Dual Fuel Reaction Mechanism 2.0 including NO\textsubscript{x} Formation and Laminar Flame Speed Calculations Using Methane/Propane/\textit{n}-Heptane Fuel Blends

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Abstract: This study presents the further development of the TU Wien dual fuel mechanism, which was optimized for simulating ignition and combustion in a rapid compression expansion machine (RCEM) in dual fuel mode using diesel and natural gas at pressures higher than 60 bar at the start of injection. The mechanism is based on the Complete San Diego mechanism with \textit{n}-heptane extension and was attuned to the RCEM measurements to achieve high agreement between experiments and simulation. This resulted in a specific application area. To obtain a mechanism for a wider parameter range, the Arrhenius parameter changes performed were analyzed and updated. Furthermore, the San Diego nitrogen sub-mechanism was added to consider NO\textsubscript{x} formation. The ignition delay time-reducing effect of propane addition to methane was closely examined and improved. To investigate the propagation of the flame front, the laminar flame speed of methane–air mixtures was simulated and compared with measured values from literature. Deviations at stoichiometric and fuel-rich conditions were found and by further mechanism optimization reduced significantly. To be able to justify the parameter changes performed, the resulting reaction rate coefficients were compared with data from the National Institute of Standards and Technology chemical kinetics database.

Keywords: dual fuel combustion; methane–propane–\textit{n}-heptane mixtures; ignition delay time; reaction kinetics; reaction rate coefficient; Arrhenius parameter; sensitivity analysis; NO\textsubscript{x}; laminar flame speed

1. Introduction

In the Paris Climate Agreement, it was negotiated that measures have to be taken to keep global warming below 2 °C [1]. To achieve this, a significant reduction of greenhouse gases is required. Electrification in the mobile sector plays a major role in achieving this goal, but also in the field of conventional combustion technology, optimization of existing and development of highly efficient technologies and advanced fuels [2,3] can make an important contribution. For example, in the transport sector, the use of dual fuel engines instead of pure diesel engines offers the potential for emission savings [4]. In the dual fuel combustion process, a mixture of air and natural gas is compressed by the piston and ignited by injection of a diesel pilot. In this operation mode, low-calorie fuel gases such as biogas can be used [5]. For emission reasons, the gas content should be as large as possible in the combustion process. Due to the high global warming potential of methane [6], which is a major component of natural gas, it is essential in dual fuel combustion that methane is completely converted and not emitted unburned. The dual fuel combustion process is very complex and not yet understood in detail.

In [7], the dual fuel combustion process was investigated experimentally and by simulations. Since diesel and natural gas consist of a huge number of different hydrocarbons, the consideration of all species...
in the simulation would lead to an unmanageable simulation time. Therefore, surrogate fuels were defined for the simulation. \( n \)-heptane is a common diesel substitute in dual fuel investigations\cite{8-10} and was used as a surrogate. It is therefore well suited as diesel substitute, since with a cetane number (which describes the flammability of the fuel) of 56\cite{11}, \( n \)-heptane is in the range of the diesel cetane number, which has to be 51 or higher according to the DIN EN590 standard of October 2009. In analogy to diesel fuel, it is necessary to define a substitute fuel for natural gas. A frequently used substitute fuel is methane\cite{8,10}. To better reflect the methane number (which is a measure of the knock resistance) of natural gas, a mixture of methane and propane was defined as a surrogate. In [7], in the first step, the ignition delay times (IDTs) of homogeneous methane–propane–\( n \)-heptane mixtures were investigated with a rapid compression machine (RCM) and a shock tube (ST) at PCFC (Physico Chemical Fundamentals of Combustion), RWTH Aachen\cite{12,13}, followed by the comparison of the measured values with simulation results using various \( n \)-heptane mechanisms available in the literature. For the simulations in [7], as well as the actual study, the program LOGEresearch (Version LSv1.09, LOGE AB, Lund, Sweden)\cite{14} was used. The simulation of the RCM measurements was performed with the module “rapid compression machine” in LOGEresearch at a specific fuel composition, fuel–air equivalence ratio, starting temperature, and starting pressure of the mixture before compression. The RCM facility effects describe the non-ideal behavior of the test facility and the machine-specific compression of the mixture. The effects are considered in the simulation by reading in the effective volume profile derived from the pressure profile of the associated non-reactive RCM measurement in which oxygen was replaced by an inert gas. Details on determining the effective volume curve are available in\cite{12,15}.

As shown on the left side of Figure 1, the IDT is defined as the time between the point when the piston of the RCM reached its end position and the maximal pressure increase due to ignition of the mixture. The simulation of ST measurements was performed with the module “rapid compression machine” too, but with the difference that the temperature and pressure values reached in the ST after the shockwave reflection were used as starting values. The IDT is thus defined as the time difference between the simulation start and reaching the maximal pressure increase due to ignition as shown on the right side of Figure 1. A device-specific pressure increase of 8\%/ms was considered in the ST-simulation. The constant volume (CV) module of LOGEresearch was used to perform CV simulations at specified initial conditions, like pressure, temperature, and simulation time. The IDT definition is identical to that of the ST simulations.

![Figure 1. Simulated pressure curve and ignition delay time (IDT)-definition for rapid compression machine (RCM) (left) and shock tube (ST) (right).](image-url)

When comparing the simulation results using different \( n \)-heptane mechanisms in [7] over the entire parameter range considered, the most promising results were achieved with the Complete
San Diego mechanism with \(n\)-heptane extension [16]. The second step in [7] comprised the study of inhomogeneous mixtures. The investigation of the ignition of a diesel spray injected into air and a natural gas–air mixture experimentally as well as theoretically by computational fluid dynamics (CFD) simulations showed in part large deviations of the IDTs, which motivated the adaptation of the Complete San Diego reaction mechanism with \(n\)-heptane extension. By means of sensitivity and flow analyzes, reactions for the mechanism adaption were identified. The adapted mechanism is able to describe ignition phenomena in the context of natural gas–diesel dual fuel combustion. However, when considering the ignition properties of methane–propane mixtures, it could be established that the IDT-reducing effect of the propane addition to methane was overestimated. This was pointed out in [7], but a detailed treatment had to be postponed to follow-up investigations. Some changes made to the Arrhenius parameters are quite large, resulting in a specific application area of the mechanism. Due to the identified optimization potential in order to obtain a larger parameter range for the application, the mechanism was further developed. The present study deals with the detailed investigation of the kinetic-controlled ignition process focusing on homogenous fuel mixtures in order to avoid a superposition of the actual ignition properties of the mixture with the jet preparation and the non-uniform distribution of the fuel influencing the ignition process in the case of inhomogeneous mixtures. A total of 10 different homogeneous mixtures with various proportions of methane, propane and \(n\)-heptane in the pressure range 60 to 100 bar were investigated. An overview of the mixtures is given in Table 1. Details on the selection of the homogeneous mixtures used are available in [7].

### Table 1. Overview of the homogeneous mixtures used for the optimization of the reaction mechanism including the respective proportion of methane, propane and \(n\)-heptane in the mixture, each in mol\%, the fuel–air equivalence ratio \(\phi\), the pressure \(p\) in bar, and the temperature \(T\) in K.

| Test Facility                      | Fuel Composition | \(\text{p}\) | \(\text{T}\) | Ref.     |
|------------------------------------|------------------|--------------|------------|---------|
|                                    | Mix CH\(_4\) [mol\%] | CH\(_3\)C\(_8\) [mol\%] | C\(_2\)H\(_8\) [mol\%] | \(\phi\) [-] | [bar] | [K] |         |
| Rapid compression machine          | 1 100 0 0        | 0.526        | 100        | 906–941 [13] |
|                                    | 2  95 5 0        | 0.526        | 100        | 888–916 [13] |
|                                    | 3  90 10 0       | 0.526        | 100        | 803–898 [12] |
|                                    | 4  70 30 0       | 0.526        | 100        | 826–865 [13] |
|                                    | 5  92.68 4.88 2.44 | 0.594        | 60         | 701–877 [12] |
|                                    | 6  90.48 4.76 4.76 | 0.661        | 60         | 671–781 [12] |
|                                    | 7  92.68 4.88 2.44 | 0.594        | 100        | 709–817 [12] |
|                                    | 8  97.56 0 2.44  | 0.599        | 60         | 720–869 [12] |
| Shock tube                         | 9  86.36 4.55 9.09 | 0.796        | 60         | 748–1187 [12] |
|                                    | 10 90.91 0 9.09  | 0.816        | 60         | 785–1284 [12] |

### 2. Materials and Methods

The mechanism presented in [7] is based on the Complete San Diego mechanism with \(n\)-heptane extension [16]. As this base mechanism has been expanded since the work presented in [7] and now consists of 303 reactions instead of 301, the most recent sub-mechanism files were downloaded from the San Diego mechanism database (Complete San Diego mechanism CK_2016-12-14, Heptane Chemistry CK_2015-03-01). In addition, the nitrogen sub-mechanism (Nitrogen Chemistry CK_2018-07-23) has been added in order to be able to calculate the formation of NO\(_x\) during combustion. The compound mechanism (MechA) consists of 344 reactions and considers 75 species.

The further development process is explained in the following and is shown graphically in Figure 2. First, the Arrhenius parameter changes made in [7] were transferred to the mechanism MechA. Second, a re-evaluation of the Arrhenius parameter changes was made. In the third step, the overestimation of the IDT-reducing effect of the propane addition to methane was investigated. In the fourth step, the laminar flame speed of methane–air mixtures was simulated and compared with experimental values taken from the literature. Derived from this comparison, the final adaptation of the mechanism was performed. It should be noted that during the whole optimization process the
thermodynamic and transport data remained unchanged and therefore correspond to the original data files of the Complete San Diego mechanism.

**Figure 2.** Schematic representation of the mechanism development process presented in the actual study.

### 2.1. Update of Arrhenius Parameters Adaption

At first, the IDTs were calculated using the compound mechanism MechA (Complete San Diego mechanism, \(n\)-heptane, and nitrogen sub-mechanism). In the next step, the parameter changes made in [7] were transferred to the compound mechanism resulting in MechB. A comparison of the simulated IDTs using MechA and MechB is shown in Figure 3.

**Figure 3.** Experimental data (symbols) [12,13] versus model prediction (lines) using the mechanism MechA (solid lines) and MechB (dashed lines). The respective content of methane, propane, and \(n\)-heptane is given in mol% and corresponds to the values in Table 1.

In the mechanism presented in [7], the Arrhenius parameters of eight reactions were adjusted, including three methane reactions and five reactions of the \(n\)-heptane sub-mechanism. The main target of the adaption was to reduce the difference between the pressure curve (and derived therefrom the point of ignition) measured in a RCEM, operated in dual fuel mode with diesel and natural gas, and the corresponding CFD simulation results. The current study concentrates on the kinetically controlled ignition processes, especially in homogeneous mixtures, in order to exclude influences on the ignition due to inhomogeneities in the fuel–air mixture caused by diesel spray injection. As can be seen in...
Figure 3, the IDT calculated with MechB at an n-heptane content of about 9 mol% is underestimated for a temperature lower than 1000 K in which the reactions of the n-heptane sub-mechanism have a major impact on overall reactivity. Therefore, the changes made in the n-heptane sub-mechanism were re-evaluated. As mentioned before, some of the changes made to the Arrhenius parameters are large and partly outside the range that can be argued with data from the literature, which is an additional reason to re-evaluate the adjustments of all reactions considered.

2.1.1. Update of Methane Reaction Adaption

The methane reactions used for the adjustment in MechB are listed in Table 2. The largest change of the Arrhenius parameters was made in reaction 42. Reaction 44 and 45 were adapted only slightly to fine-tune the mechanism. To compare the reaction rate coefficients before and after adaption with an as large as possible number of reference data from literature, the NIST (National Institute of Standards and Technology) chemical kinetics database [17] was accessed. For reaction 42, 84 database entries [18–90] over the temperature range 178 to 3000 K were used. In the case of reaction 44 and 45, six [68,72,89,91–93] and three [68,72,94] entries, respectively, in the temperature range 300 to 2500 K were available. Using the reference data, the reaction rate coefficients for each data set in the specified temperature interval were calculated with a temperature resolution of 1 K. With these data points, a nonlinear fit based on the extended Arrhenius approach (1):

\[ k = A \cdot T^\beta \cdot e^{\frac{E_A}{RT}} \] (1)

with the reaction rate coefficient \( k \), the pre-exponential factor \( A \), the temperature exponent \( \beta \), the activation energy \( E_A \), the temperature \( T \), and the universal gas constant \( R \), was performed with the program Origin (OriginPro 2017, OriginLab Corporation, Northampton, MA, USA) [95], where Equation (1) has been used in the rewritten form (2):

\[ k^* = \log(k) = A^* + \log\left(\frac{1000}{x}\right)^\beta - \frac{E_A \cdot x}{1000 \cdot \ln(10) \cdot R} \] (2)

with \( x = 1000 \cdot T \) and \( A^* = \log(A) \) for the fitting procedure.

| Reaction Number | Reaction Equation |
|-----------------|-------------------|
| 42              | \( \text{CH}_4 + \text{OH} \leftrightarrow \text{H}_2\text{O} + \text{CH}_3 \) |
| 44              | \( \text{CH}_4 + \text{O}_2 \leftrightarrow \text{CH}_3 + \text{HO}_2 \) |
| 45              | \( \text{CH}_4 + \text{HO}_2 \leftrightarrow \text{CH}_3 + \text{H}_2\text{O}_2 \) |

The effect of adjusting the Arrhenius parameters on the reaction rate coefficients is shown in Figures 4–6. In addition to the reaction rate coefficients, the graphs also show the fit function as well as the 95% prediction band in green and the 95% confidence band in red of the fit function. The confidence band is mostly so narrow that it is usually covered by the fit curve. The data from the NIST database are represented as black open circles. Due to the plot density with a temperature resolution of 1 K, the NIST data points usually appear as black lines.
Figure 4. Comparison of the reaction rate coefficient of reaction 42 (CH$_4$ + OH $\leftrightarrow$ H$_2$O + CH$_3$) of MechA to MechC as well as the fitted rate coefficient using reference data from the NIST (National Institute of Standards and Technology) database.

Figure 5. Comparison of the reaction rate coefficient of reaction 44 (CH$_4$ + O$_2$ $\leftrightarrow$ CH$_3$ + HO$_2$) of MechA to MechC as well as the fitted rate coefficient using reference data from the NIST database.
Due to the difference between the measured and calculated IDT for mixtures containing about 9 mol% \( n \)-heptane (mix 9 and 10 in Table 1), a sensitivity analysis was performed with LOGEResearch using mix 9 to determine the most influential reactions to total reactivity. The starting point of the sensitivity analysis is found in Equation (3):

\[
\frac{\partial Y}{\partial t} = P(Y, u, T) + \omega(Y, T)
\]

where \( Y \) is the \( n \)-dimensional vector of the mass fractions of the \( n \) species considered by the mechanism, \( T \) is the temperature, \( u \) the velocity field, \( P \) represents the spatial differential operator, and \( \omega \) the chemical source term. In the course of the analysis, the influence of a small perturbation of the reaction rate coefficient on the concentration of a selected species is investigated. A detailed mathematical description can be found in [96,97]. All species considered by the mechanism, as well as the temperature, can be selected as an analysis target in LOGEResearch. Since the IDT- and temperature-sensitivity are correlated as shown by Ji et al. [98], the temperature was chosen as the analysis target in this study. For the sensitivity analysis, MechA was used to avoid any influence from the Arrhenius parameter adjustments made. As an example, Figure 7 shows the time-dependent sensitivity curve of reaction 45 (\( CH_4 + HO_2 \leftrightarrow CH_3 + H_2O_2 \)) of MechA to MechC as well as the fitted rate coefficient using reference data from the NIST database.

As can be seen in Figure 4, at temperatures in excess of approximately 400 K, the reaction rate coefficient of reaction 42 in MechB lies within the 95% prediction band of the fit function, but below all reference data. This was due to the fact that the target in [7] was to optimize the mechanism for a specific parameter range. However, since the focus of the current study is on developing a mechanism for a larger parameter range, the parameter adjustments carried out in [7] were revised so that for temperatures higher than 300 K the resulting temperature-dependent reaction rate coefficient of reaction 42 in the resulting mechanism MechC is within the range of reference data. In the case of reaction 44 and 45, only minor adjustments were made for fine-tuning, with the pre-exponential factors \( A \) remaining unchanged, the temperature exponent \( \beta \) being increased and decreased from 0 to 0.02 and –0.05, respectively, and the activation energy \( E_A \) being reduced by 7.7% and 6.7%, respectively, compared to the original parameters of the San Diego mechanism.

2.1.2. Update of \( n \)-heptane Mechanism Adaption

Due to the difference between the measured and calculated IDT for mixtures containing about 9 mol% \( n \)-heptane (mix 9 and 10 in Table 1), a sensitivity analysis was performed with LOGEResearch using mix 9 to determine the most influential reactions to total reactivity. The starting point of the sensitivity analysis is found in Equation (3):

\[
\frac{\partial Y}{\partial t} = P(Y, u, T) + \omega(Y, T)
\]

where \( Y \) is the \( n \)-dimensional vector of the mass fractions of the \( n \) species considered by the mechanism, \( T \) is the temperature, \( u \) the velocity field, \( P \) represents the spatial differential operator, and \( \omega \) the chemical source term. In the course of the analysis, the influence of a small perturbation of the reaction rate coefficient on the concentration of a selected species is investigated. A detailed mathematical description can be found in [96,97]. All species considered by the mechanism, as well as the temperature, can be selected as an analysis target in LOGEResearch. Since the IDT- and temperature-sensitivity are correlated as shown by Ji et al. [98], the temperature was chosen as the analysis target in this study. For the sensitivity analysis, MechA was used to avoid any influence from the Arrhenius parameter adjustments made. As an example, Figure 7 shows the time-dependent sensitivity curve of reaction 274 (\( C_7H_{16} + OH \leftrightarrow HCO + CH_3CCH_3 \)) of the mixture was considered. In the diagram, this is the n-dimensional vector of the mass fractions of the n species considered by the mechanism, as well as the tested species.
274 ($C_7H_{16} + OH \leftrightarrow H_2O + n-C_7H_{15}$). In addition, the pressure curve and the first derivative of the pressure curve is shown. When searching for the maximum positive or negative sensitivity value, only the range of values between the simulation start and ignition (maximum of first derivative of pressure curve) of the mixture was considered. In the diagram, this range is highlighted in blue. The temperature-dependent course of the maximal sensitivity values can be seen in Figure 8 for the 16 most sensitive reactions.

Based on the differences between the measured and calculated IDTs and the course of sensitivities, the changes in Arrhenius parameters made to the $n$-heptane sub-mechanism were re-evaluated. As a result, instead of five $n$-heptane reactions, the number of reactions used for adaptation could be reduced to one lumped reaction (reaction 302 in Figure 8), which considers the branching decomposition $n-C_7-OQOOH \leftrightarrow OH + CH_2O + CO + C_2H_4 + n-C_3H_7$. The change made in this reaction is a reduction of the activation energy by about 1%. A comparison of the reaction rate coefficients of reaction 302 in its original state (MechA), with the parameter changes transferred from [7] (MechB) and after revision of the parameter changes (MechC) is shown in Figure 9. Because this reaction is not included in the NIST database, no comparison with literature data is apparent.
\( n\text{-C}_7\text{OQOOH} \leftrightarrow \text{OH} + \text{CH}_2\text{O} + \text{CO} + \text{C}_2\text{H}_4 + n\text{-C}_3\text{H}_7 \). The change made in this reaction is a reduction of the activation energy by about 1%. A comparison of the reaction rate coefficients of reaction 302 in its original state (MechA), with the parameter changes transferred from [7] (MechB) and after revision of the parameter changes (MechC) is shown in Figure 9. Because this reaction is not included in the NIST database, no comparison with literature data is apparent.

**Figure 9.** Comparison of the reaction rate coefficient of reaction 302 \( n\text{-C}_7\text{OQOOH} \leftrightarrow \text{OH} + \text{CH}_2\text{O} + \text{CO} + \text{C}_2\text{H}_4 + n\text{-C}_3\text{H}_7 \) of MechA to MechC.

### 2.2. Investigating the Influence of Propane Addition

In Figure 3, amongst others, the IDT of a methane–air mixture without propane addition and a propane admixture of 5, 10, and 30 mol% is shown. It can be observed that the deviation between measured and calculated IDTs increases with increasing propane concentration, suggesting that the IDT-reducing effect of the propane addition is overestimated by the mechanism. In order to determine which reactions have a significant effect on IDT in a methane–propane–air mixture, a sensitivity analysis towards temperature was performed with MechA. For the analysis, mix 4 in Table 1 with a propane content of 30 mol% was used. The left side of Figure 10 shows the temperature-dependent progressions of the 10 most sensitive reactions. For the sake of completeness, the measured IDTs and the values calculated with MechA for methane–propane mixtures with 0, 5, 10, and 30 mol% propane content (mix 1 to 4 in Table 1) are shown on the right-hand side of Figure 10.
Figure 10. Sensitivity towards temperature simulated with MechA and mix 4 from Table 1 (left); measured IDTs (symbols) and simulated values (lines) using MechA for different methane–propane mixtures (right). The content of methane and propane is given in mol% and corresponds to mix 1 to 4 in Table 1.

Based on the course of the reaction sensitivities and the temperature-dependent deviation between measured and calculated IDTs for the various methane–propane mixtures, five reactions were selected for the mechanism adaptation. Figure 11 shows an extract of the propane oxidation scheme derived from MechA. The five reactions selected for adaptation, including the OH- and HO₂-radical attack on propane, the oxygen addition on the propyl and hydroperoxyalkyl radical as well as the decomposition of carbonylhydroperoxide, are marked in red. In addition to the corresponding reaction numbers, the species with which the educts react are indicated. All reactions used for the adaption process are summarized in Table 3.

Figure 11. Extract from the propane oxidation scheme derived from MechA. Reactions with modified Arrhenius parameters to improve the calculation of the propane influence on the IDT are labeled in red.
Table 3. Overview of the reactions used to adjust the calculation of the propane influence on the IDT.

| Reaction Number | Reaction Equation |
|-----------------|-------------------|
| 235             | $\text{C}_3\text{H}_8 + \text{OH} \leftrightarrow n\text{-C}_3\text{H}_7 + \text{H}_2\text{O}$ |
| 238             | $\text{C}_3\text{H}_8 + \text{HO}_2 \leftrightarrow n\text{-C}_3\text{H}_7 + \text{H}_2\text{O}_2$ |
| 244             | $n\text{-C}_3\text{H}_7 + \text{O}_2 \leftrightarrow \text{C}_3\text{H}_6 + \text{HO}_2$ |
| 247             | $\text{C}_3\text{H}_6\text{OOH} + \text{O}_2 \leftrightarrow \text{OC}_3\text{H}_5\text{OOH} + \text{OH}$ |
| 248             | $\text{OC}_3\text{H}_5\text{OOH} \leftrightarrow \text{CH}_2\text{CHO} + \text{CH}_2\text{O} + \text{OH}$ |

As described in the previous chapter, reference data from the NIST chemical kinetics database were used, if available, to evaluate the effect of changes in the Arrhenius parameters on the reaction rate coefficients. In the case of reaction 235, six entries [39,79,99–102] were available in the temperature range 250 to 1220 K. For reaction 238, two entries [103,104] could be found in the database for temperature values between 300 and 2500 K. However, for adjusting the Arrhenius parameters of reaction 238, the parameters used in the AramcoMech 3.0 [105] mechanism served as template. In total, nine sources [18,73,103,106–111] were available for comparison purposes for reaction 244 between 296 and 2000 K. No reference data were included in the NIST database for reactions 247 and 248, which is why a graphical comparison with reference data is missing. Therefore, care was taken not to make too large changes to the parameters. The pre-exponential factors and the temperature exponents of the reaction 247 and 248 remained unchanged, the absolute values of the activation energy were increased by 7.1% and 9.3%, respectively. Figures 12–16 shows the temperature-dependent course of the reaction rate coefficients before (MechA) and after parameter adjustment (MechD).

![Figure 12.](image-url)
Figure 13. Comparison of the reaction rate coefficient of reaction 238 ($\text{C}_3\text{H}_8 + \text{HO}_2 \leftrightarrow n\text{-C}_3\text{H}_7 + \text{H}_2\text{O}_2$) of MechA, MechD and AramcoMech 3.0 as well as the fitted rate coefficient using reference data from the NIST database.

Figure 14. Comparison of the reaction rate coefficient of reaction 244 ($n\text{-C}_3\text{H}_7 + \text{O}_2 \leftrightarrow \text{C}_3\text{H}_6 + \text{HO}_2$) of MechA and MechD as well as the fitted rate coefficient using reference data from the NIST database.
2.3. Laminar Flame Speed Calculation

After ignition by injection of a diesel pilot in dual fuel combustion, the flame front spreads into the surrounding natural gas–air mixture in the combustion chamber. To correctly reproduce the propagation velocity of this front, the mechanism must be able to correctly calculate the laminar flame speed. In order to assess the extent to which the mechanism can reproduce the laminar flame speed, a comparison was made between simulated laminar flame speed values of methane–air mixtures (since methane is the main component of natural gas) and measurements taken from the literature.

**Figure 15.** Comparison of the reaction rate coefficient of reaction 247 (C$_3$H$_6$OOH + O$_2$ $\leftrightarrow$ OC$_3$H$_5$OOH + OH) of MechA and MechD.

**Figure 16.** Comparison of the reaction rate coefficient of reaction 248 (OC$_3$H$_5$OOH $\leftrightarrow$ CH$_2$CHO + CH$_2$O + OH) of MechA and MechD.
methane is the main component of natural gas) and measurements taken from the literature. The LOGEResearch module “Freely Propagating” was used to simulate the flame speed. In addition to the gas composition, temperature, pressure, and fuel–air equivalence ratio, the gridding settings must be defined for the flame speed calculation. The grid used consisted of 1000 points with a minimum discretization size of $10^{-9}$ m and a maximum discretization size of $5 \times 10^{-2}$ m. In the simulation, the effect of thermal diffusion was taken into account; the influence of radiation effects was neglected. The experimental determined flame speed values were taken from the supplementary materials of the publication of Ranzi et al. [112]. The gas mixtures investigated include methane–air mixtures with a start temperature of 300 to 400 K in the pressure range of 10 to about 20 bar and a fuel–air equivalence ratio between 0.7 and 1.4. The comparison between measured and calculated laminar flame speeds is shown in Figure 17.

![Figure 17](image-url)

**Figure 17.** Measured laminar flame speeds (symbols) of methane–air mixtures [112] as function of the fuel–air equivalence ratio $\phi$ at different pressures and temperatures in comparison with simulated values (lines) using MechD.

For a fuel–air equivalence ratio of less than 0.9, the experimental values can be reproduced quite well by the simulation. When increasing the equivalence ratio, a deviation between the calculated and measured values is determinable, whereby the simulation underestimates the laminar flame speed. To improve the reproduction of the laminar flame speed, the “Freely Propagating” module from LOGEResearch was used to perform sensitivity analyses using MechD for detecting influential reactions to the flame speed. For each of the five parameter sets shown in Figure 17, a sensitivity analysis was performed and the 10 most sensitive reactions were filtered out. The reactions, which were among the 10 most sensitive reactions for all five investigated parameter sets, are shown in Figures 18 and 19.
Based on the sensitivity progressions and the detected deviations between measured and calculated laminar flame speed, reactions 1, 25, and 56 (listed in Table 4) were selected for the mechanism adjustment.
Table 4. Reactions selected for adjusting the laminar flame speed calculation.

| Reaction Number | Reaction Equation                   |
|-----------------|-------------------------------------|
| 1               | H + O$_2$ ↔ OH + O                  |
| 25              | CO + OH ↔ CO$_2$ + H                |
| 56              | CH$_3$ + H (+M) ↔ CH$_4$ (+M)       |

In the case of reaction 56, not individual Arrhenius parameters were adapted, but the entire data set was changed to the dataset used in the mechanism AramcoMech 3.0, also including the third body collision coefficients and the LOW and TROE parameters. When adjusting the Arrhenius parameters of reaction 1 and 25, a comparison with reference data from the NIST database was made, with 68 entries [68,69,72,73,113–168] for reaction 1 and 83 entries [25,26,36,37,43,51,68,73–75,134,137,140,164,169–219] for reaction 25 available for this purpose in the temperature range 250 to 5500 K and 80 to 3150 K, respectively. Figures 20 and 21 show the reaction rate coefficients before (MechD) and after adaption (TU Wien dual fuel mechanism 2.0) and the reference data from the NIST database. For the adjustment of the Arrhenius parameters of reaction 25, the reaction rate coefficients used in the mechanism of Zsely et al. [220] and Varga et al. [221] served as guideline, therefore the corresponding rate coefficients are presented in Figure 21.

![Figure 20](image.png)

**Figure 20.** Comparison of the reaction rate coefficient of reaction 1 (H + O$_2$ ↔ OH + O) of MechA and TU Wien dual fuel mechanism 2.0 as well as the fitted rate coefficient using reference data from the NIST database.
The comparison of the IDT simulated with the Complete San Diego mechanism with heptane and nitrogen extension (MechA) with the mechanism MechB, in which the Arrhenius parameter changes carried out in [7] were transferred, was already shown in Figure 3. In the following Figure 22, the comparison between the mechanism MechB and the final version TU Wien dual fuel mechanism 2.0 is presented, in which the parameter changes carried out in MechB were re-evaluated, the propane influence on the IDT was corrected and the flame speed calculation was adapted.

3. Results and Discussion

In the course of the mechanism optimization process, in total the Arrhenius parameters of 12 reactions were adjusted. Table 5 provides an overview and a brief explanation why the respective reactions were used for the adaption process and which mechanism resulted from the individual adaptation steps.

Table 5. Overview of the reactions used for the mechanism adaption, the purpose of the adaptation and the resulting mechanism.

| Step | React. | Reaction Equation | Purpose | Mech. |
|------|--------|-------------------|---------|-------|
| 1    | 42     | CH₄ + OH ↔ H₂O + CH₃ | Update of adjustments made in [7] | MechC |
|      | 44     | CH₄ + O₂ ↔ CH₂ + HO₂ |                     |       |
|      | 45     | CH₄ + HO₂ ↔ CH₂ + H₂O₂ |                     |       |
|      | 302    | n-C⁷-OQOOH ↔ OH + CH₂O + CO + C₂H₄ + n-C₃H₇⁻ |                     |       |
| 2    | 235    | C₃H₈ + OH ↔ n-C₃H₇ + H₂O | Correcting propane influence on IDT | MechD |
|      | 238    | C₃H₈ + HO₂ ↔ n-C₃H₇ + H₂O₂ |                     |       |
|      | 244    | n-C₃H₇ + O₂ ↔ C₂H₆ + HO₂ |                     |       |
|      | 247    | C₃H₂OOGH + O₂ ↔ OC₃H₃OOG + OH |                     |       |
|      | 248    | OC₃H₃OOGH ↔ CH₂CHO + CH₂O + OH |                     |       |
| 3    | 1      | H + O₂ ↔ OH + O | Correcting flame speed calculation | TU Wien dual fuel mech. 2.0 |
|      | 25     | CO + OH ↔ CO₂ + H |                     |       |
|      | 56     | CH₃ + H (+M) ↔ CH₄ (+M) |                     |       |

3.1. IDT Calculation with TU Wien Dual Fuel Mechanism 2.0

The comparison of the IDT simulated with the Complete San Diego mechanism with heptane and nitrogen extension (MechA) with the mechanism MechB, in which the Arrhenius parameter changes carried out in [7] were transferred, was already shown in Figure 3. In the following Figure 22, the comparison between the mechanism MechB and the final version TU Wien dual fuel mechanism 2.0 is presented, in which the parameter changes carried out in MechB were re-evaluated, the propane influence on the IDT was corrected and the flame speed calculation was adapted.
3. Results and Discussion

In the course of the mechanism optimization process, in total the Arrhenius parameters of 12 reactions were adjusted. Table 5 provides an overview and a brief explanation why the respective reactions were used for the adaption process and which mechanism resulted from the individual adaptation steps.

| Step | React. | Reaction Equation | Purpose | Mech. |
|------|--------|-------------------|---------|-------|
| 1    | 42 CH₄ + OH → H₂O + CH₃ | Update of adjustments made in [7] | MechC |
| 44  | CH₄ + O₂ → CH₃ + HO₂ | | |
| 45  | CH₄ + HO₂ → CH₃ + H₂O₂ | | |
| 302 | n-C₇-OQOOH → OH + CH₂O + CO + C₂H₄ + n-C₃H₇ | | |
| 2   | 235 C₃H₈ + OH → n-C₃H₇ + H₂O | Correcting propane influence on IDT | MechD |
| 238 | C₃H₈ + HO₂ → n-C₃H₇ + H₂O₂ | | |
| 244 | n-C₃H₇ + O₂ → C₃H₆ + HO₂ | | |
| 247 | C₃H₆OOH + O₂ → OC₃H₅OOH + OH | | |
| 248 | OC₃H₅OOH → CH₂CHO + CH₂O + OH | | |
| 3   | H + O₂ → OH + O | Correcting flame speed calculation | TU Wien dual fuel mech. 2.0 |
| 25  | CO + OH → CO₂ + H | | |
| 56  | CH₃ + H (⁺M) → CH₄(⁺M) | | |

3.1. IDT Calculation with TU Wien Dual Fuel Mechanism 2.0

The comparison of the IDT simulated with the Complete San Diego mechanism with heptane and nitrogen extension (MechA) with the mechanism MechB, in which the Arrhenius parameter changes carried out in [7] were transferred, was already shown in Figure 3. In the following Figure 22, the comparison between the mechanism MechB and the final version TU Wien dual fuel mechanism 2.0 is presented, in which the parameter changes carried out in MechB were re-evaluated, the propane influence on the IDT was corrected and the flame speed calculation was adapted.

Figure 22. Experimental data (symbols) [12,13] versus model prediction (lines) using the mechanism MechB (dashed lines) and the final TU Wien dual fuel mechanism 2.0 (solid lines). The diagram in the upper left corner highlights the comparison between measured and calculated IDTs of methane–propane mixtures. The respective content of methane, propane, and n-heptane is given in mol% and corresponds to the values in Table 1.

By adapting the Arrhenius parameter of the reactions 235, 238, 244, 247, and 248, the TU Wien dual fuel mechanism 2.0 can reproduce the IDT-reducing effect of propane addition to a methane–air mixture well as shown in the diagram in the upper left corner of Figure 22. With the maximum investigated addition of 30 mol% propane, at which a significant deviation between the simulated and measured values was detected before the mechanism adaptation, the calculated values now lie within the uncertainty of the measured values. For the most part, an approximation of the calculated values to the experimental data can also be seen for the other investigated methane–propane mixtures. In the case of mixtures with an n-heptane content of less than 5 mol%, an almost continuous approximation to the experimental values can be observed. Since the n-heptane sub-mechanism changes transferred from [7] were adjusted and approximated to the original parameters of the San Diego mechanism, the simulated IDTs of the mixtures with the highest investigated n-heptane content of approximately 9 mol% show an increase in the temperature range from 850 to 1100 K, whereby the measured values at 950 K are therefore reproduced well, but between 1010 and 1080 K the IDT is overestimated.

3.2. Laminar Flame Speed Calculation with TU Wien Dual Fuel Mechanism 2.0

To adapt the laminar flame speed calculation, the Arrhenius parameters of the reactions 1, 25, and 56 were modified. The changes made had only a marginal effect on the calculated IDTs in the investigated parameter range, therefore the representation of the IDTs calculated with MechD is skipped. By the reaction parameter adjustment, the deviation between the measured and calculated laminar flame speed values could be reduced significantly. A comparison of the simulation results before and after the adjustment of the Arrhenius parameters of reaction 1, 25, and 56 is shown in Figure 23.
3.3. Influence of Nitrogen Sub-Mechanism on IDT and Laminar Flame Speed Calculation

To determine the influence of the nitrogen sub-mechanism on the calculation of the IDT and the laminar flame speed, the nitrogen sub-mechanism was removed from the TU Wien dual fuel mechanism 2.0 for test purposes, followed by a re-run of the simulations. In Figures 24 and 25, the simulation results with the TU Wien dual fuel mechanism 2.0 are shown as lines, the simulation results with the mechanism without the nitrogen sub-mechanism are indicated with symbols.

Figure 23. Measured laminar flame speeds of methane–air mixtures [112] as function of the fuel–air equivalence ratio $\phi$ in comparison with simulated values before (MechD; dashed lines) and after the Arrhenius parameter adaption of reactions 1, 25, and 56 (TU Wien dual fuel mechanism 2.0; solid lines).

Figure 24. IDT simulation with the TU Wien dual fuel mechanism 2.0 (lines) and the TU Wien dual fuel mechanism 2.0 without the nitrogen sub-mechanism (symbols). The respective content of methane, propane and $n$-heptane is given in mol% and corresponds to the values in Table 1.
Figure 24. IDT simulation with the TU Wien dual fuel mechanism 2.0 (lines) and the TU Wien dual fuel mechanism 2.0 without the nitrogen sub-mechanism (symbols). The respective content of methane, propane and \( n \)-heptane is given in mol% and corresponds to the values in Table 1.

Figure 25. Simulated laminar flame speed values as function of the fuel–air equivalence ratio \( \phi \) using the TU Wien dual fuel mechanism 2.0 (lines) and the TU Wien dual fuel mechanism 2.0 without the nitrogen sub-mechanism (symbols).

The comparison shows that the nitrogen sub-mechanism has a negligible influence on the calculation of the IDT in the parameter range under consideration. The same applies to the calculation of the laminar flame speed, where no differences can be seen when the nitrogen sub-mechanism is taken into account or neglected.

It can be stated that by the modification of the TU Wien mechanism for dual fuel combustion presented in [7], the mechanism TU Wien dual fuel mechanism 2.0 was developed, which can reproduce the IDT of the investigated homogeneous methane, methane–propane, methane–\( n \)-heptane, and methane–propane–\( n \)-heptane mixtures in the pressure range 60 to 100 bar well and provides improved results in the calculation of the laminar flame speed of methane–air mixtures. The mechanism and associated transport and thermodynamic files are available online and can be downloaded from supplementary materials.

4. Conclusions

To describe the dual fuel combustion process and the ignition by injection of a diesel pilot into a natural gas–air mixture, the TU Wien mechanism for dual fuel combustion based on the Complete San Diego mechanism with heptane extension was developed and presented in a previous study. With this mechanism, it is possible to reproduce pressure curves measured with a rapid compression expansion machine operated in dual fuel mode using diesel and natural gas, satisfactorily. The mechanism was attuned to the rapid compression expansion machine measurements to achieve a high agreement between experiments and simulations, which results in a specific field of application for the mechanism. In order to simulate the ignition and combustion process within a manageable period of time, diesel and natural gas had to be replaced by substitutes due to the large number of species contained in the fuels. \( n \)-heptane was used as a one-component substitute of diesel, a mixture of methane and propane served as natural gas surrogate.

To obtain a mechanism applicable for a wider parameter range as well as to be able to calculate the formation of NO\(_x\) during combustion, the TU Wien dual fuel mechanism has been extended and further developed, leading to the TU Wien dual fuel mechanism 2.0 presented in this study. The focus in the optimization process was on the kinetically controlled ignition process. Therefore,
the ignition properties of homogeneous mixtures with different proportions of methane, propane, and $n$-heptane were investigated as shown in Table 1, whereby, depending on the composition, the fuel–air equivalence ratio varied between 0.526 and 0.816, the pressure value between 60 and 100 bar, and the temperature ranged from 671 to 1284 K. The simulated values were compared with rapid compression machine and shock tube measurement results. As a first step, the Arrhenius parameter changes made in the previous study were revised to ensure that the reaction rate coefficient changes are supported by literature data taken from the National Institute of Standards and Technology chemical kinetics database. Since the ignition delay time-reducing effect of propane addition to a methane–air mixture was overestimated, by means of a sensitivity analysis using a mixture consisting of 70 mol% methane and 30 mol% propane, reactions with a significant impact on the ignition delay time were determined. By adapting the Arrhenius parameters of five reactions from the propane oxidation scheme, the overestimated ignition delay time-reducing effect of propane addition to methane–air mixtures was corrected.

After ignition by injecting a diesel pilot into the natural gas–air mixture in the dual fuel combustion process, the flame front spreads into the entire combustion chamber. In order to reproduce the flame propagation precisely, the mechanism must be able to correctly calculate the laminar flame speed. Since the background gas in the combustion chamber (mixture of natural gas and air) consists mainly of methane, the laminar flame speed of methane–air mixtures at pressures between 10 and about 20 bar, temperatures of 300 to 400 K and fuel–air equivalence ratios in the range of 0.7 to 1.4 was simulated and compared with experimental values from literature. The comparison revealed an underestimation of the laminar flame speed by the simulation at a fuel–air equivalence ratio higher than 0.9. By means of sensitivity analyses, those reactions were determined, which were suitable for adapting the mechanism in the corresponding fuel–air equivalence ratio range. A total of three reactions were used for the laminar flame speed adaptation process.

In both the ignition delay time calculation and the calculation of the laminar flame speed, a partly significant reduction of the difference between measurement and simulation results could be achieved by adapting the original mechanism. Especially, the improved consideration of the ignition delay time-reducing effect of propane addition to methane–air mixtures should be emphasized. Despite its compactness, the mechanism, which consists of 344 reactions and takes into account 75 species, is able to approximate the ignition delay time well over a large part of the investigated parameter range. With measured values between 0.06 ms and 92 ms, ignition delay times over about three orders of magnitude are covered.

In order not to restrict the possible field of applications of the mechanism by the optimization process, a careful adjustment of the Arrhenius parameters was performed to ensure that the resulting changes in the reaction rate coefficients could be justified by means of literature data. Therefore, more than 200 entries from the National Institute of Standards and Technology database were used to compare the adjusted reaction rate coefficients with data from the literature, where available. By specifying the temperature dependent courses of all modified reaction rate coefficients in this article in comparison to the available reference data, the user of the mechanism is able to determine and assess to what extent the mechanism is suitable for use under the envisaged condition.

**Supplementary Materials:** The following are available online at [http://www.mdpi.com/1996-1073/13/4/778/s1](http://www.mdpi.com/1996-1073/13/4/778/s1), Adapted reaction mechanism and associated thermodynamic- and transport data (ZIP).

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