LUND UNIVERSITY
Faculty of Science

Optimization of species transport data for reduced kinetic mechanisms

Anton Linnér

LUND
UNIVERSITY

Abstract

In order to construct more efficient and environmentally friendly fuels, knowledge about the combustion process of the fuels needs to be expanded. This can be done by running simulations in computational fluid dynamics. In order to efficiently run simulations, reduced kinetic mechanisms of lesser complexity are used. Increasing the accuracy and knowledge of the chemical reactions involved in these mechanisms is a field that has been frequently researched. The aspect of species or energy transport has received less attention. The purpose of this paper is to see if optimization of the transport properties could combat the loss in accuracy commonly followed by the reduction process of a mechanism .This was done by using a code that successively modified the transport properties and evaluated the results of simulations which were created using the modified properties. This was done for two fuels, methanol and propane, which are different in structure and size. The results showed a significant increase in accuracy for both fuels when the parameters were optimized. Optimization of the collision diamter showed tha highest impact for both propane and methanol. In the case of methanol, optimization of the well depth and dipole moment also showed significant improvements. This makes the optimization of transport properties a field with promising influence on reduced kinetics.

i

Acknowledgments

Contents

List of Abbreviations

CFD   Computational Fluid Dynamics

ACR   Ant Colony Reduction

C.M   Complete Mechanism

R.M.F   Reduced Mechanism - Fully Optimized

R.M.P   Reduced Mechanism - Partially Optimized

R.M   Reduced Mechanism - Unoptimzed

1 Introduction

Throughout the nineteenth and twentieth century, combustion has been the main process used in transport and industrial engines. It is to this day the dominating energy source for transportation, and of significant importance for industry and residental heating. [1].

Global climatic changes have been observed due to the effect of greenhouse gases released into the atmosphere. One source of greenhouse gases is combustion engines. Pollution is prevalent in other forms than the release of greenhouse gases, an example is soot[1] particles which can have an effect on human well being, as well as engine functionality. Constructing engines with a more effective energy output and finding alternative fuels is of interest since it helps to reduce the effect on global climate (and global and local pollution).

In addition to doing physical experiments, computational fluid dynamics (CFD) is used for modelling in combustion research by simulating the behavior of fluids. The development of powerful computers with high computing power in recent history has made it possible to make increasingly complex models of combustion experiments [2]. In combustion, a rapid succession of chemical reactions converts the fuel and oxidizer (commonly oxygen) to products like carbon dioxide, water and many other chemical components. To create accurate combustion experiments can prove to be difficult since there are many things to take into account. Taking the effect of gravity on a flame as an example, gravity will cause hot air to rise and for some airflow and turbulence to occur. This effects the shape of the flame since the air around the flame is not uniform in temperature. Therefore, gravity plays a role in determining the air characteristics and airflow around the flame. If there were to be no gravity, the air around the flame would be close to uniform in its characteristics and would change its shape, see Figure 1.
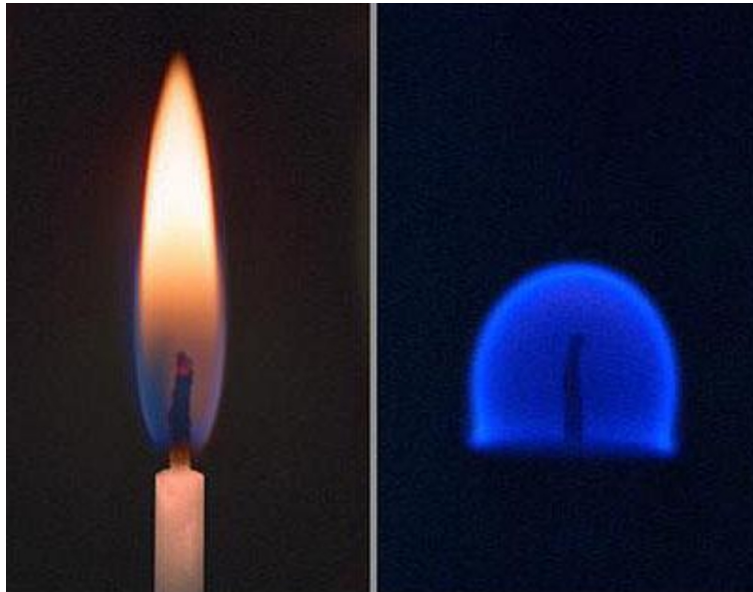
Figure 1: A flame on earth (left) and in space (right). The lack of gravity in space causes the symmetrical shape of the flame [3].

---

[1]Soot is a carbon heavy mass which is the result of incomplete combustion

Two important factors when creating a full model of combustion are the chemical kinetics and the transport properties (see Figure 2). Chemical kinetics describe the rate of reaction and which chemical steps are taken in order to get to the final product. The transport properties describe molecular transport and how heat is transferred in the system. Computational power is still limiting the use of these models, since the process of computing chemical kinetics and transport properties is very demanding.
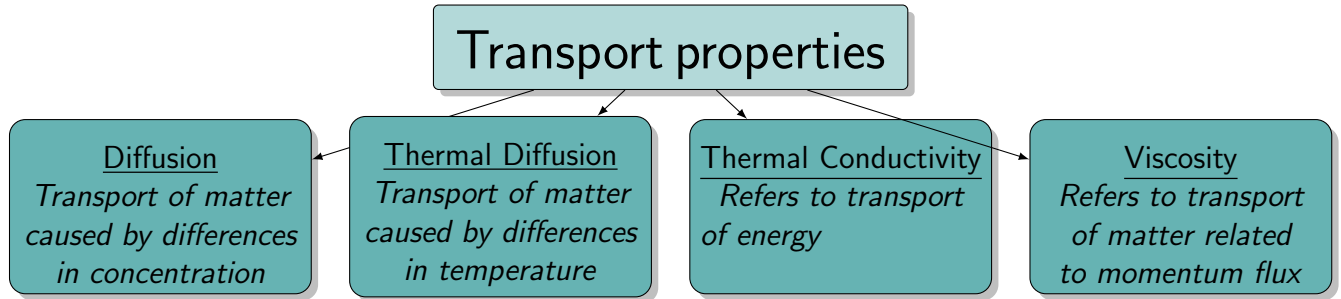
Figure 2: Outline of transport properties used in a combustion system

One way to decrease the complexity of the CFD models is to simplify the chemical kinetics. This can be done by analyzing the reaction steps in order to determine which intermediary steps can be omitted. This means that we *reduce* an otherwise complete reaction mechanism.

There are different ways of reducing a mechanism, but commonly some decrease in accuracy is to be expected as a result of omission of reactions. The purpose of the project presented in this report is to see if the optimization of the transport properties could compensate for the loss in accuracy for highly reduced mechanisms. For this purpose, simulations using two different fuels (methanol and propane) were conducted and transport properties were optimized and evaluated. These fuels were chosen because of their difference in geometrical structure and complexity, in order to give an insight in how this might affect the usefulness on optimizing the transport properties. This is part of a larger project where accurate reduced mechanisms are developed by using 0D and 1D simulations (described in Section 2.1), to later be implemented in CFD (using 2D and 3D simulations).

The optimization of transport properties has not been looked into before to any significant degree, in contrast to optimization of the chemical kinetics which has gotten substantially more attention as illustrated by Figure 3 for comparison of overall process.
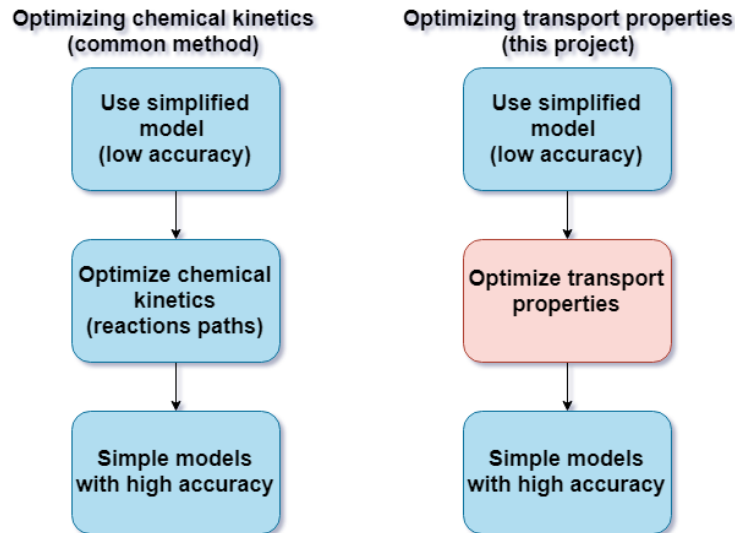
Figure 3: Comparison of the common way of finding a simple combustion model using optimization of chemical kinetics compered to using optimization of transport properties

This report first outlines the different aspects a model in combustion should include and predict, including a description of the chemistry involved. The reduction process of a mechanism is then briefly discussed and a more detailed description on the role of transport properties in different scenarios is presented. Important parts of the theory used to obtain the transport properties is included in order to better understand the role they play in a combustion simulation. A more detailed description of the parameters used to calculate the transport properties is provided in order to discuss their influence in the optimization process. Lastly, the results of the optimization for the two fuels are connected to the concepts discussed in the previous part describing the theory behind the parameters.

2 Background

2.1 Combustion modelling

Combustion models differ in level of complexity. For a laminar flame, 0D simulations (which only consider time evolution) and 1D simulations (considering time evolution *and* spatial propagation along one axis) are sufficient. This is not the case for a turbulent flame, which is characterized by its turbulent propagation in many spacial directions. Therefore, more dimensions are needed to simulate turbulent flames accurately. This means that they are generally more demanding to simulate.

Depending on the application of the combustion process (e.g. gasoline engine, Bunsen burner or candle) there will be different factors limiting the combustion. Three situations to distinguish between are [4]

* *Low chemical reaction rate* relative to the transport of molecules, making the chemical kinetics a limiting factor.

* *High chemical reaction rate* relative to the transport of reactants, making transport a limiting factor

* A combination where both the rate of reaction and the transport of molecules become relevant.

A high chemical reaction rate is important in the ignition phase of a flame. This is due to the fact that enough radicals[2] need to be created in order to have a self-sustaining flame. In a diffusion flame the oxidizer (commonly air) and the fuel are initially separated and will therefore have to mix at a molecular level through diffusion as they meet. Therefore the transport of molecules (diffusion) is a heavily limiting factor and it is important to take it into account [4]. However, chemical kinetics and molecular/energy transport often affect each other. It is therefore not always clear which of the two is the limiting factor. A high transport of the energy (transport property) means that heat flows from the reaction zone to the fuel. This will increase reaction rate due to the higher energy of the fuel. Therefore it is important to take both aspects into account in combustion models.

The properties that a model should be able to reproduce are:

- **Ignition/ignition delay** The process of a reaction evolving in time towards a stable flame is important. An application where this is important is in engines where ignition timing is highly influential. Transport properties do not influence this process significantly since the limiting factor is how fast the reactions occur.

- **Flame speed** How quickly the flame propagates. To predict the flame speed is important to avoid unwanted detonation (supersonic flame propagation).

- **Extinction rate** To which rate a flame is extinguished. This is an important quality to predict in order to make sure all fuel in an engine is used. If part of a flame is extinguished it will be possible for unburnt fuel to leave the reaction zone [5].

---

[2]Radicals are highly reactive chemical components

Additionally, information on the molar fraction composition at different regions of the flame is useful in regards to predicting the amount of pollution from the combustion.

Knowledge regarding the sensitivity of the above mentioned combustion properties on molecular transport or kinetic properties will allow for simplifications to be made without a significant decrease in accuracy. This is useful since it is important to make sure to save computational power when it is possible. A sensitivity analysis will therefore help understand which factors in the model have the largest impact on the accuracy of the outcome.

2.2   Combustion chemistry

When considering models describing the reactions of combustion, one aspect is knowing how many reactions will occur in a certain amount of time for the specific species involved. Here the transport aspect is not considered since it is assumed that the reacting elements are at the point of reaction and not limited by access. Arrhenius equation is used to express the rate coefficient [6], k, as:

$$k = AT^{\beta}\exp\left[-\frac{E_a}{RT}\right] \tag{1}$$

where A being the pre-exponential factor, T^{β} is the temperature dependance in the pre-exponential factor, E_a is the activation energy, T is the temperature and R is the ideal gas constant. The unit of k is dependant on the reaction order. For a reaction of order m, the unit is $mol^{1-m}L^{m-1}s^{-1}$.

Even for a simple combustion process there might be a large amount of reaction steps and species. Especially if there is a high amount of energy released in the process, enabling easier creation of radicals. In combustion engines the fuels commonly used are large hydrocarbons with complex chemistry. For simplicity, a small fuel molecule is here used to explain the basic principles in combustion chemical kinetics. The fuel H_2 (hydrogen gas) reacts with oxygen gas, O_2, creating water. The overall reaction is:

$$2H_2 + O_2 \rightarrow 2H_2O$$
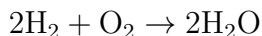
The detailed mechanism is shown in Table 1, where all the elementary reactions are numbered. To start the reaction process, there needs to be an initiation step. The following step is called a chain initiation.

$$H_2 \rightarrow H + H. \tag{R5}$$

This step creates hydrogen radicals which will enable further reactions. In Table 1, the M stands for an arbitrary molecule or atom. This is sometimes needed in order to dissociate a molecule (hydrogen in the case of R5). It is also needed to *prevent* dissociation when a recombination of atoms or ions release a large amount of energy. The M molecule will then absorb energy from the process, preventing the newly formed molecule to immediately disassociate.

The hydrogen atoms formed can then interact with the oxygen molecules

$$H + O_2 \rightarrow OH + O. \tag{R1}$$

5

Both the oxygen atom and hydroxyl molecule (OH) are radicals which will be the driving force of the reactions in the chain. When there is an increase in radicals, as in step R1, it is called chain branching. Due to the high reactivity of the radicals, chain branching is one reason the mechanisms become increasingly complex. So far, the reactions have resulted in the creation of radicals from hydrogen or oxygen-gas. If there is a reaction without a net increase in radicals, as in

$$OH + H_2 \rightarrow H + H_2O, \tag{R3}$$

it is called chain propagation.

When the concentration of stable molecules is low, the remaining radicals that were created in the first steps (R1 and R2) will react with each other to create water

$$OH + H \rightarrow H_2O. \tag{R8}$$

This is called chain termination since the reactive radicals are consumed, resulting in a stable water molecule. If the amount of chain branching is higher than the amount of chain termination, it could result in a rapid increase in reactivity. This is needed in the ignition phase, but an uncontrolled incease in reactivity could lead to a chain reaction explosion.

Table 1: Complete mechanism for H_2/O_2 combustion [4].

Number	Reaction
1	$H + O_2 \rightarrow OH + O$
2	$O + H_2 \rightarrow H + OH$
3	$OH + H_2 \rightarrow H + H_2O$
4	$O + H_2O \rightarrow OH + OH$
5	$H_2 + M \rightarrow H + H + M$
6	$O + O + M \rightarrow O_2 + M$
7	$O + H + M \rightarrow OH + M$
8	$H + O + M \rightarrow H_2O + M$
9	$H + O_2 + M \rightarrow HO_2 + M$
10	$HO_2 + H \rightarrow H_2 O_2$
11	$HO_2 + H \rightarrow OH + OH$
12	$HO_2 + O \rightarrow OH + O_2$
13	$HO_2 + OH \rightarrow H_2O + O_2$
14	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
15	$H_2O_2 + M \rightarrow OH + OH + M$
16	$H_2O_2 + H \rightarrow H_2O + OH$
17	$H_2O_2 + H \rightarrow H_2 + HO_2$
18	$H_2O_2 + O \rightarrow OH + HO_2$
19	$H_2O_2 + OH \rightarrow H_2O + HO_2$

2.3   Reducing a chemical mechanism

For hydrogen/oxygen combustion the reaction is fully described using 8 species and around 19 reactions (see Table 1). For methane, the number of species required are 50 and a few hundred chemical reactions are needed to describe the combustion. When looking at larger hydrocarbon fuels there might be hundreds of species and thousands of reactions necessary to consider to describe the full chemical scheme. For each reaction the Arrhenius equation (1) is used in order to know the rate of reactions and for each species the transport coefficients has to be found in order to determine the transport of that species. Models that fully describe chemical reactions are therefore reserved for small hydrocarbon fuels since the complexity of chemistry for the larger fuel molecules is too time consuming for computers to handle. This is problematic since larger hydrocarbon fuels are used in practical applications [7].

Using a simplified a description of the reaction process is often times necessary due to these limitations. Denotations of different mechanisms vary from author to author [8], in the following, denotations used in this work are provided. When referring to a *complete mechanism*, all reaction steps are considered, as described so far in Section 2.3. As already mentioned, this is very complicated and will rarely be done when fuels that are more complex than methane are used. When reducing the amount of intermediary steps considered in a complete mechanism it is commonly called a *detailed mechanims* or a *skeletal mechanism*. In a detailed or skeletal there is a reduction in reaction steps considered and species included. The important reactions and species are still included, making the reaction keep its important characteristics. The degree to which a detailed/skeletal mechanism is reduced can vary from a slight decrease in species and reactions to a substantial reduction.

There is more than one reduction method to use when deciding which steps to exclude from a complete mechanism described by Tamás Turányi and Alison S. Tomlin, chapter 7 [6]. The method used in this project was presented by Pichler and Nilson [9], and is briefly summarized in Section 4.

2.4   Transport properties in modeling

As mentioned in Section 2.1, the influence of transport properties can depend on what kind of flame is studied (e.g. premixed flame or diffusion flame), what kind of burner is being used and what kind of molecules are involved. The transport properties are specific for each molecule or molecule-molecule interaction, which is the reason transport property calculations are so demanding.

In Section 2.1 a diffusion flame was presented as an example where the transport properties are important. A diffusion flame will mix the fuel and oxidizer at the reaction point, making fast mixing (diffusion) important. This was shown in research for laminar flame speeds and extinction rates done by S. G. Davis and C.K. Law [10]. This shows that the fuel compound size does not have an effect on the laminar flame speeds for premixed higher alkanes. The extinction strain rates of premixed n-decane and n-dodecane flames show the same behaviour [11]. But for *non-premixed* flames of n-alkanes (from n-pentane to n-tetradecane), the extinction strain rates can be shown to be effected by the size of the fuel. The result of a sensitivity analysis suggested that the extinction strain rates of the premixed flames were overall not sensitive to the fuel diffusivity [12]. This suggests that the molecular transport

aspect is of lesser importance for the extinction strain rate of such a flame. However, the analysis showed that the extinction strain rates of the non-premixed flames were sensitive to the fuel diffusivity , making it more important to take molecular transport into consideration.

In this project, the transport parameters available for optimization are shown in Table 2.

Table 2 :Transport parameters available for optimization.

Parameter	Symbol
Collision diameter	σ
Potential well depth	ε
Dipole moment	μ
Polarizability	α
Rotational relaxation number	Z_{rot}

These parameters are more thoroughly described in Section 3.

3 Theory regarding transport properties

There are two kinds of transport to consider in combustion processes [13], as shown in Figure 2.

- Transport of the molecules (matter) described by diffusion, thermal diffusion or viscosity.

- Transport of energy described by thermal conduction.

When modelling combustion, the transport of molecules is of interest since it describes to what degree the molecules mix with each other. The movement of molecules due to concentration differences in the gas is described by *diffusion* or *mass diffusion* [13].

Thermal diffusion describes the movement of molecules when they are subject to a temperature gradient. This is related to how much of the energy exerted on a gas mixture is converted to translational energy for each species in the mixture, in comparision on how much is converted to internal energy (i.e. intramolecular vibrational and rotational energy).

Thermal conductivity describes heat transfer. Heat can be transferred through a raise in temperature (translational motion) or through intramolecular vibrational and rotational motion. In a monatomic gas, the transfer of heat will be through temperature and not through transfer of internal[3] energy.

The *viscosity* of a gas will also effect the way the gas flows. A high viscosity means a high resistance to change in flow. To simplify further, it means to which degree one portion of the fluid will drag an adjacent portion of the fluid with it. This will affect the movement of molecules in the gas.

Energy transfer in a gas has an effect when it comes to reactions at the point of combustion and in the creation of radicals. This is due to energy being able to reach and initiate a reaction that otherwise would be energetically unfavorable.

There are two ways to obtain the coefficients describing the transport properties, either through a mixed average analysis or through a multicomponent analysis. A mixed average analysis will calculate the property of a species in relation to an average of the rest of the mixture. In a multicomponent analysis, the property will be calculated for each species interacting with every other species separately. The multicomponent analysis is a more thorough analysis, which means it will be more computationally demanding and time consuming. For certain scenarios and for certain properties, a mixed average analysis is sufficient and should therefore be used to save computational power. This is commonly used in CFD where the multicomponent option is too demanding.

3.1 Mixed average analysis

In this section, the transport coefficients equations are obtained from the Chemkin Theory manual [13] and described thoroughly in [14].

The first step is to obtain the pure species viscosities, pure species thermal conductivies and the binary diffusion coefficients. Using these, it will be possible to calculate the mixed average viscosities, conductivies, diffusion coefficents and thermal diffusion ratios.

---

[3]There are no internal vibrational or rotational energy states in a single atom

The pure species viscosities and conductivities are temperature dependant, as are the binary diffusion coefficients. To avoid calculating these properties for each temperature in a system with changing temperature, their temperature dependant parts are fit at the start of each new configuration. Using these fits will make it easier to obtain these properties compared to calculating them for each temperature.

3.1.1 Pure species properties and binary diffusion coefficient

The **viscosity coefficients** for a pure species, k, are

$$\eta_k = \frac{5}{16} \frac{\sqrt{\pi m_k k_B T}}{\pi \sigma_k^2 \Omega^{*(2,2)}}, \tag{2}$$

where σ_k is the Lennard-Jones collision diameter, m_k is the mass, k_b is the Boltzmann constant, T is the temperature and $\Omega^{*(2,2)}$ is a collision integral. The collision integral depends on the reduced temperature, T_k^*, and the reduced dipole moment δ_k^*. For the reduced quantities the reader is refered to the Chemkin theory manual [13] for a summarized description or to Dixon-Lewis [14] for a thorough description. Collision integrals will be discussed more in Section 3.1.4. The **binary diffusion coefficients** are given by:

$$D_{kj} = \frac{3}{16} \frac{\sqrt{2\pi k_B^3 T^3/m_{jk}}}{P \pi \sigma_{jk}^2 \Omega^{(1,1)*}}, \tag{3}$$

where m_{jk} is the reduced mass, σ_{jk} is the reduced collision diameter for species j and k and P is the pressure. Without going into great detail on the reduced quantities, it should be noted that a correction to the reduced collision diameter is added when a polar and non-polar molecule interact. This correction depends on the reduced polarizability, which describes the effect an external electric field (from the polar molecule) has on the non-polar molecule.

The pure species **thermal conductivity** is obtained through the equation

$$\lambda_k = \frac{\eta_k}{W_k}(f_{trans}C_{v,trans.} + f_{rot.}C_{v,rot.} + f_{vib.}C_{v,vib.}), \tag{4}$$

where $C_{v,trans.}, C_{v,rot.}$ and $C_{v,vib.}$ are the specific heat capacities relating to translational, rotational and vibrational motion of the atoms/molecules. For a monoatomic species, Equation 4 will be reduced to only the translational part due to the fact that atoms do not have vibrational or rotational states. f_{trans}, f_{rot} and $f_{vib.}$ are variables that are summarized in Chemkin theory manual [13]. It is worth noting that they contain the rotational relaxation number, Z_{rot}, which relates to the transfer of rotational energy between molecules.

3.1.2 Fitting procedure

The temperature dependant parts of the pure species viscosity and thermal conductivity as well as the binary diffusion coefficients are fitted in order to avoid re-calculating them as the temperature changes [13]. The fit for viscosity is

$$\ln \eta_k = \sum_{n=1}^{N} a_{n,k}(\ln T)^{n-1}, \tag{5}$$

where $a_{n,k}$ are the fit coefficients for species k.

The fit for thermal conductivity is

$$\ln \lambda_k = \sum_{n=1}^{N} b_{n,k} (\ln T)^{n-1}, \tag{6}$$

where $b_{n,k}$ are the fit coefficients for species k.

The fits for *each* pair of species binary diffusion coefficient is

$$\ln D_{kj} = \sum_{n=1}^{N} d_{n,kj} (\ln T)^{n-1}, \tag{7}$$

where $d_{n,kj}$ are the fit coefficients for each species pair kj.

3.1.3 Mixed average properties

The mixed average viscosities are obtained by using the pure species viscosities in Equation 2,

$$\eta = \frac{\sum_{k=1}^{K} X_k \eta_k}{\sum_{j=1}^{K} X_k \Phi_{kj}} \tag{8}$$

where

$$\Phi_{kj} = \frac{1}{\sqrt{8}} \left(1 + \frac{W_k}{W_j} \right)^{-1/2} \left(1 + \frac{\eta_k}{\eta_j}^{1/2} \left(\frac{W_j}{W_k} \right)^{1/4} \right)^2, \tag{9}$$

X_k is the molar fraction of the species k and W_k is the molecular weight of species k.

The mixed average thermal conductivities are obtained through

$$\lambda = \frac{1}{2} \left(\sum_{k=1}^{K} X_k \lambda_k + \frac{1}{\sum_{k=1}^{K} X_k / \lambda_k} \right). \tag{10}$$

For the mixture average diffusion coefficients we have

$$D_{km} = \frac{1 - Y_k}{\sum_{j \neq k}^{K} X_j / D_{jk}}, \tag{11}$$

where Y_k is the mass fraction. The thermal diffusion ratios are used to measure the velocity of thermal diffusion. These ratios are defined as

$$\Theta = \sum_{j \neq k}^{K} \theta_{kj}, \tag{12}$$

where θ_{kj} is

$$\theta_{kj} = \frac{15}{2} \frac{(2A_{kj}^* + 5)(6C_{kj}^* - 5)}{A_{kj}^*(16A_{kj}^* - 12B_{kj}^* + 55)} \frac{W_k - W_j}{W_k + W_j} X_k X_J, \tag{13}$$

where A_{kj}^*, B_{kj}^* and C_{kj}^* are ratios of certain collision integrals [13]. Therefore the temperature dependent part of θ_{kj} (coming from the collision integrals) can be fit as well.

11

3.1.4   Collision integrals

The collision integrals are functionals which give information on how much the distribution of certain species differs from the distribution in a collision free environment.

The collision integrals are sensitive to the potential used to calculate them. In this project, the Stockmayer potential obtained by Monchick and Mason [15] or the Lennard-Jones potential is used to interpolate these integrals.

The potential used for the collision integrals depend on if the collision considered is between two polar molecules, two non-polar molecules or if it is one polar and one non-polar molecule. For two *non-polar* molecules/atoms colliding the potential used is the Lennard-Jones potential (Equation 14). This is also the potential used for a *polar/non-polar* interaction. In that case, a slight correction is applied for the collision diameter and well depth using the reduced polarizability, $\alpha*$, [14]. For the interaction between two *polar* molecules, the Stockmayer potentials are used, see Equation 15.

$$V_{LJ} = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right], \tag{14}$$

$$V_{Stock} = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] - \frac{\mu_1 \mu_2}{r^3} \cdot \Phi(\theta_1, \theta_2, \phi), \tag{15}$$

where r is the radius, μ_1, μ_2 are the dipole moments of the two molecules. $\Phi(\theta_1, \theta_2, \phi)$ is a function depending on the angels of the dipoles to the center connecting axis (θ_1, θ_2) and ϕ is the azimutal angle between the molecules. In both of these potentials the Pauli repulsion and Van der Waal interaction is taken into account (the 12th power term and the 6th power term respectively). However, in the Stockmayer potential an extra term relating to the dipole moments of the molecules is added.

4 Method

In this project Chemkin was used to simulate a premixed laminar flame. A reference target was simulated using an experimentally validated complete mechanism for the given fuel/oxidizer combustion process. The complete mechanism was then reduced using an ant colony reduction code (ACR) [9]. Optimization of transport parameters were implemented within the present project and used in combination with the reduced mechanism to run new simulations. The results were validated against the reference target using a response function implemented in the code. This was done using the fuels methanol and propane.

4.1 Chemkin simulation software

Chemkin simulates the flame using given reaction rate coefficients, thermodynamic data and transport data. By using the reaction rate coefficients described in Equation 1, thermodynamic data and transport parameter data used to calculate the coefficients in Section 3, the behaviour of the flame was modelled. This was done in order to simulate a premixed 1D laminar flame where the burning velocity and molar fraction of certain components of the mechanism was determined[4]. Mixed average analysis was applied according to Section 3.1 for the diffusion coefficient, thermal diffusion ratios, thermal conductivity and viscosity.

4.2 The ACR mechanism reduction tool

Since a full kinetic mechanism, referred as a *complete* mechanism in Section 2.3, is time consuming and demanding even for 1D simulations in Chemkin, a reduction is necessary. This is done using a code which evaluates the reaction steps of the complete mechanism and selects the steps in the reaction which are occurring at a certain rate using ant colony optimization. The code includes an optimization part for the reaction rate coefficients, see Figure 4. The code included a response function which compared the output of the simulations in order to evaluate their agreement with the reference mechanism. In this project the code was extended to include optimization of transport parameters.
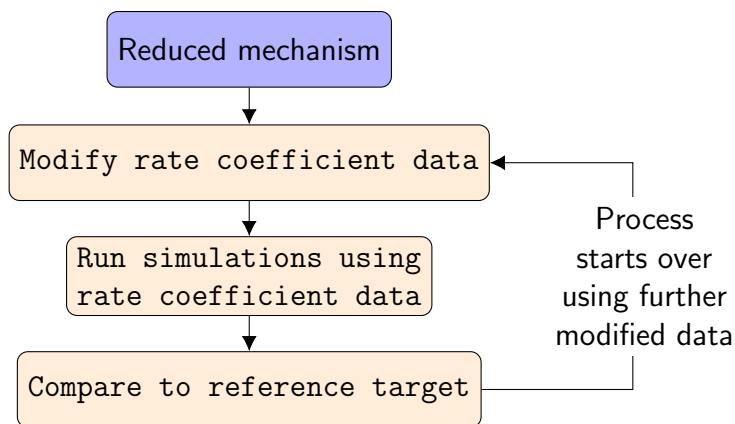

Figure 4: Flowchart of the optimization process for reaction rate coefficients

---

[4]The molar fractions were determined at several points in the flame

4.3   Optimization of transport data

When optimizing the transport data, the reaction coefficients and the thermodynamic data were not changed when running the simulations since the purpose of this project is to single out the effect of changes in the given transport parameter data.

The part of the code in Section 4.2 which was used to modify the reaction rate coefficients was changed to modify transport parameters for the different molecules and atoms, see Figure 5.

```
N2                  1     97.530      3.621      0.000      1.760      4.000
H2                  1     38.000      2.920      0.000      0.790    280.000
H                   0    145.000      2.050      0.000      0.000      0.000
O2                  1    107.400      3.458      0.000      1.600      3.800
O                   0     80.000      2.750      0.000      0.000      0.000
H2O                 2    572.400      2.605      1.844      0.000      4.000
OH                  1     80.000      2.750      0.000      0.000      0.000
HO2                 2    107.400      3.458      0.000      0.000      1.000
CO                  1     98.100      3.650      0.000      1.950      1.800
CO2                 1    244.000      3.763      0.000      2.650      2.100
CH3                 1    144.000      3.800      0.000      0.000      0.000
CH2O                2    498.000      3.590      0.000      0.000      2.000
HCO                 2    498.000      3.590      0.000      0.000      0.000
C2H5                2    247.500      4.350      0.000      0.000      1.500
C2H4                2    238.400      3.496      0.000      0.000      1.500
C2H3                2    265.300      3.721      0.000      0.000      1.000
C2H2                1    265.300      3.721      0.000      0.000      2.500
HCCO                2    150.000      2.500      0.000      0.000      1.000
C3H8                2    303.400      4.810      0.000      0.000      1.000
IC3H7               2    303.400      4.810      0.000      0.000      1.000
NC3H7               2    303.400      4.810      0.000      0.000      1.000
C3H6                2    307.800      4.140      0.000      0.000      1.000
```

Figure 5: Transport data for molecules and atoms used in propane combustion. The data is given in the following order: Species, geometrical configuration, collision diameter, well depth, dipole moment, polarizability, rotational relaxation number

Chemkin used these parameters to create a laminar flame simulation. The code is then designed to compare the flame properties of these simulations to a reference value created from a mechanism of known quality. The transport parameters are then modified again and the process is repeated. The process is demonstrated in Figure 6.
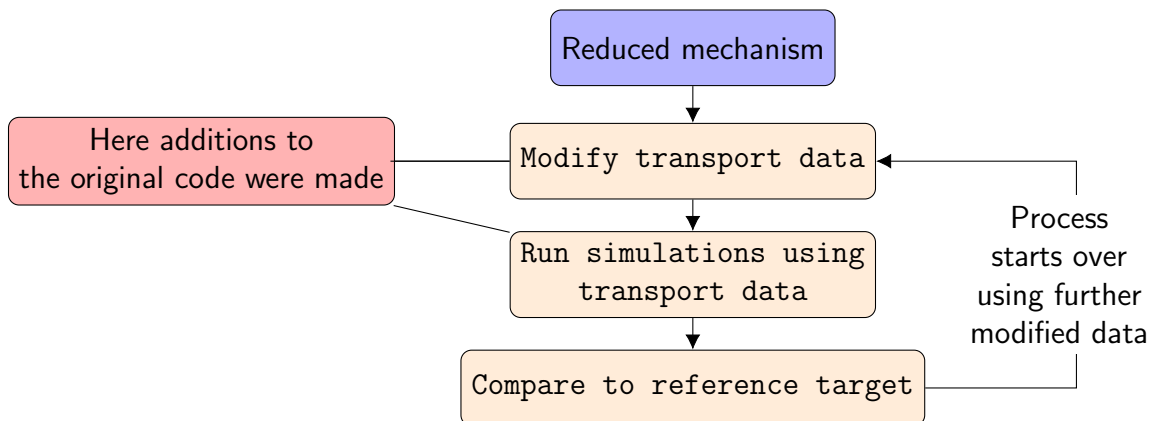

Figure 6: Flowchart of the optimization process for transport data

Geometric configuration was not changed in the transport data since the knowledge of the atoms/molecules shape was assumed to be known. The remaining parameters were optimized.

For both fuels (methanol and propane) the parameters were changed both separately and simultaneously. This was done in order to get insight in both the sensitivity of each parameter and to which magnitude the results would be improved for optimizing all relevant parameters simultaneously. For methanol, the transport parameters were optimized for a select set of temperatures (300 K, 400 K and 500 K) and a constant pressure (30 atm) and equivalence ratio (ϕ=1). This was done to see if the temperature dependence of the collision integrals and transport parameters affected the results of the optimization. The transport parameters for propane were optimized for different equivalence ratios[5] (ϕ=0.7, 1, 1.2) and pressure (1 atm and 5 atm).

The two fuels were chosen based on their structure. Methanol has a more spherical structure compared to propane which in turn could result in a larger amount of reaction steps that include molecules with spherical structure. This might influence the results since the Lennard-Jones potential assumes spherical symmetry and the Stockmayer potential only has a correction for the dipole moment of polarized molecules. An optimization for relatively non-spherical fuel molecules would be presumed to be particularly influential.

---

[5]Equivalence ratio, ϕ, describes the fuel/oxidizer ratio compared to the stoichiometric fuel/oxidizer ratio

5 Result and discussion

In this section the results obtained from running simulations using the reduced mechanism with and without optimized transport parameters are compared to reference values gathered from the complete mechanism. The values obtained when using the complete mechanism are regarded to be accurate and the goal is to be as close to these values as possible. As mentioned in Section 4, the parameters were both optimized separately to determine the sensitivity of change in each parameter, and simultaneously to determine the magnitude of improvement in a full optimization. The results from full optimization, optimization of the most influential parameter and no optimization for the reduced mechanisms will be compared to the values from the full mechanism.

5.1 CH_3OH - Methanol

5.1.1 Laminar burning velocity

The laminar burning velocity of CH_3OH, shown in Figure 7, had a significant increase in accuracy using the optimized transport data.
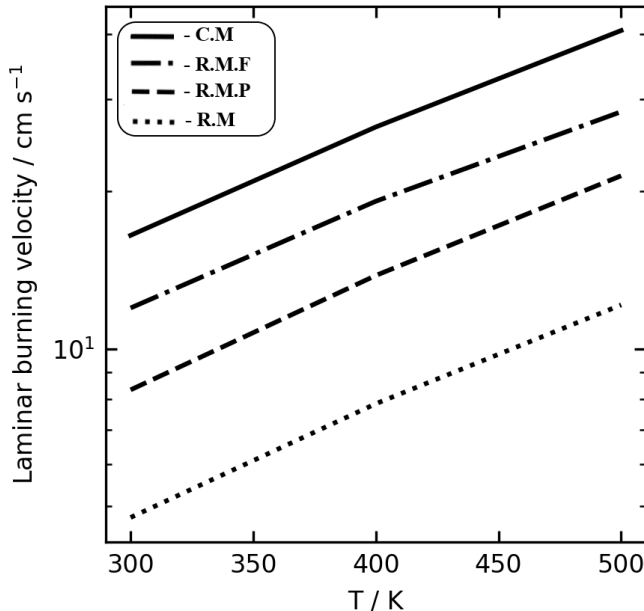

Figure 7: The laminar burning velocity as a function of temperature. **C.M** - Complete reference mechanism. **R.M** - Reduced mechanism (unoptimized). **R.M.P** - Reduced mechanism (only collision diameter optimized). **R.M.F**- Reduced mechanism (all parameters optimized).

The full-drawn line represents the complete mechanism (**C.M**) used as a reference. This was reduced using ACR (see Section 4) and optimized. The dotted line (**R.M**) represents the reduced mechanism without optimization. A significant decrease in accuracy of the laminar burning velocity was observed as a result of the reduction process. This mechanism would

not be suitable for further use in CFD due to the accuracy loss. The reduced mechanism was optimized both by optimizing each parameter separately and by optimizing them simultaneously. The dashed-dotted line represents the reduced mechanism when all the transport parameters were optimized (**R.M.F**) and the dashed line represents the reduced mechanism when it was partially optimized (**R.M.P**) with regards to the parameter it showed the highest sensitivity to. The parameter to which the laminar burning velocity had the highest sensitivity to was the collision diameter.

5.1.2 Overall response

The optimization of transport data substantially improved the overall response score, as shown in Figure 8a and 8b. The overall response score is determined using comparisons of mole fractions and selected flame properties between the reduced and complete mechanisms. For a response score of 1, there is a complete agreement.

For both the fully optimized and the unoptimized mechanism the response score was higher if the mixture temperature was higher. Since this was the case for both the optimized and unoptimized reduced mechanism, this might indicate that the optimization is not heavily temperature dependent in this temperature range.

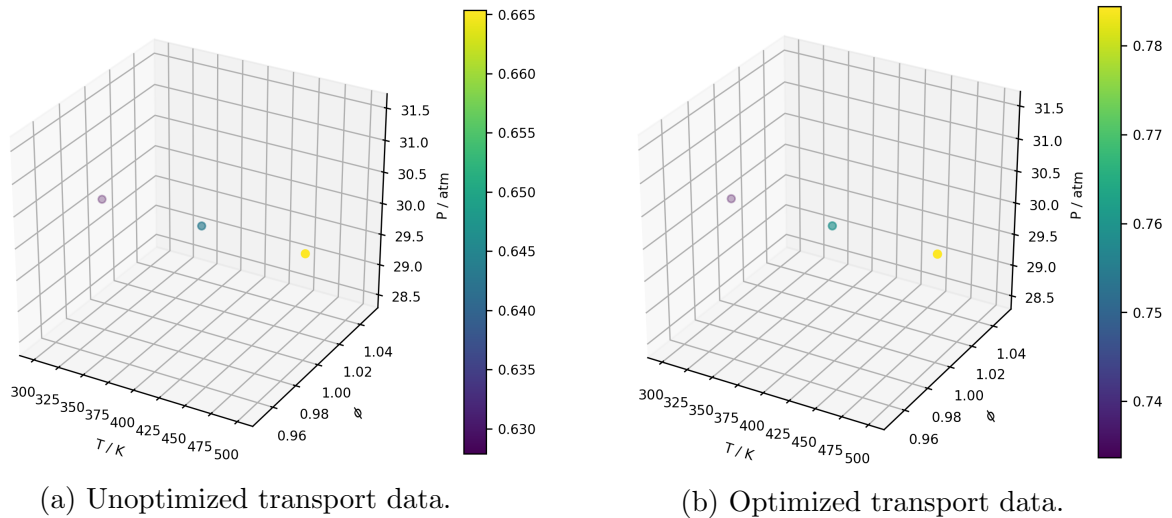(a) Unoptimized transport data. (b) Optimized transport data.

Figure 8: Response score for unoptimized and optimized transport data at different temperatures. Note the different scaling on the color axis.

When the transport parameters were optimized separately, it revealed varying improvements in accuracy. In Figure 9, the effect of the three parameters that the optimization showed largest sensitivity to are shown. The other parameters showed an improvement in accuracy lower than 5 %.
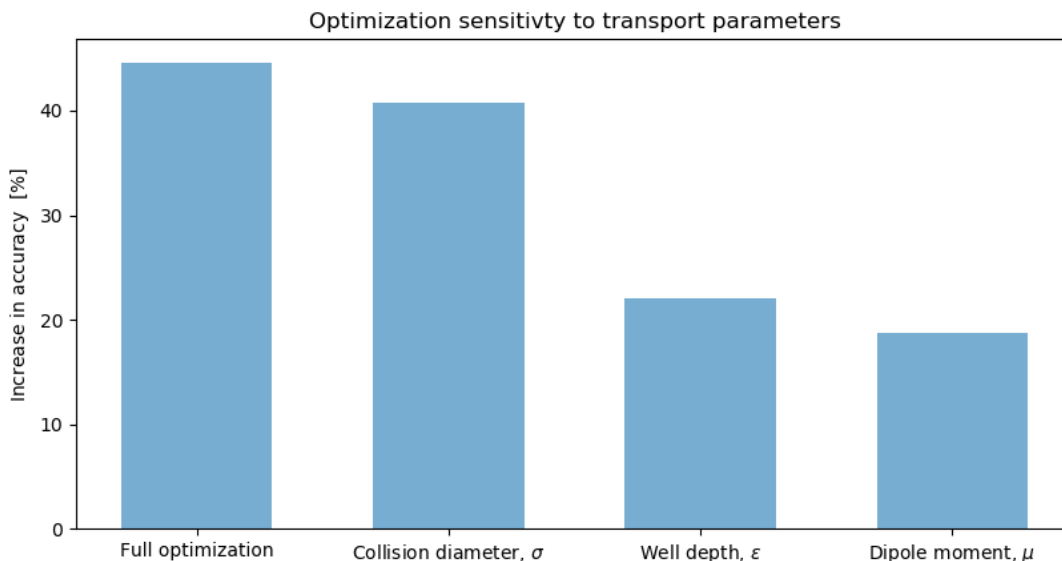

Figure 9: Increase in overall response score when optimizing collision diameter, well depth and dipole moment compared to full optimization.

Optimizing the collision diameter had a noticeably higher impact than optimizing the other parameters. The well depth and dipole moment still provided a notable increase in accuracy when optimized, making them important to take into account when optimizing methanol.

5.2 C_3H_8 - Propane

5.2.1   Laminar burning velocity

Figure 10 shows that the unoptimized reduced mechanism (dotted line) is inefficient when predicting the burning velocity compared to the complete mechanism (full drawn line) at different equivalence ratios. A significant increase in accuracy was observed both when all parameters were optimized (dashed-dotted line) and only the collision diameter was optimized (dashed line) for the reduced mechanism. This signifies that the collision diameter played a significant role in predicting the burning velocity for the optimized reduced mechanism.
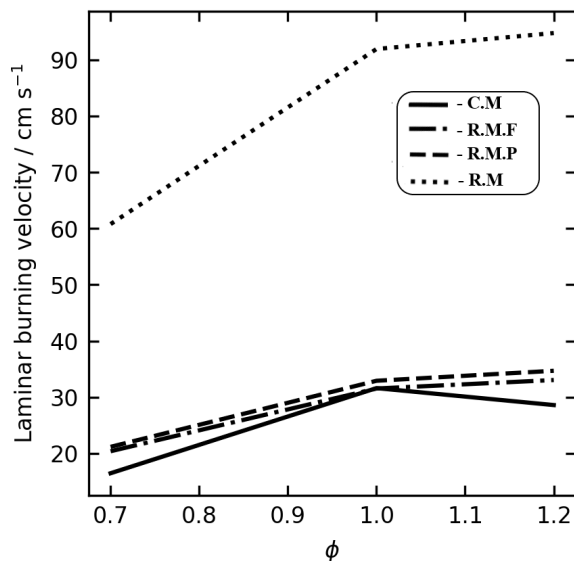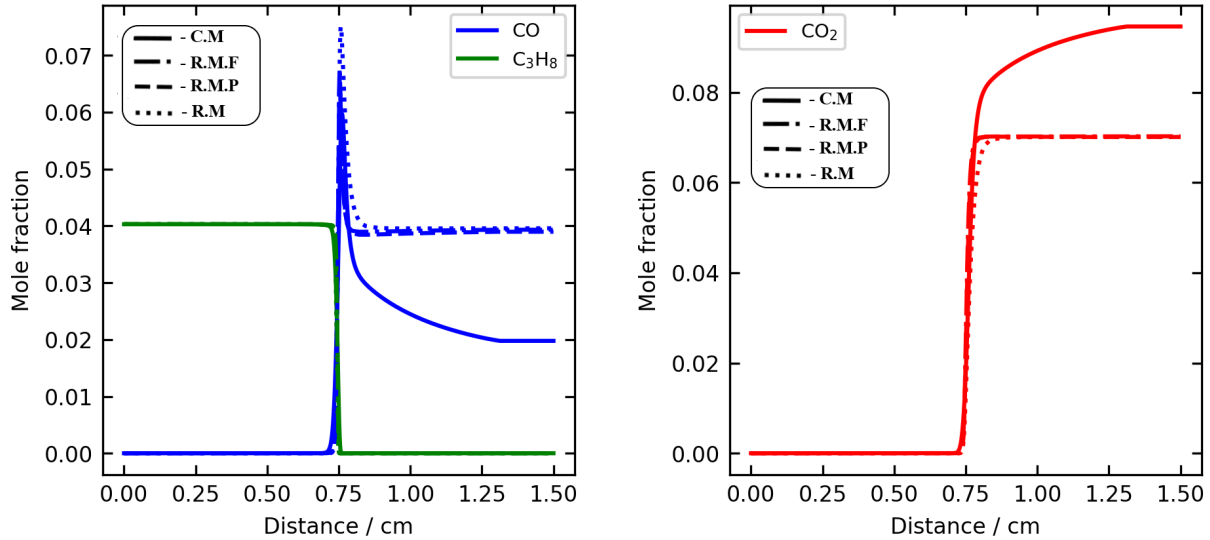

Figure 10: Laminar burning velocity as a function of ϕ. **C.M** - Complete reference mechanism. **R.M** - Reduced mechanism (unoptimized). **R.M.P** - Reduced mechanism (only collision diameter optimized). **R.M.F**- Reduced mechanism (all parameters optimized).

5.2.2 Molar fraction

The transport optimization had only modest success in improving molar fraction predictions shown in Figure 8a/8b .

(a) Molar fraction at pressure 1 atm and at a ϕ value of 1

(b) Molar fraction at pressure 1 atm and at a ϕ value of 1

Figure 11: The molar fractions for different species at different places in the combustion process. **C.M** - Complete reference mechanism. **R.M** - Reduced mechanism (unoptimized). **R.M.P** - Reduced mechanism (only collision diameter optimized). **R.M.F**- Reduced mechanism (all parameters optimized).

The unoptimized mechanism (dotted line) did not predict the molar fractions of carbon monoxide, propane or carbon dioxide accurately when compared to the complete mechanism (full line). Neither optimization of only the collision diameter (dashed line) or full optimization of all transport parameters (dashed-dotted line) improved the molar fraction predictions significantly.

5.2.3   Overall response score

A noticeable improvement in overall response score was observed when optimizing the transport data. Regardless of pressure or if the combustion was fuel-lean ($\phi < 1$), fuel-rich ($\phi > 1$) or stoichiometric ($\phi = 1$) there was an improvement in the overall response score.

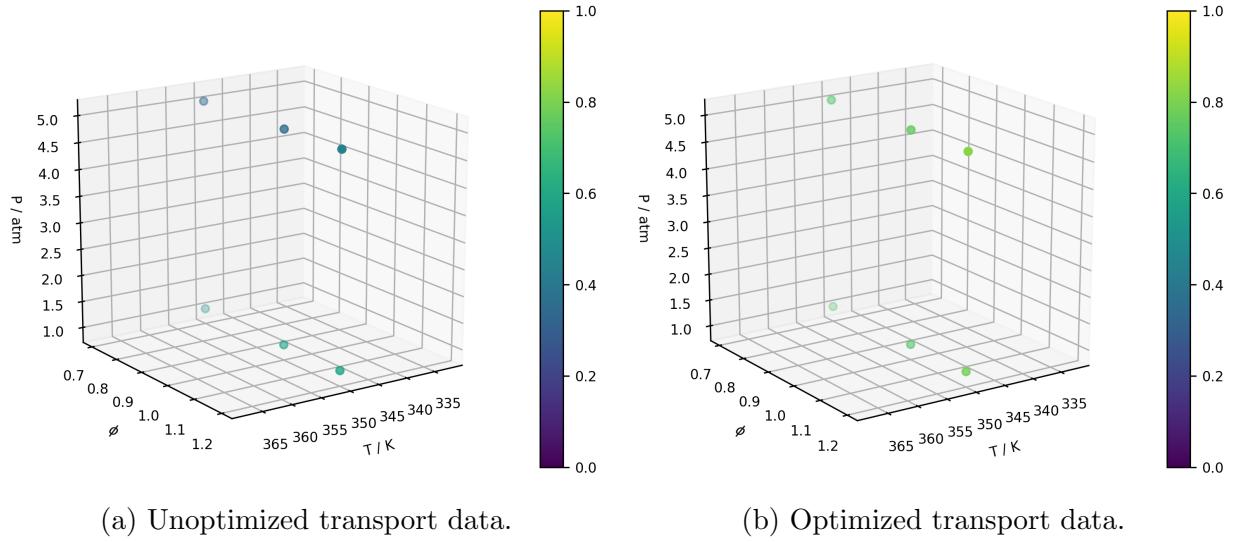(a) Unoptimized transport data.   (b) Optimized transport data.

Figure 12: Response score for unoptimized and optimized transport data at 350 K at different equivalence ratios.

The result of optimizing the each parameter separately showed that collision diameter had a dominant role in the optimization process of propane, see Figure 13. Only the three parameters with largest impact on the influence on the optimization are shown. The remaining parameters did not show a significant influence in the optimization process.
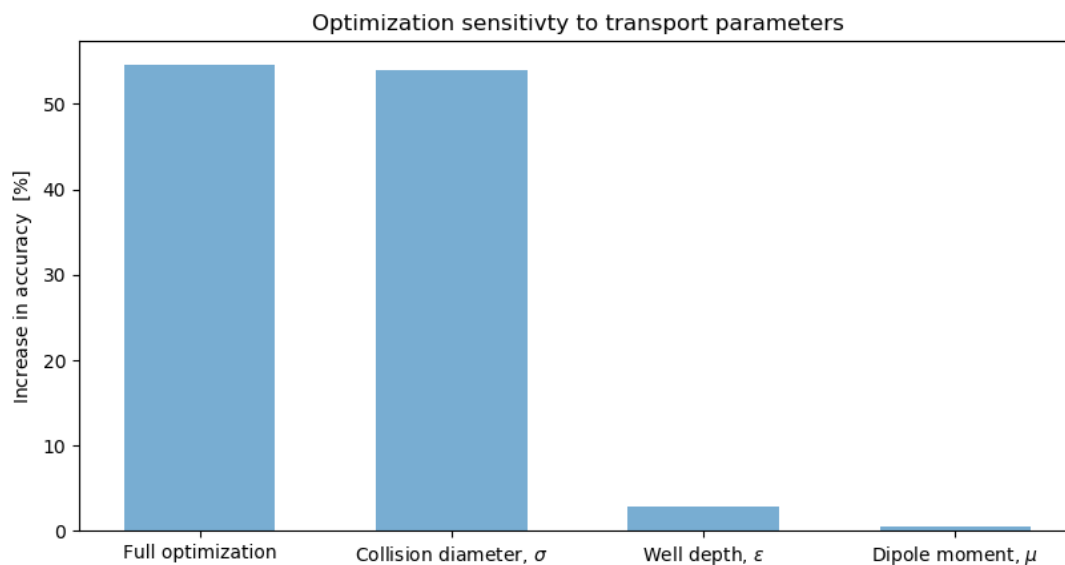

Figure 13: Increase in overall response score when optimizing collision diameter, well depth and dipole moment compared to full optimization.

6   Summary and conclusions

In this project, modified code was used to optimize transport data and evaluate their impact on combustion simulations. This was done using two kinds of fuel molecules, methanol and propane.

For both methanol and propane the laminar burning velocity and the overall response score showed significant improvement when the reduced mechanisms were optimized with regards to the transport parameters. For methanol, the improvement did not seem to depend on the temperature as indicated in Figure 7, where the same improvement can be seen throughout the temperature range. This gives reason to believe that the optimization for the transport properties at a certain temperature will be valid for other temperature ranges. In a combustion process where wide temperature ranges are common, it would be beneficial to optimize the properties for one temperature and use it for the entirety of the temperature range. Methanol showed highest sensitivity to optimization of the collision diameter followed by the well depth and dipole moment.

The burning velocity for propane shown in Figure 10 was in almost complete agreement with the reference mechanism at all equivalence ratios. The dominant factor in this optimization was the collision diameter which stood for close to all of the improvement in accuracy. This can be compared to methanol where even though the collision diameter was the largest affecting factor, it had a much less dominant affect than in the case for propane. This could relate to the different structures for the fuels. Propane has a less spherically symmetric structure compared to methanol, making the Lennard-Jones and Stockmayer potentials less accurate representations of the molecule. This could manifest in the high sensitivity of the collision diameter, since it is the dominant term of the potentials (see Equation 14 and 15).

The overall response score for propane showed a greater increase for a pressure at 5 atm than 1 atm. This could be partially accounted for by the fact that the unoptimized reduced mechanism did not suffer a great loss in accuracy at 1 atm, making it unable to be greatly improved upon.

The sensitivity to the collision diameter for both fuels shown in Figure 9 and 13 could be accounted to the fact that spherically symmetric potentials are poor descriptions for both fuels. This gives reason to believe that optimization for fuels of non-spherical structure might have a larger impact. The sensitivity to optimization of the dipole moment in propane was close to zero. Since the dipole moment is mainly used for interactions between two polar molecules (using the Stockmayer potential), the lack of sensitivity could be explained by the fact that the propane mechanism only had one polar molecule (see the transport data file in the Appendix). The influence optimization of the dipole moment had on methanol could be explained by the fact that methanol is a polar molecule with a strong dipole.

Knowledge about the species and how the species react in a reduced mechanism might therefore be important in order to know which transport parameters will affect the optimization process. Alternatively, knowledge on the effect of the transport parameters for different species and reactions might affect how one chooses to reduce a mechanism. It is not meaningful to optimize a mechanism with regards to transport parameters it is not sensitive to. The molar fractions for carbon monoxide, propane or carbon dioxide shown in Figure 11b and Figure 11a were the one case where no significant increase in accuracy could be seen. A possible explanation for this is that the mixed average analysis does not take into

account molecules with a mole mass larger than 5 when calculating the thermal diffusion ratios. Carbon monoxide, propane or carbon dioxide all have a higher molecular mass than 5, and since the thermal diffusion ratios relate to how the molecules transport when subject to a temperature gradient, this might effect the result of predicted mole fractions at different regions of the flame. It is possible the multicomponent analysis option where all molar masses are included would give more insight regarding the molar fractions compared to the mixed average analysis. However. the mixed average option is the method commonly used in CFD simulations which is the field the reduced mechanisms are constructed for. Therefore using the mixed average option is more relevant for real applications.

A strong recommendation for further mechanism development is to optimize the collision diameter, since it showed to be the most important parameter for both the studied fuels. It is likely that it will be even more influential for larger fuel molecules, which could be a relevant topic for further studies. Regarding the importance of dipole moment and well depth for the polar molecule methanol, this is something that could be further studied for various other fuels with dipole moments.

In conclusion, there was a significant improvement in accuracy when the transport properties were optimized for both methanol and propane. A strong recommendation for further mechanism development is to optimize the collision diameter to which both methanol and propane showed strong sensitivity towards. This sensitivity might extend to even larger fuel molecules for which optimization of collision diameter could prove to be more influential.

References

[1] S. Chu and A. Majumdar, "Opportunities and challenges for a sustainable energy future," *nature*, vol. 488, no. 7411, p. 294, 2012.

[2] C. K. Westbrook, Y. Mizobuchi, T. J. Poinsot, P. J. Smith, and J. Warnatz, "Computational combustion," *Proceedings of the Combustion Institute*, vol. 30, no. 1, pp. 125–157, 2005.

[3] B. Dunbar, "Flames on earth and space (1998)," Jun 2013.

[4] P.-E. Bengtsson, *Chemical Kinetics*.

[5] D. Lignell, J. Chen, and H. A. Schmutz, "Effects of damköhler number on flame extinction and reignition in turbulent non-premixed flames using dns," *Combustion and Flame - COMBUST FLAME*, vol. 158, pp. 949–963, 05 2011.

[6] T. Turanyi and A. S. Tomlin, "Analysis of kinetic reaction mechanisms."

[7] C. K. Law, "Combustion at a crossroads: Status and prospects," *Proceedings of the Combustion Institute*, vol. 31, pp. 1–29, 01 2007.

[8] R. Hilbert, F. Tap, H. El-Rabii, and D. Thévenin, "Impact of detailed chemistry and transport models on turbulent combustion simulations," *Progress in Energy and Combustion Science*, vol. 30, pp. 61–117, 12 2004.

[9] C. Pichler and E. J. K. Nilsson, "Reduced kinetic mechanism for methanol combustion in spark-ignition engines," *Energy & Fuels*.

[10] S. G. DAVIS and C. LAW, "Determination of and fuel structure effects on laminar flame speeds of c1 to c8 hydrocarbons," *Combustion Science and Technology*, vol. 140, no. 1-6, pp. 427–449, 1998.

[11] K. Kumar and C.-J. Sung, "Laminar flame speeds and extinction limits of preheated n-decane/o-2/n-2 and n-dodecane/o-2/n-2 mixtures," *Combustion and Flame*, vol. 151, 10 2007.

[12] A. Holley, X. You, E. Dames, H. Wang, and F. Egolfopoulos, "Sensitivity of propagation and extinction of large hydrocarbon flames to fuel diffusion," *Proceedings of the Combustion Institute*, vol. 32, no. 1, pp. 1157 – 1163, 2009.

[13] *Chemkin theory manual*.

[14] G. N. Dixon-Lewis and T. G. Cowling, "Flame structure and flame reaction kinetics ii. transport phenomena in multicomponent systems," *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, vol. 307, no. 1488, pp. 111–135, 1968.

[15] L. Monchick and E. A. Mason, "Transport properties of polar gases," *The Journal of Chemical Physics*, vol. 35, no. 5, pp. 1676–1697, 1961.