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Ants walking in renewable fire

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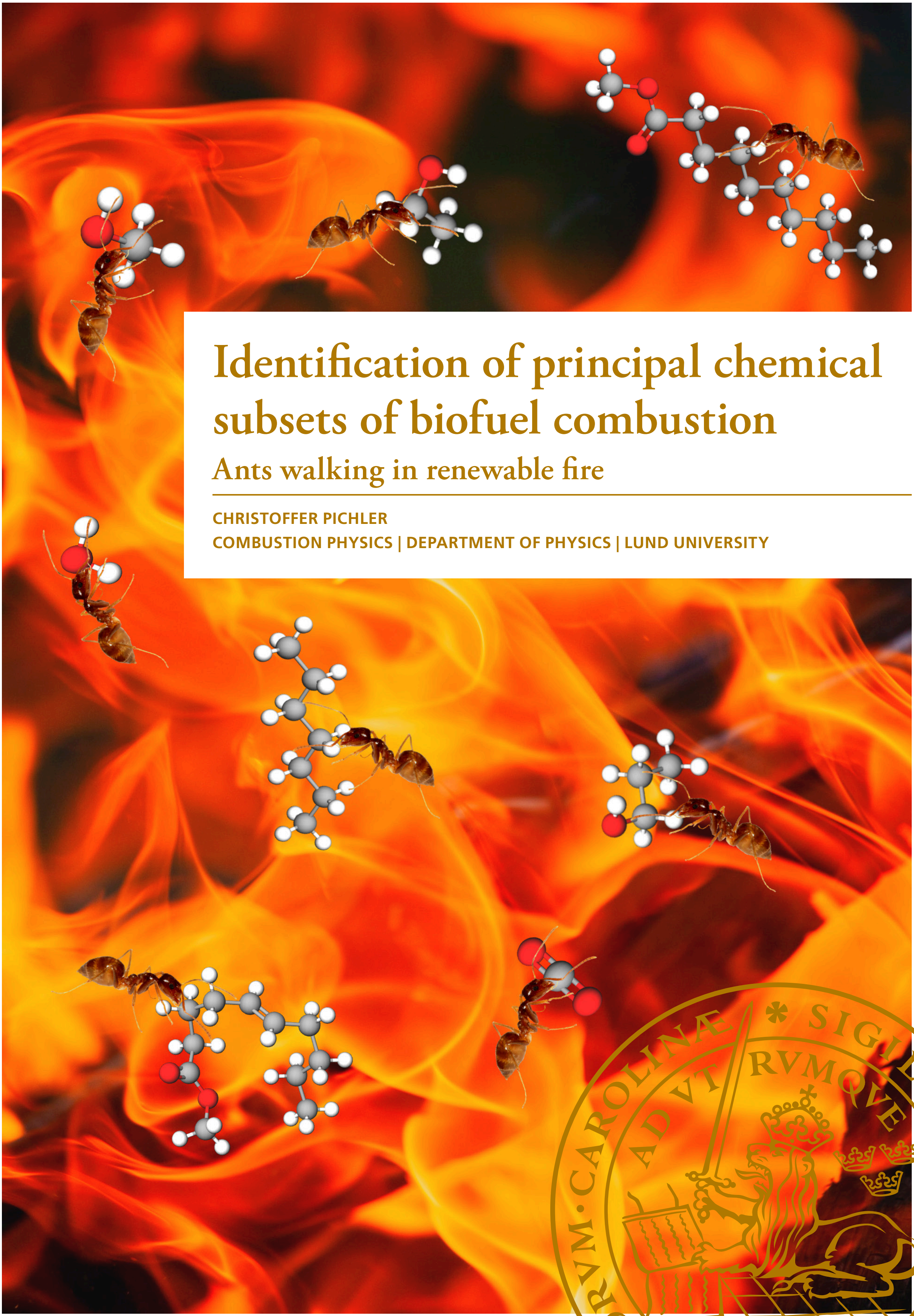

Identification of principal chemical subsets of biofuel combustion

Ants walking in renewable fire

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Christoffer Pichler

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Abstract

The work in this thesis was carried out to highlight important chemical pathways in skeletal mechanisms for the three smallest alcohol fuels (methanol, ethanol and n-propanol), two representative fuel alkanes n-heptane and n-decane, and finally the biodiesel surrogates, methyl-decanoate, methyl-5-decenoate, and methyl-9-decenoate. This aim was set up to further the efforts of creating Computational Fluid Dynamics (CFD) suitable mechanisms, which in turn can be used by the industry to improve, for example, engines or gas turbines, or by academia to further understand turbulent combustion. The work in this thesis was divided into three parts: development of a novel reduction method, pathway analysis of biofuels, and pathway analysis of petroleum and biodiesel surrogates.

Ant Colony Reduction (ACR) is a semi-stochastic reduction algorithm that has been applied successfully on kinetic mechanisms for several biofuels (methanol, ethanol, n-propanol, methyl-decanoate and methyl-decenoate), alkanes, and volatile organic compound oxidation in atmospheric chemistry simulations. The method was developed within the framework of the present thesis work, as a new approach to the mechanism reduction problem, as much research has been carried out on various established reduction methods. It has been shown that in some cases the mechanisms reduced using the ACR method outperforms previously published reduced mechanisms by having a lower number of reactions or species while preserving the same accuracy compared to a chosen reference mechanism.

The pathways analysis of the biofuel mechanisms was conducted in order to identify the principal reaction subsets for different combustion modes. It was then shown that similarities can be seen for each combustion mode for each of the smallest alcohols, methanol, ethanol and n-propanol. By understanding these subsets, an initial guess for the next alcohol fuel would be facilitated. Several trends were identified that was true for all the alcohol fuels, but there were also new reaction paths that was important for the new skeletal mechanism when the chain length of the alcohol was longer. Since the alcohol at some point has to decompose to two fragments, where only one can contain oxygen, alkane combustion chemistry became more important for n-propanol and ethanol than for methanol.

A similar approach to the biofuel pathway analysis was conducted for n-heptane, for which separate reduced mechanisms were produced for the combustion phenomena ignition, flame propagation and extinction. The reference mechanisms for n-heptane are much larger than for the small alcohols, often resulting in larger skeletal mechanisms as well. After investigation, it was shown that for high temperature ignition and laminar burning velocity, it is not necessary to have too much detail in the chemistry. Even extinction and low temperature ignition mechanisms were below 150 reactions each, but when one mechanism for all conditions were constructed, the mechanism had 230 reactions. From the pathway analysis, the important reactions for each subset was identified and can serve as an initial guide for future reduction work on large hydrocarbon fuels.

The methodology was also applied to biodiesel surrogates, methyl-decanoate, methyl-5-decenoate and methyl-9-decenoate. Once again, the mechanisms were larger in size due to the complexity of the reference mechanism. It was found that for the methyl-decenoates, the skeletal mechanisms were smaller since the number of possible, and important, intermediates are lower. Compared to other published skeletal mechanisms for the biodiesel surrogates, the sizes of these mechanisms are much smaller, between 200-861 reactions for low temperature ignition, while still retaining high predictability compared to their reference mechanism.

Key words: Reduced kinetics, biofuels, n-heptane, alcohols, Ant-Colony Reduction, combustion chemistry

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Table of Contents

Abstract

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Populärvetenskaplig sammanfattning

Utveckling av förbränningsmotorer är viktigare än någonsin då det finns en stor oro för klimatförändringar som ett resultat av användning av fossila bränslen. En lösning är att ta fram effektivare motorer som drar mindre bränsle för lika mycket arbete. En annan lösning är att hitta nya, alternativa, bränslen som inte bidrar till klimatförändringar. Utöver den här problematiken så finns det allt hårdare utsläppskrav för att behålla en bra luftkvalité i våra städer.

Biobränslen är en lovande kategori av alternativa bränslen, som skapas av bland annat växter. När vi odlar bränslet fångas lika mycket koldioxid in från atmosfärer, som det frigörs när vi sedan använder bränslet. Detta gör att vi får koldioxidneutral förbränning och därmed bidrar dessa bränslen inte till den globala uppvärmningen. Till dess att biobränslen är ekonomiskt hållbara så bör samhället istället använda fossila bränslen så effektivt som möjligt, för att minimera de negativa konsekvenserna av användningen.

För att bli mer effektiv med nuvarande, eller alternativa, bränslen så behövs nya motorer. Det är dyrt att ta fram nya fysiska prototyper för motorer bara för att testa en ny design, eftersom det kan krävas hundratals iterationer innan en tillräckligt bra effektivisering har uppnåtts och utsläppskraven har uppfyllts. Istället kan man använda förbränningssimuleringar som ett verktyg för att underlätta utvecklingen av nya bränslen och effektivare motorer.

Moores lag säger att tillgänglig beräkningskraft per krona i våra datorer dubblas vartannat år, vilket gör det mer attraktivt för varje år som går att investera i simuleringsverktyg för industriutveckling. Även då vi har tillgång till billigare beräkningskraft idag än någonsin tidigare, så är dessa motorsimuleringar krävande. Simuleringen av en virtuell motor kan delas upp i två delar, den fysiska och den kemiska. Den fysiska delen, flödessimuleringen, kräver att det simulerade utrymmet, till exempel insidan av en cylinder i en motorprototyp, delas upp i så många små boxar som möjligt så att upplösningen blir optimal. Det är vanligt att ett utrymme måste delas upp i miljontals boxar. Utöver det så måste även kemin, förbränningen, simuleras separat i varje box. Det krävs väldigt små och optimerade kemiska modeller, och det är där vår nyutvecklade reduktionsmetod, Ant-Colony Reduction (ACR) kommer in i bilden.

ACR skapar kompakta kemiska modeller (mekanismer) från enormt stora modeller. Algoritmen är baserad på hur myror hittar mat. Myrorna går slumpvis omkring runt sin myrstack tills en av dem hittar mat. Myror kommunicerar med dofter, så myran kommer att ta med en del av maten tillbaka till stacken och på vägen lägger den ut ett doftspår. Doftspåret lockar andra myror som därmed också hittar maten. Spåret håller i sig tills maten är slut, eftersom varje myra som hittar mat i slutet av spåret kommer att lägga ut ny doft. Upptäcker däremot en annan myra, som aldrig följde det första doftspåret, mat vid en närmare plats, så kommer även den att ta med sig mat hem och lägga ut ett doftspår. Myrorna har nu två dofter som de kan välja på, men det kortare spåret till mat kommer att vara starkare eftersom det blir mer doft per avståndsenhet. På det sättet hittar myrorna dynamiskt den snabbaste vägen till mat, även ifall omständigheter skulle förändras. Likt de riktiga myrorna så kan virtuella myror leta efter förbränningsprodukter genom att vandra runt i en kemisk modell, och därmed hitta de snabbaste vägarna från bränsle (myrstacken) till förbränningsprodukter (maten). Vilka molekyler som är förbränningsprodukter beror på vilket bränsle som används, men för biobränsle eller fossila bränslen är det koldioxid och vatten. I det här arbetet har ACR metoden applicerats på kemiska modeller för metanol, etanol, n-propanol, metyl-dekanoat, och metyl-dekenoat som är biobränslen, men även på n-heptan som är ett fossilt bränsle.

För n-heptan, en enkel representation av bensin (som egentligen består utav tiotals molekyler), så har det visats i det här arbetet att ACR kan skapa en modell med 230 reaktioner, och behålla liknande överensstämmelse med verkligheten som en modell med 11 790 reaktioner. Beräkningskostnaden för en modell är ungefär proportionell mot kvadraten av antalet reaktioner, vilket i det här fallet betyder en minskning med en faktor 2600. Genom att använda den kompakta modellen som har skapats med ACR så kan mycket mer datorkraft användas till effektivt simuleringsarbete.

Med en billigare utvecklingsprocess för motorindustrin är vi ett steg närmare att nå ekonomiskt hållbara gröna alternativ som samhället efterfrågar.

List of Papers

I. Pichler, Christoffer, and Elna JK Nilsson. "Reduced kinetic mechanism for methanol combustion in Spark-Ignition engines." Energy & Fuels 32.12 (2018): 12805-12813. [**Published**]

This paper explains the basic principles of the Ant-Colony Reduction methodology, and shows a proof-of-concept case of methanol combustion at Spark-Ignition engine conditions. Comparisons with other reduced mechanisms for methanol was conducted for laminar burning velocity, ignition delay times, and species profiles in jet-stirred reactors.

I carried out the simulations and developed the reduction methodology demonstrated in the article. I also did most of the data analysis and created the figures. Elna Nilsson helped with the manuscript, discussion section, structured the work, and proposed suitable reference mechanisms.

II. Pichler, Christoffer Stefan, and Elna JK Nilsson. "Analysis of important chemical pathways of n-heptane combustion in small skeletal mechanisms." *Energy & Fuels* (2019). [**Published**]

In this paper an improved version of the Ant-Colony Reduction methodology was outlined, and the scope was extended to include pathway analysis for n-heptane. Principal reaction sets and species were identified, which should facilitate future studies on the topic. Several skeletal mechanisms were presented, with sizes up to 230 reactions, for high and low temperature ignition, flame propagation, and extinction.

I carried out the simulations, reduction, and optimisation while Elna Nilsson decided conditions of interest. Much of the pathway analysis was done by both authors together, with an emphasis on Elna Nilssons expertise. Figures were created by me.

III. Pichler, Christoffer, and Elna JK Nilsson. "Pathway analysis of skeletal kinetics for small alcohol fuels at engine conditions." [**In review, Fuel**]

The successful pathway analysis found in Paper II was combined with alcohol combustion, started in Paper I. In Paper III, the alcohol fuels methanol,

ethanol, and n-propanol were studied, and several useful trends were highlighted. It was also shown that to construct compact skeletal mechanisms with high accuracy, it is beneficial to tailor the mechanism to a single combustion mode.

In this article, I did the simulations, data analysis, preparatory work and pathway analysis. Under supervision of Elna Nilsson, who also contributed significantly to the discussion section.

IV. Pichler, Christoffer, and Elna JK Nilsson. "Composition of skeletal mechanisms for ignition of biodiesel surrogates." [**Submitted, Combustion and Flame**]

In this paper, the Ant-Colony Reduction methodology was applied to ignition delay time simulations for bio-diesel substitute fuels. The original sizes of the detailed mechanisms are between 9700 to 11800 reactions and between 2600 and 3300 species. After reduction the smallest mechanism is 75 reactions and 42 species, and the largest mechanism is 1367 reactions and 404 species. The largest skeletal mechanism is still a factor 2000 times faster to calculate than the corresponding detailed mechanism. Differences between high and low temperature ignition chemistry is highlighted, and for the different fuels, the need for further development of the methodology is identified.

I applied the reduction methodology to the large detailed mechanisms, ran all the simulations and prepared most of the figures. Elna Nilsson wrote the manuscript and analysed the chemistry.

Related work

R-I. Li, Rui, et al. "Comparative analysis of detailed and reduced kinetic models for CH4+ H2 combustion." Fuel 246 (2019): 244-258.

R-II. Joelsson, Lars Magnus T., Christoffer Pichler, and Elna JK Nilsson. "Tailored chemical mechanisms for simulation of urban air pollution." *WIT Transactions on Ecology and the Environment* 230 (2018): 165-176.

R-III. Joelsson, L. M. T., C. Pichler, and E. J. K. Nilsson. "Tailored reduced kinetic mechanisms for atmospheric chemistry modeling." *Atmospheric Environment* (2019).

Abbreviations

Acetic acid	CH_3COOH
Ant-Colony Optimisation	ACO
Ant-Colony Reduction	ACR
Best-Worst Ant System	BWAS
Carbon dioxide	CO_2
Compression ignition	CI
Computational fluid dynamics	CFD
Dimethyl ether	DME
Direct numerical simulations	DNS
Directed relation graph	DRG
Directed relation graph aided sensitivity analysis	DRGASA
Directed relation graph with error propagation	DRGEP
Directed relation graph with error propagation aided sensitivity analysis	DRGEPSA
Ethanol	C_2H_5OH
Extinction strain rate	ESR
Formaldehyde	CH_2O
Formic acid	CHOOH
Genetic algorithm	GA
Hydroxyl	OH
Ignition delay time	IDT
Laminar burning velocity	LBV
Large eddy simulation	LES
Methanol	CH3OH
Methyl-cyclohexane	MCH
Methyl-decanoate	MD
Methyl-5-decenoate	MDe5
Methyl-9-decenoate	MDe9
Multiple Ant-Colony System for Vehicle Routing Problems with Time Windows	MACS-VRPTW
N-decane	$n\text{-}C_{10}H_{22}$
N-heptane	$n\text{-}C_7H_{16}$
N-propanol	$n\text{-}C_3H_7OH$
Negative temperature coefficient	NTC
Nitrous oxides	NO_X
Ozone	O_3
Path Flux Analysis	PFA
Polycyclic aromatic hydrocarbons	PAH
Primary reference fuels	PRF
Principal Component Analysis	PCA
Quasi-steady state approximation	QSSA
Sensitivity analysis	SA
Simulated error minimisation connectivity method	SEM-CM
Spark-Ignition	SI
Third body species	M
Volatile organic compound	VOC

Chapter 1.
Introduction

Combustion processes are fundamental for power generation and transportation in modern society. Ever since the invention of the steam engine in the late 17th century, the use of coal and other fossil fuels have been a cornerstone of the industrial era. In a recent report by Kalghatgi et al. [1], the authors conclude that the internal combustion engine will be a fundamental part of society for the foreseeable future, making research on this topic highly relevant. The point of internal combustion engines is to extract chemical energy bound in a fuel and convert it into useful work. By oxidising the fuel to carbon dioxide and water, stored energy is released, which is converted into work using an engine or gas turbine. As Kohse-Höinghaus points out in a recent report [2], the field of combustion is much wider than just engines and power generation, since it also includes, among other applications, waste incinerators, industrial furnaces, heating solutions, steel, ceramics, cement and glass production. It is fair to state that combustion is a fundamental concept that is required to maintain the current form of society and will thus have to be around for the foreseeable future.

Today, fossil fuels are the most utilized fuels since they have high energy density, both in respect to weight and volume, while also being cheap to produce. It is possible to synthetically produce fuels with similar properties and energy density, but that comes at a high cost. Fossil fuels include coal-based fuels, natural gas, and oil derivative hydrocarbons, such as petroleum, diesel, and kerosene.

Combustion of fossil fuels contributes to the anthropogenic greenhouse effect. By emitting carbon dioxide that has been captured from the atmosphere thousands of years ago, the net-total contribution of carbon dioxide to the atmosphere in the immediate time frame is positive. The anthropogenic greenhouse effect increases the average temperature of the planet, causing climate change and disturbs ecosystems. There are many models and predictions that indicate that there will be major repercussions for habitable areas and food production if the anthropogenic greenhouse effect is further increased [3-6]. To avoid unwanted effects on the climate and to reduce the adverse effects of combustion on people and the local environment, new fuels has to replace the traditional fossil fuels [2].

Due to the imminent risk of climate change, as reported by Blunden et al. [7], new fuels are being developed to replace fossil fuels and one promising category is biofuels. Biofuels comes in many shapes and forms, such as wood pellets, alcohols, ethers, or any gas that can be extracted from, for example, plant decomposition. Using biofuels have two important benefits over traditional fossil fuels, carbon neutrality and renewability; together, these two concepts makes the category interesting as alternative fuels. Biofuels are produced from trees, crops, plants, algae, and animal- and municipal waste. This ensures carbon neutrality, since the carbon dioxide that is being emitted when the fuel is consumed, was captured when the plant was grown. Furthermore, this makes biofuels a renewable source of energy, unlike fossil fuels which is being produced at an extremely slow rate but consumed very quickly.

Alcohol is a subclass of biofuels, which have been given much attention recently. Alcohol molecules consist of a hydrocarbon chain with one or several hydroxyl (OH) groups attached to it. Unlike the four shortest alkanes, even the shortest alcohol, methanol (CH_3OH), is liquid at room temperature. This property makes the alcohols suitable to use as a substitute for petroleum and diesel, since it makes full use of the current infrastructure, which is designed for liquid fuel. Moreover, since alcohols produced from renewable sources are biofuels, they are carbon neutral and renewable. It is methanol and ethanol (C_2H_5OH), the mono-ols with the shortest carbon chains, which is given the most attention as replacement fuels.

In the report by Kalghatgi et al. [1], the authors formulate four challenges for the future of the transport sector, if the emission goals for greenhouse gases are to be achieved. The first two challenges are: "Fuels tailored to engines with cycle and system advances that increase overall conversion of chemical energy to useful work" and "Renewable fuels that are chemically converted to equivalent petroleum products matched to the combustion engine that optimizes performance". As discussed, short alcohol fuels resemble petroleum for some important combustion properties, thus qualifying research on this topic to work on the second challenge. Furthermore, the industry is designing new engines to adapt to new fuels, in order to handle the first challenge. To facilitate the process of developing new engines, the industry utilises fully modelled engine simulations. In order to obtain accurate combustion predictions, there is a need for reduced kinetics.

Reduced kinetics is a small set of chemical reactions that accurately approximates the properties of interest but does so without many real reactions that barely affect the chosen targets. A mechanism, a set of reactions, can then be used by kinetic software to simulate, for example, the combustion process. According to the report by Kohse-Höinghaus, creating reduced kinetics for real life applications is one step towards transitioning to renewable fuels [2]. In this thesis, a newly developed methodology for constructing reduced kinetics is presented, together with several examples where the methodology has been applied to biofuel and fossil fuel substitutes. The reduction is followed with pathway analysis to further understand the principal reaction subsets for ignition, flame propagation, and extinction for reduced kinetics at Spark-Ignition (SI) engine conditions.

Studying the turbulent conditions inside a running engine or gas turbine is a challenging task, which can be performed through computer modelling. Computational Fluid Dynamics (CFD) is an umbrella term for all categories of algorithms that model turbulent flow. Two examples of subcategories are the Large Eddy Simulation (LES) [8] and Direct Numerical Simulation (DNS) [9]. In general, LES has a lower spatial resolution than DNS, but can in turn model more complex system. The turbulent flow is modelled using the

Navier-Stokes equation, which describe the motion of viscous fluids and gases. LES models the Navier-Stokes equations, but ignores the smallest length scales, which reduces the computational cost on the expense of accuracy. In contrast, DNS models the full extent of the equations. As it is with all modelling, computational cost is a big concern. Having a highly resolved DNS simulation might not be worth it, due to limitations in computational capacity, if the only system that can be modelled is an inert cube of air. On the other hand, a low resolution LES simulation of the flow field inside a compression ignition engine could also be of little value, unless gas mixing is properly resolved. Finding the proper trade-off between level of detail and computational cost is a significant challenge in CFD engineering.

In order to run a complete computer model of an engine, the gas phase chemistry has to be modelled. Since this adds even more computational cost to the simulation, a time efficient approach is to use an LES algorithm when modelling turbulence-chemistry interaction. Even with simplifications in the fluid-dynamic part of the simulation, the chemistry model has to be very compact in order to not scale up the computational cost significantly. In a recent review by Hochgreb, the author expresses a need for kinetic modellers and experimentalists to work closer together to solve questions from real applications [10]. On the modelling side, there is a lack of reduced kinetics that can handle high pressure combustion, sprays and soot formation, while still being computationally feasible for CFD simulations.

Comprehensive, or detailed, mechanisms contain hundreds or thousands of species and up to tens of thousands of reactions to accurately predict the complete combustion process. Like the CFD algorithms, if the "chemical-resolution" is high, the associated computational cost is also high.

Reduced kinetics is the trade-off between the accurate results of a comprehensive chemistry description and computational cost. A reduced mechanism is a scaled down version of a comprehensive mechanism. There are various degrees of reduction that can be implemented. Skeletal reduction, which will be the focus of this thesis, is the process of removing reactions and species, without making any approximations to the remaining parts. Global mechanisms, on the other hand, uses just a few (< 10) reactions, but can still provide good predictability for some combustion targets in a limited condition range. A common methodology, lumping, is used to combine several species or reactions into one, which means that the individual species concentrations are no longer discernible, and the new compound behaves as some sort of linear combination of the initial species. This technique can reduce the size of the model significantly. A common approach to reaction lumping by is using Quasi-Steady State Approximation (QSSA), applied by many authors, for example Schneider et al. [11], and Zhang et al. [12]. QSSA skips over species that are produced by one reaction and consumed by another, thus removing one species and combining two reactions into one. Lumping also occurs in the large comprehensive models, in order to scale them down to computationally feasible size, although the extent of the lumping is usually restricted to larger molecules with little reliable thermodynamic data available. A lumped comprehensive model is sometimes called “complex” instead, to indicate that approximations have been made, but most of the chemistry is still intact.

It is often the case that less than 20 % of the species in the comprehensive mechanism is of interest for the engine development process. For example, if the goal is to reduce NO_x emissions in a Compression Ignition (CI) engine with methanol, species such as acetic acid is not in itself of interest, so if the NO_x chemistry barely interacts with this species, it can be removed. Similar, in the case of an CI-engine, it is most likely operated at lean conditions, which means that all reactions and species that are mainly formed in rich conditions can be removed. This hunt for reactions and species to remove is important as the maximum size of mechanisms suitable for LES is around 20-40 species and 50-100 reactions [13-15]. This approximation will always cause deviation in the results compared to the comprehensive model, but with smart choices of which species to remove, the deviations can be kept small while the computational cost is reduced drastically.

The focus of this thesis is to construct small and computationally cheap skeletal mechanisms for biofuels and study the chemical pathways. In order to develop the methodology, additional attention has been given to the chemical aspects by performing pathway analysis of skeletal mechanisms for common fuel, such as small alcohols, n-heptane and large ester fuels. To our knowledge, this is the first systematic study revealing important reaction subsets for the different combustion modes.

The mechanisms presented in papers I-IV are used as examples of considerations that have to be made when constructing small skeletal mechanisms suitable for CFD simulations. Paper I presents a mechanism for methanol combustion in SI-engines. Paper II demonstrates the size differences of different combustion modes of n-heptane, and highlights the importance of narrowing down the condition space, to only cover relevant conditions of the target application, before reduction. Paper III, is a thorough study of the chemical pathways in small alcohol combustion, and how the complexity of the skeletal mechanism increases with the fuel’s carbon chain length. The final paper, IV, demonstrates that a similar reduction methodology for is also possible for large biodiesel fuels, methyl-decanoate, methyl-5-decenoate, and methyl-9-decenoate.

Chapter 2.

Brief overview of the field

The study carried out in this thesis is based on the need for more knowledge about reduced kinetics of biofuels. As mentioned in the introduction, reduced kinetics is essential for accurate CFD simulations of combustion processes. The most common approach is to remove reactions and species from a comprehensive mechanism. It is possible to build a new mechanism from the ground up, as have been demonstrated by Chinnick et al. [16], but in this thesis the focus will be on the reduction approach.

In order to create accurate reduced kinetics, detailed kinetics has to be constructed with excellent agreement with experimental data. If comprehensive mechanisms that can reproduce experimental data did not exist, it would be very difficult to construct a small mechanism with that capability.

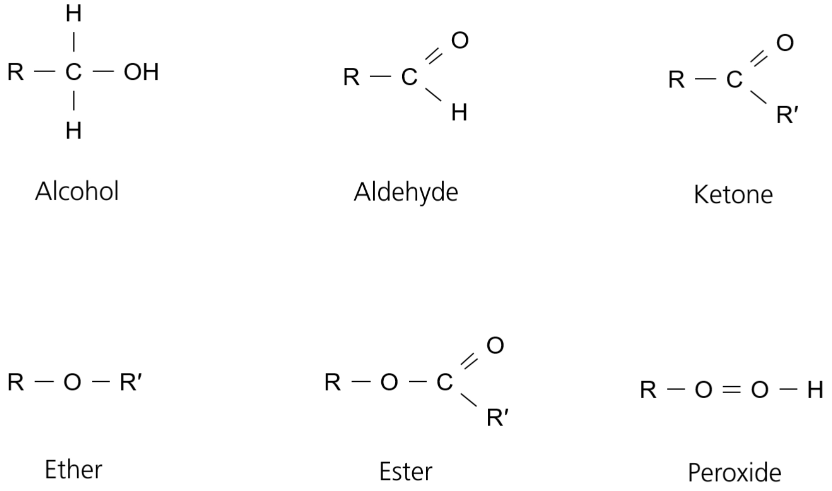
The reason for the recent increased attention given to reduced kinetics of biofuels is due to the need for new carbon dioxide neutral fuels, and without the reduced kinetics, it is more difficult to develop and optimise engines to the new fuels. There exist plenty of variations of biofuels, some of which are discussed in further detail later in this chapter. In this thesis, Paper I & III focuses on the alcohol subclass of biofuels, specifically for SI-engines, while Paper IV presents skeletal models for methyl-ester fuels, biodiesel for CI-engines.

This chapter gives an overview of important concepts, functional group, and biofuels, which has chemical characteristics that are defined by the functional groups. This is followed by a brief description of detailed kinetics and some well-known mechanisms from the literature. Finally, established reduction methods are presented, before the novel semi-stochastic Ant-Colony Reduction (ACR) method is described in Chapter 3. The newly developed ACR method, first presented in Paper I in this thesis, combines the strengths of deterministic and stochastic methods. This makes it possible to create the compact and optimised reduced skeletal mechanisms, for a given range of conditions, while still retaining good agreement with each corresponding detailed mechanism.

2.1 Functional groups

In general, any fuel produced from a biological organism is a biofuel. As previously mentioned, common sources are plants, crops, trees, and animal- and municipal waste. Usually, these fuels are oxygenated hydrocarbons, but the combustion properties vary based on the primary functional group of the fuel, hydrocarbon chain length, degree of saturation and branching.

Figure 1 shows the structure of common functional groups found in biofuel and hydrocarbon combustion kinetics. Alcohols and esters are the two types of biofuels discussed in this thesis, but during combustion, these molecules will transition through several of the other classes, such as aldehydes, ketones, ethers, and peroxides [17]. The first group, alcohols, is a hydrocarbon chain with one or several hydroxyl groups bound to carbon atoms. These molecules are stable and several of them have been explored as fuels in paper I and III.



Alcohol

Aldehyde

Ketone

Ether

Ester

Peroxide

Figure 1. Structure of six common oxygenated species found in reaction mechanisms for combustion of biofuels and hydrocarbons. R and R′ are hydrocarbon chains.

While oxidizing alcohols, depending on the location of the hydroxyl group, an aldehyde or ketone could be produced as an intermediate species. These two groups have a carbonyl group, double bonded oxygen, attached to a carbon atom. An aldehyde has the carbonyl group in the end of the hydrocarbon chain, and a ketone has the carbonyl attached to any of the carbon atoms not at either end of the chain. A very common aldehyde that show up in biofuel combustion is formaldehyde (CH_2O), an important emission to track. Formaldehyde is carcinogenic, stable, and produced in larger quantities for incomplete combustion of, for example, methanol and ethanol in internal combustion engines.

Further oxidation of aldehydes can lead to formation of carboxylic acid. As the name suggests, carboxylic acids are acidic and can cause problems if a sufficient concentration is accumulated inside engine systems [18].

Esters and ethers are functional groups that connect two hydrocarbon chains through an oxygen atom. Esters also have a carbonyl group bound to one of the carbon atoms attached to the oxygen bridge. These are formed from reactions of alcohols and carboxylic acids. Both esters and ethers are stable molecules, which are used as fuels. Methyl-decanoate, one of the fuels from Paper IV, is an example of a large diesel-like ester that can be produced from biomass and contains eleven carbon atoms. On the shorter end of the spectrum, dimethyl ether (DME) is the smallest ether, only containing two carbon atoms, and can be used as a biofuel substitute for propane gas, or even as a diesel substitute [19].

Another prominent functional group in, especially, lower temperature combustion is the peroxide. Peroxides are defined by two bound oxygen atoms with a single bond to a hydrocarbon chain. The notation OOQOOH in a species' name indicates that there are two peroxide groups attached to the same hydrocarbon chain, and these species are important when modelling Negative Temperature Coefficient (NTC) behaviour of ignition delay times. This will be covered in more detail in Section 4.3.2 Low temperature ignition.

All the mentioned functional groups also exist in radical form. By abstracting a hydrogen atom from the hydrocarbon chain, or from a hydroxyl group, a radical is produced. Most species in the combustion reaction mechanisms presented are radicals, as these are very important intermediates for the propagation of combustion. An example of a radical is CH_2OH, created by an alcohol, methanol, losing a hydrogen atom through a hydrogen abstraction reaction. This species reacts much quicker than the stable methanol and will thus keep the reaction chain going. When more radicals are created than consumed by a reaction, it is called a chain branching reaction, since each of the radicals will quickly participate in new reactions. If the same number of radicals are consumed as is produced, the reaction is called chain propagating, as the reactivity of the overall system has not changed. The final type of reaction is the chain terminating reaction, when more radicals are consumed than produced. When the temperature decreases, then chain terminating reactions are favoured and the radicals react to form stable species, either as one of the functional groups above, or as some other species.

2.2 Biofuels

Although the mechanisms presented in this thesis only include fuels belonging to a few of these functional groups, many of the groups are represented in some stage of the combustion process for each fuel. The three biofuels that were studied in Paper I and III are the three smallest alcohols, methanol, ethanol, propanol, shown in Figure 2, and the focus of Paper IV is on the ester fuels methyl-decanoate, methyl-5-decenoate, and methyl-9-decenoate, shown in Figure 3. Figures 2 and 3 were made using MolView [20]. The fuels included in this thesis were chosen due to their relevance in society and the need for further knowledge to better utilise them. These fuels were all studied under SI conditions to validate the methodology and highlight the reaction paths, even though methanol, methyl-decanoate, and the two methyl-decenoates are more suitable for CI-engines. A major difference between SI and CI engines, is that the range of relevant equivalence rations is larger in a CI-engine, and that the maximum pressure is usually higher, up to 200 bar. The difference in ignition method also makes fuels more suitable for one of the engine types. SI-engines need fuel with high octane number, a rating based on how much the fuel can be compressed before auto-igniting, where high number fuels ignite later [21]. CI-engines, on the other hand, requires a fuel with a high cetane number. The cetane number indicates how well a fuel ignites under CI-engine conditions [21]. Given the results of the Papers I-IV, it would be possible to construct additional mechanisms for the CI conditions as well.

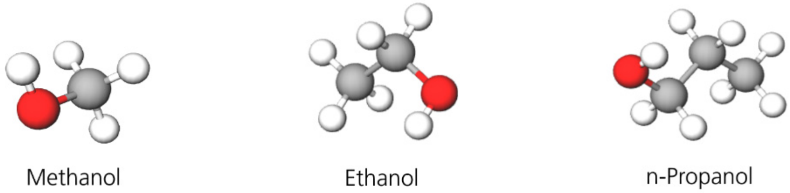
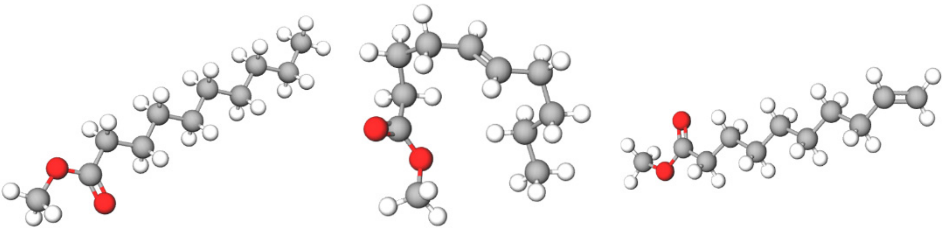


Figure 2. The three shortest alcohols, methanol, ethanol and n-propanol. The atoms are carbon (grey), hydrogen (white), and oxygen (red).

Methanol is currently mostly target towards heavy duty engines, such as trucks and cargo ships [22]. The fuel yields higher engine power, higher brake thermal efficiency and slightly higher nitrous oxides compared to traditional fuels [23, 24]. An upside of using methanol is that the fuel can be produced from various crops [24]. Although there are ethical concerns associated with converting food into fuel, fortunately, methanol can also be produced from non-food sources, such as municipal- and agricultural waste, and also gasification of wood [24]. Methanol is poisonous and soluble in water, which means that if a large tank of methanol is spilt in nature, the quality of the water supply in the immediate area would deteriorate to some extent, but not as much as a similar petroleum spill [25].

Ethanol has been investigated as a potential substitute fuel primarily for cars [18]. It has already made an impact on the car racing industry, and several of the fastest cars to this day runs on ethanol, as stated by Koeningsegg [26]. The increased combustion efficiency compared to petroleum, which leads to better performing cars, is similar to that of methanol. Unlike methanol though, ethanol is mainly produced from food sources, often from corn or sugarcanes. Another issue with ethanol is that the vapour pressure is low at room temperature, 15 kPa at 311 K compared to 60 kPa for petroleum [27], and is thus difficult to ignite. This issue is further amplified during the winter, in some countries, when cars must start at temperatures around zero degrees Celsius. Now, this is solved by using ethanol blend, rather than pure ethanol. In Sweden, E85 is the dominant blend, which consists of 85 % ethanol and 15 % petroleum, having a vapour pressure around 35 kPa at 311 K [27] (and is changed to E75 during the winter, which increases vapour pressure to 50 kPa [27]). Brazil, as a country with warm climate, has replaced much of its petroleum needs with ethanol primarily produced from sugarcanes [27].

Propanol is the third smallest alcohol, and the smallest alcohol with two isomers. Either the hydroxyl group can be bound to the end of the carbon chain, forming n-propanol (used in Paper III), or the group can be bound to the middle carbon atom, forming i-propanol. Some properties of the two isomers are different, and the reaction paths, since the fuel radicals created after hydrogen abstraction have different structure. At the time of writing, there is still no application for propanol fuel, since it is expensive to manufacture, but the academic interest remains due to the increased complexity of the chemistry compared to the two smaller alcohols, and the possibility to gain general understanding of alcohol combustion.



Methyl-decanoate

Methyl-5-decenoate

Methyl-9-decenoate

Figure 3. Three methyl-esters, the saturated methyl-decanoate and the two unsaturated methyl-5-decenoate, and methyl-9-decenoate. The atoms are carbon (grey), hydrogen (white), and oxygen (red).

Methyl-decanoate is a large saturated ester, with ten carbon atoms in the main chain and a methyl group bound by an ester bond. The large carbon chain makes the properties of the fuel resembling diesel fuels, meaning that methyl-decanoate falls in the subcategory of biodiesel. The primary attribute of diesel-like fuels is that they have a high cetane number, typically above 40. High cetane number indicates that the fuel quickly ignites, while a low cetane number shows that the fuel has long ignition delay time [21], i.e. time between first reaction and the specific ignition event indicator (for example pressure increase, or OH-radical formation).

Methyl-5-decenoate and methyl-9-decenoate are both unsaturated esters, similar to methyl-decanoate in structure, except having a double bond between two carbon atoms in the main hydrocarbon chains. For methyl-5-decenoate, the double bond is five atoms away from the ester bond, and for the methyl-9-decenoate, it is 9 atoms away from the ester bond. Both methyl-5-decenoate and methyl-9-decenoate have similar properties as methyl-decanoate, and thus a similar reasoning applies to them as well. According to Westbrook et al. [28], the presence of a double bond, or allylic group, in the fuel slows down ignition at low temperatures by inhibiting the formation of the OOQOOH species and its accelerative effects on ignition delay times, as discussed further in Section 4.3.2. A similar experimental study was carried out by Wang et al. [29] confirming the analysis of Westbrook et al. The experimental results showed that for high temperature ignition, the ignition delay time is independent of location of double bond, but for low temperature ignition there is a deviation of a factor 2.

Burning any carbon-based fuel will emit carbon dioxide, but due to incomplete combustion the carbon dioxide will be accompanied by various other partially oxidised molecules. Even though biofuels ensure that the carbon dioxide emission does not contribute to global warming, there are several other pollutant gases that cause health issues and damage to crops and ecosystems. For alcohol combustion in engines, there is a significant emission of oxygenated species, such as formaldehyde (CH_2O) [30], formic acid ($CHOOH$), and acetic acid (CH_3COOH). Formaldehyde is carcinogenic, making the exhaust toxic to humans [31-34]. Furthermore, the production of acids has a corrosive effect on the engine, which is not present when burning non-oxygenated hydrocarbons [18]. These are engine design challenges that need to be resolved before a sustainable transition from fossil to alcohol fuels can be done.

2.3 Chemical kinetics

An important concept when describing combustion is the equivalence ratio, Φ. Every fuel-oxidizer mixture has a stoichiometric gas concentration ratio, i.e. the ratio where there are just enough oxidizer molecules per fuel molecule to form complete combustion products. A simple case is the methane-oxygen stoichiometric balanced, global, reaction

$$\mathrm{CH_4} + 2\ \mathrm{O_2} \leftrightarrow \mathrm{CO_2} + 2\ \mathrm{H_2O}$$

where the stoichiometric ratio would be 0.5, since there are two oxygen molecules per methane molecule. The equivalence ratio is then calculated as the actual ratio between fuel and oxidizer, divided by the stoichiometric ratio. Temperature, pressure and equivalence ratio are usually the three parameters that are used to describe the initial conditions of kinetic simulations and experiments. This triplet of information can sometimes be complemented with dilute gas concentration to fully describe the initial condition.

Kinetic reaction mechanisms describe a chemical system and include many chemical reactions. A global reaction, as the one above, describes a whole process, while an elementary reaction describes a single collision of molecules. For example, the reaction

$$\mathrm{CH_4} + \mathrm{OH} \leftrightarrow \mathrm{CH_3} + \mathrm{H_2O}$$

is an elementary reaction, since it describes the breaking of an C-H bond in the methane (CH_4) molecule, and formation of an O-H bond for the hydroxyl radical (OH). Combining many elementary reactions forms a global reaction. Each chemical reaction consists of reactants, products, and a reaction rate constant. In the elementary reaction example above, methane (CH_4) and hydroxyl radical (OH) are the reactants and methyl radical (CH_3) and water (H_2O) are the products. The reaction rate constant is commonly parameterised by the modified Arrhenius expression (1)

$$k = AT^{n}e^{-\frac{E}{k_B T}} \quad (1)$$

where T is the temperature, k_B is Boltzmann's constant, A is the pre-exponential factor, n is the temperature co-efficient and E is the activation energy [35]. Each of these reactions describes the change with respect to time of a few species, making the whole mechanism a set of differential equations. Using numerical methods, the concentration of each species in the system can be calculated at any point in time for any initial condition. Adding to this entropy and enthalpy changes, heat release, temperature, and pressure changes can also be calculated.

There are many research groups that develop comprehensive mechanisms for various fuels. The San Diego mechanism [36] models up to C4-hydrocarbons, nitrous oxides (NO_x), methanol and DME. The Aramco Mechanism 3.0 [37] models up to C10-hydrocarbons, and many oxygenated compounds. The CRECK research group at

Politecnico di Milano has developed a combination of a detailed and lumped mechanism [38] for primary reference fuels (PRF), polycyclic aromatic hydrocarbons (PAH), biomass, alcohols, ethers, and methyl-esters. From Lawrence Livermore National Laboratory, there are mechanisms for butanol, iso-pentanol, alkanes, alkenes, PAH, DME, methyl esters, and surrogate fuels, such as biodiesel surrogate [39-41]. In an article by Capriolo et al. [42] the Konnov mechanism have been updated to include laminar burning velocities for propanal.

The process of combustion is a sequence of reactions that oxidises fuel to complete combustion products (commonly carbon dioxide and water) [43]. This process is driven by radicals interacting with the species, using their reactive nature to decompose stable species and advancing the process. Given the importance of radicals, there are three main types of reactions occurring as previously mentioned: Chain-branching, net-positive radical formation; chain-propagation, net-neutral radical formation; and chain-termination, net-negative radical formation [43]. The three modes of combustion, ignition, flame propagation, and extinction, are dominated by various degrees of these reaction types.

Ignition starts with endothermic chain-branching reactions that builds up the radical pool until exothermic reactions can occur [43]. Depending on the fuel and the conditions, there can be competition between chain-branching and chain-terminating reactions, meaning that a change in temperature could either favour a faster reacting system (if the chain-branching reactions are favoured) or a slower reacting system (if the chain-terminating reactions are favoured). An example of this competition is the H + O_2 reaction, which could either react to form HO_2, a slow-reacting radical (chain-terminating), or OH + O (chain-branching). There are also chain propagation reactions, for example,

$$H_2 + OH \leftrightarrow H + H_2O,$$

which does not change the reactivity of the system, since one radical is consumed while another is produced.

Flame propagation is the stable conversion of fuel to complete combustion products, given an already established radical pool [44]. This phenomenon is usually simulated by a steady-state simulation as the flame should be self-sufficient, given a constant flow of fuel and oxidiser, and can maintain the radical pool and temperature. Since there is a high temperature zone and radicals present, endothermic chain-branching reactions are not as important as heat releasing reactions that form complete combustion products, such as

$$CO + OH \leftrightarrow CO_2 + H.$$

Extinction occurs when the conditions change in the flame to favour more chain-terminating reactions until the radical pool is depleted. This can be induced by, for example, lowering the temperature, changing the pressure, or changing the composition of the fuel-oxidiser mixture [45]. In the case of counter-flow diffusion flames, such as the ones simulated in Papers II & III, increased stretching of the flame front will eventually extinguishes the flame [46].

The principal chemistry for each combustion mode is not the same. For example, fuel decomposition reactions without radicals are crucial in the ignition phase, but almost irrelevant when the radical pool has been established for flame propagation and extinction. Similar, certain chain-terminating reactions and formation of larger species are not that relevant in the high temperature chemistry of flame propagation but influences the outcome of ignition and extinction simulations greatly. The details of the differences between the combustion modes are further explored in Chapter 4.

2.4 Established reduction methods

Reduction of comprehensive mechanisms has been a relevant topic the last decades, since more complex chemistry can be considered for CFD simulations as the computational power of society grows. Many reduction strategies have been developed, and in this section, a few prominent ones will be presented.

The Directed Relation Graph (DRG) method was proposed by Lu and Law, [47] and has been the starting point for development of a myriad of similar reduction algorithms. Lu and Law also applied the DRG method to n-heptane and iso-octane to demonstrate the potential of the algorithm [48]. The DRG method measures the error induced by directly dependent species in a mechanism, and then removes all connections that are weaker than a specified threshold. If a given species A is connected by a single reaction with B and C, then the algorithm estimates how the error in production of A is dependent on removing B or C, respectively. This error value is always the same, given that the initial conditions are constant, which makes the algorithm deterministic. The threshold can easily be varied to produce a small enough mechanism from a computational perspective, while maximising the accuracy of the system. The main weakness of this algorithm is that it only takes into account direct dependencies of species and cannot see further down the reaction tree.

DRG with Error Propagation (DRGEP) was proposed as a solution to the shortcomings of the base DRG method [49]. This variant allows the error induced by removing a species further down the reaction tree to propagate to previous species, not directly dependent on the removed species. If the given species A is connected to B and C, and B is further connected with D, then in DRGEP, the connection A-D is also considered when calculating the error of removing species. Pepiot and Pitsch [49] proposed this approach and applied it to n-heptane, showing that higher accuracy could be obtained with the same number of species in the reduced mechanism compared to the original DRG method.

Another variant of the DRG method is DRG-Aided Sensitivity Analysis (DRGASA), where sensitivity analysis, a common tool in mechanism development, was used to better estimate the strength of the connection between species. Zheng et al. [50] used this approach to generate a reduced model for ignition temperature of counter-flow burners for 1,3-butadiene. This method is a development by combining well-known Sensitivity Analysis reduction (SA), as for example Liao et al. [51] used for methanol reduction, with DRG. Although this approach has a better estimator of connection strength, it lacks the bigger picture approach that is the basis of DRGEP.

The combination of DRGEP and DRGASA is called DRGEPSA, and the idea was to combine the strengths of both variants of DRG in order to create an even better algorithm. Niemeyer et al. [52] presented the method and demonstrated the improved capabilities for n-heptane, iso-octane and n-decane.

Besides all variants of DRG, another common reduction approach is the Principal Component Analysis (PCA). Vajda et al. [53] presented PCA for hydrogen-bromine reaction and formaldehyde oxidation. Although the initial case was not for combustion, Brown et al. [54] applied PCA for hydrogen-air- and methane-air combustion for premixed laminar flames, perfectly stirred reactors and plug flow reactors. The PCA method divides the reaction space into influential and non-influential portions, which is then used to remove reactions and species. Using sensitivity analysis, sensitivity coefficients are calculated for each reaction in the mechanism. By constructing an objective function in a specific way and using the Gauss approximation, a matrix with eigenvalue a corresponding to the impact on accuracy of removing reaction a is obtained. By using a threshold, similar to the DRG method, only influential reactions (with an eigenvalue above the threshold) are kept. Similar to the DRG method, this is also a deterministic algorithm which will always produce the same result if the same input, mechanism and conditions, are given with a fixed threshold on the eigenvalues.

The Simulated Error Minimization Connectivity Method (SEM-CM) [55] is an approach that builds a reduced mechanism from zero reactions, rather than removes reactions from the full set. SEM-CM starts by defining important species and combustion targets (e.g. pollutants, ignition delay time, or laminar burning velocity), and the minimum set of species and corresponding reactions to describe the important set is selected. All species that are not yet selected but would contribute with at least one additional reaction (called the “complementary set”), are found. After simulation of the temporary mechanism, deviations in targets and important species concentrations from the complex mechanism are recorded and stored in a database. The smallest complementary set with the smallest error is added to the mechanism, and the process repeats until a mechanism with enough accuracy is found. The main advantage of this deterministic algorithm, compared to previously mentioned DRG and PCA, is that this approach directly links mechanism size with accuracy and thus makes it easy to construct a mechanism that is just good enough for the target application.

Another approach to the reduction process is the Decoupling methodology, demonstrated for diesel surrogate chemistry [56]. According to several studies [38, 57-59], laminar burning velocity, extinction, heat release and the source of hydrocarbon emissions all depends mostly on the $C_0 – C_2$ chemistry. This led to the main idea behind the decoupling methodology: Using a detailed mechanism for the $C_0 – C_1$ chemistry, with a slightly reduced model for $C_2 – C_3$ species, and a very coarse model for $C_4 – C_n$ (n being the number of species of the target fuel). Chang et al. [56] demonstrated that with just eight species in the $C_4 – C_{10}$ part of the mechanism, an accurate reduced mechanism could be constructed for n-decane, using a skeletal version of the $C_2 – C_3$ set and a detailed $C_0 – C_1$ set. Furthermore, by adding another eight species, the same model could also accurately predict iso-octane. With another nine species, it was also accurate for methyl-cyclohexane (MCH) and required another eleven species for toluene. This is impressive results, given that the comprehensive mechanisms for these species are several thousand reactions and between several hundred to a bit over a thousand species. The fact that by adding a few large species on top of the same base mechanism works for all of these hydrocarbons, demonstrates that by identifying a proper base set of species is the most important part of the reduction process. The difference between this approach and the previously mentioned is that this is more of a strategy to constructing the final mechanism than determining specific reactions to use. The best size of the detailed base chemistry set is debatable, with Zettervall et al. [60] having only full detail on the C0 – C1 chemistry, while the HyChem mechanism by Wang et al. [61, 62] has full detail on the C0 – C4 chemistry. Both groups show promising results with the Decoupling methodology. After choosing the base set, and making a few breakdown reactions for the fuel, the intermediate set still has to be a reduced skeletal mechanism for this approach to work. This intermediate set then must be acquired by using another reduction method, but just for the intermediate chemistry region.

The last reduction methodology discussed is the Genetic Algorithm (GA) approach. GA is a common optimisation method, using stochastic (random) search, in an intelligent manner, to find an optimal set of species and corresponding reactions [63]. Sikalo et al. applied this method to GRI-Mech 3.0 [64] for methane, reducing it from 325 reactions and 53 species to 58 reactions and 26 species [65]. It is important to not just randomly test combinations of reactions and species, since there would be thousands upon thousands of combinations, but do it in a structured and smart way.

Assume that a complex mechanism for methane combustion contains 150 reactions. There are a total of 10^{45} unique combinations of reactions, but many of these are not very interesting to evaluate. The way GA goes around this obstacle is to have many agents that communicate with each other about their findings. Each agent is given a specific combination to evaluate, and after determining the accuracy, only the best few are allowed to advance to the next generation. In this step, the remaining agents exchange reactions with each other, some new agents are created with random additions/subtractions from an existing agent, and the process is repeated. The name, and approach, is inspired by biological genetics, where each reaction is a “gene” for the individual, and the best performing agents can reproduce by exchanging genes with each other. In contrast to the deterministic approaches previously mentioned, the result of this method is determined by the random numbers generated. If the algorithm is properly toned, in theory, it would eventually converge towards the same optimal solution, but in practice the result is always a little different. This means that there could always be a slightly better mechanism than the one found. Another implication is that an important subset that might have a low statistical impact, according to the deterministic methods, could be included with the stochastic methods, resulting in a significantly better mechanism than the deterministic counterpart.

Chapter 3.

Ant-Colony Reduction

In this chapter, the kinetic mechanism reduction method Ant-Colony Reduction (ACR) will be discussed. The objective of the method is to generate small, tailor-made, computationally efficient skeletal mechanisms for a given combustion application. The method was developed by the author and used to create the reduced mechanisms presented in this thesis and the related papers.

ACR is a semi-stochastic build-up skeletal mechanism generating algorithm. It is based on the more general Ant-Colony Optimisation (ACO) algorithm, which is a subset of graph optimisation algorithms. The method selects species and reactions, based on a semi-stochastic approach and keeps building the mechanism until an appropriate size and accuracy is acquired. The semi-stochastic nature of ACR is used to harness the inherent strength of both statistical and probabilistic methods.

The first step is to identify the range of conditions and specify the targets of interest, for example, ignition delay, laminar burning velocity, or species profiles. In general, a single application, e.g. combustion in an SI-engine, only includes a limited range of conditions. If the rest of the chemistry is ignored, the mechanism can be made smaller with the same accuracy for the conditions of interest, than if the complete space of possible conditions is considered. Throughout the chapter, the strengths and current limitations of the method will be examined, supported by examples of cases where ACR have been used.

The following two sections outline the established theory and the class of algorithm that ACR is based on. First, there are some general overview of optimisation algorithms, which is followed by the section on Ant-Colony Optimisation.

3.1 Optimisation algorithms

The goal of optimisation, in general, is to find

$$\min_x f(x)$$

for some objective function f [66]. This minimum quantity is often called the “global minimum”. In addition to the global minimum, there might be several local minima, each one being the lowest value of the objective function f, within a small enough subset of x around that point. The value of the global minimum is the same as the lowest value of all existing local minima.

In convex optimisation, it is assumed that *f* is a convex function, which means that it is mono-modal, and thus as long as the search travels along the gradient, the global minimum will eventually be discovered [66]. There are several powerful algorithms to make this journey from an arbitrary point in the domain to the global minimum using limited computational power; examples include Newton's method [66], Gradient Descent [66], Quasi-Newton's method [67], Barrier methods [66] and the Ellipsoid method [68]. Most of these algorithms utilise as much information as possible about *f* by observing the gradient and the Hessian of the function *f*. For practical applications, an analytical gradient or Hessian might not be available. Instead, approximations are used in different ways to circumvent this issue. Although, even if the gradient of the function *f* is available, the risk of the optimisation algorithm getting stuck in a local minimum is high, since the search will always travel along the approximated gradient and no matter how many iterations that the method is allowed to run, the results will be the same. This behaviour could be detrimental to the success of the optimisation of a real-life problem where *f* is not convex. DRG and PCA, which were discussed in Section 2.4, are based on the deterministic approach, and thus inherit the strengths and weaknesses mentioned above. Especially the risk of getting stuck in a local minimum can lead to larger mechanism sizes than necessary for the skeletal mechanism.

Another class of optimisation algorithms is the stochastic methods. Instead of determining a search direction by observing the gradient, these methods perform random search around the initial point. When a new local minimum is discovered, the focus of the random search is shifted towards a new region around the newly discovered minimum. By expanding the region of interest with each iteration, given enough computational power, the algorithm would eventually find a way out of the local minimum and continue searching for the global minimum. Note that it is not possible to know if the new local minimum is the global minimum, since the number of local minima is unknown. This can only be determined with certainty by exploring the entire input domain, which is most often not feasible.

There are a number of stochastic methods such as Simulated Annealing [69], Particle Swarm Optimisation [70], Stochastic Hill Climbing [71], Genetic Algorithm [72], and Differential Evolution [73]. Each method has its own way of utilising random search points in order to do an efficient search of the domain space. The function value in each evaluated random point will somehow affect the selection of the next set of random points, in order to eliminate areas where the global minimum most likely is not present. Unlike the deterministic algorithms used in convex optimisation, there is no guarantee that any improvement is made, even though the initial point is not a local minimum. These algorithms thus suffer from slow convergence and could waste plenty of resources, searching a region which is completely unnecessary since the search is driven by random numbers.

As a rule of thumb, deterministic algorithms have a tendency to get stuck in local minima and will always find the same minimum if the search is restarted, while the stochastic methods do not suffer from the same problem. On the other hand, deterministic algorithms utilise additional information about the objective function f, which leads to low computational cost in order to converge towards a local minimum, while stochastic algorithms could do an expensive random search before finding anything, which could be even worse than the local minimum found by the deterministic counter-part. The idea of combining deterministic efficiency traits with a stochastic global search method is an interesting thought, maximising the best of both algorithms. This is the main idea behind the semi-stochastic approach of the ACO algorithms [74].

3.2 Ant-Colony Optimisation

The ACO algorithm is inspired by ants' interactions in order to find food [74]. Each ant roams around outside the ant hill randomly, but the terrain is most likely not homogeneous; some paths will be easier to walk, and others more strenuous (or even dangerous). The probability for the ant to choose an easier path to traverse is higher than it chooses the opposite. After travelling around for a while, if it eventually finds food, the ant deploys pheromone along the path it took. All the ants can smell the pheromone, and as they walk randomly around the grounds, there is higher probability that an ant will select a path with pheromone on it. Over time, the pheromone evaporates, erasing the path to the (now maybe depleted) food source. Each ant carries the same amount of pheromone, which means that an ant that finds a shorter path to the food source will deposit more pheromone per unit length than an ant that finds a longer path. These concepts will allow the colony of ants to quickly form up along a common path to find food, while also allowing the colony freedom to search for new (e.g. shorter) path to food and eventually switch path if the new path is better.

Although the behaviour of the ants in the algorithm does not exactly replicate the behaviour of actual ants, the concept makes for a powerful algorithm that has applications in many fields. In combustion research, within the present work, the algorithm has been adapted to reduce kinetic mechanisms, with the name Ant-Colony Reduction (to clearly mark it as a reduction method and not confuse it with rate parameter optimisation algorithms).

3.3 Examples of application of ACO

The ACO class of algorithms has been applied to many discrete optimisation problems, as outlined by Dorigo and Stützle [75]. Cordon et al. [76] developed an algorithm called Best-Worst Ant System (BWAS) to solve instances of the Travelling Salesman Problem [77]. An extension of the problem, but with a multi-objective component, is the vehicle routing problem with time windows, which was solved using an algorithm the authors, Gambardella et al. [78], called Multiple Ant Colony System for Vehicle Routing Problems with Time Windows (MACS-VRPTW). Another routing problem, found in telecommunication networks, was approached using ant-like agents by Bonabeau et al. [79].

ACO type algorithms are very successful at finding solutions to different kind of routing problems, by identifying the most efficient pathway through a maze of possibilities. As seen with the MACS-VRPTW, the algorithm is also suitable for multi-objective problems. In this case, the route length and travel time for each vehicle should be minimised, in a system with non-uniform travel times for each segment of the route. This is similar to the problem of skeletal reduction, except for in the skeletal reduction case the two objectives are to minimise the computational time of the kinetic simulation while maximising the accuracy of the predicted combustion properties calculated using the new mechanism compared to the original reference mechanism.

Intuitively, choosing the fewest reactions should yield the fastest mechanism, but due to stiffness and the size of the set of species associated with the set of reactions, this is not always true. Solution size, additional computations, and memory management associated with having many species can increase the computational time significantly, and thus a good compromise between number of reactions and species has to be found. Furthermore, the choice of both species and reactions greatly affect the accuracy of the mechanism, which ties the two optimisation objectives together. The other factor, stiffness, is due to having incompatible timescales of the reactions, and is an inherent property in systems of differential equations. Systems with a mix of different timescales requires many time steps to fully resolve, and thus requires many more calculations compared to an equally large system with homogenous timescales.

The ACR algorithm, within the scope of the papers in this thesis, has demonstrated great potential in solving this multi-objective optimisation problem. As previously stated, many real-life applications have kinetic systems that are computationally expensive to model using state-of-the-art comprehensive mechanisms. Currently, the ACR method has been adapted to several different fields of kinetic modelling, including alcohol combustion (Paper I & III), n-heptane combustion (Paper II), and atmospheric modelling of nitrous oxides, volatile organic compound (VOC), and ozone (O_3) (Related work R-II & R-III).

Chapter 4.

Combustion subsets

The combustion process can be divided into three main modes: ignition, propagation and extinction. Applications for kinetic modelling can consist of any combination of these, and the chemistry for each mode has its own characteristics. In order to make the most compact skeletal mechanism for a given application, it is important to understand these differences so that irrelevant chemistry is not included. This chapter focuses on discussion about creating skeletal mechanisms that preserve global combustion properties for the combustion modes, i.e. Ignition Delay Time (IDT) for ignition, Laminar Burning Velocity (LBV) for flame propagation, and Extinction Strain Rate (ESR) for extinction. While not within the scope of this thesis, if pollutant formation is included, additional species specific reactions and species have to be included and is not necessarily unique for each combustion mode. This chapter use examples of combustion subsets for n-propanol and n-heptane, taken from Papers II & III and show the main idea behind the methodology of Papers II-IV. Each mechanism, except the merged ones, was developed to reproduce only the specific combustion property associated with the specified combustion mode in order to obtain the minimum set of species and reactions for each combustion mode.

The n-heptane skeletal reaction mechanisms from paper II are developed using ACR and are based on the CRECK mechanism [80, 81], and the n-propanol mechanisms from paper III are based on the mechanism by Gong et al. [82]. Subsets of the n-propanol mechanisms are also found in the methanol and ethanol mechanisms, further discussed in Chapter 5, and are used for the analysis. All the mechanisms are developed for internal combustion engine conditions, equivalence ratios of 0.7 – 1.3, initial temperatures in the range 300-700 K, and pressure between 1-50 bar. In Chapter 5, size reduction and loss of accuracy is discussed. It is shown that the reduced mechanisms presented in Figures 4-10 are valid representations of the principal chemistry sets for their respective combustion mode.

The simulations referred to in this and the following chapter have been carried out using either CANTERA 3.4 [83] or CHEMKIN [84], with CANTERA being used for Paper II-IV and CHEMKIN for Paper I. Simulations that were not part of any paper have all been carried out using CANTERA.

4.1 Flame propagation

The first combustion mode discussed is flame propagation, as it requires the simplest chemistry of the three modes. The simplicity comes from the need to preserve the overall radical pool and heat release, without having any competing reactions that create non-monotone behaviour. These effects can be observed for low temperature ignition, and will be discussed in details in section 4.4. The term radical pool refers to the overall fraction of species in the entire mixture that are radicals (e.g. OH, CH3, O, H).

Flame propagation is modelled using a steady-state laminar premixed one-dimensional flame, considering diffusion and transport properties as well as kinetics. LBV was selected as a measure of how well the reduced mechanisms from Paper I-III agree with the complex reference mechanisms. LBV is experimentally determined through mainly four methods, discussed by Egolfopoulos et al. [85], and is a fundamental property to accurately model.

Figure 4 shows the reaction paths available to the carbon atoms of the fuel, n-heptane (NC7H16), in the skeletal mechanism ACR57-FP, all the way to the complete combustion product, carbon dioxide (CO2). This mechanism consists of 28 species and 57 reactions. The main characteristic to note from this reaction diagram is that it is streamlined. The fuel breaks down in a single path. The fuel radical decomposes using two irreversible reactions. After some additional decomposition reactions, the remaining species contain one or two carbon atoms. At this point, the species follow straight paths towards CO2.

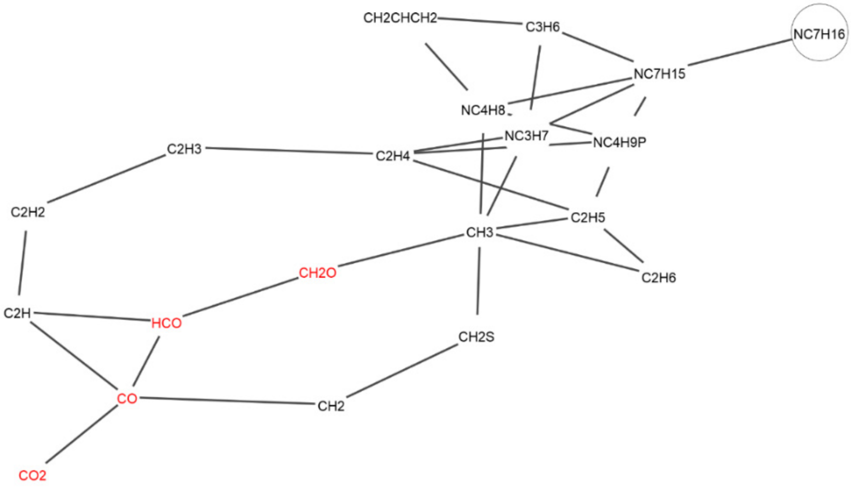


Figure 4. A skeletal mechanism, ACR57-FP, containing 28 species and 57 reactions for flame propagation of n-heptane (NC7H16) and air. Only carbon containing species have been included for clarity, and species containing at least one oxygen atom have been coloured red. A line between two species indicates that at least one reaction connects the two.

4.2 Flame extinction

The next combustion mode to be discussed is extinction. In many ways similar to flame propagation, extinction is more dependent on the diffusive properties of the overall mixture, according to Holley et al. [86], while still retaining the need for accurate heat release and the concentration of the radical pool. There are studies that have shown that skeletal mechanisms that reproduce ESR well are larger than those that reproduce LBV [13]. This holds true for our study of n-heptane combustion, with the extinction mechanism containing 44 species and 133 reactions is shown in Figure 5. This extinction mechanism is twice the size of the flame propagation mechanism, while retaining similar accuracy.

Yet, when the same methodology was conducted for n-propanol, the extinction mechanism was half the size of the flame propagation mechanism, while also retaining similar accuracy. The n-propanol extinction mechanism, containing 22 species and 46 reactions, is shown in Figure 4 and only has 2 non-oxygenated species. The C_1 and C_2 set of both mechanisms are quite similar, which indicates that ESR is mostly dictated by this oxygenated C_1 and C_2 chemistry, combined with a set of necessary fuel breakdown reactions that retain the correct diffusivity of the mixture, similar to the conclusions of Holley et al. for n-alkanes [86]. Since n-propanol requires fewer fuel breakdown reactions, the mechanism can become much smaller.

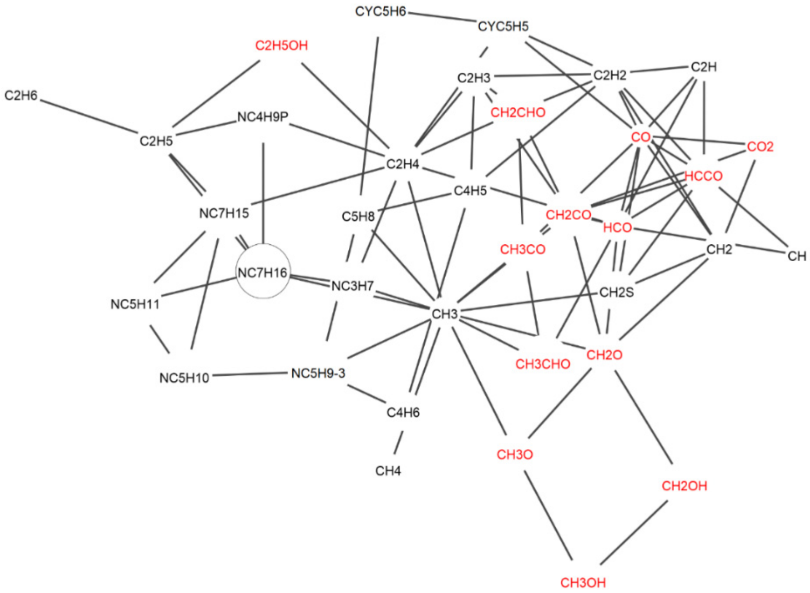


Figure 5. A skeletal mechanism, ACR133-NPE, containing 44 species and 133 reactions for extinction simulations of n-heptane (NC7H16) and air. Only carbon containing species have been included for clarity, and species containing at least one oxygen atom have been coloured red. A line between two species indicates that at least one reaction connects the two.

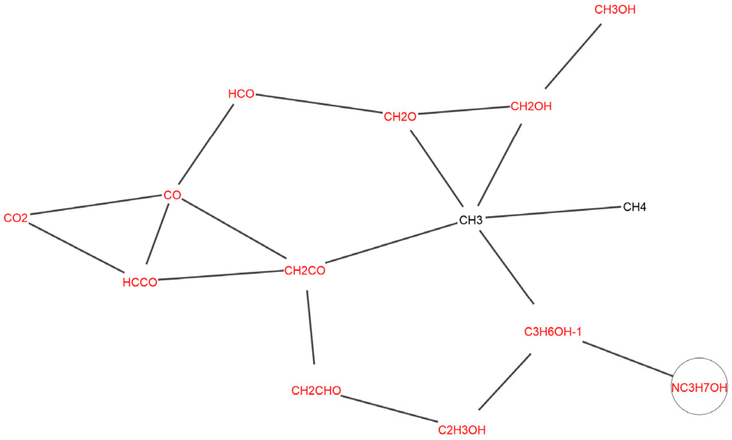


Figure 6. A skeletal mechanism, ACR46-NPE, containing 22 species and 46 reactions for extinction simulations of n-propanol (NC3H7OH) and air. Only carbon containing species have been included for clarity, and species containing at least one oxygen atom have been coloured red. A line between two species indicates that at least one reaction connects the two.

The general trend for extinction mechanisms is that they contain plenty of C_1 and C_2 chemistry. This is quite apparent in Figure 5, as there are only two minor branches containing C_4 and C_5 species, respectively, while the rest is smaller fragments [87]. This is explained by most of the heat release occurs in the later stages of combustion, the formation of water and carbon dioxide. Since the extinction phenomenon is highly dependent on temperature, this is one of the primary concerns for accurate ESR prediction. There is also a higher emphasis on alcohol and carbonyl species compared to the flame propagation mechanism, seen in Figure 4, likely as an effect of controlling the heat release to a higher extent than for flame propagation.

The common extinction mechanism trend, containing many C_1 and C_2 species with emphasis on alcohols and carbonyls, also holds true for the n-propanol mechanism shown in Figure 6. Unlike the n-heptane counterpart, this mechanism is much smaller than the flame propagation mechanism for n-propanol. The reason for this can better be understood by analysing the mechanisms of the two shorter alcohol fuels, methanol and ethanol. The first thing to note is that a complete skeletal mechanism (including all three combustion modes) for methanol is quite straight forward. Methanol is the smallest alcohol, and, as shown in Figure 7, the mechanism only has to contain a maximum of two reaction paths to describe ESR at engine conditions, since the chemistry is simple. For ethanol, it becomes more complex, due to isomerisation of fuel radicals and non-oxygenated carbon fragments that form from decomposition of the C-C bond. However, the oxygenated path is, once again, straight forward with just a single branch like the methanol chemistry. Since the extinction mechanism should have a high content of oxygenated C_1 and C_2 chemistry, it is a combination of two simple mechanisms, and the result is a mechanism with two main reaction paths and some short side-branches, likely kept as heat release control and to preserve the overall diffusivity of the mixture.

The diffusivity is more important for extinction [86], compared to the flame propagation discussed previously, since the extinction simulation is a counter-flow diffusion flame, compared to the laminar premixed flame used in the flame propagation simulation. In the premixed propagation case, the diffusive properties between the cells of the one-dimensional steady-state grid is not imperative for the reactions to occur. Even if diffusion was disabled all together, reactions would still occur (even though the results might not be representative of reality). In a diffusion flame, it is impossible for the fuel and oxidiser (air in these cases) to react without diffusing together. This restriction adds additional emphasis on the transport properties of the mixture, compared to the premixed flame propagation simulation, meaning that a larger fuel requires larger intermediates to keep the transport speed similar to the original mechanism.

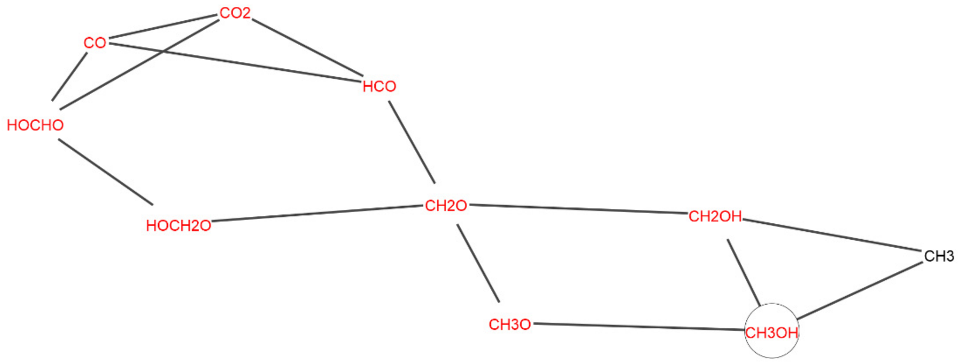


Figure 7. A skeletal mechanism, ACR55-C1, containing 18 species and 55 reactions for combustion of methanol (CH3OH) for ignition, flame propagation, and extinction simulations at SI-conditions. Species containing at least one oxygen are marked with red, and a line between two species indicates that they are connected by at least one reaction.

4.3 Ignition

The most kinetically complex combustion mode is ignition. Ignition simulations are zero-dimensional, transient simulations, i.e. all species in the mixture are constantly in contact and can react, and thus there is neither diffusion nor transport taking place. Furthermore, since the simulation is not a steady-state simulation, there is no initial established radical pool, which assists in breaking down the fuel and forming additional radicals, maintaining the pool. Instead, a fuel decomposition reaction is essential for the ignition to occur at all. In addition, the kinetics is temperature and pressure sensitive, which is especially prominent for ignition since the mode spans over a larger range of conditions. In particular, initial temperature has a large impact on the ignition chemistry that the ignition mode is commonly divided into high and low temperature ignition.

4.3.1 High temperature ignition

The simplest case of the two is the high temperature ignition. At low temperatures, there are a larger number of competing reactions which increases the chemical complexity. Many of these branches are not relevant at high temperature, resulting in smaller mechanisms if only high temperature ignition must be considered. The IDT discussed in this section, the measure of the reactivity of the mixture, is defined as the maximum gradient of OH radical concentration in for the transient solution.

Figure 8 shows an n-propanol mechanism designed for high temperature ignition at engine conditions. The fuel decomposition reaction here is NC3H7OH (+M) ↔ CH2OH + C2H5 (+M), which was not found in the mechanism in Figure 6. The "M" species indicates any third-body species, and does not participate in the reaction, and the brackets indicate that the reaction is pressure sensitive. There are also four other hydrogen abstraction paths available in this mechanism, indicating the strong dependence on fuel breakdown and initial chemistry for accurately predicting IDT compared to the reference mechanism. Heat release also has a role to play in ignition, as radical formation increases drastically with higher temperatures, and thus many oxygenated C_1-species are also present.

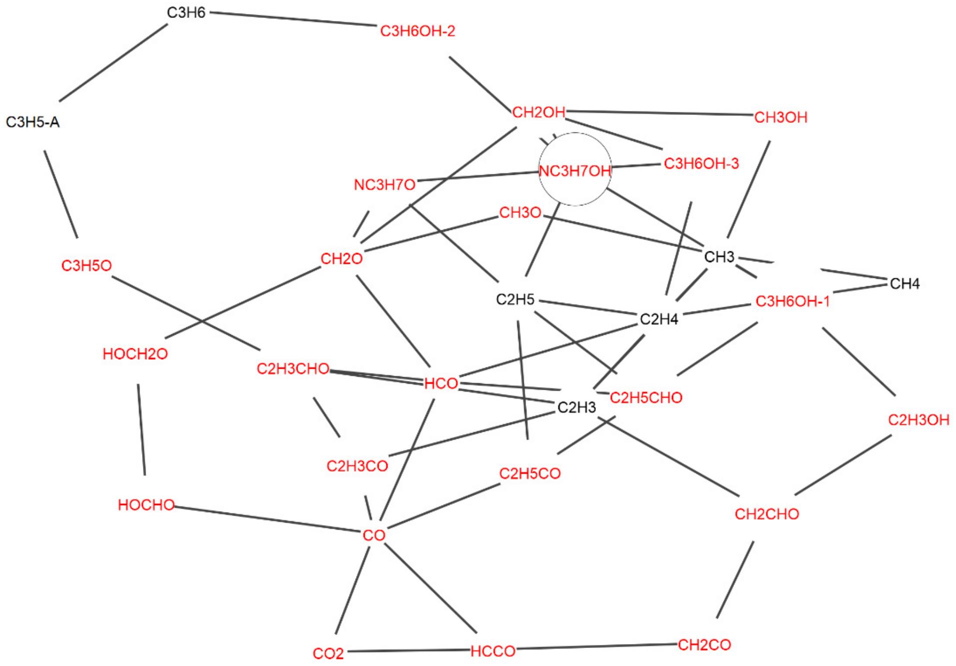


Figure 8. A skeletal mechanism, ACR95, containing 39 species and 95 reactions for high temperature ignition of n-propanol (NC3H7OH) and air. Only carbon containing species have been included for clarity, and species containing at least one oxygen atom have been coloured red. A line between two species indicates that at least one reaction connects the two.

Overall, the high temperature ignition mechanism for n-propanol is similar to the laminar burning velocity mechanism. The fact that there is a majority of oxygenated compounds is not an inherent property of the ignition phenomenon, but rather an effect of the oxygenated fuel that was used. Since only one fuel decomposition reaction was included, producing one oxygenated and one alkane specie, there is only one reaction path that contains a non-oxygenated carbon species, and this is in a few steps oxygenated as well. The detail of this branch is rather low, likely due to that the fuel decomposition is only important to start of the chain reaction, but then the actual OH concentration is more reliant on the four hydrogen abstraction paths. The opposite effect can be observed in the n-heptane high temperature ignition mechanism, found in Figure 9, where many species, 14 out of 23 (excluding C_1), are non-oxygenated.

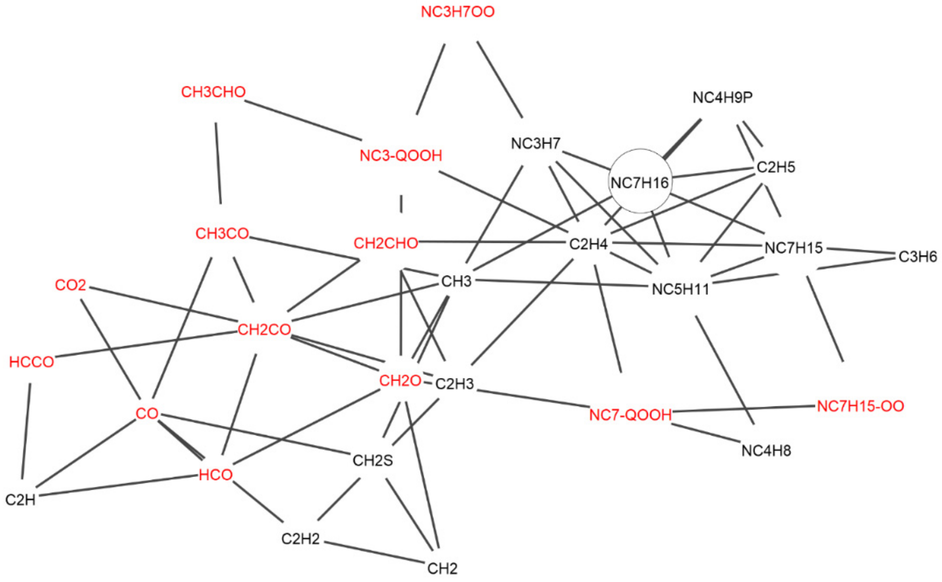


Figure 9. A skeletal mechanism, ACR88-HTi, containing 37 species and 88 reactions for high temperature ignition of n-heptane (NC7H16) and air. Only carbon containing species have been included for clarity, and species containing at least one oxygen atom have been coloured red. A line between two species indicates that at least one reaction connects the two.

4.3.2 Low temperature ignition

As previously mentioned, constructing compact skeletal mechanisms for low temperature ignition is challenging as there are many reactions required to accurately describe the process and predict the OH concentration. For n-propanol, many carboxyl and carboxyl radicals are included, shifting the principal reaction pathways from carbonyl. The reaction pathways that are important at high temperatures still matters at low-temperatures, but they are no longer dominant. Another difference is that at lower temperature, the H abstraction from the hydroxyl group is not included in the reduced mechanism, but it is present at the higher temperatures. An example of an n-heptane skeletal mechanism developed for low temperature ignition is shown in Figure 10. In the case of fuels with longer carbon chains, there is a certain branch of reactions that makes the ignition happen faster (shorter IDT) while the temperature is being decreased. The temperature range, in which this phenomenon occurs, is called the Negative Temperature Coefficient (NTC) region. As outlined by Prince et al. [88] and Xu et al. [62] and also observed in Paper II, this happens because the OOQOOH species can react in a chain branching manner, but this reaction is competing with the decomposition reaction to QOOH, which decreases the reactivity of the system and is preferred at higher temperatures, meaning that there is a point where the increase in reactivity due to the OOQOOH chain-branching path has a greater impact on the build-up of OH concentration than the decrease in initial temperature, thus forming the NTC region on in the IDT dependence on temperature; Further discussion on NTC behaviour, with n-heptane IDT at engine conditions as an example, is found in section 5.2.3.

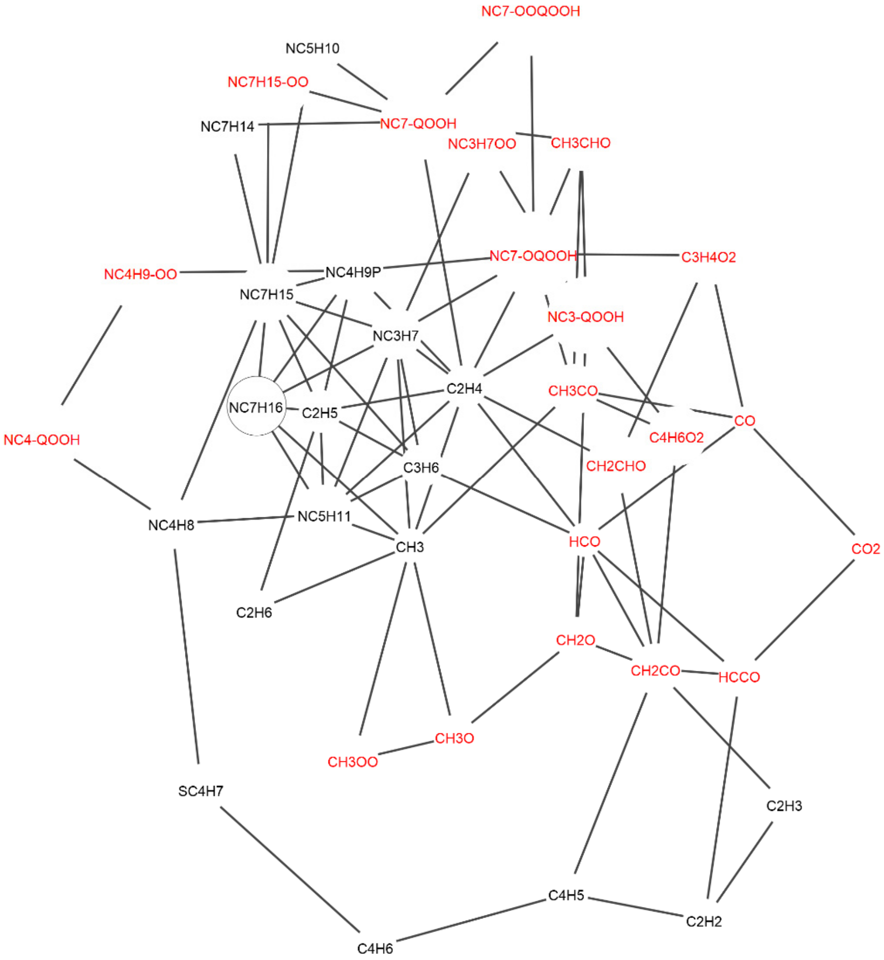


Figure 10. A skeletal mechanism, ACR102-LTi, containing of 48 species and 102 reactions for low temperature ignition of n-heptane (NC7H16) and air. Only carbon containing species have been included for clarity, and species containing at least one oxygen atom have been coloured red. A line between two species indicates that at least one reaction connects the two.

Chapter 5.

Accuracy and size

In the previous chapter, several skeletal mechanisms for a few biofuels and n-heptane were presented and their reaction pathways were analysed. Although there were several important conclusions from this analysis, they hold little value if the accuracy of the mechanisms is low, or if the size is too large for implementation in LES. In this chapter, these two properties will be quantified to show that the skeletal mechanism generation using ACR for specific combustion subsets is a viable methodology for reduced kinetics. For some fuels the reduced mechanisms are small enough for use in LES, for others they are on the large side but suitable as starting points for further reduction.

5.1 Skeletal mechanism size

Table 1 shows all mechanisms discussed in the previous chapter, alongside a few mechanisms for comparison from the literature. Since skeletal mechanisms can be developed for different conditions, the combustion modes are noted at the end of each row, since some literature mechanisms are developed for a large range of conditions. The "merged" method refers to that the mechanism was generated by combining several smaller mechanisms developed using ACR. For example, ACR230-C7 was created by taking all unique species and reactions from ACR57-FP, ACR88-HTI, ACR102-LTI, and ACR133-NPE. This approach was shown to yield smaller mechanisms than when ACR was applied directly onto a larger condition space.

In Table 1, reduced mechanisms from the literature are presented for most of the fuels used in papers of this thesis, with exception for MDe5 and MDe9. The mechanisms were chosen based on similar target condition ranges as the mechanisms developed using ACR. In comparison, the ACR mechanisms contain between 20-60 % fewer reactions and species. Furthermore, the compact size, given the high accuracy, of the low temperature skeletal mechanisms is unmatched by any other mechanism in the literature for n-heptane, MD, MDe5, and MDe9.

Table 1. A list of skeletal mechanisms, their size, reduction methodology and the combustion modes for which they were validated. The reaction size is calculated by counting each irreversible reaction once, and each reversible reaction twice. The available modes are Homogenous Ignition (HI), Laminar Flame Propagation (FP), Non-Premixed Extinction (NPE).

Name	Fuel	Size		Method	Modes
		Species	Reactions		
ACR57-FP	n-C_7H_{16}	28	57	ACR (Paper II)	FP
ACR88-HTI	n-C_7H_{16}	37	88	ACR (Paper II)	HI
ACR102-LTI	n-C_7H_{16}	48	102	ACR (Paper II)	HI
ACR133-NPE	n-C_7H_{16}	44	133	ACR (Paper II)	NPE
ACR230-C7	n-C_7H_{16}	65	230	Merged (Paper II)	HI, FP, NPE
Lu [48]	n-C_7H_{16}	188	842	DRG [48]	HI
ACR55-C1	CH_3OH	18	55	ACR (Paper I)	HI, FP
Liao [51]	CH_3OH	19	80	SA [51]	HI, FP
ACR74-C1	CH_3OH	19	74	Merged (Paper III)	HI, FP, NPE
ACR155-C2	C_2H_5OH	36	155	Merged (Paper III)	HI, FP, NPE
Minuzzi [89]	C_2H_5OH	56	377	DRGSA [50]	HI, FP
ACR46-NPE	n-C_3H_7OH	22	46	ACR (Paper III)	NPE
ACR95-HTi	n-C_3H_7OH	39	95	ACR (Paper III)	HI
ACR97-FP	n-C_3H_7OH	36	97	ACR (Paper III)	FP
ACR154-LTi	n-C_3H_7OH	46	154	ACR (Paper III)	HI
ACR199-C3	n-C_3H_7OH	52	199	Merged (Paper III)	HI, FP, NPE
Liu [90]	n-C_3H_7OH	57	267	DRGEP [49]	HI, FP
ACR100-HT-C	n-$C_{10}H_{22}$	47	100	ACR (Paper IV)	HI
ACR140-LT-C	n-$C_{10}H_{22}$	63	140	ACR (Paper IV)	HI
ACR123-HT-C	MD	54	123	ACR (Paper IV)	HI
ACR157-LT-C	MD	65	157	ACR (Paper IV)	HI
ACR258-HT	MD	95	258	ACR (Paper IV)	HI
ACR810-LT	MD	322	810	ACR (Paper IV)	HI
Dievert [91]	MD	530	2396	PFA [91]	HI, FP, NPE
ACR186-HT	MDe5	61	186	ACR (Paper IV)	HI
ACR361-LT	MDe5	150	361	ACR (Paper IV)	HI
ACR78-HT	MDe9	42	78	ACR (Paper IV)	HI
ACR200-LT	MDe9	93	200	ACR (Paper IV)	HI

For comparison of size, Table 2 show each of the complex reference mechanisms that were used in Papers I-IV. As can be seen, the skeletal mechanisms presented in Table 1, are but a fraction of the original size. Although, mechanisms like AramcoMech 2.0 and CRECK are developed for tens of fuels, the reduction is still significant. The comprehensive mechanisms by Herbinet et al. are only developed for one specific fuel and does not contain any lumping or discrimination of reaction paths. The fact that CRECK is lumped explains why CRECK and the Herbinet mechanisms have a similar number of reactions, yet a large species disparity.

Table 2. List of complex mechanisms used for reduction with the ACR algorithm. The specified fuel shows the fuel that was used for the reduced mechanism, the full list of fuels that the mechanism is validated for could be longer.

Name	Size		Fuel (Paper)	Ref
	Species	Reactions		
AramcoMech 2.0	493	5131	CH_3OH (I & III) & C_2H_5OH (III)	[92]
Gong	137	1695	n-C_3H_7OH (III)	[82]
CRECK_n-heptane	300	11790	n-C_7H_{16} (II)	[80, 81]
CRECK_n-decane	416	16433	n-$C_{10}H_{22}$ (IV)	[93-95]
Herbinet-MD	2878	9742	methyl-decanoate (IV)	[96]
Herbinet-MDe5	2649	10487	methyl-5-decenoate (IV)	[96]
Herbinet-MDe9	3298	11964	methyl-9-decenoate (IV)	[96]

5.2 Accuracy of skeletal mechanism

From Table 1, most of the skeletal mechanisms generated using ACR have an appropriate size for LES (20-40 species and 50-100 reactions) [13-15]. In the following, the accuracy compared to the respective reference mechanism is shown to be sufficiently high. The term accuracy is quantified as the average absolute deviation for condition triplet (temperature, pressure, and equivalence ratio) used as development targets for each mechanism. Complex models, such as the CRECK mechanism that was used as the starting point of reduction in Paper II, are constructed to accurately predict experimental data, and are published in conjunction with thorough validation. In the present work the complex mechanisms were only used for construction of reduced mechanisms within the range of parameters they were originally validated for. This means that if the accuracy of the reduced mechanism, compared to the complex mechanism, is high enough, the reduced mechanism accurately represents experimental data. In this section, validation figures are presented for three common combustion parameters, laminar burning velocity, extinction strain rate, and ignition delay time, which the skeletal mechanisms generated by the ACR method was developed to reproduce.

5.2.1 Laminar burning velocity

For flame propagation, the Laminar Burning Velocity (LBV) is an important parameter for a mechanism to reproduce. This quantity is directly related to the turbulent burning velocity, which affects reactive flows in CFD simulations [97]. This was measured experimentally by several research groups [98-100], and the correlation between laminar and turbulent burning velocity is dependent on Reynolds number, but independent on fuel-oxidiser ratio. For example, if the turbulent burning velocity of the model is too low, a CFD simulation might show that for a given set of conditions, the flame propagation inside an SI-engine is not quick enough to combustion all of the fuel-air mixture, even though it would in practice. The conclusions that could be drawn from these results might hinder, rather than further, development of new engines.

LBV is the quantity that shows how quickly a flat flame would propagate though an infinite space of premixed fuel and air. [44] The quantity is measured experimentally in many different setups that has evolved over the years, the most common methods are spherical expanding flame, counter flow, and heat flux method [85]. Bradley et al. [101] used a spherical bomb setup, where a flame propagates from the centre of a container towards the edges, to investigate laminar burning velocity of n-heptane and air. Due to flame stretching, these results have an elevated uncertainty compared to the two newer methods in the following. Smallbone et al. [102] used a counter-flow setup to study the LBV of n-heptane and air, and Alekseev et al. [103] used the heat flux method. Especially the latter has lower experimental scatter due to the low impact of flame stretching.

Figure 11 shows LBV as a function of equivalence ratio for the ACR generated n-propanol mechanisms (Paper III) and their reference mechanism, the complex mechanism by Gong et al. [82]. There is general agreement between the mechanisms, with a maximum deviation of less than 8 % at the fuel rich side. Reproducing rich combustion is more complex than lean combustion since fuel radicals can react with each other or with other radicals or stable species when there is a lack of oxygen. It is thus expected that skeletal mechanisms, with barebones amount of chemistry, may have some deviation at higher equivalence ratios.

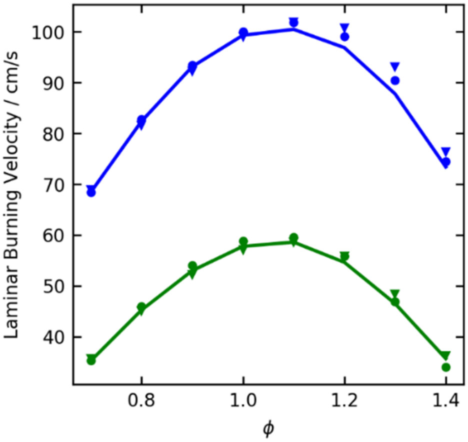


Figure 11. Laminar burning velocity for n-propanol at 500 K initial temperature, and 1 atm (blue) and 10 atm (green). Gong mechanism is represented as lines, circles represent ACR97-FP and triangles represent ACR199-C3.

Similar results can be seen for LBV for the other mechanisms from Papers I and II, with slightly higher average deviation for the n-heptane mechanisms, but still having a maximum deviation of less than 10 %. Since the accuracy of the mechanisms are high, the proper chemistry has been captured in the skeletal mechanisms, giving the analysis in the previous chapter meaning. Similar results can be observed for the extinction strain rate and ignition delay time in the following two sections.

5.2.2 Extinction strain rate

Extinction Strain Rate (ESR) is the measure of the strain of a flame. Strain rate can be increased systematically by stretching the flame, which affects the reaction zone and shortening the reaction time scale compared to transport time scales. ESR is commonly conducted in a counter-flow diffusion burner setup, where fuel is emitted from one nozzle and the oxidizer from another nozzle, opposite to the first one. In the simulation setup, this becomes a one-dimensional steady-state problem, and the strain rate is changed by increasing the mass flow of fuel and oxidizer and changing both the radial and axial flow velocities.

Figure 12 shows an example of result from an ESR simulation for n-heptane combustion using a counter-flow diffusion setup. The maximum temperature of the flame is recorded for each strain rate, until the temperature drops below 1500 K, where the flame is considered extinguished. The larger skeletal mechanism, ACR133-NPE, is performing well, but slightly under-predicts the maximum temperature, while the merged ACR230-C7 almost identically reproduces the complex CRECK mechanism.

This shows that some chemistry that is only found in the ignition or propagation mechanism also played some minor role in the extinction simulation. This chemistry could be identified and included in the ESR mechanism if perfect agreement with the reference mechanism is required. For n-alkanes, extinction require the most complex chemistry of the three flame modes [86], which is also observed for the n-heptane mechanisms from Paper II.

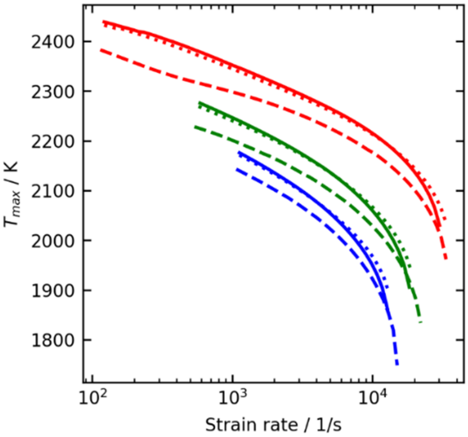


Figure 12. Extinction strain rate simulation for n-heptane at 5 atm (blue), 10 atm (green), and 50 atm (red). Full lines represent the complex mechanism CRECK, dashed lines represent ACR133-NPE, and dotted lines represent ACR230-C7. The figure is from Paper II.

Figure 13 shows results of ESR simulation for n-propanol, and the specific mechanism for extinction, ACR46-NPE, reproduces the Gong mechanism well. Contrary to the conclusion for n-heptane, ACR46-NPE is the smallest of all the sub-mechanisms for n-propanol, just shy of one quarter of the reactions of the merged mechanism, ACR199-C3. The largest deviations are found at the highest pressure, 40 atm, which indicates that only half the strain rate is required to extinguish a flame simulated by ACR46-NPE compared to the mechanism by Gong et al. Even though the mean deviation is sufficiently low, having one point with high deviation could impact the effectiveness of the mechanism for CFD simulations.

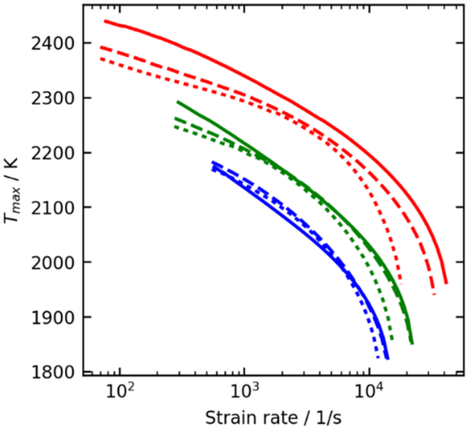


Figure 13. Extinction strain rate simulation for n-propanol at 5 atm (blue), 10 atm (green), and 40 atm (red). Full lines represent the complex mechanism Gong, dashed lines represent ACR46-NPE, and dotted lines represent ACR199-C3. The figure is from Paper III.

5.2.3 Ignition delay time

Ignition Delay Time (IDT) is a quantity that measures the initial reactivity of a chemical system. The definition used for IDT various for different studies, but in this thesis, it is defined as the maximum gradient of OH concentration for time resolved zero-dimensional homogenous simulations. Experimentally, IDT is commonly determined by using a shock tube and measuring the time between initial shock and either maximum luminescence or maximum pressure gradient [104]. A shock tube is a device that has a premixed, preheated mixture in one compartment and a pressurised inert gas in an adjacent compartment. The experiment starts by the separating wall between the compartments is removed and the pressure increasing to the target pressure in the fuel-oxidizer mixture. The time from the removal of the wall to the defined ignition event occurs is the IDT.

The reason why the increase in OH concentration was used in this work is that the formation of OH radicals is closely related to the formation of excited OH radicals, which is one of the main sources of luminescence, one of the common experimental definitions of IDT. Furthermore, implementing restrictions on the reduction to preserve a rather irrelevant quantity as the luminescence would cause the skeletal mechanisms to be much larger, without containing additional information about relevant information of the combustion process. On the other hand, OH concentration is a fundamental component for proper combustion, and having a restriction to include OH and preserve the formation timing, has a low negative impact on the reduction process in terms of size, and might even help with preserving high accuracy.

IDT is affected by choice of fuel, equivalence ratio, temperature, pressure, and concentration of dilute gas. A rough approximation is that the logarithm of IDT is inversely proportional to temperature (in Kelvin) of the initial gas, given that the other conditions are constant. Figure 14 shows IDT for n-propanol in the temperature range of 700 – 1700 K, displayed in the typical fashion as log IDT on the y-axis and 1000 / T on the x-axis. Although there is a linear relation between these quantities in this case, by including the low temperature region, T < 1100 K, the size of the mechanism increased by a little more than 50 %, according to Table 1. It is often observed that the low temperature chemistry for ignition is quite complex and requires more reactions and species than the high temperature ignition. At high temperature, species decompose quickly and follows a single, or a few, paths.

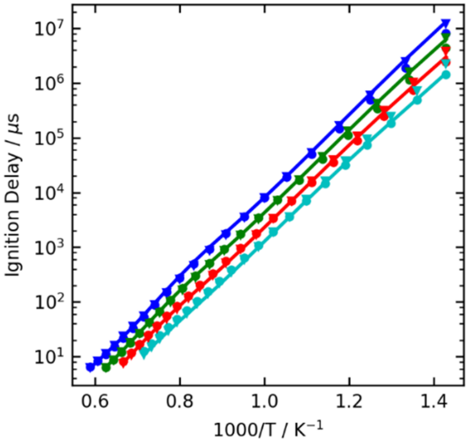


Figure 14. Ignition delay times for n-propanol and air mixture at equivalence ratio 1.4 and 5 atm (blue), 10 atm (green), 20 atm (red), and 40 atm (teal). The lines represent the complex Gong mechanism, the circles represent ACR154-LTI, and triangles ACR199-C3. Figure is from Supplementary Materials for Paper III.

When the hydrocarbon chain increases in length, the proportionality trend is not observed over all temperatures. For example, when the fuel is n-heptane or methyl-decanoate, an NTC region can be observed, where the IDT decreases, even as the inverse temperature is increased (and the temperature is decreased). Figure 15 shows IDT for a similar temperature region used in Figure 14, but for n-heptane.

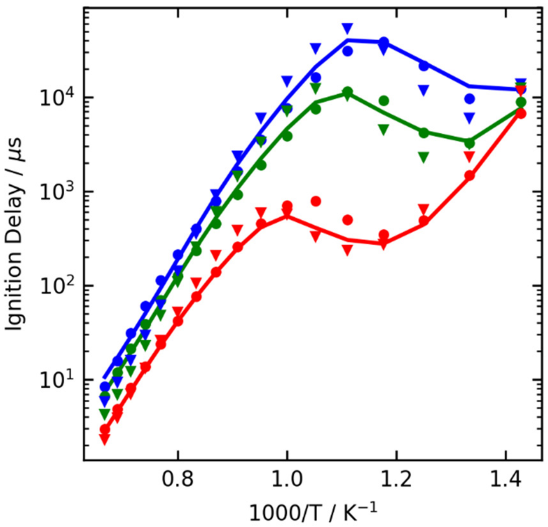


Figure 15. Ignition delay times for n-heptane and air mixture at equivalence ratio 1.0 and 5 atm (blue), 10 atm (green), and 50 atm (red). The lines represent the complex CRECK mechanism, the circles represent ACR102-LTI, and triangles ACR230-C7.

Chapter 6.
Conclusion

The aim of this thesis was to construct compact skeletal mechanisms and study the chemical pathways of biofuels. This aim was achieved by using the novel semi-stochastic reduction method called ACR to create small and tailor-made skeletal mechanisms for biofuels, methanol, ethanol, n-propanol, methyl-decanoate, and methyl-decenoate, as well as for petroleum substitute n-heptane. Given the successful application of the ACR methodology within the present work, this approach is a promising method for creating LES suitable mechanisms for larger fuels as well.

The work carried out in Paper I & III was to produce several small skeletal mechanisms for the first three alcohols, usable at SI-engine conditions. It was shown good agreement between the skeletal mechanisms and the original reference mechanism, AramcoMech 2.0 [92]. The analysis of chemical pathways that are required to recreate IDT, LBV and ESR can help future work in the field to create even more optimised mechanisms. Extending this reasoning to Paper II & IV, shows that the results of investigating pathways can be applied to a large variety of fuels.

In addition, the results of Paper III show that the extinction mechanism for n-propanol is the smallest mechanism of the three combustion modes. This is contradictory to the findings of Esposito and Chelliah, who stated that ESR, in general, require more reactions and species to model accurately [13]. In Paper II, we investigated the alkane n-heptane, a fuel more closely related to ethylene that was used in the study of Esposito and Chelliah, since neither contains a hydroxyl group. For n-heptane, the same trend, ESR requiring more reactions and species, was found to be true.

Overall, the analysis showed that there is a strong dependency on details of the C_1 and C_2 chemistry for flame propagation and extinction, with an emphasis on species containing a carbonyl group. The extinction mechanisms have a more detailed fuel decomposition subset than the flame propagation mechanisms. The high temperature ignition mechanisms followed a similar trend to that of flame propagation and extinction, with simple fuel breakdown chemistry, but was followed with more detailed C_0 and C_1 chemistry, rather than including details in C_2 as well. For low temperature ignition, on the other hand, more complex chemistry had to be included. For the short carbon-chain alcohol fuels, there was increased attention given to the carboxyl species, and for the larger fuels peroxide chemistry was also present.

Furthermore, the high temperature ignition mechanisms for methyl-esters developed in Paper IV are significantly smaller than the mechanism developed by Dievert et al

[91], although that mechanism is developed to also include species profiles, LBV and ESR. Our high temperature ignition mechanisms are still around a factor two too large for LES, and a need for a complementary method, such as lumping, is identified to ensure a sufficient size reduction of the mechanisms. For the low temperature ignition case, our mechanisms are the first to accurately reproduce the ignition behaviour with only 200-810 reactions, depending on the fuel.

The limitation on the analysis carried out in the papers is that it was only concerned with preserving the global combustion properties, while ignoring other important aspects such as accurately modelling species profiles, heat release, and pressure increase during simulation. Although some of these properties are implicitly dependent on the global combustion properties, it is not safe to assume that the pollutant emission from a skeletal mechanism is accurate if the mechanism was only validated against global combustion properties.

Given the successful application of the methodology and the current limitation on scope, future work could include pathway analysis of formation of common pollutants. Comparison of pathways between different fuels for the same pollutant would be interesting to investigate, in order to find some common minimum set of reactions and species for each pollutant. Moreover, linking the chemistry of certain pollutants with the chemistry of some global combustion property could reveal more efficient ways of creating LES suitable skeletal mechanisms in the future, by minimising the number of validation targets, while still retaining confidence in that the mechanism will accurately reproduce the formation of the desired pollutant.

Acknowledgements

As one book closes, another one opens. At this time, I'd like to express my gratitude to all the people who have helped me on my scientific journey. I am listening to peaceful piano music from the Legend of Zelda games while writing this, so to fully, logically and emotionally, understand the words, I suggest the reader to do the same.

It has been four eventful years, and I have developed much as an individual during my time at Combustion Physics. Maybe not in the way that some people would have liked, but at least I have learnt a few things to where I am now.

Firstly, I'd like to extend my gratitude to my primary supervisor, *Elna Heimdal Nilsson*. The spring of 2016, you had to make a choice. Hire a qualified, well-educated, chemistry student with an interest in biofuel combustion, or me. I think we both can agree that you sometimes regret that choice. Especially whenever you read a first draft of a manuscript and wonder where all the references are located. Although we might never see eye to eye regarding if combustion is physics, chemistry or mathematics, I believe that you are okay with that. Even though I am right.

Secondly, *Minna Ramkull* deserves a big applaud for having the patients to deal with my many, *many*, visits to the third floor. After every trip, after every little issue at the start of my PhD education, you had to help me out with something. Even though you have explained it probably ten times, I still have no clue how to properly calculate deduction for hotel breakfast or included lunch during conference trips. And honestly, does this "Proceedo"-system actually exist or do you just use the word to scare young PhD students?

A grateful thanks is extended to each of my three officemates that I had during my time at Combustion Physics. *Vladimir Alekseev*, you had the disputable honour of, for almost two years, being interrupted in your work 2-8 times per day with questions about Chemkin, chemistry, or random politics that I read about. You helped me overcome some major obstacles in the early stages of my method development. When you left, *Marco Lubrano Lavadera* tagged in. I would like to say I have become more self-sufficient over the years, but you can agree that the only thing that has changed from the list above, is that I now swear over Cantera instead of Chemkin. Overlapping with both of these was *Gianluca Capriolo*. I never saw your desk, but I am sure we shared an office anyway.

On the practical side of things, *Igor Buzuk* has been helpful. I am happy that you have without any complaints assembled computer after computer for me and always been the most supportive when I am confused about practical things. Like how e-mail accounts work around here. Or how to enter the workshop. The latter one was just the first step in a series of questions about these "tools" that were located inside.

More closely related to my scientific work, a few people have been extra useful. In no particular order, thank you to *Mattias Richter, Alexios Matamis*, *Christer Fureby, Niklas Zettervall*, and *Magnus Joelsson*. The first two knows plenty of facts about engines. Like real engines. Not only the zero-dimensional ones that I can simulate. *Mattias*, I can never understand when you are joking. Thank you for teaching me to doubt everything I hear, and as you said, that is what makes me a great scientist. *Alexios*, your kid is so cute, good luck with the second one as well. Also, I have learnt quite a bit about engines and laser diagnostics while MATLAB coding/cursing with you. *Christer* and *Niklas*, given that we are located quite the distance apart, I still have received valuable feedback about turbulent combustion from both of you during conferences, courses and other opportunities to meet. Who knew that Reynolds numbers, Lewis numbers, and all the other numbers, actually are quite useful to understand? An extra thank you to *Christer* for agreeing to be my co-supervisor. *Magnus*, you tested my method and provided valuable feedback while also showing that you could adapt the approach to atmospheric science.

Now to the scary section of the division, Professor *Marcus Aldén* and Professor *Alexander Konnov*. From day one, I have been slightly terrified of you two, and you have managed to maintain it throughout my time at the division. Being scared makes my brain go on full alert whenever your names are mentioned, you are nearby, or I think you have to consider something I said or wrote. This made me take things more seriously than I otherwise would have, and for this, I thank you both. I hope this does not disappoint you; and if it does, please do not let me know until I have found a new hiding spot.

Although not everyone is mentioned by name, many people at our division have had an impact on me as a person, if not professionally. I promised that this text would stay professional, so I will keep this part short. Two positive examples are *Joakim Jönsonne* and *Karolina Dorozynska*. *Joakim*, is there anything I have written that you have not read? By the way, thank you for proof-reading my Acknowledgement chapter as well! You are also a great and reliable friend. You help me with basically everything except science. Also, you almost fully repaired my phone once, that was almost cool! *Karolina*, we hated each other from the first time we met at an activity for SPIE/OSA Student Chapter at Lund University. Although, thinking back on it, I think the hate actually grew over time. But just as it grew, it also faded and today I would consider you one of my closer friends. I know you have my back, except when we play games, then I know you don't.

At long last, I can hear the playful piano notes from YouTube drawing to a close, and thus I shall conclude this text. First though, a few quick mentions of gratitude with a single word for context. You guys understand what I refer to, and the rest… too bad, I guess. *Cecilia Bille* – lunch; *Yupan Bao* – guns; *Xin Liu* – laoshi; *Sandra Török* – lab; *Saeed Derafshzan* – world-politics; *Haisol Kim* – reliability; *Manu Mannazhi* – badminton; *Maria Ruchkina* – fashion; *Dina Hot* – positivity; *Torsten Methling* – Cantera; *Johan Zetterberg* – catalysis; *Wubin Weng* – words; *Samuel Jansson* – break; *Sebastian Pfaff* – typography; *Elin Malmqvist* – talking; *Sven-Inge Möller* – jokes.

Thank you.

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