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Investigation of reaction properties to facilitate chemical lumping of kinetic mechanisms

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Abstract

Combustion process are used to improve modern society, but it comes with problems, like global warming and air pollution. Computer simulations are used to study combustion process to allow more efficient use of the fuel or decrease the creation of pollution. The main problem with simulations of combustion process is that they are very time consuming, as both physical effects and chemical reactions must be in the simulation. The chemical reactions are typically simplified to shorten the time needed. The project reported here is part of a larger project with the aim of creating a program that can reduce the size of an chemical kinetics mechanism. The goal of the project reported here is to create two methods that, through chemical lumping, reduces the size of mechanisms, which in turn will reduce the time needed for simulations of combustion process. Both methods were tested on one mechanism with methanol as fuel. One was also tested on another mechanism with both methanol and propane as fuel. The method tested on two mechanisms gave worse results than the original mechanisms, while the other was on par with the original mechanism. Both methods shows potential, but further work is needed before they can be implemented into the reduction program.

Contents

1   Introduction

Modern society relies heavily on the combustion of fuels to transport goods and people. This is how most cars, boats and airplanes get their energy. Trains and electric cars use electricity, but the electricity is usually partially generated through combustion. This is a problem as the combustion of fossil fuels increases the concentration of carbon dioxide in the atmosphere, which exacerbates global warming. Other substances that lowers the quality of the air are also created during combustion, like soot. To combat this, numerous scientists are working on environmental friendly technology. However global warming and pollution are both problems that needs to be solved quickly and the environmental-friendly technology is not ready yet. This is why much effort is dedicated to improve existing technology so that it produces less pollution and is more efficient [1]. More efficient engines needs less fuel.

One important tool used to understand combustion processes is computer simulations. Some properties of a combustion process are often possible to determine experimentally, like temperature, but others are extremely difficult to study experimentally, like the concentration of most species. Combustion simulations allow scientists to study these properties. One important step in creating efficient engines is to find optimal starting concentrations of the fuel and oxygen. This can often be achieved in combustion simulations by repeating the simulation with different starting parameters. However the main challenge of combustion simulations is that they are very time-consuming.

One of the reasons why the simulations are time-consuming is that many reactions take place concertedly in a combustion process. The fuel molecule does not immediately react with the appropriate amount of oxygen and create water and carbon dioxide. This happens step by steps, in which the fuel looses a hydrogen or gains an oxygen atom. The fuel molecule could also break into pieces. All of these reactions have been collected into kinetic mechanisms and the mechanisms are then used in the combustion simulations. A typical mechanism contains hundreds or thousands of reactions, depending on the size of the fuel. Smaller mechanisms gives faster simulations. Considerable amount of work has therefore been put into reducing the size and complexity of the mechanisms [2]. Chemical lumping is one method of mechanism reduction, where reactions or species are lumped together. On the other hand, the accuracy of the results typically decreases when the mechanism is reduced.

The project reported here is part of a larger project that uses Ant Colony Reduction (ACR) to automatically reduce the size of mechanisms without loosing to much accuracy. The goal of this project is to investigate possibilities to create algorithms that in turn creates shortcuts in the mechanisms. Two methods to achieve this was proposed and tested. One of the methods uses symmetry among the reactions and the other uses the speed of the reactions to create shortcuts.

The goal of the project reported here is to investigate possibilities to create shortcuts in the mechanism. Two methods to achieve this was proposed and tested. One of the methods uses symmetry among the reactions and the other uses the speed of the reactions to create shortcuts. This project is part of a larger project with the aim to create a program that automatically reduces mechanisms without loosing to much accuracy in their predictive power. The larger project uses a method called Ant Colony Reduction (ACR) and the purpose of this project is to create methods that can be used together with ACR to reduce mechanisms. Two optimization algorithms with ACR were also tested and compared to using only ACR. In short, this project aims to create two methods that can improve the larger project with reducing mechanisms. Reducing mechanisms will in turn make combustion simulations much faster and will thereby improve them. This will improve the usability of combustion simulations and this will lead to a better understanding of combustion processes. The understanding of combustion processes can then be used to improve the usage of combustion in society.

2 Background

2.1 Combustion simulations

A combustion process has three main characteristics. These are ignition, flame propagation and extinction of the flame. The combustion itself is a sequence of rapid chemical reactions. The reactions depend heavily on the fuel, not only because the actual reactions vary between two different fuels, but also because common reactions will impact the end result differently. The characteristics of the combustion process will therefore depend on the reactions. The characteristics of a combustion process can be studied with both dedicated experiments and simulations.

It is often possible to decrease the size of the simulation when the simulation is dedicated to finding out certain properties of the combustion process instead of everything. One possible way to decrease the size of the simulation is to decrease the number of spatial dimensions. This does not only decrease the size of the simulation, but also simplifies it, as compilations like turbulence and diffusion are simpler or disappears completely in simulations of lower dimensions [3]. 3D and 2D simulations can simulate entire flames, while simulations with lower dimensions can be made to separately determine ignition delay, laminar burning velocity and extinction strain rate. The project reported here will work with 0D simulations. This means that only the chemistry of the combustion process will be taken into account.

2.2 Kinetic mechanisms

As mentioned in the introduction, a mechanism is a collection of reactions and species. There are different types of mechanism, depending on the number of reactions in the mechanism. The smallest mechanism is the global or single-step mechanism. As the name implies, it contains only one reaction. This is usually the one where the fuel reacts with oxygen, forming water and carbon dioxide. Such a reaction for methanol is shown in reaction 1 below.

$$2CH_3OH + 3O_2 \rightarrow 4H_2O + 2CO_2 \tag{1}$$

The next size of mechanisms are the semi-global mechanisms. These usually contains only the species with the highest concentrations and relevant reactions connecting these species. Such mechanism typically contains 4–10 species [3]. On the opposite side of global mechanisms are the complete mechanisms. These mechanisms contains all of the species and reactions relevant to the combustion process. Between the complete and the semi-global mechanisms are the detailed and skeletal mechanisms. The difference between these two types of mechanism is not well defined, but a detailed mechanism is a reduced complete mechanism, while a skeletal mechanism is heavily reduced complete mechanism. In detailed mechanisms, the main chemical pathway is still in the mechanisms, while the skeletal mechanism involve only the bare minimum of reactions. These mechanism types vary in size depending on the fuel. For example, the LLNL (Lawrence Livermore National Laboratories) mechanism for heptane involves 561 species and 2539 reactions [4], while detailed mechanisms for hydrogen usually contain only 8 species. [3]
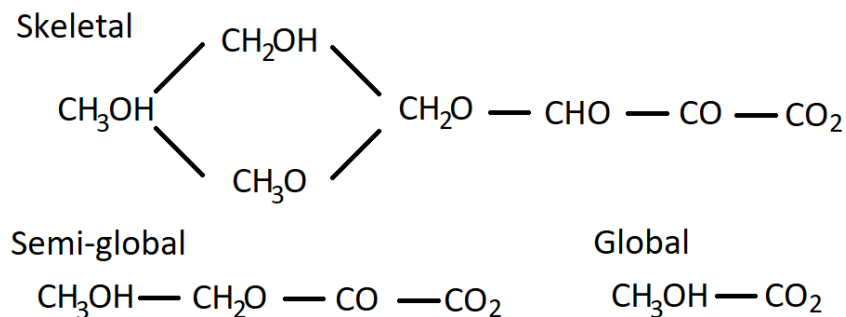
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Figure 1: Carbon containing species in a typical skeletal, semi-global and global mechanism for methanol. The lines between the species represent reactions and the reaction for the global mechanism was shown in Eq. 1.

The different mechanism types can be divided into two groups, one containing the global and the semi-global mechanisms and the second containing the other three. The main difference between the groups is that the second group have a unbroken chain of species containing carbon from the fuel to carbon dioxide, while the first group simplifies the chemistry by skipping some of these species. The unbroken carbon chain can be seen in Figure 1 together with examples of the carbon chains from semi-global and global mechanisms for methanol.

The semi-global and global mechanisms has simplified the chemistry behind the combustion process, while the other types of mechanisms are simplified by leaving out species and reactions that are deemed unnecessary. This means that simulations using the semi-global and global mechanisms are much faster, but the accuracy is much lower. The entire combustion process take place at the same time rather than in a long string of reactions. This does not only ignore most of the intermediate species, but it also releases all of the stored energy at the same time. Mechanisms from this group are mainly used to obtain qualitative trends.

Complete mechanisms give accurate results, but the size of the mechanism makes it impractical to use in simulations of anything except the smallest of fuel molecules. Detailed and skeletal mechanisms have sacrificed some of their accuracy to decrease the number of reactions. The detailed mechanisms used in this project are the SanDiego mechanism with 57 species and 268 reactions and the AramcoMech 2.0 mechanism, in the following referred to as Aramco, with 493 species and 2716 reactions [5, 6]. Both Aramco and SanDiego are detailed mechanisms, but Aramco is a bigger and therefore more accurate mechanism. Aramco can also be used for more fuels and a larger range temperatures and pressures than SanDiego. However the size of Aramco makes it hard to use. The mechanisms was chosen because Aramco is currently one of the best mechanisms for fuels with three or less carbon atoms, while SanDiego is a good mechanism with a much smaller size. The goal of the project reported here is to create methods that reduces the size of mechanisms. It is therefore important that the methods developed here works on multiple mechanisms. It would have been better to use more mechanisms, but time constraints limited it to two.

2.3   Chemical kinetics

Chemical reactions are usually represented by a stoichiometric equation. The global reaction for the combustion of methanol was shown in Eq. 1 and below the reaction where methanol reacts with a hydroxyl radical can be seen.

$$CH_3OH + OH^{\bullet} \rightleftharpoons CH_2OH + H_2O \tag{2}$$

Such stoichiometric equations indicate the molar ratios between the various species in the reaction [7]. The

$\rightleftharpoons$ means that the reaction is reversible, which means that the reaction can take place in both directions. The reaction in Eq. 1 was irreversible, which means that the products will not spontaneously react with each other and form the reactants. This is symbolized with an arrow pointing in the direction of the reaction ($\rightarrow$). It is sometimes possible for a set of reactants to have different reaction paths. Reaction 3 is another example in which both methanol and a hydroxyl radical are the reactants.

$$CH_3OH + OH^\bullet \rightleftharpoons CH_3O + H_2O \tag{3}$$

This is the reason for the branch seen in the skeletal mechanism in Figure 1. The paths converge again when formaldehyde, CH_2O, is formed. So far, all reactions mentioned have only had two reactants. A three-body reaction has three reactants and is usually much less likely to happen. The reason is that the concentration of the species are usually low, which means that a collision of all three reactants is usually rare. The rate do typically increase with the pressure. Reaction 4 is an example of a certain type of three-body reactions called a termolecular reaction. The third species in these reactions is called M. This is not one species, but a collection of species that helps with the reaction [7].

$$CO + O + M \rightleftharpoons CO_2 + M \tag{4}$$

The reason that the species of the M molecule does not matter in the reaction is because of how the reaction happens. First the two other species reacts and creates the end product, but in an excited state. This means that the molecule is not in its ground state and has the energy needed to fall apart back into the reactants. The M species then collides with the excited molecule and takes some of the energy, preventing it from falling apart [8]. This bypasses the problem of the three reactants colliding at the same time and termolecular reactions are therefore not generally slower than two-body reactions. Not all reactions are equally important in a combustion process. Some reactions are faster than others and will therefore have a bigger impact on a number of aspects like heat release and final product formation. The speed of a reaction can be seen from its reaction rate, r [7]. The rate of the reaction is defined by

$$r = \frac{1}{s}\frac{dS}{dt}$$

where S is the concentration of species S, s is the stochiometric coefficient of it in the reaction and t is time [7]. r does not depend on which species in a reaction one looks at, but it does depend on the reaction. It also depends on the temperature, T. This can be seen from the rate constant, k. r can be approximated with

$$r = k \prod S_i^{c_i}$$

where S_i is the concentration of the i:th species in the reaction and c_i is a positive real number or zero [7]. This formula is important as it shows a clear difference between reactions with different amount of species. The concentration of gases is generally quite low. The methods proposed later in this report will take two two-body reactions and create one three-body reaction meant to model the two reactions. If the k constant is unchanged then the low concentration of the species will decrease the reaction rate compared to the two original reactions. The value of k will therefore be changed by the methods to compensate for this. The value of the change was calculated from some estimations of the temperature and pressure (see Method) with the ideal gas law,

$$\frac{N}{V} = \frac{k_B T}{P}$$

where N is the number of molecules, V is the volume, k_B is the Boltzmann constant, T is the temperature and P is the pressure of the gas. The ideal gas law has been written so that the left side gives the concentrations, as the concentration is the number of molecules divided by the volume. The temperature dependence of k is given by the Arrhenius equation

$$k = Ae^{-\frac{E_A}{RT}}$$

where A is a constant, R is the gas constant and E_A is the activation energy of the reaction. In combustion simulations, a modified version of the Arrhenious equation is normally used.

$$k = AT^n e^{-\frac{E_A}{RT}}$$

where n is a constant. The modified Arrhenius equation is used when describing high temperature gas-phase kinetic systems, like in a combustion process. Thus, every reaction is modelled by three parameters A, n and E_A in combustion simulations. These are then used to find r, which tells how fast the reaction is.

2.4   Reduction and optimization using the ACR method

There are four categories of ways to reduce a mechanism [3]. The first is skeletal reduction where species and reactions are taken away from a detailed mechanism. The new skeleton mechanism is a subset of the original detailed mechanism. The second category is chemical lumping. Similar species or reactions are lumped together to decrease the amount of species and reactions. This category works well at reducing mechanisms meant for large hydrocarbons, as these have a large number of isomers with similar properties. The third category analyses the time-scale of the reactions and couples species together. The fourth category reduces the computational stiffness of the simulation. Stiffness is a measure of how well different parts of a system match regarding to time dependence. In a stiff system the time dependence does not match.

The method used in this project is called Ant Colony Reduction, ACR, [9] and it belongs to the first category of mechanism reduction described above. The method is a semi-stochastic method developed from ant colony optimization, a meta-heuristic optimization algorithm [10, 11]. This means that running ACR multiple times on the same mechanism will produce different skeletal mechanisms of different lengths and accuracy. The program MechMod [14] was used to create a mechanism containing only irreversible reactions using SanDiego as a starting point. This mechanism will later be refereed to as SanDiego-irr. This was done because one of the methods require irreversible mechanisms, but there are reasons to do this anyway. The reversible reactions are, in simulations, two irreversible reactions clumped together. Breaking them apart allows the ACR program to remove one of the reactions, instead of keeping both. The ACR program was used together with two optimization algorithms to improve the response scores of the mechanisms created by ACR. This will later be refereed to as hybrid optimization.

The accuracy of any given mechanism was measured by its response. A mechanism can be used to calculate different properties of a combustion process, like the ignition or the concentration of the species. The response was calculated by taking a normalized root mean square of the properties. The reference values for any given property was set to be the value calculated using the detailed mechanism SanDiego or Aramco, depending on the origin of the mechanism being tested. The root mean square deviation, RMS, can be calculated from

$$RMS = \sqrt{\frac{1}{N} \sum_t^N x_t^2}$$

Where x_t is the difference between the values calculated with the detailed mechanism and the mechanism

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being tested at time t and N is the number of data points. The value from the root mean square was then normalized so that different properties could be compared. The program Chemkin was used as the chemistry solver [15].

3 Method

Two methods to find and create shortcuts in mechanisms was developed. One that uses the symmetry among reactions and one that uses the reaction rates to find shortcuts. The first will be refereed to as symmetry and the second as speed in the following. Both methods belongs to the lumping methods described in Section 2.4. They are described more in their respective sections below. The symmetry method was tested on Aramco, SanDiego and SanDiego-irr with methanol as the fuel, as well on Aramco with propane as fuel. An irreversible mechanism was made of SanDiego, because the speed method requires that the reactions are irreversible. SanDiego-irr was also tested as it was a better comparison for the mechanisms created from SanDiego-irr than SanDiego. Both of the methods are supposed to be applicable on any mechanism and that was the reason for using more than one mechanism. Another reason was that the results from the two mechanisms can be compared for a more accurate representation of the ability of the methods.

The symmetry method was used on SanDiego, SanDiego-irr and Aramco for methanol and only on Aramco for propane. The mechanisms created with the symmetry method will be refereed to with "Symmetry" followed by the name of the original mechanism. For example, the mechanism created by using the symmetry method on SanDiego-irr will be refereed to as Symmetry-SanDiego-irr. The speed method was used on SanDiego-irr for methanol and the resulting mechanism will be refereed to as Speed.

As mentioned in the previous section, ACR is a semi-random process. This means that all mechanisms had to be tested by ACR multiple times. The number of tests was chosen based on experience and time constraints. The Aramco and SanDiego mechanisms was run through the ACR program 17 times each and SanDiego-irr and Aramco was hybrid optimized 16 times. Otherwise all mechanisms where hybrid optimized 12 times for methanol and 8 times for propane. The exception being SanDiego with one extra run because of human error and symmetry on SanDiego where the trend became apparent after 9 runs. Table 1 shows how many times ACR and the hybrid optimisation was used. Symmetry-SanDiego was tested by first running the hybrid optimization on the mechanism and then on the results from the first hybrid optimization. This will be refereed to as Symmetry-SanDiego-Twice later in this rapport. The average length and response from the tests was then calculated and used to compare the different mechanisms.

Table 1: Shows how many times ACR or the hybrid optimization was used on the mechanisms for the two different fuels. The hybrid optimization uses ACR, but the ACR used as a part of the hybrid optimization are not included in the ACR column.

Fuel	Mechanism	ACR	Hybrid optimization
Methanol	SanDiego	17	13
Methanol	SanDiego-irr	0	16
Propane	SanDiego-irr	0	8
Methanol	Symmetry-SanDiego	0	9
Methanol	Symmetry-SanDiego-Twice	0	4
Methanol	Symmetry-SanDiego-irr	0	12
Methanol	Speed	0	12
Methanol	Aramco	17	16
Propane	Aramco	0	8
Methanol	Symmetry-Aramco	0	12
Propane	Symmetry-Aramco	0	8

The two methods have some differences, but also some similarities. As mentioned in Section 2.3, every reaction has three parameters associated with it. While the hybrid optimization program can improve the values, a first guess is necessary. This first guess is generated in the same way for both of the methods when they generate a new reaction from two other reactions. Species that the two reactions have in common are added together if they are on the same side or subtracted if they are on different sides of the reaction. For example, Reactions 2 and 3 have water on the right side of the reaction and none on the left side. A new

reaction created from these two would therefore have two water on the right side of the reaction. Then the constants from the reaction with the smallest rate of production was chosen. The A constant was increased with a factor of $1.6 \cdot 10^4$, because the starting reactions were two-body reactions while the new became a three-body reaction. As mentioned earlier, three-body reactions depends more heavily on the concentration of the species than two-body reactions and the A constant was therefore increased to compensate for this (see Section 2.3). The value of the factor was calculated by taking 0.5% of the concentration calculated from the ideal gas law at 1000 K and atmospheric pressure and then inverting it. The methods do not remove the original reactions. Another similarity between the methods is that they only create shortcuts among species with the same number of carbon atoms as the fuel or less. The reason for this restriction is that the simulations done in this project do not deal with species with longer carbon chains than the fuel. The length limit can easily be changed if the method is to be used in a project where carbon chains longer than the fuel are of interest. This means that the symmetry method was used twice on the Aramco mechanism with different number of allowed carbon. Another restriction on which shortcuts are made is that the shortcuts may not exclude some specific species. The species that were not allowed to be excluded by the methods are H_2O, CO_2, CO, OH and CH_2O. These species are either end-products or their concentrations are important. For example, CH_2O is poisonous and the concentration is measurable in experiments. Which species are important depends on the simulation and the list can easily be changed.

3.1 Reaction symmetry

This method relies on the fact that many species can be transformed into another species in many different ways. An example of this is shown in Figures 1 and 2. Reactions 2 and 3 showed that methanol can react with hydroxyl radicals, but what they did not show was that the products can react again with a hydroxyl radical and create formaldehyde. Methanol has four hydrogen atoms, but the hydrogen is either attached to the carbon or the oxygen. This means that the hydroxyl radical, a radical which needs one hydrogen to form a stable water molecule, can take hydrogen either from the carbon or the oxygen. The product of the reaction can then react with hydroxide again and loose the other hydrogen. Overall the methanol molecule reacts with two hydroxides and forms two water and formaldehyde, but there are two different ways this can happen. This creates a general symmetry that can be seen in Figure 2.
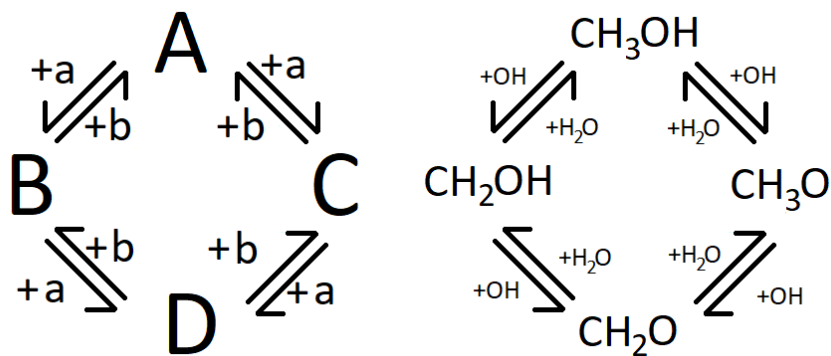

Figure 2: Left shows the general symmetry created by species A reacting with a and forming B+b or C+b. C and B then reacts with a again and forms D+b. The right part shows an example of this symmetry.

The hydroxyl radical is not the only species that can react with methanol. Another example of a species that can react like the hydroxyl radical is hydrogen radical. The difference is that hydrogen gas is created instead of water. The two possible symmetries can be seen in Figure 3. Note that the symmetry from Figure 2 is a special case of the new symmetries when the radicals in all of the reactions are the same. The importance of any reaction depends on the rate constant and the concentration of the species involved in the reaction. The symmetry method finds these places of symmetry and creates a shortcut. When creating the shortcut

reaction the method first creates two support reactions as described in the previous subsection. Then it adds the two reactions together to create the new reaction. The rate of production of the new reaction is the sum of the rates of production from the two supporting reactions. The rate constants is equal to the rate constants of the supporting reaction with the largest rate of production. For example, when the method creates a shortcut from methanol to formaldehyde with the reactions showed in Figure 2. It first creates two supporting reactions, one where CH_2OH is skipped and one where CH_3O is skipped. Both reactions has the same stoichiometric equation, but with different rate constants. Then the new reaction is created by adding the rate of production of the two supporting reactions together.
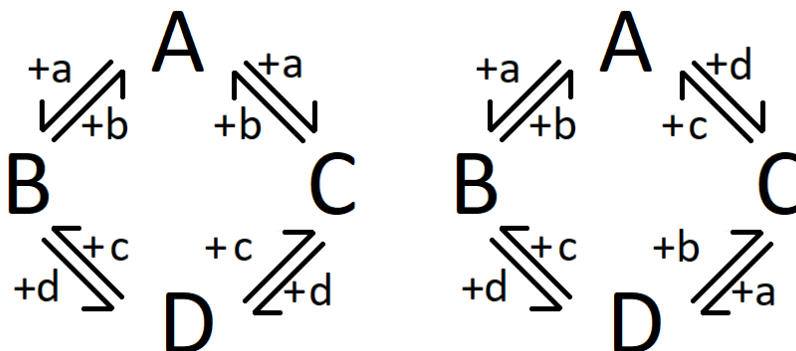

Figure 3: Both panels show variations of the symmetry relation shown in Figure 2.

3.2 Reaction speed

Different reactions have different reaction rates. This method employs the fact that the reaction rate of some reactions are several orders of magnitude larger than others. The method goes through all reactions involving a species. The rate of production from reactions where the specie is a reactant are added together. Reactions with a rate of production that was more than a tenth of the total rate of production was put into a list. The same was done for all of the reactions in which the species in question was produced. If a species had only one reaction in either list then new reactions were created combining the single reaction with every reaction in the other list. This can be seen in Figure 4. This was done for all of the species in the mechanism except those with one carbon atom more than the fuel and the species mentioned at the end of the first section of the method.
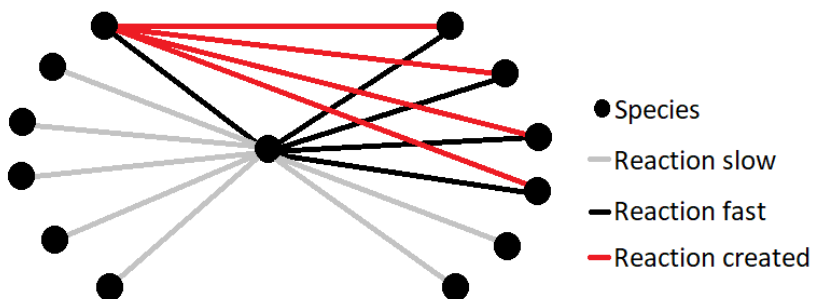

Figure 4: The speed method. The black dots represent species while lines represents reactions. Gray lines are reactions that contributes less than a tenth of the total rate of production, while black lines represents reactions that does. The red lines are the reactions created by the method. The reactions on the left side has the main species as a reactant, while the reactions on the right side has the main specie as the product.

4 Results

The symmetry method was used to create four new mechanisms with the detailed mechanisms as starting points. Symmetry-SanDiego with 446 reactions, Symmetry-SanDiego-irr with 1950 reactions and Symmetry-Aramco with 3548 reactions for methanol and 5453 reactions for propane. The number of species was not changed compared to the original mechanisms. The speed method created a new mechanism with 544 reactions for methanol. The original SanDiego has 268 reactions and SanDiego-irr has 536 reactions. Both has 57 species. The original Aramco mechanism had 493 species and 2716 reactions.

The effect of the optimization in the hybrid optimization was investigated by running ACR and the hybrid optimization on SanDiego and Aramco with methanol as fuel. As mentioned in Section 2.4, ACR is a part of the hybrid optimization and the difference between the two is the optimization algorithms in the hybrid optimization. The results are shown in Figure 5 where each point represents a mechanism of a certain size and response. The mechanisms produced from ACR and the hybrid optimization had, within statistical uncertainty, the same average response and number of reactions for SanDiego. The average length of the mechanisms produced from Aramco was the same, but the average response increased. As mentioned in Section 2.4, the response is a measure of how accurate a mechanism is and a larger response corresponds to a more accurate mechanism. Using a smaller mechanism in a simulation will take less time than a large mechanism. The response and size of a mechanism will therefore give a good estimation of how well a mechanism will work in a simulation.
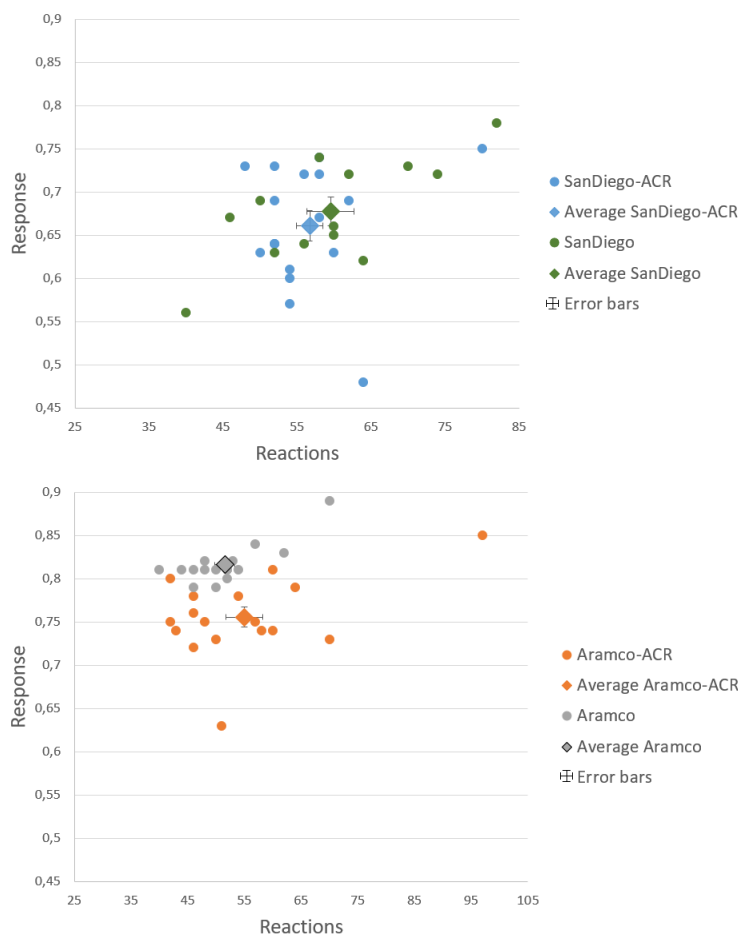

Figure 5: Shows the response and the number of reactions of the mechanisms resulting from running ACR and the hybrid optimization on SanDiego (above) and Aramco (below) with methanol as fuel. The Average of the mechanisms are shown as clover shaped points and the standard error is shown as lines from the

average. The average of the Aramco mechanism has been outlined to increase it's visibility.

The hybrid optimization was used on the mechanisms created by the symmetry method. The mechanisms created by the hybrid optimization was then compared to the mechanisms created with the hybrid optimization from the detailed mechanisms. Methanol was used as fuel. The response and number of reactions in the resulting mechanisms can be seen in Figure 6 and 7. The mechanisms produced from Symmetry-SanDiego had a lower average response and a higher average length than the mechanisms produced from SanDiego. The standard error on the average response of the mechanisms produced from Symmetry-SanDiego when the hybrid optimization was used twice overlaps the standard error from both SanDiego and Symmetry-SanDiego, but the average length was longer than average of the two other. The mechanisms produced by using the hybrid optimization on Symmetry-Aramco had on average more reactions and a lower response than the mechanisms produced from Aramco. The reason that only three mechanisms are presented for Symmetry-SanDiego-irr is that the hybrid optimization was used eight times, but only managed to create three mechanisms. The average length of these three reactions where smaller than the average length of the mechanisms created by the hybrid optimization program used on SanDiego-irr. These mechanisms where shorter than the mechanisms created from SanDiego. The mechanisms from Symmetry-SanDiego-irr had a lower response than the mechanisms from SanDiego-irr and the mechanisms from SanDiego-irr had a lower average response than the mechanisms created from SanDiego.
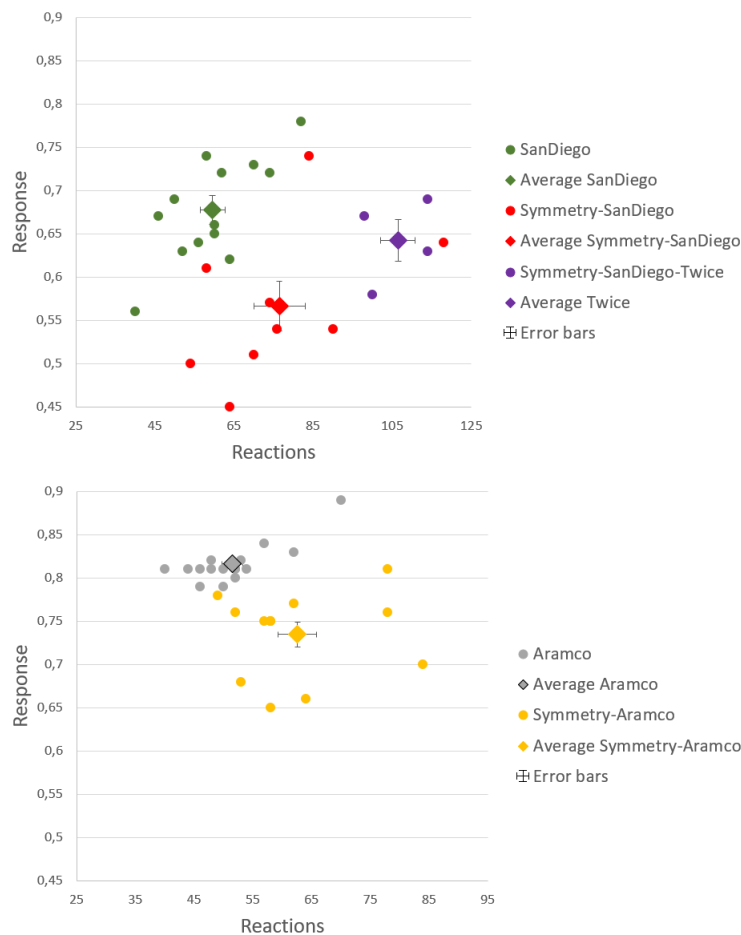

Figure 6: Shows the response and the number of reactions of the mechanisms resulting from using the hybrid optimization on SanDiego and Symmetry-SanDiego above. The hybrid optimization used twice on Symmetry-SanDiego can also be seen above. The response and the length of the mechanisms produced by the hybrid optimization on Aramco and Symmetry-Aramco can be seen below. Methanol was used as fuel.

The Average of the mechanisms are shown as clover shaped points and the standard error is shown as lines from the average. The average of the Aramco mechanism has been outlined to increase it's visibility.
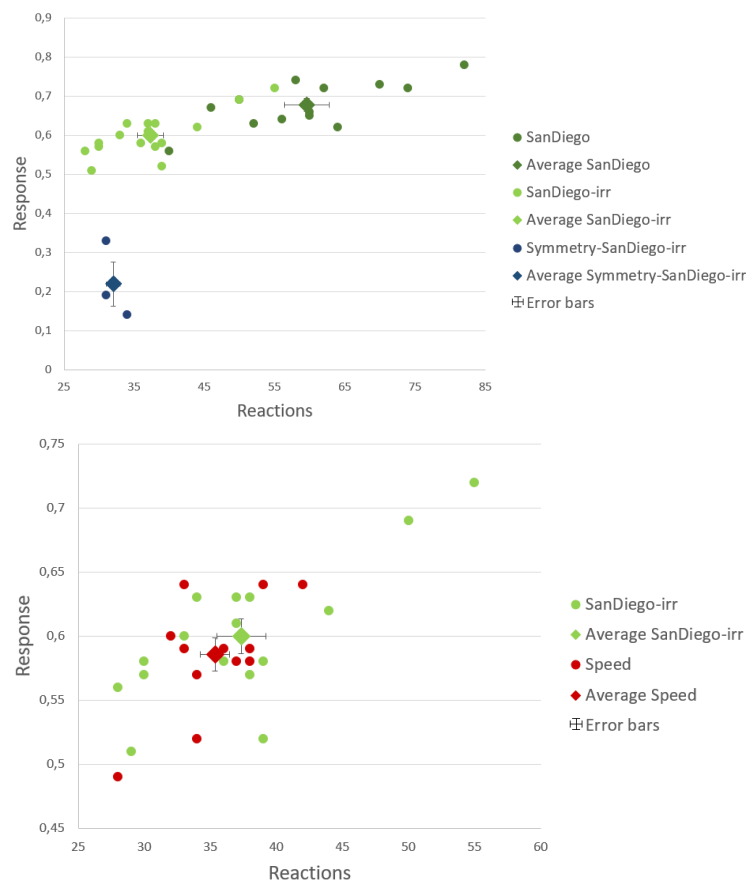

Figure 7: Shows the response and the number of reactions of the mechanisms resulting from using the hybrid optimization on SanDiego, SanDiego-irr and Symmetry-SanDiego-irr (above) and SanDiego-irr and Speed (below) with methanol as fuel. The Average of the mechanisms are shown as clover shaped points and the standard error is shown as lines from the average.

The mechanism created by using the speed method on SanDiego-irr was tested in the same way as the mechanisms created by using the symmetry method with methanol as fuel. The response and the length of the mechanisms created by using the hybrid optimization on Speed and SanDiego-irr can be seen in Figure 7. The average response and the length of the mechanisms created from Speed and SanDiego-irr was, within statistical uncertainty, the same. The hybrid optimization failed to create any mechanisms from Symmetry-Aramco and Symmetry-irr when propane was used as the fuel. The mechanisms created with the hybrid optimization on Aramco for propane had an average length of 300±10 reactions and average response of 0.866±0.003.

5 Discussion

The mechanisms produced by the hybrid optimization had on average a higher or equal response to the mechanisms produced by ACR. The length of the mechanisms produced by the hybrid optimization was equal to the length of the mechanisms produced by ACR. This was expected as the hybrid optimization uses ACR to reduce the mechanisms and then optimizes the mechanisms.

The mechanisms created by the symmetry method gave worse results than the original mechanisms. In fact, the average response were lower and the mechanisms were also on average longer. This is not expected as the hybrid optimization should have been able to create the same mechanisms from the mechanisms created by the symmetry method as from the originals. As mentioned earlier, ACR is a skeletal reduction method and it chooses a subset of reactions to create a new mechanism off. Neither the symmetry method nor the speed method removes any of the original reactions. ACR should therefore still be able to choose a subset of reactions that originated in the original mechanisms. These mechanisms should have the same length and response as the speed and symmetry methods does not change the constants of the original reactions. While there are some data points from the symmetry method which comes close to the original, the averages are in these cases close enough for there to be an overlap. It was also not expected that running the hybrid optimization twice on Symmetry-SanDiego resulted in mechanisms that where longer than if the hybrid optimization was only used once. It is possible that the second optimization could not reduce the mechanisms any further. There were mechanisms from using the hybrid optimization once on Symmetry-SanDiego that had more reactions. It is therefore not unreasonable to think that the mechanisms produced from using the hybrid optimization twice are of equal length as the once produced by using hybrid optimization only once.

The mechanisms produced by using the hybrid optimization on Speed was on average slightly shorter and had a bit lower response than the mechanisms created from SanDiego-irr. However, further testing is required to conclusively determine if the hybrid optimization on Speed results in shorter mechanism than SanDiego-irr. A lager mechanism is bad, while a mechanism with a higher response is good. Increasing the size of a mechanism while decreasing the response can be good, depending on how large the changes are and for what the mechanism is intended to be used. If the mechanisms produced by using the hybrid optimization on Speed are smaller and has slightly less response than the original, then the speed method might be useful.

The hybrid optimization managed to reduce and optimize the Aramco mechanism for propane and it reduced the Symmetry-Aramco mechanisms for methane. It was therefore unexpected that the hybrid optimization would fail to reduce Symmetry-Aramco for propane. This is not only bad because the method failed, but also because lumping methods typically works better on larger fuels. The reason for this might be because the complexity of the system increases with the length of the fuel. Symmetry-Aramco performed worse than Aramco for methanol. Both in length and response and this might been amplified by the complexity. One possible reason for the symmetry methods performance might be that the reactions created by the symmetry method were usually three-body reactions. As mentioned in Section 2.3, three-body reactions depends more on the concentration of the species than two-body reactions. Too compensate for this the A constant for the new reactions were increased, but the increase was based on an estimation. The estimation corresponds to 0.5 % the concentration of a gas at atmospheric pressure at 1000 K. This might be a bad estimation for a number of reasons. The most important one is probably that the concentration of any species varies during the combustion process, while the increase of A was constant. The optimization happens after the ACR and if the ACR does not find anything then it does not happen at all. As stated in Section 2.4, the optimization algorithms are meta-heuristic. This means that they might not have been able to find the optimal value of the constants even if the ACR had worked. The method could therefore probably been improved by a better first guess.

Another thing that might have increased the length of the mechanisms created by the hybrid optimization was that ACR sometimes picked both the shortcut and the reactions from the original that the shortcut was made from. This might not have a large effect on the response, because the optimization could decrease the constants to compensate. However, it would increase the length of the mechanisms. One way to prevent this would be to remove the original reactions in favor of the shortcuts. However, the reason that this was

not done is because some of the original reactions are important. The intent was that ACR would find the important reactions among the original and which could be exchanged with the new shortcuts. If a pattern appeared then the methods could have been changed to replace the unimportant reactions with shortcuts.

The standard error has been used when calculating the error of the averages. This might not be the true error as the length and the response of the mechanisms are not independent. While the dependency between the variables was not strong, it can be seen in Figure 7. The mechanisms created by the hybrid optimization on SanDiego and SanDiego-irr does not gather round the average in a circle, but in an ellipse where the major axis is not perpendicular to the x-axis or the y-axis. Another reason that the shown error might be incorrect is that the ACR gives the best mechanism it could find and the data should have been evaluated according to extreme value theory. As the goal of this project was to evaluate the methods and the results were either clearly distinct from each other or very close together. Changing how the error of the averages was calculated should not change any of the comparisons. Though it should be noted that the error on the average response calculated for Symmetry-SanDiego-irr is probably in the same order of magnitude as the other errors and that the three mechanisms coincidentally had similar lengths.

6 Outlook

This project was a first attempt on creating lumping methods within the bigger reduction project. Both of the methods shows potential, even though they did not give better results than the original mechanisms. The reason for this was that, as mentioned in the Discussion, they can be improved. For example, by improving the first guess of the A constant. The methods could also be better implemented into the ACR program. The mechanisms created by using the hybrid optimization on the Symmetry mechanisms contained both the original reactions and the new shortcuts. One way to prevent this would be to remove the originals, another would be to force ACR to choose between the original and the shortcuts. This was not attempted in this project, because of time constraints and it was outside the scope of the project.

Another idea would be to use the methods on the mechanisms created by the ACR instead of on the detailed mechanisms. This would lead to a more manageable number of new shortcuts and the shortcuts could be tried individually or in small groups. The good shortcuts would then be easier to find, while many of the unimportant shortcuts would never be created because the reactions would have already been removed.

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