
<tr>
<td>i-Butene</td>
<td>50</td>
<td>62</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>15</td>
<td>28</td>
</tr>
<tr>
<td>2-Methylpropanal*</td>
<td>138</td>
<td>137</td>
<td>143</td>
</tr>
<tr>
<td></td>
<td>158</td>
<td>152</td>
<td>132</td>
</tr>
</tbody>
</table>

*The -al is the sum of the aldehyde (-al) + alcohol (-ol) tautomer form
4.5.4 **Opposed-flow diffusion flame**

The mechanism was also tested against the opposed-flow diffusion flame data measured by Grana et al. [153] using the Opposed Flow Flame Module in Chemkin-Pro [76]. The experimental and modeling results are presented in Figure 4-16.

The opposed flow diffusion flame was solved as an adiabatic system, with the experimental profile used as initial guess for the solver. The predicted temperature profile matches the experimental curve reasonably well: the maximum temperature is within 5% of the experimental values and well within the +/- 200 K uncertainty reported by the experimentalists. The predicted temperature curve has a narrower reaction zone than the experimental one and the flame front leads by ~1.2 mm on the reactant side and lags by ~0.7 mm on the oxidizer side. The peak axial temperature position is within 0.5 mm of the experimental value. The model predicts the concentration profiles of all major species reasonably well (It must be noted that +/- 200 K uncertainty in temperature represents a 20% uncertainty in the predicted peak concentration and ~ 0.5 mm uncertainty in the peak position of the intermediate species) as seen in Figure 4-16.
Opposed Flow Diffusion Flame

- **H2**
- **O2**
- **CO2**
- **CO**
- **H2O**

Mole fraction vs. Distance from fuel duct [mm]

<table>
<thead>
<tr>
<th>Distance from fuel duct [mm]</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.25</td>
</tr>
<tr>
<td>2</td>
<td>0.20</td>
</tr>
<tr>
<td>4</td>
<td>0.15</td>
</tr>
<tr>
<td>6</td>
<td>0.10</td>
</tr>
<tr>
<td>8</td>
<td>0.05</td>
</tr>
<tr>
<td>10</td>
<td>0.00</td>
</tr>
</tbody>
</table>

**BuOH**

<table>
<thead>
<tr>
<th>Distance from fuel duct [mm]</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.10</td>
</tr>
<tr>
<td>2</td>
<td>0.08</td>
</tr>
<tr>
<td>4</td>
<td>0.06</td>
</tr>
<tr>
<td>6</td>
<td>0.04</td>
</tr>
<tr>
<td>8</td>
<td>0.02</td>
</tr>
<tr>
<td>10</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Opposed Flow Diffusion Flame

- **C2H4**
- **C2H2**
- **C3H6**

Distance from fuel duct [mm]

Mole fraction

Opposed Flow Diffusion Flame

- **C2H6**
- **iC4H8**

Distance from fuel duct [mm]

Mole fraction
The flux analysis of iso-butanol decomposition in this flame is shown in Figure 4-17. The predominant decomposition path is the C-C bond fission of iso-butanol to give iso-propyl radical and hydroxymethyl radical with the maximum reaction rate occurring ~4.7 mm from the fuel port. Hydrogen abstraction by hydroxyl radical to give 1-hydroxy-2-methylpropyl and the C-C bond fission of iso-butanol to give methyl and 1-(hydroxymethyl)ethyl radical are other reaction pathways contributing significantly to iso-butanol consumption, but have a peak rate a factor of 6 smaller than the predominant decomposition path.
The peak values of CO, CO₂, H₂O and H₂ are predicted reasonably well. The axial position corresponding to peak position is slightly shifted towards the oxidizer side when compared to experimental profiles, but well within the experimental uncertainty. The model predicts the peak concentration profiles of ethene, acetylene, ethane, propene and i-butene within 50% of the experimental value. Two species which the model currently does not predict well are formaldehyde and acetaldehyde overpredicted and underpredicted by a factor of 2 respectively. Figure 4-18 gives the flux analysis for major pathways leading to production of the aldehydes.
Figure 4.18: Simulated rate of production for A) formaldehyde and B) acetaldehyde for opposed flow diffusion flame.
Figure 4·18 A gives the flux analysis of formaldehyde. As seen from the figure the model predicts that there is net production of CH₂O up to ~4.8 mm from fuel port, with peak production rate ~4.67 mm from fuel port. Beyond ~4.8 mm there is a net consumption of CH₂O with maximum consumption rate at ~4.93 mm. The iso-butanol decomposes to give iso-propyl radical and hydroxymethyl radical, the hydroxymethyl radical then undergoes β-scission to give formaldehyde and H radical and this is the major path of production of formaldehyde up to ~5 mm from fuel port, beyond which the reaction of molecular oxygen with CH₂ radical is predicted to be the main formation route of formaldehyde. From 4.3 to 5.1 mm from the fuel port the main decomposition routes for formaldehyde are hydrogen abstraction by H atom and OH radical using the rate coefficients from GRI-Mech 3.0 [185]. The maximum consumption by OH occurs around 5.13 mm beyond which it rapidly decreases and becomes less important.

Figure 4·18 B gives flux analysis predicted for acetaldehyde. Like formaldehyde there is net production of acetaldehyde near the fuel port, while at the oxidizer side (5 – 5.3 mm from fuel port) there is net consumption. The predominant decomposition route is predicted to be hydrogen abstraction from acetaldehyde by H atom to give acetyl radical with maximum rate ~5 mm from the fuel port. The production of acetaldehyde is from the well skipping reactions of propene + O atom and ethene + OH, predicted to have peak rates ~5 mm from the fuel port. Acetaldehyde is also formed by the well skipping reaction of H atom with vinyl alcohol and direct tautomerization of vinyl alcohol.

4.5.5 Laminar flame speeds

Laminar flame speeds are important properties of premixed flames and play an essential role in determining critical performance properties (i.e. knock, unburned hydrocarbon emissions) for spark ignition engines. The model is compared against available experimental data of iso-butanol/air laminar burning velocities measured by Veloo and Egolfopoulos [149] and Liu et al. [150]. The results were obtained in a range of equivalence ratios from 0.7 to 1.5 at 1 and 2 atm, but statistically at the same unburned gas temperature, i.e., there is no significant difference between the sets at 343 and 353 K because the uncertainty in temperature measurements was close to 20-30 K as reported by Liu et al. [150]. For the 1 atm study the model is able to accurately reproduce the peak flame speed at the correct stoichiometry (~ 1.1) and the flame speeds for the fuel lean case.
However the model underpredicts the flame speeds for the rich case especially for experimental data by Liu et al. [150] as seen from Figure 4-19. It must be noted here that the experimental data for laminar flame speed for iso-butanol at 1 atm by Veloo et al. [149] and Liu et al. [150] is in good agreement within the reported uncertainty for the lean and stoichiometric flames, but deviates beyond the reported uncertainty range for the fuel rich flames. Hence the uncertainty in the laminar flame speed measurement is quite significant on the rich side and it is possible that much of the discrepancy between predictions vs. data is due to experimental uncertainties. The experimental data for flame speeds at higher pressure is only available from Liu et al. [150] and the model predictions are similar to 1 atm case, i.e. the experimental data is well predicted for the fuel lean flames but underpredicted for the rich flames.

Figure 4-19: Simulated (line) and experimental (symbol) zero-strain laminar flame speed of iso-butanol air mixtures as a function of equivalence ratios (Experiment: 1 atm ○ Veloo et al. [149], Δ Liu et al. [150] and 2 atm □ Liu et al. [150]).
The results of the sensitivity analysis for the rich flame at $\varphi = 1.4$, are reported in Figure 4-20. The reactions with high sensitivity are the chain branching reaction $\text{H} + \text{O}_2 = \text{O} + \text{OH}$, thermal decomposition of methane ($\text{CH}_4 = \text{CH}_3 + \text{H}$) and ketene ($\text{CH}_2\text{CO} = \text{HCO} + \text{H}$) to respective radical and H atom. Among these reactions the decomposition of ketene is most uncertain (~ order of magnitude) as the rate coefficient is calculated using a group contribution method implemented in RMG. The fuel rich flame also has notable sensitivity to fuel decomposition reactions like iso-butanol decomposing to iso-propyl radical and hydroxymethyl radical. Sensitivity analysis to heat of formation of species to laminar flame speed was also carried out and the thermochemistry for most of the sensitive species come from the active thermochemical tables (ATcT) [206] except for iso-butanol whose thermochemistry has been calculated using CBS-QB3 values with bond additivity corrections and has 1-2 kcal/mol uncertainty in the enthalpy.

The peak flame speed occurs close to stoichiometric condition and the sensitivity analysis at $\varphi = 1$ reveals the thermal decomposition of formyl radical and the reaction of vinyl radical with molecular oxygen have high sensitivity.

\[
\text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M} \quad (1)
\]

\[
\text{C}_3\text{H}_3 + \text{O}_2 = \text{HCO} + \text{CH}_2\text{O} \quad (2)
\]
The rate of decomposition of formyl radical has been recently reviewed by Li et al. [207] and the authors recommended the low pressure limit value of $k_1$(cm$^3$ mol$^{-1}$ s$^{-1}$) = 4.75x10$^{11}$T$^{0.66}$exp(-14870 (cal/mol)/RT) based on weighted least-square fitting to all experimental data. They also recommend a collision efficiency of 12 for water, since water is the major product of combustion this efficiency strongly affects the flame speed prediction. If collision efficiencies based on the ethanol reaction mechanism by Marinov [186] are used (collision efficiency of 5 for water) it underpredicts the peak flame speed by 3 – 4 cm/s.

Figure 4-21 presents a comparison between the most recent experimental [208, 209] and theoretical [210-212] rate constants for reaction (2). The rates from RRKM calculations obtained by Mebel et al. [211] are close to the considered experimental results and are the values used in the present model. However, the Arrhenius expressions suggested by Bozzelli and Dean [210] and Marinov et al. [212], which are represented by the upper and lower dashed lines in the shadow region in Figure 4-21, respectively are significantly slower than the experimental data. Except for the current mechanism and one for butanol oxidation proposed by Moss et al. [160], the expression suggested by Mebel et al. [211] has not been applied. For instance, Sarathy et al. [213] preferred to increase empirically the values of $k_2$ by a factor of 1.7 over the Mebel et al. [211] rate constant, while Grana et al. [153] chose kinetic parameters ($k_2$(cm$^3$ mol$^{-1}$ s$^{-1}$)=1.0x10$^{12}$exp[-4000(cal/mol)/RT]) that are in great disagreement with the measured rates over almost the entire range of temperature in Figure 4-21. Although the rate coefficient presented by Marinov et al. [212] for reaction (2) have not been applied for iso-butanol models, it was currently considered because it was widely accepted in combustion mechanisms for ethanol and primary reference fuels [186, 214]. Moreover, it seems that Marinov et al. [212] has concluded a decrease in rate constants was needed as temperature is increased to have good predictions on ethanol flames. The authors feel that these reaction need special attention by kinetics community as even factor of 2 in the rate coefficients can noticeably affect the predicted flame speed.
Figure 4-21: Comparison of literature rate coefficients for \( \text{C}_2\text{H}_3 + \text{O}_2 = \text{HCO} + \text{CH}_2\text{O} \) (Knyazev et al. [208], Bozzelli and Dean [210], Mebel et al. [211], Marinov et al. [186] and Baulch et al. [215]). Present model uses Mebel et al. [211] value.

The current mechanism for \( \text{iso-butanol} \) using the Mebel et al. [211] rate expression, gives predictions in accord with the experiments measured by Veloo and Egolfopoulos [149] and Liu et al. [150].

4.5.6 Ignition delay time

The last set of experiments for which the mechanism is validated are the autoignition delays for \( \text{iso-butanol} \) [160, [154], [155]. The experiments were modeled using the Closed Homogenous Batch Reactor module in CHEMKIN-PRO. The reported ignition delay is the time at which half the maximum [OH] is achieved; these times correspond well to the time at which maximum \([\text{C}_2\text{H}]_x[\text{O}]\) is achieved and the time at which peak pressure rise rate is observed.

4.5.6.1 High temperature shock tubes

4.5.6.1.1 Stanford shock tube experiments

Stranic et al. [154] measured autoignition delay times for \( \text{iso-butanol} \) behind reflected shock waves over a wide range of experimental conditions: 1250 to 1600 K, 1 to 43 atm and equivalence ratios of \( \varphi = 1 \) and 0.5. Overall as seen from Figure 4-22 the model performs very well for the entire pressure range and at both the lean and stoichiometric conditions,
the maximum deviation is within a factor of 2 for all conditions. Even with excellent agreement to the data, it is valuable to look at flux and sensitivity analysis to understand the major decomposition pathways for iso-butanol and sensitive parameters which are estimates to be looked into for future studies. Figure 4-23 gives the iso-butanol flux analysis for the simulation of iso-butanol autoignition, with 3 % initial concentration of O₂, φ =1, P =1 bar, and T =1400 K. Initially the C-C bond fission to form iso-propyl radical and hydroxymethyl radical is the dominant decomposition route for iso-butanol. After 10 μs there is enough buildup of OH radicals such that the flux through H abstraction of iso-butanol by hydroxyl radical becomes the dominant decomposition pathway leading to formation of 1-hydroxy-2-methylpropyl and 3-hydroxy-2-methylpropyl radical.
Figure 4-22: Experimental [154] (shapes) and simulated (lines) autoignition delay for iso-butanol at high temperatures. The stated pressures are used for modeling the shock tube experiments.
The shock tube ignition time is sensitive mainly to small molecule reactions, most of which have been discussed in previous sections. Additionally the C-C bond fission of *iso*-butanol to give *iso*-propyl radical plus hydroxymethyl radical is also sensitive. The rate coefficient for this has been recently calculated by Zhou et al. [187] and has been incorporated in the present model.
4.5.6.1.2 Rapid Compression machine experiments

Ignition delays were measured in a rapid compression machine (RCM) by Weber and Sung [155, 156] for iso-butanol at \( \phi = 1 \), pressure of 15 and 30 atm with temperature range from 750 to 850 K. These studies provide an insight into the low temperature reactivity of iso-butanol. Figure 4-24 gives the comparison of the measured and predicted ignition delays for constant volume simulations (heat loss has not been incorporated). Incorporating the heat loss will increase the ignition delay by about a factor of 2.

![Iso-Butanol: 3.38% fuel, \( \phi = 1.0 \)](image)

Figure 4-24: Experimental [155] (symbols) and simulated (lines) autoignition delay for iso-butanol at low temperature. The stated pressure correspond was used for modeling the RCM experiments. These simulations do not include the experimental heat losses, so the model vs data agreement is not as good at low temperature as it appears in this plot.

The flux analysis (Figure 4-25) for iso-butanol at \( \phi = 1 \) and 750 K reveal that the hydrogen atom abstraction by hydroxyl radical and O atom are the major routes of consumption.
beyond 0.2 sec. Earlier most iso-butanol consumption is by hydroperoxy radicals. As discussed in previous sections currently there is a significant uncertainty associated with iso-butanol + HO$_2$ rate coefficients (current study uses CBS-QB3 RRHO rate coefficients). It is therefore clear that given the model’s strong dependence on these reactions that more accurate values are needed either from theory or from experiments.

![Figure 4-25](image-url)

**Figure 4-25**: Simulated rate of production of iso-butanol during adiabatic isochoric autoignition ($P = 30$ atm, $T = 750$ K and $\phi = 1$). Hydrogen abstraction by HO$_2$ is the dominant consumption path during the pre-ignition period.

### 4.6 Conclusion

A detailed, robust reaction mechanism for iso-butanol has been constructed using an automated, open-source software package, Reaction Mechanism Generator (RMG). The
model has been validated against multiple types of experiments – flames, jet-stirred reactors, shock tubes – including new speciation data for pyrolysis of iso-butanol in a plug flow reactor. The validation targets selected cover a wide range of reaction conditions – diffusion and premixed, rich and lean, over a pressure range of 1-45 atm and a temperature range of 850-1800 K.

In general good agreement is seen for the prediction of the product distribution under pyrolysis conditions including soot precursors like 1,3-cyclopentadiene and benzene. The model also has reasonable predictions for most high temperature oxidation experiments. The current mechanism predicts the centerline concentration of all species formed in an iso-butanol doped methane diffusion flame including aromatics such as benzene well. The model is able to accurately reproduce the peak flame speed at the correct stoichiometry (~1.1) and the flame speeds for the fuel lean case, but slightly underpredicts the flame speeds for the rich case. The model also predicts the concentration profiles of all major species in the opposed-flow diffusion flame experiments measured by Grana et al. [153] well. Moreover, the calculated ignition delay times agree well with the ignition delays measured by Stranic et al. [154]. The performance for the jet stirred reactor experiments can be improved because the model significantly overpredicts the rate of consumption of iso-butanol especially for temperatures lower than 850 K. The discrepancy between the model and experiment can be attributed to the large uncertainties in calculated HO₂ + iso-butanol rate constants (since no hindered rotor were included in the rate calculation the uncertainty is an order of magnitude at T~ 800 K) and in the OH + iso-butanol product branching ratios. It is clear that having access to improved rate coefficients for the hydrogen abstraction reactions by HO₂ with uncertainty lower than a factor 2 will be a significant step forward and allow development of better predictive kinetic models for alcohol oxidation. Another source of discrepancy between the model and experiments at low temperature is the peroxy chemistry as the current model rates are based on alkane-like rate constants and might have an incomplete treatment of all the pathways. It is recommend that the current model be used for applications where the temperature > 850 K. Further theoretical and quantum chemical studies are needed in understanding the rates of alcohol peroxy pathways and extending the model to lower temperatures.
Chapter 5

*Extending alcohol mechanisms to n- and iso-pentanol*

This chapter focuses on extending the butanol mechanisms to higher alcohols. Pentanol is a five carbon alcohol which can be produced from natural microbial fermentation or engineered microorganisms. Its higher carbon number presents several advantages over smaller alcohols such as ethanol: higher energy content, lower vapor pressure and better fuel compatibility. The intermediate size of pentanols gives them fuel characteristics in between that of alkanes and alcohols [216]. In this study, we generate a detailed reaction networks for n- and iso- pentanol combustion with RMG. We validate the high temperature chemistry by new experimental pyrolysis data obtained in a plug flow reactor. We further simulate the laminar flame speeds and ignition delays at high temperatures with the RMG model and identify significant differences from previously published pentanol models. This work highlights the mature state of RMG-database for modeling alcohol combustion, as only a limited number of reaction rates had to be updated to predict the experimental data accurately.
5.1 Introduction

To reduce global dependence on traditional fossil fuels in internal combustion engines, many have proposed a shift to straight or blended bio-fuels. Biofuels produced from biomass show strong potential for reducing harmful emissions and alleviating petroleum shortages, making research in this area very attractive [217-220]. Bio-alcohols in particular have gained a lot of traction, with great advances in recent years for ethanol and butanol. As the first-generation biofuel, ethanol is widely studied and is used as a transportation fuel throughout the world. However, ethanol has several drawbacks, including its hygroscopicity, corrosivity, and low energy density. This has motivated research on higher carbon alcoholic fuels such as butanols and pentanols. The previous work by Harper et al. [113, 221], Van Geem et al. [162] and Chapter 4 of this thesis focused on developing comprehensive kinetic mechanism for all butanol isomers using RMG. This work focuses on developing oxidation and pyrolysis models for two important pentanol isomers $n$- and iso-pentanol.

$n$-Pentanol is a promising candidate for diesel blends due to its low autoignition temperature, higher reactivity than butanols and higher heating value[220, 222, 223]. Furthermore, it is much easier to blend $n$-pentanol into conventional hydrocarbon fuels due to its longer carbon chain. $n$-Pentanol [224] also displays a negative temperature coefficient (NTC) very similar to that of alkanes [225], which indicates that this fuel may be applicable to auto-ignition controlled engines. Campos-Fernandez et al. [222] recently studied pentanol/diesel blends in a direct-injection compression ignition engine. Their results indicate that the blends have better combustion characteristics than diesel while delivering similar engine performance in terms of power output, brake-specific fuel consumption, and torque. It is proposed by Fernandez et al. that blends with up to 25% $n$-pentanol can replace diesel fuels in existing engines.

Though $n$-pentanol is a promising alternative fuel candidate, few studies regarding its combustion kinetics exist in the literature. Togbe et al.[226] published the first kinetic model on $n$-pentanol oxidation validated by experimental jet-stirred reactor (JSR) data and laminar flame speeds. Except for the primary carbon atom, hydrogen abstractions from all carbon sites were assigned the same reaction rate coefficient, and simulated results from the mechanism showed large deviations from experimental ignition delays [227] and
Laminar flame speeds [16]. Heufer et al. [228] developed an improved detailed oxidation mechanism of \( n \)-pentanol covering both low and high temperature chemistry. In that study, the bond energies of C–H and C–C were calculated using quantum chemistry. The mechanism agrees well with ignition delay and JSR data, though it has large discrepancies with the laminar flame speeds obtained by Togbe et al. There are also no studies on kinetics of \( n \)-pentanol pyrolysis in the literature.

\textit{iso}-Pentanol on the other hand is a bio-derived gasoline substitute [229]. Yang et al. [230] studied the use of \textit{iso}-pentanol in a HCCI engine and found that \textit{iso}-pentanol displays intermediate temperature heat release (ITHR) characteristics which is important for better engine control. To explore the applicability of \textit{iso}-pentanol as a gasoline alternative several combustion studies were conducted. Dayma et al. [231] experimentally measured speciation data for oxidation of \textit{iso}-pentanol in JSR. Tsujimura et al. [216] developed a kinetic model for \textit{iso}-pentanol oxidation and validated it against ignition delay times measured in a shock-tube (ST) at high temperatures and a rapid compression machine (RCM) at low temperatures. Tang et al. [232] also measured the high temperature ignition behavior of \textit{iso}-pentanol and found that \textit{iso}-pentanol is less reactive than \( n \)-pentanol. Recently, Sarathy et al. [233] developed a detailed model for \textit{iso}-pentanol combustion with updates to the Tsujimura et al. [216] model. They validated their model against new and existing experimental data at pressures of 1–60 atm, temperatures of 650–1500 K and equivalence ratios of 0.25–4.0, covering both premixed and non-premixed environments. However one area where the model was not validated was under pyrolysis conditions.

The goal of this work is to provide detailed oxidation and pyrolysis kinetic mechanism for \( n \)-pentanol and \textit{iso}-pentanol. These models are validated against existing experimental data and also new experimental pyrolysis data obtained in a plug flow reactor at the Laboratory for Chemical Technology (LCT), Ghent University.
5.2 Experimental and the simulation method

5.2.1 The pyrolysis setup

A bench-scale pyrolysis setup at the Laboratory for Chemical Technology (LCT) was used to conduct \( n \)-pentanol and \( iso \)-pentanol pyrolysis experiments. Here, we provide a brief description of the setup. Details of the setup can be found elsewhere [111]. Note that the same setup was also used to obtain datasets for \( n \)-butanol [113] and \( iso \)-butanol pyrolysis [137].

The experimental setup, shown in Figure 5-1, consists of three parts: the feed section, the reaction section, and the analysis section. The peristaltic pump is used to pump liquid pentanol into an evaporator at 523K. The diluent, \( N_2 \), is heated separately to reach the same temperature. The \( N_2 \) and pentanol are mixed before entering the reactor.

The reactor is made of Incoloy 800HT with a length of 1475mm and tube diameter of 6mm. Eight thermocouples are placed along the reactor which measure the gas temperature. The reactor is in a vertical position in a rectangular furnace divided into four.
separate sections, each having an electrical heater and controlled by one of the thermocouples. An extra heater between the outlet of the reactor and the analysis section compensates for any heat loss. The pressure in the reactor was controlled by a back pressure regulator downstream from the outlet of the reactor. The coil inlet pressure (CIP) and the coil outlet pressure (COP) were measured by two manometers situated at the inlet and outlet of the reactor, respectively. The pressure drop is found to be negligible.

The details of the analysis section have been described in previous studies [111, 164, 234]. The hot reactor effluent enters a heated sampling system kept at 523K. A sample of the effluent is injected on a dedicated C+ gas chromatograph, i.e. a so-called refinery gas analyzer (RGA), after removal of the C5+ fraction through condensation. This GC is equipped with two thermal conductivity detectors (TCD), for quantification of the permanent gasses, and a flame ionization detector (FID), for quantification of C4- hydrocarbons. The diluent, N2, was used as internal standard. Furthermore, a gas chromatograph dedicated to quantifying small oxygenated species (water, formaldehyde, methanol) analyzes the reactor effluent without prior condensation. Propene, quantified on the RGA, was used as secondary internal standard. Finally, the hot reactor effluent is injected on a GCxGC equipped with a FID, used for quantification, and a time-of-flight mass spectrometer (TOF-MS), used for identification. This GC is able to detect the majority of species in the effluent stream, ranging from methane to pyrene. Methane, quantified on the RGA, was used as secondary internal standard.

This methodology allows online analysis of the complete effluent composition and avoids separate gas, condensate analysis.

For each studied condition, we repeated the experiment at least three times to ensure reproducibility. We closed the mass balances within 5%. The experimental operating conditions for the pyrolysis of \textit{n-} and \textit{iso-} pentanol are listed in Table 5.1. Using these conditions, we study the effect of temperature and dilution on product distribution at similar residence times.
Table 5.1: Experimental conditions for the pyrolysis of \( n \) and \( iso \) pentanol.

<table>
<thead>
<tr>
<th></th>
<th>High Dilution</th>
<th>Low Dilution</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_{mg} / K )</td>
<td>913-1073</td>
<td>913-1073</td>
</tr>
<tr>
<td>COP / ( 10^5 )Pa</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Hydrocarbon flow rate / g s(^{-1})</td>
<td>( 3.02 \times 10^{-2} )</td>
<td>( 4.39 \times 10^{-2} )</td>
</tr>
<tr>
<td>Nitrogen flow rate / g s(^{-1})</td>
<td>( 1.69 \times 10^{-2} )</td>
<td>( 1.06 \times 10^{-2} )</td>
</tr>
<tr>
<td>Conversion / %</td>
<td>20-100</td>
<td>20-100</td>
</tr>
</tbody>
</table>

5.2.2 Reaction mechanism generation

We use the open source software package Reaction Mechanism Generator (RMG) [235] to generate pentanol kinetics models. RMG constructs a reaction network at a set of given initial conditions and error tolerances, using 40 reaction family templates to build the reactions, including H abstraction, β-scission, and recombination reactions [235]. The thermal properties of species are estimated using Benson’s group additivity scheme [236]. The transport properties, such as Lennard-Jones parameters, are estimated using empirical correlations based on species’ critical properties. The user has the option to provide libraries with values for the reaction rate coefficients, thermodynamic and transport properties. These libraries will overwrite RMG estimates in the model generation. RMG can also be seeded with an existing reaction network. All species and reactions in such a seed mechanism, along with the species supplied in the initial condition, will be included in the model. The rate-based algorithm will then enlarge the mechanism to meet the user termination criterion.

In this study, we construct the pentanol mechanism using a small molecule (C\(_1\)-C\(_2\)) reaction network developed by Metcalfe et al. [237] as the seed mechanism. This mechanism has been extensively validated over a wide range of C\(_1\)-C\(_2\) experiments.
The rate-based network generation algorithm in RMG requires a set of initial conditions, including feed composition and reactor conditions, as well as a criterion for terminating network generation.

For pentanol oxidation, reactor conditions correspond to pressures of 1.0, 10 and 20 atm, and temperatures of 700 K, 1000 K and 2000 K while feed composition corresponds to four equivalence ratios (0.5, 1.0, 2.0, 4.0) in air. The criteria for terminating the simulation was set to be 90% fuel conversion with an error tolerance of 0.1.

For the pentanol pyrolysis condition, the RMG network generation is at a pressure of 1.0 atm and a temperature range of 900-1200 K. The initial composition was set according to the pyrolysis experimental conditions. The termination criterion was set to be residence time of 1 sec with an error tolerance of 0.05.

The pentanol pyrolysis and oxidation models are merged in order to yield a model valid over the entire range of conditions. Separate models for n- and iso-pentanol were generated using RMG.

5.2.3 Quantum calculations

5.2.3.1 Methodology

Zhao et al. [238] theoretically studied the dominant reaction channels for the thermal decomposition of three pentanol isomers (n-, iso-pentanol and 2-methyl-1-butanol) at CBS-QB3 level of theory. Apart from the study by Zhao there is no other theoretical study on the rate coefficients for n- or iso-pentanol.

Recently published pentanol models [16, 216, 233] made use of approximations to obtain the required rate coefficients or fell back on theoretical results performed on similar species, such as butanols. Due to their importance for speciation, rate coefficients for important hydrogen abstraction reactions and β-scissions were calculated within the conventional transition state framework:

$$k_x(T) = \kappa(T) \frac{k_B T}{h} \frac{q_x}{\prod_{\text{reactant-i}} q_{\text{reactant-i}}} e^{\frac{\Delta E_B}{RT}}$$  \hspace{1cm} (5-1)
where $k_*$ is the high-pressure limit rate coefficient, $k_B$ Boltzmann’s constant, $T$ the temperature, $h$ Planck’s constant, $q$ the partition function per volume, $\Delta E_0$ the zero-point energy corrected energy barrier and $R$ the universal gas constant. The Eckart method [188] was used to calculate the tunneling contributions, $\kappa(T)$, using the formalism presented in ref. 31 [239]. Some of the studied reactions, mainly hydrogen abstraction reactions and $\beta$-scission reactions involving OH, have a low lying van der Waals minimum near the entrance or exit channel and a two transition state model should be used. However, at the temperatures of interest, i.e. around 1000 K, the inner transition state, which is entropically more restricting than the outer transition state, will be the dominating bottleneck for reaction. Consequently, rate coefficients for these reactions can be obtained accurately using only the inner transition state.

The electronic energies of the species involved were calculated with CBS-QB3 [240-242] with the vibrational frequencies calculated using B3LYP/6-311G(2d,d,p) [242] using a scaling factor of 0.99. All internal rotations were treated as 1-D hindered rotors by solving the 1-D rigid rotor Schrödinger equation using the reduced moment of inertia $I_{230}^2$ evaluated at the equilibrium geometry. The 1-D hindered rotor potentials were calculated using B3LYP/6-31G(d) with a step size of $10^\circ$ and relaxing all other degrees of freedom [243]. In some cases relaxed optimizations caused the transition states to break to the reactants or products, mainly loose transition states, and in those cases unrelaxed scans were used instead. All of the electronic energy calculations were performed using Gaussian 03 [116] and the rate coefficients were calculated using CANTHERM [130].

5.2.3.2 n-Pentanol fuel decomposition

In previous studies, it has been demonstrated that hydrogen abstraction reactions[162, 221] dominate the initial step of fuel consumption of primary and secondary alcohols. In Table 5-2 Arrhenius parameters and rate coefficients at 1000 K are presented for hydrogen abstraction reactions from $n$-pentanol by hydrogen, methyl and OH radicals.

Just as for $n$-butanol, the $\alpha$ hydrogen atom, i.e. adjacent to the O atom, is the most easily abstracted. This is particularly the case for OH, of which the rate coefficient for $\alpha$ hydrogen abstraction by OH is at least a factor 5 faster than the competing hydrogen abstraction reactions. The H radical is less selective towards the C-atom it abstracts from.
At 1000 K, the rate coefficient obtained for H· abstraction from the α-site is within a factor 2 with those obtained from the other carbon atoms.

Hydrogen abstraction from the oxygen atom by H is a factor 10 lower at 1000 K. This is in contrast with the rate coefficients obtained for hydrogen abstraction from the hydroxyl group by methyl and OH, which are of the same order of magnitude as those obtained for H abstraction from the β and γ site in n-pentanol. The hydrogen abstractions from the δ and ε sites of n-pentanol come from the analogous alkane rate coefficients.

**Table 5-2: Rate coefficients (mol⁻¹ cm³ s⁻¹) for hydrogen abstraction reactions by H, CH₃ and OH from n-pentanol calculated using CBS-QB3 and the 1D-HR treatment for torsional modes.**

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Arrhenius parameters</th>
<th>Rate coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>n</td>
</tr>
<tr>
<td></td>
<td>cm³ mol⁻¹</td>
<td>s⁻¹</td>
</tr>
<tr>
<td>H</td>
<td></td>
<td></td>
</tr>
<tr>
<td>⍠OH + H → ⍠O· + H₂</td>
<td>2.9×10⁴</td>
<td>2.88</td>
</tr>
<tr>
<td>⍠OH + H → ⍠OH· + H₂</td>
<td>7.8×10⁵</td>
<td>2.46</td>
</tr>
<tr>
<td>⍠OH + H → ⍠OH· + H₂</td>
<td>4.4×10⁵</td>
<td>2.56</td>
</tr>
<tr>
<td>⍠OH + H → ⍠OH· + H₂</td>
<td>2.9×10⁶</td>
<td>2.32</td>
</tr>
<tr>
<td>CH₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>⍠OH + CH₃ → ⍠O· + CH₄</td>
<td>1.4×10⁻³</td>
<td>4.45</td>
</tr>
</tbody>
</table>

177
Besides H abstractions from the parent fuel, the radical mechanism governing the pyrolysis and combustion will be governed by β-scission reactions. In Table 5-3 Arrhenius parameters and rate coefficients at 1000 K for 7 relevant β-scissions are shown.

As is usually observed alkoxy radicals rapidly β-scission. The lowest activation energy and highest rate coefficient is obtained for β-scission in the pentoxy (CH₃(CH₂)₄O) radical which yields formaldehyde and 1-butyl.

The α-radical, CH₃(CH₂)₃CHOH, will predominantly decompose to 1-propyl and vinylalcohol. At 1000 K the rate coefficient for this reaction is more than one order of magnitude larger than for the competing but more endothermic β-scission reaction to pentanal + H.

Two thirds of the β-radicals, CH₃(CH₂)₃CHCH₂OH, decomposes to prop-2-en-1-ol and ethyl, while one third reacts to 1-pentene and OH radicals, as shown in Table 5-3.
The γ-radical, $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_2)_2\text{OH}$, will mainly decompose to 1-butene and $\text{CH}_2\text{OH}$, while a minor path leads to but-3-en-1-ol and $\text{CH}_3$.

The δ- radical, $\text{CH}_3\text{CHCH}_2(\text{CH}_2)_2\text{OH}$ will mainly decompose to propene and $\text{CH}_2\text{CH}_2\text{OH}$ radical. The ε-radical, $\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_2)_2\text{OH}$ will primarily decompose to ethene and $\text{CH}_2\text{OH}$ radical. In this work, we do not calculate the rates from the δ- and ε-radicals as we expect the rates to be similar to that for alkanes.

The intra-molecular hydrogen migrations are estimated from the n-butanol rate coefficients calculated by Zhang et al. [244]. The intra-molecular hydrogen migration from the δ-radical to the pentoxy radical is seen to be important for the high temperature pyrolysis system.
formation of aromatics

In this work special attention is paid to the formation of aromatics like benzene. Here, we reassess some of the rate coefficients reported in literature (by Sharma et al. [95]). Since Sharma et al. did not report the high-pressure limit rate coefficients, we report the rates of the corresponding reactions in Table 5-4.
Table 5.4: High-pressure limit rate coefficients for Fulvene + H going to Benzene + H reactions calculated using CBS-QB3 and the 1D-HR treatment for torsional modes.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Arrhenius parameters</th>
<th>Rate coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A$</td>
<td>$n$</td>
</tr>
<tr>
<td></td>
<td>s$^{-1}$ or mol$^{-1}$ cm$^3$ s$^{-1}$</td>
<td>kcal mol$^{-1}$</td>
</tr>
<tr>
<td>Fulvene + H$^+$ to Benzene + H$^+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fulvene + H$^+$ to Benzene + H$^+$*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fulvene + H$^+$ to Benzene + H$^+$*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fulvene + H$^+$ to Benzene + H$^+$*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fulvene + H$^+$ to Benzene + H$^+$*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fulvene + H$^+$ to Benzene + H$^+$*</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5.3  n-Pentanol results and discussion

5.3.1 Pyrolysis experiment

Figure 5-2 displays the measured experimental conversion of n-pentanol versus the set temperature in the reactor along with the model predictions. The model is simulated using CHEMKIN-PRO [245] plug flow reactor model with the experimental initial conditions and the temperature profile. Previous studies have validated the plug flow assumption for this reactor [113]. Experimentally the conversion is 20% at 913 K and is approximately 100% at 1073 K. The model agrees well with the experimental results throughout the temperature range. The observed conversion was similar for the low and high dilution conditions throughout the temperature range.
Figure 5-2: $n$-Pentanol conversion as a function of the average reactor temperature (symbols: experiment; lines: simulation; square: low dilution, 1 mol $n$-pentanol/ 1 mol $N_2$; circle: high dilution, 1 mol $n$-pentanol/4 mol $N_2$).

Figure 5-3 illustrates the yields of the major products in the $n$-pentanol pyrolysis experiments as compared with the simulation results. The RMG model accurately predicts carbon monoxide, methane, ethane and all major alkenes. As both datasets were obtained at similar residence time, the difference in the measured and simulated profiles is mainly due to the dilution of the feed. For example, both ethene and ethane profiles depend on the reactivity of the ethyl radical. High dilution favors decomposition to ethene and hydrogen while low dilution causes hydrogen abstraction forming ethane to gain importance.
Figure 5-3: The major pyrolysis products at two dilution conditions as a function of temperature (symbols: experimental; lines: simulation results; black square: low dilution, 1mol \( n \)-pentanol/ 1mol \( N_2 \); red circle: high dilution, 1mol \( n \)-pentanol/ 4 mol \( N_2 \)).
Figure 5-4 presents the model-predicted fuel consumption pathways and major product formation channels at 10% and 90% \textit{n}-pentanol conversion, with $T = 1000$ K, $P = 1.7$ bar for 1 mol \textit{n}-pentanol : 4 mol N$_2$. At both conversions \textit{n}-pentanol is primarily consumed by hydrogen abstraction by H ($\sim 33\%$), CH$_3$ ($\sim 33\%$) and OH ($\sim 8\text{-}22\%$) radical to yield six different C$_5$H$_{10}$O radicals. Hydrogen abstraction reaction from the $\alpha$-carbon accounts for the highest consumption of \textit{n}-pentanol, consistent with previous \textit{n}-propanol [246, 247], \textit{n}-butanol [113, 248] and \textit{n}-pentanol [233] studies.

The \textit{n}-pentoxy radical decomposes through $\theta$-scission to primarily yield formaldehyde + \textit{n}-butyl radical, which subsequently fragments to ethene + ethyl. The dominant reaction route for $\alpha$-C$_5$H$_{10}$OH radical is C-C $\theta$-scission to \textit{n}-propyl radical + vinyl alcohol. The vinyl alcohol can undergo unimolecular or assisted keto-enol tautomerization forming acetaldehyde. A small fraction of $\alpha$-C$_5$H$_{10}$OH radical is converted to pentanal by $\theta$-scission of the O-H bond. $\theta$-C$_5$H$_{10}$OH radical can either form a OH radical + 1-pentene or ethyl radical + prop-2-en-ol. The latter pathway is computed to be slightly favored in the investigated pyrolysis conditions. 1-Butene and propene can be formed by C-C $\theta$-scission reactions of $\gamma$-C$_5$H$_{10}$OH and $\delta$-C$_5$H$_{10}$OH radicals, respectively. A fraction of the $\delta$-C$_5$H$_{10}$OH radicals undergo intra-molecular hydrogen abstraction to give \textit{n}-pentoxy radical. The rate coefficient estimate for this 1,5 hydrogen shift reaction comes from literature calculations of \textit{n}-butanol, i.e. hydrogen shift of the $\delta$-butanol radical to \textit{n}-butoxy by Zhang et al. [244]. Ethene, the most abundant alkene, is produced through $\theta$-scission reactions from various radicals such as $\varepsilon$-C$_5$H$_{10}$OH, CH$_2$CH$_2$OH and \textit{n}-propyl. 1-pentene is also formed by unimolecular dehydration of the parent alcohol at higher temperatures.
Figure 5-4: Reaction pathway analysis for n-pentanol pyrolysis (1 mol n-pentanol : 4 mol N₂) in a plug flow reactor operated at P = 1.7 bar and T = 1000 K. rates are expressed relative to the total n-pentanol consumption rate and the values for 10% conversion are written in normal font while those for 90% conversion are written in bold.

Figure 5-5 shows the yield of soot precursors over a wide temperature range. Reasonable agreement can be observed between the experimental and simulation results for the soot precursors 1,3-butadiene (1,3-C₄H₆), acetylene, benzene and 1,3-cyclopetadiene. However, the current model is unable to predict the toluene formed during the pyrolysis experiments. Various pathways to toluene formation were explored theoretically, including cyclopentadienyl plus acetylene, cyclopentadienyl plus ethene, phenyl plus CH₃ reactions. However none of the pathways is computed to be fast enough to explain the amount of toluene formed in the experiments. It must be noted that the model of Heufer et al.[228] accurately predicts the major non-aromatic products; however it does not predict any aromatic species. Future work will focus on understanding formation of aromatics below 1100K.
As mentioned earlier, one of the aims of this work is to understand benzene formation. Figure 5-6 gives the computed major formation pathways for benzene during \( n \)-pentanol pyrolysis for two different temperatures \( T = 1000 \) K and \( T = 1100 \) K. Conventionally most kinetic models which include benzene formation include only the vinyl radical + butadiene pathway [93, 249-251] and the cyclopentadienyl + CH\(_3\) pathway [95]. The automatic mechanism generation by RMG not only finds these two pathways for benzene formation.
but also two additional pathways which are important under pyrolysis conditions-butadiene + allyl radical and cyclopentadienyl + ethyl radical.

The butadiene + allyl radical pathway calculated to be the dominant pathway (~70% of the benzene formation rate) for temperatures below 1000 K. It involves formation of the C7H11 adduct which undergoes intra-molecular hydrogen migration followed by cyclization to give 2-methyl-cyclohex-3-enyl radical. The 2-methyl-cyclohex-3-enyl radical undergoes β-scission to give 1,3-cyclohexadiene. The 1,3-cyclohexadiene will further undergo hydrogen abstraction and β-scission to give benzene. The butadiene + allyl radical pathway has a much higher flux than the butadiene + vinyl radical pathway because the concentration of allyl radical is ~10^3 higher than the vinyl radical concentration in the system. The rates used for the butadiene + vinyl radical pathway come from the recent experimental and theoretical study by Buras et al. [252] while the allyl + butadiene pathway rates have been estimated using RMG group contribution method and so have a higher uncertainty.

For temperatures > 1100 K the cyclopentadienyl radical will undergo addition with CH₃ and ethyl radicals to form methyl-cyclopentadiene and ethyl-cyclopentadiene respectively. The methyl-cyclopentadiene undergoes hydrogen abstraction followed by 1,3-addition and ring expansion reaction to eventually yield benzene. This pathway has been theoretically studied by Sharma et al. [95] and the rate coefficients have been re-evaluated in this work. The ethyl-cyclopentadiene undergoes 1,5-sigmatropic shifts and bond scission to give methyl-cyclopentadienyl radical, which goes on to form benzene as discussed above.
Figure 5-6: Predicted major formation pathways to benzene for \( n \)-pentanol pyrolysis in a plug flow reactor operated at \( P = 1.7 \) atm and \( T = 1000 \text{K} \) (bold italics) and \( T = 1100 \text{K} \) (normal text). Rates are expressed relative to the total benzene formation rate. All minor channels are not shown in the picture and in certain cases these channels can add up to a significant flux.

5.3.2 Laminar flame speed experiment

Figure 5-7, shows the comparison of RMG model, NUI model published by Heufer et al. [228] and the Li et al. model [16] against Li et al.’s experimental laminar flame speed data [16]. All three models yield similar results at lean conditions and agree well with the experimental data. Slight deviations from the experiment are seen for rich conditions for all three models, with the current model giving the best prediction while the NUI model over-predicts and the Li et al. model under-predicts the experimental data. However, the differences between the three models are not large; and well within the experimental uncertainty range for the laminar flame speed measurement.

189
Given the deviations at the rich condition, sensitivity analyses for all three models help identify the reactions that strongly affect the model predictions and elucidate the differences between the three models. Figure 5·8 shows the normalized reaction sensitivities for the three models for laminar flame speed predictions at an initial temperature of 433K, initial pressure of 0.1MPa and equivalence ratio of 1.4. The sensitivity analysis shows that the laminar flame speeds are sensitive to the chemistry of small molecules, especially H₂/C₁-C₂ reactions, and are not dependent on the fuel. The chain branching reaction, H+O₂=O+OH, is the most sensitive reaction in all three models. Differences among the models in estimates of the rate coefficients for the sensitive reactions lead to the disparities in the predicted laminar flame speed. The different models also predict different branching ratios for the n-pentanol decomposition, leading to different amounts of C₃ and C₂ species. Laminar flame speeds are sensitive to C₃ reactions only for the Li model. The C₃ reactions have negative sensitivities, shown in Figure 5·8, and retard the overall laminar speed in the Li et al. model; this effect is much less important in the other models.
Figure 5.7: The comparison of the laminar flame speed of n-pentanol simulated with three mechanisms. Experimental data from ref. [16].
Figure 5.8: Sensitivity analysis of n-pentanol laminar flame speed for three models at $T_u = 433$ K, $P_u = 0.1$ MPa and $\phi = 1.4$.

5.3.3 Ignition delay experiment

The RMG model is also validated against the high temperature $n$-pentanol autoignition delay times measured by Tang et al. [227] and compared against the NUI and Li et al. models in Figure 5-9. We used the Closed Homogenous Batch Reactor module in CHEMKIN-PRO to model the experiments. The simulations are carried under adiabatic isochoric (constant-volume) conditions. This neglects some non-idealities in the shock-tube and RCM experiments. The predicted ignition delay is defined here as the time at which half the maximum $[\text{OH}]$ is achieved; these times correspond well to the time at which maximum $[\text{C}_2\text{H}] \times [\text{O}]$ is achieved and the time at which peak pressure rise rate is observed.
The ignition delay times were simulated under highly diluted conditions at pressures of 1 bar and 2.5 bar and equivalence ratios of 0.25, 0.5, and 1.0. From Figure 5-9, we can see that the three models exhibit reasonable agreement with the experimental data at pressure of 1.0 bar for the lean mixtures in Figure 5-9 (a) and (b). However, both the Li and the NUI models predict slower ignition delays for the stoichiometric conditions as seen in Figure 5-9(c). Model simulations using the RMG model match the experimental observations over the entire pressure and high temperature range under both lean and stoichiometric conditions. The maximum deviation is about a factor of 2.

Figure 5-9: Comparison of experimental [227] (shapes) and simulated (lines) autoignition delay for $n$-pentanol oxidation at high temperatures. The three mechanisms used are this work (solid line), Ref. [16] (dash line), and Ref. [228] (dash dot line). The stated pressures are used for modeling the shock tube experiments. Figure 5-10 shows the sensitivity analysis on the OH radical production at $T = 1400$ K, $P = 1$ bar, $\phi = 1.0$ for 0.5% $n$-pentanol and 40% fuel conversion. For the Li model, the most sensitive ignition promoting reaction is $\text{H} + \text{O}_2 = \text{OH} + \text{O}$, similar to the results from the
laminar flame speed sensitivity analysis. Furthermore, according to Li et al. model the ignition delay times are sensitive to H\textsubscript{2}/C\textsubscript{1}–C\textsubscript{3} molecule reactions and not to fuel-specific reactions.

While the RMG and NUI model-predicted ignition delays are sensitive to some of the same reactions as the Li model, according to those models the most significant promoting reaction is CH\textsubscript{3}+HO\textsubscript{2}=OH+CH\textsubscript{2}O and the most significant retarding reaction is HO\textsubscript{2}+OH=H\textsubscript{2}O+O\textsubscript{2}. For these two models, ignition delay times are also sensitive to unimolecular fuel decomposition reactions and hydrogen abstractions from the fuel.
Figure 5-10: Reaction sensitivity analysis for OH radical production with three mechanisms at 1.0 bar, 1400K, and $\varphi = 1.0$ for 0.5% $n$-pentanol and 40% fuel conversion.

Figure 5-11 gives the reaction pathway fluxes for the three models at 1400 K, 1.0 bar, $\varphi = 1.0$ for 0.5% $n$-pentanol and 40% fuel conversion. For all three models, $n$-pentanol consumption is primarily by hydrogen abstraction occurring at the six different sites, with a small fraction consumed through the unimolecular decomposition. The RMG and NUI models have similar branching ratios for all sites except the $\gamma$ and $\varepsilon$ carbons. The Li model however has significantly different branching ratios. For the RMG and NUI models, H abstraction from the $\alpha$ site is dominant, and very little abstraction occurs at the hydroxyl group, consistent with the bond energies [233]. In the Li model, H abstractions from the $\alpha$, $\beta$, $\gamma$, $\delta$ sites have the same branching ratio due to assignment of the same reaction rates by the hydroxyl group. There is also significant amount of abstraction from the hydroxyl group in the Li model.

The pentoxy radical decomposes to formaldehyde and $n$-butyl radical in both the RMG and NUI models while in the Li model it first isomerizes to $\gamma$, $\delta$, $\varepsilon$ - C$_5$H$_{10}$OH radicals, and these then undergo decomposition to smaller species. The $\alpha$-C$_5$H$_{10}$OH radical $\beta$-scissions to give vinyl alcohol + $n$-propyl radical in all three models. However, in the RMG model the $\alpha$-C$_5$H$_{10}$OH radical also has a significant branching to pentanal + H atom at 1400 K. In the RMG model, the $\beta$-C$_5$H$_{10}$OH radical consumption is mainly by the bond scission between the $\gamma$- and the $\delta$-carbon, predominantly producing prop-2-en-1-ol while in the NUI and Li model, the $\beta$-C$_5$H$_{10}$OH radical undergoes a competing $\beta$-scission reaction to give almost 50% 1-pentene. The NUI model over predicts the 1-pentene yield in the pyrolysis experiments.
The $\beta$C$_5$H$_{10}$OH and $\alpha$C$_5$H$_{10}$OH radicals decompose to propene + CH$_2$CH$_2$OH radical and ethene + CH$_2$(CH$_2$)$_2$OH radical respectively in the RMG and NUI models, however in the Li model these radicals also isomerize to $\alpha$C$_5$H$_{10}$OH and $\beta$C$_5$H$_{10}$OH radicals respectively. These differences lead to the observed deviations in simulation results between the models.

Figure 5-11: Reaction pathway analysis for $n$-pentanol oxidation ($\varphi = 1.0$) in an isothermal batch reactor simulation at $P = 1$ bar and $T = 1400K$. Rates are expressed relative to the total $n$-pentanol consumption rate. The values are at 40% conversion. (bold: RMG model; italic: NUI model; normal: Li model).

The three models were also validated against the experimental results on autoignition delay times measured at low temperature and high pressure by Heufer et al. [224]. Figure 5-12 gives the comparison between the experimental and predicted ignition delay for constant volume adiabatic simulations using the three models. Incorporating the experimental heat loss will increase the predicted low temperature ignition delay by about a factor of 2. The RMG and NUI models yield accurate predictions for the intermediate temperature regime. However at low temperatures, the experimental data shows alkane-
like NTC behavior in good agreement with the NUI model. The RMG model is in fairly good agreement with the NUI model (and the experimental data) for the 30 bar case, but the RMG model’s NTC curve is offset by about 100 K from the 9 bar case. The Li model does not incorporate the low temperature peroxy chemistry and is very inaccurate below 100 K.

![Figure 5.12: Experimental [224] (symbols) and simulated (lines) autoignition delay for n-pentanol at low temperature. The stated pressure correspond was used for modeling the RCM experiments. These simulations for all models do not include the experimental heat losses, so the model vs data agreement is not as good at low temperature as it appears in this plot. RMG model uses the NUI ketohydroperoxide decomposition rate.](image)

Previous RMG butanol models [113, 137] were unable to predict ignition under low temperature conditions as shown by Zhu et al. [253]. The initial RMG generated n-pentanol model also had similar drawbacks. Analysis from Chapter 2 and sensitivity analysis indicate that low temperature ignition delay is strongly affected by the rate of decomposition of the ketohydroperoxide. The original RMG estimates this rate in the recombination direction \( \text{OQ'O + OH} \rightarrow \text{OQ'OOH} \) as \( 10^{13} \) (cm\(^3\)/mole-s) and uses the thermochemistry of the species to obtain the decomposition rate. The NUI model [228] uses an estimate of \( A = 10^{16} \) (s\(^{-1}\)) and \( E_a = 39 \) kcal/mol for the decomposition. Figure 5.13 gives the comparison of the ketohydroperoxide decomposition rate as estimated by RMG and the NUI model. RMG’s predicted rate is about a factor of 100 slower than the NUI rate causing the original RMG model predictions to be much longer than the experimental measured values. The RMG model used for making the ignition delay predictions (Figure 5.12) uses the same ketohydroperoxide decomposition rate as the NUI model. However future work
must focus on obtaining better estimates for this rate. Since the ketohydroperoxide contains at least one carbonyl group and one OOH group there is significant hydrogen bonding and the partition functions obtained using single 1d HR approximations can have significant errors [42]. Advanced methods like MS-T calculations [254] should be used for obtaining the thermochemistry of the species involved in this reaction. However, intermolecular hydrogen bonding might be expected to stabilize the ketohydroperoxide and slow the decomposition rate and not increase it. Similarly the cyclic peroxide route evaluated by Jalan et al. [42] would be expected to slow ignition, not accelerate it. Perhaps there are other pathways forming radicals missing in the models and the fast decomposition of ketohydroperoxide is compensating for missing routes. Further work in carefully evaluating low temperature pathways is needed.

198

![Graph](image)

**Figure 5-13:** Comparison of RMG and the NUI model [228] decomposition rate for a ketohydroperoxide formed during n-pentanol oxidation. RMG reverse rate coefficient is estimated using the thermochemistry obtained from Benson groups.

### 5.4 *iso*-Pentanol results and discussion

The *iso*-pentanol kinetic model is validated against new experimental pyrolysis data obtained in a plug flow reactor at the Laboratory for Chemical Technology (LCT), Ghent University. In addition, we also validate the mechanism against a wide range of literature
data sets i.e. jet stirred reactor oxidation studies by Dayma et al. [231] and ignition delays by Tsujimura et al. [216].

5.4.1 Pyrolysis experiment

Figure 5.14 gives the measured experimental conversion of iso-pentanol versus the set temperature in the reactor along with the model predictions. The model is simulated using CHEMKIN-PRO [245] plug flow reactor with the initial conditions and the temperature profile obtained from the experiments. Experimentally the conversion of iso-pentanol is ~18% at 913 K and is approximately 100% at 1073 K. The model agrees well with the experimental results throughout the temperature range.

![Figure 5.14: iso-Pentanol conversion as a function of the average pyrolysis reactor temperature (symbols – experimental: • N₂ diluted: 4 molN₂/mol iso-pentanol, – RMG model predictions).](image-url)

Figure 5.15 and Figure 5.16 gives the yield of the major products and alkenes formed during iso-pentanol pyrolysis experiments and compared with the simulation results. The RMG model is able to accurately predict most major products like hydrogen, carbon monoxide, methane, ethane and all major alkenes within a factor of two. Though formaldehyde is correctly predicted by the kinetic model, the methanol yield is underpredicted by about a factor of 3. The major route to formation of methanol is by
hydrogen abstractions by CH₂OH radicals from the parent fuel. These rates are estimates based on theoretical results for similar reactions of CH₂OH abstracting from n-butanol, however due to severe coupling of the hindered rotors in the transition state the computed rates are uncertain by more than a factor of 10. Most of the CH₂OH radicals undergo β-scissions to give formaldehyde (CH₂O), the rate coefficient estimate comes from the small molecule seed which has been well established in literature. The sum of CH₂O and methanol is underpredicted suggesting an error in the initial formation of CH₂OH.
Figure 5-15: Comparison of the experimental (symbols) and simulated (lines) yields of the major products at diluted (4 mol \(N_2/mol \text{iso-pentanol}\)) (symbols are experimental measurements, – RMG model predictions).
Figure 5-17 presents the model-predicted fuel consumption pathways and major product formation channels at 80% iso-pentanol conversion, with T = 1000 K, P = 1.7 atm for 1 mol iso-pentanol : 4 mol N₂. iso-Pentanol is primarily consumed by hydrogen abstraction from H, CH₃ and OH radicals to yield five different iC₅H₁₀O radicals. Abstraction from the α-site accounts for the highest consumption of iso-pentanol. The α-iC₅H₁₀OH radical primarily undergoes C-C β-scissions to give vinyl-alcohol + iso-propyl radical. The iso-propyl radical will further undergo C-H β-scissions to give propene + H atom. β-iC₅H₁₀OH radical can either form OH + iso-pentene or 2-butenol + CH₃ with the latter pathway computed to being preferred. iso-Butene and propene are formed by C-C β-scissions of γ-iC₅H₁₀OH and δ-iC₅H₁₀OH radicals, respectively. Almost 50% of the δ-
iC₆H₁₀OH radical undergoes C-C β-scissions to give 1-butenol + CH₃ radical. Unlike n-pentanol where ethene is the major alkene formed during pyrolysis in iso-pentanol the major alkene product is propene.

Figure 5-17: Reaction pathway analysis for iso-pentanol pyrolysis (1 mol iso-pentanol : 4 mol N₂) in a plug flow reactor operated at P = 1.7 bar and T = 1000 K, rates are expressed relative to the total iso-pentanol consumption rate for 80% conversion.

Figure 5-18 shows the yield of soot precursors over a wide temperature range. Reasonable agreement can be observed between the experimental and simulation results for soot precursors - 1,3-butadiene (1,3-C₄H₆), acetylene, benzene and 1,3-cyclopentadiene. However, similar to the n-pentanol model the iso-pentanol model is also unable to predict the toluene formed during the pyrolysis experiments. Since the major pathways for formation of benzene are similar to that discussed for n-pentanol it will not be discussed again. The small amount of toluene predicted by the model is formed by recombination of iso-butenyl radical + allyl radical to give 2-methyl-1,5-hexadiene which undergoes hydrogen abstraction and β-scission to give 2-methyl-hexatriene. This will then undergo intra-diels-
alders reaction to give methyl-cyclohexadiene intermediate. The methyl-cyclohexadiene will eventually form toluene via H abstraction followed by β-scission.

Figure 5-18: Comparison of the experimental (symbols) and simulated (lines) yields of soot precursors and smaller aromatics formed at diluted (4 mol N$_2$/mol isopentanol). (symbols are experimental measurements, – RMG model predictions).
5.4.2 Jet Stirred Reactor

The mechanism was also validated against the jet-stirred reactor data (JSR) measured by Dayma et al. [231]. Figure 5-19 gives the model prediction for major species for $\phi = 1.0$ at $P = 10$ bar and $t = 0.7$ s. As seen from Figure 5-19 that the predictions show good agreement with the experimental data; however, the simulation results reveal that the fuel consumption occurs at slightly lower temperature ($\sim 30$ K) than the experimental measurement. Figure 5-20 gives the flux analysis for the consumption of iso-pentanol for all three equivalence ratios. For all three experiments hydrogen abstraction reactions by OH and H radicals are the most important with the abstraction from the $\alpha$- and $\gamma$- (tertiary) site being the most important. The rate coefficients for abstraction by OH reactions come from the calculated rates for analogous sites from iso-butanol [255] and $n$-butanol [248] calculations and have an estimated uncertainty of more than a factor of 2. In the lean case hydrogen abstraction by O atom forming C$_5$H$_{11}$O radicals becomes significant. In the rich case at high temperatures the C-C bond scission reactions contribute significantly to the fuel consumption. The fuel radicals formed are primarily consumed via O$_2$ addition under low temperatures and lean conditions. However many undergo $\beta$-scission as the temperature is increased or O$_2$ is decreased (rich conditions).
Figure 5.19: Simulated (lines) and experimental (symbols) profiles of major species for jet stirred reactor experiment [231] for $\varphi=1.0$ and $P=10$ bar.
Figure 5-20: Simulated rate of production for iso-pentanol in the 10 atm jet stirred reactor for equivalence ratios A) 0.5, B) 1 and C) 2.
The model predictions for the concentration of CO, CO₂, H₂O, H₂, methane, ethene, acetaldehyde + vinyl-alcohol, 3-methyl-1-butanal + 3-methyl-1-butenol and propene are within a factor of two of the experimental data across the entire temperature range for all the equivalence ratios considered in the experiment.

The yield of iso-butene is over predicted by a factor of 2.5. The predicted major pathway for formation of iso-butene for all three equivalence ratios over the complete range of JSR temperatures is the β-scission of the γ-C₅H₁₁O (3-hydroxy-1,1-dimethylpropyl) radical to give iso-butene and CH₂OH radical. In the lean case the model predicts most of the γ-C₅H₁₁O radical adds molecular oxygen instead of undergoing β-scission to form iso-butene. The predominant decomposition pathway of iso-butene is abstraction of primary hydrogen by hydroxyl radical for lean and stoichiometric conditions while for the rich conditions the hydrogen abstraction by H atom is the dominant reaction especially at higher temperatures.

Acrolein (C₃H₅CHO) is the only measured experimental product which is overpredicted (~ 7x) beyond the experimental uncertainty. Studies by Sarathy et al. [233] also overpredicts acrolein concentration by similar magnitude. Acrolein is primarily formed by β-scission of allyloxy (CH₂=CHCH₂O) radical. This radical is primarily formed by well skipping reaction of allyl + HO₂ radical to give allyloxy + OH radical. The reaction rate coefficient comes from the estimate by Metcalfe et al. [237] which is within a factor of 3 of the recent theoretical calculation by Goldsmith et al. [256].

5.4.3 Ignition delay experiment

Tsujimura et al. [216] measured autoignition delay for iso-pentanol using shocktube (ST) at NUI Galway and rapid compression machine (RCM) at the University of Connecticut over a T = 650 – 1500 K and P = 7 – 20 bar. We validate our model against this experimental data and also compare against the Sarathy et al. model (LLNL) in Figure 5-21 and Figure 5-22. We used the Closed Homogenous Batch Reactor module and performed constant volume simulations in CHEMKIN-PRO to model the experiments. The predicted ignition delay is the time at which half the maximum [OH] is achieved; these times correspond well to other metrics such as - the time at which maximum [C₂H] x [O] is achieved or the time at which peak pressure rise rate is observed. The RMG and LLNL models can accurately predict the high temperature ST ignition data within a factor of 2 for
both pressures. For the low temperature autoignition both models over predict the experimental measured autoignition by a factor of 4 for $P = 7$ bar and a factor of 2 for $P = 20$ bar. For temperatures $> 1450$ K both model under predict the ignition delay by more than a factor of 4 for $P = 7$ bar.

**Figure 5-21:** Comparison of experimental (shapes) and simulated (lines) autoignition delay for iso-pentanol oxidation at $P = 7$ bar. Experimental data below 1000 K measured by RCM and above 1000 K in ST [216]. The mechanisms used are RMG (solid line), Sarathy et al. model [233] (dash line). The stated pressures are used for modeling the shock tube experiments.
A sensitivity analysis of the OH radical production for the RMG model was carried out at $T = 800$ K, $P = 20$ bar and $\phi = 1.0$. The most sensitive reactions at $t = 2$ ms and $t = 10$ ms are shown in Figure 5-23. At 800 K and $P = 20$ bar the temperature is very close to $T_{\text{stage-max}}$ (discussed in Chapter 2) hence the peroxy chain branching pathway is running out of gain. The sensitive reactions are now those that involve production of $H_2O_2$, which leads to OH formation via $H_2O_2 \rightarrow 2OH$. The hydrogen abstraction by OH and $HO_2$ radical from the parent fuel are the most sensitive reactions. Increasing the abstraction from the alpha site will decrease the radical gain since it leads to formation of stable aldehyde and hydrogen peroxide while the increasing the abstraction from the delta site will lead to formation of 3 OH radicals via the peroxy chemistry and increase fuel reactivity. The $RO_2 \Rightarrow QOOH$, $QOOH + O_2 \Rightarrow O_2QOOH$ and the competing chain terminating $RO_2 \rightarrow C_5H_{10}O$ (Alkene) + $HO_2$ reaction from the gamma radical are seen to be important. Increasing the rate coefficient for $RO_2 \Rightarrow QOOH$ and $QOOH + O_2 \Rightarrow O_2QOOH$ will increase the gain of the peroxy cycle and speed up OH radical production on the other hand increasing the $RO_2 \rightarrow C_5H_{10}O$ (Alkene) + $HO_2$ will decrease the overall gain and slow down the fuel reactivity. The
hydrogen-abstraction rates come from analogous butanol studies and have an uncertainty of a factor of 2-4. The peroxyl chemistry however comes from RMG alkane estimates and some of the rates could be uncertain by more than factor of 10. Currently very few studies on these rate coefficients exist and these rate rules should be explored in the future.

The main difference between the two times is that early on the HO₂ radical pool is building up and the HO₂ + HO₂ → H₂O₂ reaction is not sensitive, beyond 2.5 ms the HO₂ will be in quasi-steady state and the recombination reaction becomes important. At even later times it is seen that H₂O₂ decomposition to OH radical is also among the most sensitive reactions.

Figure 5-23: Sensitivity analysis of the iso-pentanol ignition delay for the RMG-generated model, S = ∂ ln [OH]/∂ ln k. Based on the model predictions at 800 K and 20 bar.
5.5 Conclusion

We present a detailed, robust reaction network for \( n \)- and \( iso \)-pentanol pyrolysis and oxidation. We validate our kinetic model against speciation data from pyrolysis experiments, laminar flame speeds, jet stirred reactor and ignition delays over a wide range of temperature (700 K – 2000 K), pressure (1-30 bar), and equivalence ratios (0.5 – 2.0). RMG model predictions and experimental results are within a factor of 2 for most cases. In addition, we also compare key experiments against literature models. The main conclusions are as follows:

(1) The current RMG model is the only model which can predict (within factor of 3) soot precursors and smaller aromatics like acetylene, 1,3-butadiene, cyclopentadiene and benzene. The only notable failure of the model’s predictive ability is for toluene predictions. Future work must focus on understanding pathways to toluene formation.

(2) At higher temperatures (\( T > 1200 \) K), RMG model accurately predicts the experimental ignition delay times within a factor of 2 under for \( n \)-pentanol.

(3) Although accurate at higher temperatures, the RMG model is unable to predict the low temperature ignition delays. The \( n \)-pentanol model predicts the NTC at a temperature of 100 K higher than the experiments. The \( iso \)-pentanol ignition delays are predicted within a factor of 4. In comparison, the LLNL model for \( n \)- and \( iso \)-pentanol can predict the ignition with reasonable accuracy. Future work is required to accurately understand the low temperature ignition of alcohols.
Chapter 6

*Investigating Reactivity Controlled Compression Ignition (RCCI) using iso-butanol and di-tert-butyl-peroxide*

### 6.1 Need for a high efficiency and clean engine

Internal combustion engines are ubiquitous to today’s world and serve as the primary technology used in transportation. However with rising fuel costs and stringent emission standards there is a growing need to increase the efficiency of internal combustion engines. This need for increased efficiency has placed the diesel or compression ignition (CI) engine in the spotlight due to its superior fuel efficiency as compared to gasoline or spark-ignited (SI) engines. Although the fuel efficiency of CI engines is generally higher than that of SI engines, they also have higher NOx and soot emissions. To run CI engines compliant with current and future emission standards, emission after-treatment devices must be used [257]. Soot is effectively removed by use of a diesel particulate filter (DPF), however the DPF imposes pressure drop which increases with soot and ash loading and in-turn leads to higher fuel consumption. Since most diesel engines operate in the lean mode the conventional three way catalyst (TWC) cannot be used for NOx reduction. For CI engines, either a lean NOx trap (LNT) or selective catalytic reduction (SCR) technology is used to reduce NOx. LNT works like a TWC and relies on the NOx reducing to N₂ through reactions with unburnt hydrocarbon and CO. The use of LNT forces the engine to periodically operate
rich affecting the fuel economy. The SCR technology uses reducing agent (urea or ammonia) stored onboard. The reducing agent is injected in the exhaust and is used to reduce the NOx providing no useful work and affecting the overall economy of the vehicle. Johnson [257] estimates that the urea based SCR to effectively cost for 1% of the fuel consumption per g/kW-hr reduction in NOx emissions. The complex after-treatment system and the high pressure fuel injection system used to reduce emissions also significantly increase the cost of the engine.

To overcome the limitations of after treatment technologies many researchers have investigated advanced in-cylinder technologies to reduce NOx and soot levels [13, 15, 18, 258]. However any such new technology has to be feasible throughout the engine load and operating conditions and often requires extensive experimental study. These experimental studies are expensive and time consuming slowing down the commercialization of these technologies. To aid in the development of these technologies, predictive tools such as computational fluid dynamics (CFD) simulations can be used. CFD allows us to do feasibility studies, identify promising fuel + engine strategy, run optimization studies and help guide the experiments. However one of the major limitations affecting the predictive ability has been the inability to use detailed chemistry in these simulations. Until recently, CFD simulations were conducted using reduced or skeletal mechanism, hence leading to loss in accuracy of the predictions. Software such as FORTE [259] has overcome this limitation by using improved sparse solvers and on-the-fly adaptive – chemistry reduction techniques to sharply decrease the chemistry solver time. We present one of the first studies for evaluating a new potential engine technology and a detailed fuel model. The use of detailed validated kinetic models allows for a more accurate prediction of the engine emissions which is of interest in optimizing the engine combustion.

6.2 Reactivity controlled compression ignition (RCCI) engine

The RCCI engine was first proposed by Kokjohn et al. [260]. It is a dual fuel engine combustion technology which uses in-cylinder fuel blending with at least two fuels of different reactivity and multiple injections of the fuel. This strategy provides greater control over the in-cylinder fuel reactivity and the combustion phasing duration and magnitude. Figure 6-1 gives a cartoon of the RCCI engine concept. In RCCI engine the low reactive fuel is first injected in the cylinder to create a well-mixed charge consisting of low
reactive fuel, intake air and recirculating gases. The intake valves closes and the piston starts to compress this mixture. The high reactive fuel is directly injected into the combustion chamber before the ignition of the premixed fuel using single or multiple injections. Addition of the high reactive fuel causes the mixture to auto-ignite. The time and duration of the heat release can be controlled by controlling the quantity and time when the high reactive fuel is injected.

![Fuel Injector](image)

**Figure 6-1:** Cartoon representation of the RCCI engine concept. The low reactive fuel + air is injected through the intake port and high reactive fuel is injected directly into the cylinder.

Kokjohn et al. [261] showed that the gasoline/diesel RCCI strategy is capable of operating over a wide range of engine loads (4.5 – 14.6 bar IMEP), with nearly zero levels of NOx, soot and acceptable levels of pressure rise rates. The thermal efficiency of RCCI engine was also higher than the conventional diesel engine operating under similar conditions. Peak gross efficiency achieved by Kokjohn was ~56% at 9.3 bar indicated mean effective pressure (IMEP) and engine speed of 1300 rpm. Other researchers have shown by optimizing the operating conditions and piston design, thermal efficiencies as high as 60% can be achieved in single cylinder experiments while maintaining the engine out NOx and soot below the US2010 mandate [16]. Thus the RCCI engine concept is a potential technology to meet the increased efficiency and stringent emission standards of the future.

In recent years the RCCI concept has been studied with number of dual fuel combinations including gasoline/diesel [261, 262], ethanol/diesel [263], $n$-butanol/bio-diesel
Single fuel strategies where a low reactive fuel + a small amount of cetane improver (like 2-ethyl-hexy-nitrate and di-tert-butyl-peroxide) are blended have also been studied [265]. A comprehensive summary of the current progress and challenges in RCCI engine development was recently published by Reitz et al. [15].

6.3 Case Study: iso-Butanol + Peroxide in RCCI engine

The focus of this work is to evaluate whether iso-butanol can be a potential future fuel for the RCCI engine concept. The “single fuel” strategy for the RCCI engine demonstrated by Splitter et al. [265] is explored. In this strategy a single low reactive fuel is used as the primary fuel. The higher reactivity fuel is obtained by blending the low reactive fuel with a small volume percent of a reactivity enhancing additive. Since iso-Butanol has a high octane number (RON = 98) it serves as the low reactive fuel and a small percentage of di-tert-butyl peroxide (DTBP) is used as reactivity enhancer (cetane improver). DTBP was selected on basis of work by Tanaka et al. [266] who showed that for gasoline like fuels 2% (mol frac) DTBP causes a significant increase in reactivity of the fuel. Figure 6-2 gives the scheme for the single fuel injection strategy for iso-Butanol + DTBP RCCI engine.

Figure 6-2: Schematic of “single fuel” injection RCCI engine strategy.

6.3.1 Single cylinder experiments

The experiments for the iso-butanol + peroxide system were conducted at the Engine Research Center (University of Wisconsin Madison) by Dan Delvescovo. Here we briefly describe the experimental setup to aid in understanding the computational setup.
A Caterpillar 3401E Single Cylinder Oil Test Engine (SCOTE) with a displacement of 2.44 liters was used for the experiments. The engine geometry and operating conditions are shown in Table 6-1 and Table 6-2. The neat iso-butanol is delivered through a low pressure port fuel injector (PFI) and the iso-butanol and di-tert-butyl peroxide (DTBP) is delivered through a direct injection common rail system. In the experiment the following variables were measured: cylinder pressure as a function of the crank angle (using a water cooled transducer), intake air flow, particulate matter (using a smoke meter) and emissions (using a Horiba emission bench). The hydrocarbon emissions were measured on a wet basis using a heated sampling system. All other emissions were sampled on a dry basis. The emissions were averaged for 30 seconds after attaining steady-state for several minutes. Further details can be found here [267].

**Table 6-1:** Stock 3401 SCOTE Geometry.

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Displacement</td>
<td>2.44L</td>
</tr>
<tr>
<td>Bore x Stroke</td>
<td>13.72cm x 16.51cm</td>
</tr>
<tr>
<td>Connecting Rod Length</td>
<td>21.16cm</td>
</tr>
<tr>
<td>Swirl Ratio</td>
<td>0.7</td>
</tr>
<tr>
<td>Number of Valves</td>
<td>4</td>
</tr>
<tr>
<td>Exhaust Valve Closing</td>
<td>-355 °CA ATDC</td>
</tr>
<tr>
<td>Intake Valve Closing</td>
<td>-143°CA ATDC</td>
</tr>
<tr>
<td>Exhaust Valve Opening</td>
<td>130°CA ATDC</td>
</tr>
<tr>
<td>Intake Valve Opening</td>
<td>-335 °CA ATDC</td>
</tr>
</tbody>
</table>

**Table 6-2:** Engine operating conditions.

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Speed [rpm]</td>
<td>1300</td>
</tr>
<tr>
<td>IMEP [bar]</td>
<td>6.29</td>
</tr>
<tr>
<td>DI timing</td>
<td>1st -56°, 2nd -36°</td>
</tr>
<tr>
<td>DI ratio between</td>
<td>70% in 1st, 30% in 2nd</td>
</tr>
<tr>
<td>Total fuel mass [mg]</td>
<td>98</td>
</tr>
</tbody>
</table>
6.3.2 Multi-Dimensional CFD

The FORTE simulation package [259] was used for the RCCI simulations. Turbulence was modeled using the RNG (Re-Normalization Group) k-ε model. The grid-independent spray breakup model of Abani et al. [268], called the gas-jet model was used. The spray injection uses a solid-cone spray model with droplet-breakup governed by KH-RT sub-models [269, 270], and the radius of influence collision model [271]. A discrete multi-component spray-vaporization model [272] considers the vaporization properties of each component. Default settings for these models were used. Details of FORTE and its sub-models can be found elsewhere [273]. Equations for all chemical species included in the detailed kinetics mechanism are directly solved in the CFD calculations through an operator-splitting method.

A 60-degree sector mesh shown in Figure 6-3 was used for the RCCI calculations. The mesh only considers one of the fuel injector's holes. This is based on the assumption that the combustion chamber is axis symmetric about the cylinder axis and these grids have periodic boundaries to the left and right of the fuel spray. The mesh has 10080 cells at IVC (intake valve closing). In this study the sensitivity of the results to the mesh resolution was not studied. However Puduppakkam et al. [274] did a sensitivity analysis on the mesh size in FORTE for the gasoline + diesel dual fuel system and concluded that the coarse mesh (~11000 cells at IVC) and the fine mesh (~40000 cells at IVC) resulted in very similar results. The CA50 (crank angle when 50% of heat is released) was within 1-1.5 degrees for the cases modeled.
Caterpillar Engine

<table>
<thead>
<tr>
<th>Sector Angle</th>
<th>60°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cells at BDC</td>
<td>~11000</td>
</tr>
<tr>
<td>Average Cell Size</td>
<td>~3°</td>
</tr>
<tr>
<td>Azimuthal Resolution</td>
<td>4°</td>
</tr>
</tbody>
</table>

**Figure 6-3:** FORTE computational sector mesh used for the heavy-duty Caterpillar engine.

In order to reduce the computation time related to solving for the chemistry both the dynamic cell clustering (DCC) and dynamic adaptive chemistry (DAC) features of FORTE were used. The DCC method [275] performs calculation on clusters of computational cells with very similar thermochemical conditions. After the chemistry calculations are completed, the method will map back the updated clusters to the cells contained in each clusters. In this study, clusters were defined to have temperature dispersion no greater than 10K and equivalence ratio dispersion no greater than 0.05. The DAC method automatically reduces the kinetics on the fly at every time step, for details see ref. [276]. In order to ensure that the important species are always tracked and not eliminated by DAC, the software allows us to give a list of important species. For this study we track the fuel (iso-Butanol), DTBP, oxygen, nitrogen, OH, HO₂, CO, CO₂, NO, NO₂, CH₂O and C₂H₂.

**Initial Conditions**

The initial conditions needed for the FORTE simulation is given in Table 6-3. The IVC temperature is determined using GT-Power [277] simulations for the RCCI engine. The IVC temperature has an uncertainty of ± 10 K at least this is significant as a 10 K can in IVC cause engine to misfire. The initial mole fraction is determined by running single zone
HCCI simulations, assuming 7% of internal gas is recycled. The system is solved for many engine cycles until a steady state is reached which determines the initial composition in the cylinder at IVC for the FORTÉ simulations. The IVC temperature is an unknown variable and treated as a free parameter which can be adjusted to match the CA50 obtained from the simulation and the experiment.

Table 6.3: Initial conditions used in the FORTÉ CFD simulation for the iso-Butanol + DTBP RCCI run.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>IVC Temp (K)</td>
<td>363</td>
</tr>
<tr>
<td>IVC Pressure (bar)</td>
<td>1.53</td>
</tr>
<tr>
<td>Total fuel mass (mg/cyc)</td>
<td>98.6</td>
</tr>
<tr>
<td>Premixed fuel mass ratio (%)</td>
<td>40.6</td>
</tr>
<tr>
<td>DI DTBP mass ratio (%)</td>
<td>20.1</td>
</tr>
<tr>
<td>Internal EGR ratio (%)</td>
<td>7.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Initial composition (mole %)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>20.4</td>
</tr>
<tr>
<td>N₂</td>
<td>78.5</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.327</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.409</td>
</tr>
<tr>
<td>iso-Butanol</td>
<td>0.442</td>
</tr>
</tbody>
</table>

6.3.3 Chemistry mechanism

One of the primary objectives of this work is to provide a first case study for using a detailed mechanism in multi-dimensional CFD software. The overall mechanism used in this work consists of 550 species and over 4400 reactions, details of the mechanism generation is given in the following sections.

6.3.3.1 iso-Butanol + DTBP mechanism

The automatic mechanism generation software (RMG) [110] was used to generate the integrated iso-Butanol + DTBP mechanism. Given the initial conditions, RMG will automatically generate all possible species and reactions from a database of reaction families and libraries, and then use a flux-based algorithm to select the most important pathways to include in the model. This process is iterated until all the important species
and reactions are found for a given user tolerance. Details describing the model generation in RMG can be found here [113].

Entire reaction networks can also be seeded for RMG network generation. For this work the iso-butanol sub-mechanism based on the validated model discussed in Chapter 4 is used. The mechanism generation was done at pressures of 10 – 40 atm, at temperatures of 800 K, 1000 K and 2000 K and at equivalence ratios of 0.3 and 1.0 in air. Since the iso-Butanol mechanism has been extensively validated under engine relevant conditions and the DTBP mechanism is well understood in literature extensive mechanism validations were not carried out for this work.

Figure 6-4 shows the predicted ignition delay of iso-butanol + DTBP mixtures as a function of the DTBP % in the mixture. As can be seen, the reactivity of the alcohol is greatly enhanced by addition of relatively small amount of DTBP. The reactivity enhancement is also non-linear with DTBP percentage. Ignition delay here was defined as the time when the peak in pressure rise rate is observed. The simulation conditions $P = 40$ bar, $T = 900$ K and $\varphi = 0.3$ are representative of the conditions seen in a real CI engine.
Figure 6.4: Predicted ignition delay as a function of DTBP mole % in iso-Butanol + DTBP mixture. The simulations conditions are representative of a real RCCI engine operation.

In order to understand the reactivity enhancement we compare the species concentration profile for iso-butanol and iso-butanol + 5% DTBP (Figure 6-5) mixture. The simulations are carried out in a constant volume adiabatic reactor system. As seen from the Figure 6-5, 90% of DTBP is consumed in less than 0.4 ms under the current simulation conditions. The DTBP decomposes by breaking the O-O peroxide bond resulting in two tert-butoxy radicals which β-scission to give acetone and CH₃ radicals. The decomposition of DTBP results in much higher concentration of CH₃ radicals as compared to the neat iso-butanol case. The CH₃ radicals will react with the oxygen in the system to form chain carrying OH radicals as shown in the reaction path in Figure 6-6. The overall increase in chain carrying radical will lead to shorter ignition delays. Acetone formed by DTBP decomposition is a relatively stable by-product and does not contribute to the radical pool. The above observations are in agreement with those of Wang et al. [278]. Wang et al. studied the reactivity boost for lower alcohols (methanol and ethanol) + DTBP mixtures.
Figure 6-5: Comparison of species profiles in constant volume adiabatic reactor between iso-Butanol and iso-Butanol with 5% DTBP mixture at $P = 40$ bar, $T = 900$ K and $\varphi = 0.3$ (Air). As seen from panel b) DTBP decomposes to give $\text{CH}_3$ radicals which get converted to OH radicals speeding up the reactivity.
6.3.3.2 Soot formation model

Soot is predicted using a two-step phenomenological soot model based on the approach of Hiroyasu [20]. The two model constants needed for this model, the soot formation pre-exponential ($A_{sf}$) and the activation energy ($E_{sf}$) were obtained from the study conducted by Kokjohn [279] for gasoline/diesel RCCI engine operation. The values used in this study are $A_{sf} = 700$ and $E_{sf} = 1250$ kcal/mol. The soot model used in the present study uses acetylene as an inception species, allowing coupling of the soot model and the chemistry solver.

6.3.3.3 NOx sub-chemistry model

NOx emissions are predicted using a reduced NO mechanism [280]. The NOx mechanism is based on the GRI NOx mechanism [185]. This mechanism has been
extensively used in previous RCCI engine computational studies [279]. The reactions included in the reduced model are

\[
\begin{align*}
N + NO &= N_2 + O \\
N + O_2 &= NO + O \\
N + OH &= NO + H \\
N_2O + O &= N_2 + O_2 \\
N_2O + O &= 2NO \\
N_2O + H &= N_2 + OH \\
N_2O + OH &= N_2 + HO_2 \\
N_2O (\pm M) &= N_2 + O (\pm M) \\
HO_2 + NO &= NO_2 + OH \\
NO + O + M &= NO_2 + M \\
NO_2 + O &= NO + O_2 \\
NO_2 + H &= NO + OH
\end{align*}
\]

6.3.4 Results and discussion

Figure 6-7 compares the average in-cylinder pressure and the corresponding apparent heat release rate (AHRR) from the FORTE simulation and the experiment. The AHRR is defined as the chemical heat release rate minus the heat loss rate from the walls of the cylinder given by (6-1) [281].

\[
AHRR = \frac{dQ}{d\theta}_{\text{chemical}} - \frac{dQ}{d\theta}_{\text{wall}} = \frac{1}{\gamma - 1} \frac{\gamma}{\gamma - 1} P \frac{dV}{d\theta}
\]

where \( \gamma \) is the average specific heat ratio for the gas in the cylinder.

As seen from the Figure 6-7 the simulations are able to fairly accurately capture the start of combustion and the amount of heat released during the experiment by using the IVC temperature of 363 K for the \textit{iso}butanol + peroxide 6 bar IMEP run.
Table 6-4 compares the predicted and experimentally measured engine performance and emission results. The fuel energy input per cycle is calculated using (6-2) where $m_{iBuOH}$ is the mass of $i$-butanol and $m_{DTBP}$ is the mass of DTBP input per cycle. $LHV_{iBuOH}$ (33 MJ/kg) and $LHV_{DTBP}$ (36 MJ/kg) are the lower heating values of $i$-Butanol and DTBP respectively.

$$E_{fuel} = m_{iBuOH}LHV_{iBuOH} + m_{DTBP}LHV_{DTBP} \quad (6-2)$$

The work done in the cycle is calculated using (6-3) where $P$ is the average cylinder pressure and $V$ is the displacement volume of the cylinder

$$W_{cycle} = \int_{cycle} PdV \quad (6-3)$$

The combustion efficiency is the measure of completeness of the combustion and is calculated as (6-4)
\[ \eta_{\text{combustion}} = \frac{E_{\text{fuel}} - m_{\text{UHC}}^{\text{EVO}} LHV_{\text{fuel}} - m_{\text{CO}}^{\text{EVO}} LHV_{\text{CO}}}{E_{\text{fuel}}} \]  
(6-4)

The gross indicated efficiency is given as the work done in the cycle (-180° ATDC to 180° ATDC) to the fuel energy input

\[ \eta_{\text{gross thermal}} = \frac{W_{\text{cycle}}}{E_{\text{fuel}}} \]  
(6-5)

The LHV\(_{\text{fuel}}\) is calculated on the relative basis of iso-butanol and DTBP in the fuel. The LHV of CO is 10.12 MJ/kg. As seen from the Table 6·4 the simulations are able to accurately predict the CA50 ~ 5° ATDC, the predicted gross indicated efficiency is ~ 49.5% and the combustion efficiency is ~ 93% which is within ±2% of the experimental values. The predicted emission also compare well with the experimental measurements within the modeling uncertainty. The unburned hydrocarbon and CO are over predicted by 10% and 40% respectively. The NO\(_x\) emission however is underpredicted by a factor of 2.

<table>
<thead>
<tr>
<th>CA50 (°ATDC)</th>
<th>Combustion Efficiency (%)</th>
<th>Gross Indicated Efficiency (%)</th>
<th>PPRR (bar/deg)</th>
<th>Emission (g/kW-hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental Results</td>
<td>Predicted Results</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.5</td>
<td>5.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>94.9</td>
<td>92.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>47.8</td>
<td>49.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.1</td>
<td>9.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO(_x)</td>
<td>0.3</td>
<td>0.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soot</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UHC</td>
<td>3.8</td>
<td>4.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>26.9</td>
<td>38.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6·4: Comparison of the experimental and FORTÉ CFD simulation predictions for the iso-Butanol + DTBP RCCI run (6 bar IMEP, 1300 rpm).
Figure 6-8 provides the breakdown of the unburned hydrocarbons predictions from the RCCI engine simulation. The unburned fuel species accounts for ~40 wt% of the UHC. Oxygenates comprising of C1-C4 aldehydes, enols and formic acid account for ~48 wt% and the smaller hydrocarbons (C1-C4) account for close to 10 wt% of the UHC. H2O2 which is not counted as UHC has a concentration of 0.4 g/kg-fuel at EVO.

![Figure 6-8: Breakdown of the predicted UHC emissions, for the 6 bar IMEP iso-Butanol + DTBP RCCI case.](image)

The predicted distribution of oxygenates formed can be seen in Figure 6-9. C4 and C3 aldehydes + enols account for a large fraction of the oxygenates (~20 wt%) and are formed by oxidation or β-scission of the primary fuel radicals. C3 aldehydes also include acetone which is formed by primary decomposition of DTBP. Acrolein and Ethynol (HCCOH) the most significant oxygenated species are formed by the oxidation of C3 enols and acetylene and account for ~10 and ~9 wt% of the UHC respectively. Formaldehyde which is often the major oxygenate species in diesel fuel accounts for only ~4 wt%. Other oxygenates predicted by the simulation are formic acid, methanol, acetaldehyde, ketene and 2-methylacrolein. The oxygenate species predicted by the model are consistent with the recent experiments by Ratcliff et al. [282]. Ratcliff et al. studied the impact of higher alcohol blends in gasoline for a light duty engine. Experiments conducted by Ratcliff with 21% iso-butanol blend report significant quantities of oxygenate species such as iso-butanal, acetone, acrolein, acetaldehyde and formaldehyde in the exhaust emissions.
The NOx predictions are significantly affected by the chemistry and the temperature in the simulations. The NOx mechanism used for these simulations might be too simplified and future work must investigate detailed validated NOx models to improve engine predictions.

### 6.4 Conclusion

This work is one of the first published case studies where a detailed kinetic model was used in multi-dimensional CFD simulations to predict engine performance. We study the effect of using *iso*-Butanol + DTBP mixtures in a heavy-duty RCCI engine. The mechanism used in this study consists of 440 species and over 5500 reactions. Using Forté software, multi-dimensional CFD simulations could be carried out in reasonable time. Each single cycle simulation takes around 14 hours on a 16-core compute node, while using 11000 cell mesh. The CFD predicted engine performance results are also compared against RCCI engine experiment. The main conclusions are as follows:

![Figure 6-9: Predicted distribution of the oxygenate species, for the 6 bar IMEP *iso*-Butanol + DTBP RCCI case.](image)
1. *iso*-Butanol + DTBP mixture yields a suitable alternative for Gasoline + Diesel mixture for RCCI engine operation. The low load (6 bar IMEP) experimental gross indicated efficiency was ~ 48% with little or no soot formed. The NOx formed during the experiment (0.3 g/kW·hr) however was slightly above the US2010 mandate (0.27 g/kW·hr) and further adjustment of the engine operation would be needed to bring it below the limit.

2. The CFD simulations are able to predict the engine performance reasonably well. The start of ignition and CA50 is predicted within 0.5° of the experiment. This is well within the uncertainty of the IVC temperature. The simulation is also able to capture the net heat release from the experiment accurately. The predicted gross indicated and combustion efficiencies are in excellent agreement with the experiment.

3. Engine out emission such as unburnt hydrocarbon, CO and NOx are predicted within a factor of 2.

4. Analyzing the predicted UHC we see that the use of *iso*-butanol as a fuel results in a significant increase of the aldehyde emissions. Acetaldehyde and formaldehyde have been classified as carcinogens by the National Institute for Occupational Safety and Health (NIOSH) [283] and the Environmental Protection Agency (EPA) [284]. Data on C4 aldehydes is not yet available but NIOSH considers it will have similar reactivity and mutagenicity as acetaldehyde [283]. Furthermore if emitted in the atmosphere unchecked, these oxygenates could undergo oxidation to yield acid formation. The use of *iso*-butanol as a fuel could therefore have significant health consequences and additional research in this area is warranted.

This thesis makes significant stride towards the goal of predictive kinetics. Given the vast improvement in computational resource and our knowledge of chemistry in the past decade, an engineer can now sit down at a computer, input information about the fuel, generate a detailed kinetic model. The kinetic model can then be run in a realistic engine simulator to yield quantitative prediction of the fuel and engine performance.
Chapter 7

**Recommendations for future work**

This thesis has made several significant contributions in improving combustion kinetic models. Particular focus has been given to improving the scientific understanding of low temperature ignition delay and formation of PAHs like indene and naphthalene under pyrolytic conditions. This thesis also contributes comprehensive kinetic models for alternative alcohol fuels like iso-butanol, n-pentanol and iso-pentanol which were validated against a large number of experimental datasets over a wide range of conditions. Lastly I, also show how these detailed kinetic models can be applied in multi-dimensional CFD simulations to assess the performance of a novel engine. This thesis makes significant progress towards the goal of accurately predicting performance of new fuels in future engines. The uncertainties in our quantitative understanding of the chemistry are comparable to uncertainties due to other experimental factors (e.g. temperature in engine, RCM and low-T shock tube experiments). However there are still a number of challenges that need to be addressed in order to improve our predictive capabilities. In this chapter we will discuss several such challenges for future work.

### 7.1 Develop understanding for low temperature ignition

Chapter 2 contributes to providing a simplified picture for low temperature ignition of straight chain alkanes. Analytical approximations for the radical growth and the first stage ignition delay are also derived. However, there are several extensions that should be explored:
1. Extending the analysis to branched alkanes

The analytical expressions provided is for straight chain alkanes, however to predict branched chain alkanes we need to include additional terms for the loss of fuel radical by β-scission reactions. The single site assumption would also not be valid and rates from every site will have to be individually accounted for in the expressions.

2. Extending the analysis to alcohols

Alcohols behave in very similar way to propane. The alpha radical in alcohol is the most dominant fuel radical produced which undergoes \( \text{O}_2 \) addition followed by concerted \( \text{HO}_2 \) elimination to give aldehyde. Therefore the branching to active radicals \( \alpha \) in alcohols will be much less than 1. Additionally the gamma site in alcohols will give two OH + one \( \text{HO}_2 \) radicals instead of three OH radicals as seen in alkanes. The generalized expression for the gain factor can be written as:

\[
f_{\text{OH}} = \sum_{i=1}^{N} n_i \alpha_i \beta_i \tag{7-1}
\]

where \( n_i \) is the number of radical produced by the \( i \)th site, \( \alpha_i \) and \( \beta_i \) are site specific branching of fuel (\( \text{R} \)) and peroxy (\( \text{RO}_2 \)) radicals. The single site assumption would not be valid, since the forward and reverse rate coefficients from the different sites in an alcohol molecule are very different.

3. Second stage ignition

The work in this thesis contributes to understanding first stage ignition in alkanes which is important under low combustion temperatures (typically 600 – 800 K for long chain alkane). However in order to predict the ignition under intermediate and high temperatures the second stage of ignition must be accounted for. Analysis of detailed mechanism by various authors [27, 28, 285] suggests during the second stage the slow decomposition of hydrogen peroxide to give two OH radicals is the primary chain branching step. Peters et al. [28] did the analysis to obtain the second stage ignition delay corresponding to time when the fuel vanishes. Peters assumed a constant temperature decomposition of hydrogen peroxide and ketohydroperoxide as
the main reactions which contribute to chain branching. It would be interesting to verify and club Peter's analysis with the current first stage ignition predictions in order to “a priori” predict the ignition of any fuel over a wide range of temperature.

7.2 Developing kinetic models for higher PAHs

Chapter 3 discusses the first elementary kinetic model to predict smaller PAHs like indene and naphthalene. The model was constructed using RMG-Java. While developing these models there were several issues which were not fully addressed and future work should be dedicated into developing better solutions.

7.2.1 Improving RMG thermochemistry estimation

The current version of RMG uses on-the-fly quantum calculations to estimate the thermochemistry of cyclic species. The calculations are performed at PM7 semi-empirical level of theory. It was seen during model generation that the PM7 calculated enthalpy of many unsaturated cyclic species had an error greater than 10 kcal/mol (see Table 7-1).

<table>
<thead>
<tr>
<th>Species</th>
<th>$H_{298}$ (kcal/mol) using CBS-QB3</th>
<th>$H_{298}$ (kcal/mol) using QM PM-7</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50.9</td>
<td>40.8</td>
</tr>
<tr>
<td></td>
<td>42.2</td>
<td>34.5</td>
</tr>
</tbody>
</table>

To overcome this limitation, enthalpies of most important species were calculated and read from a library during mechanism generation. Error cancelling reactions such as isodesmic approach was also implemented but significant errors of up to 5 kcal/mol were still observed. In the future other more accurate error cancelling approaches such as homodesmotic and hyperhomodesmotic should be pursued.
Additionally given the significant number of similar species that will be seen during pyrolysis of any fuel, high level ab-initio calculations (i.e at CBS-QB3) should be performed on the existing PM7 thermochemistry libraries generated from this work. This would not only save on model generation time for future user but also provide reliable estimates of enthalpy.

### 7.2.2 Developing rate rules for higher PAHs

Currently the rate rules for predicting indene and naphthalene from cyclopentadiene have been calculated. In future rate rules for larger PAHs, such as anthracene and phenanthrene should be developed. A potential route to these PAHs is suggested by Mulholland et al. [286] by reaction of indenyl radical with cyclopentadiene.

Among smaller aromatics RMG rate rules are still unsatisfactory for predicting toluene. Considerable literature already existing on the formation of toluene and systematic comparison of literature with current RMG estimates is required.

### 7.2.3 RMG speed up and memory issues

Modeling of higher PAHs will result in a large number of species being generated. Currently modeling a C11 system such as anthracene takes a large run time where most of the processing time is spent creating species generated via cross reactions. Parallelization of RMG for species thermochemistry generation and on-the-fly pruning to reduce the unimportant species will be crucial features as we try to model these bigger systems. Considerable efforts must be placed in future versions of RMG to have these features developed and tested.

### 7.3 Alcohol modeling

RMG’s alcohol modeling capabilities is at a mature state, the development of new alcohol mechanism should now require minimal participation by the modeler. The development of pentanol mechanisms was completed within months as compared to butanols which took over three years. The CEFRC alcohol model is perhaps one of the best tests of the predictive power of a complicated chemistry model against a wide range of experiments and conditions. Nevertheless, some areas for improvement in the future would be to develop a better understanding of the polycyclic aromatic formation during pyrolysis
and low temperature peroxy chemistry. The improvements needed for improving predictions for aromatic chemistry is described in the previous section, here we only discuss improvements needed for the low temperature ignition.

7.3.1 Investigating decomposition kinetics for ketohydroperoxide

The analysis from Chapter 2 and the sensitivity analysis for low temperature ignition delay for alcohols indicate that the rate coefficient for decomposition of ketohydroperoxide is extremely important. Figure 7-1 gives the comparison of the rate coefficient as predicted by RMG and the estimate from Sarathy et al. [159] butanol model ($A = 10^{10} \text{s}^{-1}$ and $E_a = 39 \text{kcal/mol}$) for decomposition of a representative ketohydroperoxide. As seen from the Figure 7-1 the rate predicted by RMG is about a 100 times slower at lower temperatures. This is one of the primary reasons why RMG models do not ignite under RCM conditions. However it must be noted that the Sarathy estimate is also based on the decomposition kinetics of alkane hydroperoxides [287] and has a high uncertainty. Detail investigation on the thermochemistry of ketohydroperoxide and ketoalkyloxy radical must be performed, since RMG estimates the rate of recombination of OH and O\textsuperscript{\text{2}}\textsuperscript{\text{−}} radical ($10^{13} \text{cm}^3/\text{mol}\cdot\text{s}$) and uses the thermochemistry to calculate the decomposition rate. The intermolecular hydrogen bonding makes partition functions calculated using 1d hindered rotor approximations inadequate and multi-structural approximation with torsional anharmonicity (MS-T) should be performed. The Sarathy et al. rate expression give reasonable ignition delays, however the $E_a$ appears to be less than the $\Delta H_{\text{rxn}}$, and the $A$ factor corresponds to a high temperature lifetime of 0.1 femtoseconds, much less than a vibrational period, so it seems unphysical. Perhaps this fast rate is compensating for other deficiencies in the model and further research is required.
Figure 7.1: Comparison of RMG and Sarathy et al. [ref] decomposition rate for ketohydroperoxide. RMG reverse rate coefficient is estimated using the thermochemistry obtained from Benson groups.

7.3.2 Investigating the $O_2$ dependence for low temperature alcohol ignition

Weber et al. [288] and Zhu et al. [253] have measured low temperature ignition delay for butanols with varying oxygen concentrations (10 – 40%). Both studies reported strong oxygen dependence ($\tau \sim [O_2]^{-1.7}$) of the measured ignition delay. However none of the butanol models including the RMG model developed in this thesis is able to predict it. What was more surprising is that Chapter 2 shows a very weak dependence of alkane ignition delays on oxygen ($\tau \sim [O_2]^{-0.5}$ for intermediate temperatures and low pressures). Alcohols might therefore have very different chemistry controlling the low temperature ignition. Since many of the peroxy chemistry rate rules only exist for alkane like systems, ROO and $O_2O_2OH$ surfaces for characteristic alcohols must be pursued. Coupling of rotors due to hydrogen bonding with the alcoholic group necessitates the use of MS-T method for rate/thermochemistry calculations.
Bibliography


