Predicting flammability limits for hydrocarbon gases and mixtures with nitrogen as inert gas

Master's thesis report
PECT10-3-F19

Aalborg University Esbjerg
Energy

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Titel:
Forudsigelse af brandbarhedsgrænser for kulbrinter og blandinger med nitrogen som inert gas

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31. Maj

Abstract:

At kunne forudsige brandbarhedsgrænser er vigtigt, når det kommer til sikker håndtering af brandbare gasser så som kulbrinter. Teorien omkring detter emne er ikke helt udarbejdet endnu, men der eksisterer nogle teoretiske metoder så som Le Chatelier's blandingsregel. En model var lavet til at forudsige brandbarhedsgrænser for kulbrinter og blandinger med inert gas. Modellen var opbygget som en combustor med masseflowcontrollere til at justere molarfraktionerne af gasserne i blandingen. Blandingen blev andtændt ved brug af en kort puls af hydrogen radikaler. Reaktionsmekanismen brugt i modellen var gri30, siden den har værdier for methan, ethan og propan samt andre gasser som er til stede i forbrænding. Resultater fra moddel blev sammenlignet med eksperimentelle data fra Kuchta og Zhao, og viste at være i stand til at forudsige brandbarhedsegenskaber af mindre kulbrinter, med nogle undtagelser når ethan var til stede.

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STUDENT REPORT

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Predicting flammability limits for hydrocarbon gases and mixtures with nitrogen as inert gas

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Abstract:

Predicting flammability limits of gases is of importance, when it comes to safety, when handling combustible gases such as hydrocarbons. The theory of this topic is not fully explored yet, but some theoretical approaches such as the Le Chatelier's mixing rule exists. A model was made for predicting flammability limits of hydrocarbons and mixtures with inert gas present. The model was build as a combustor using mass flow controllers, to adjust the molar fractions of gases in the mixture. The mixture was ignited using a short pulse of hydrogen radicals. The reaction mechanism used in the model was gri30, as it has properties for methane, ethane and propane along with other gases present in combustion. Results from the model were compared to experimental data from Kuchta and Zhao, and proved to be capable of predicting flammability properties of smaller hydrocarbons, with some exceptions when ethane was present.

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1 Introduction

The flammability limits of gases is an important topic to study, due to its importance in regards to safety conditions for many industrial processes. Flammable gases expose a great danger of igniting, if they are not handled correctly. A lot of data exists for single component gases, however, when a mixture of gases is present, not a lot of data is readily available, as less research has been conducted for mixtures.

When storing flammable gases in a tank, it might sometimes be necessary to vent out some of the gas, to alleviate the pressure inside the tank. If the vented gas is within the range of the flammability limits, it has the possibility of igniting. It is therefore sometimes required, to add inert gas to the vented gas as a safety measure, to prevent ignition from happening. This is an important topic for branches, such as the offshore sector, where safety is very strict, and the danger of a gas igniting could be very destructive. It is important to have a safe way to vent the natural gas extracted at the rig.

The addition of inert gas, and the effect it has on the flammability limits, is still without exact theoretical background, and relies mostly on experimental data. This is especially true for mixtures of gases, where less data is available. It would be favourable, if a general method of predicting how much inert gas is needed, could be developed. In order to do this, it is necessary to gain an understanding of which parameters that has an effect on the flammability limits.

This study explores which methods have currently been used to predict flammability limits. In understanding this it might be possible to use software to develop a general model, instead of relying on experimental data.

1.1 Problem Definition

This study seeks to develop a model capable of predicting flammability limits for hydrocarbon gases as well as mixtures of hydrocarbon gases in air. The model should also be able to include the inerting effect when nitrogen is added to the mixture. This should make the model capable of predicting, how much nitrogen is needed, to inert the gas mixture. The model will be made using Cantera as software, which is an open source software capable of calculating the kinetics for gases and mixtures. The model will be tested with only smaller hydrocarbons these being methane, ethane and propane. Only nitrogen will be used as inerting gas.

2 Literature Study

In order to determine a method for predicting the flammability limits for gas mixtures, it is important to have a good grasp of the concepts, therefore a literature study is conducted in this chapter. The chapter includes a study on flammability limits, and factors that could influence a change in a gas mixtures flammability range.

2.1 Flammability Limits

Flammability limits for gases consist of the lower flammability limit (LFL) and the upper flammability limit (UFL). These two limits define the range of fuel-air composition, for a fixed pressure and temperature, in which an ignition reaction can occur, if an external ignition source is introduced [1]. The flammability limits vary, depending on which combustion gas is present, and the medium it is contained in, for example, the limit range is wider if oxygen is the medium rather than air. It is also known that a stronger ignition source will allow for leaner mixtures to be ignited [1].

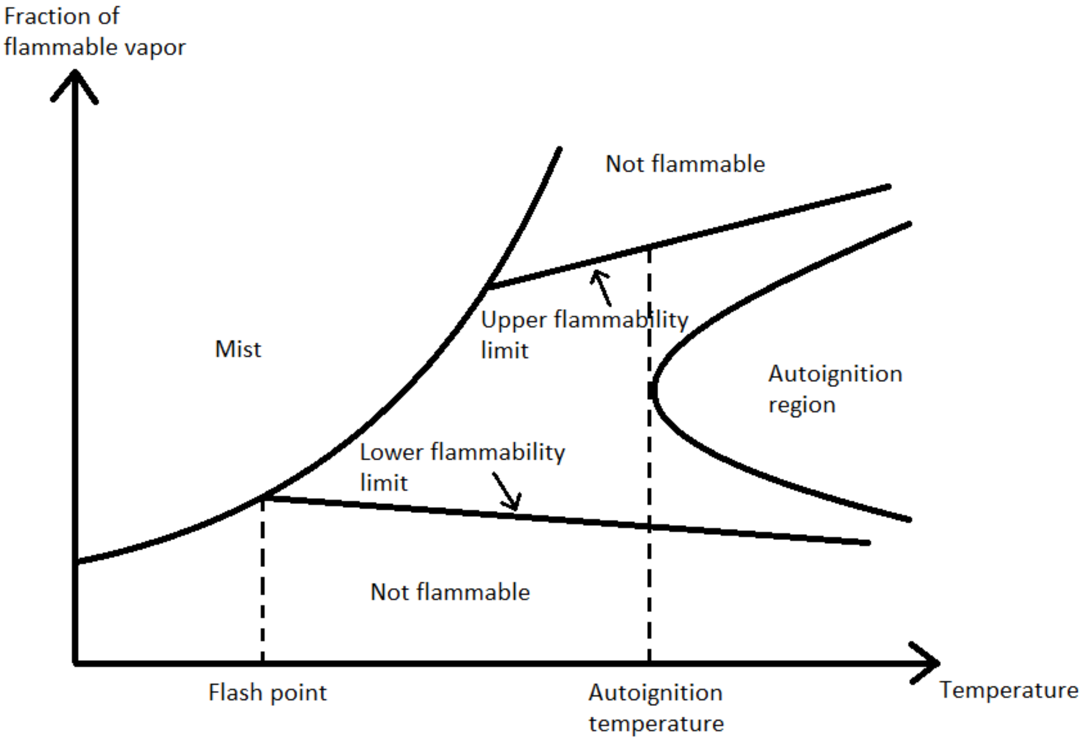

Figure 2.1: Relationship between flammability properties [2].

Figure 2.1 shows the flammability properties of a flammable vapor as the relation between flammable vapor fraction and temperature. The flash point is the lowest temperature at which the material can form a flammable mixture. The lower the flash point is, the greater the fire hazard is. Normally a flammable vapor will not ignite if the temperature is below the flash point, however, if a mist of finely divided droplets of a flammable liquid is formed, it can have the characteristics of a flammable gas and can ignite [3]. When the concentration is between the

LFL and UFL, the mixture can ignite if an ignition source is introduced. If the material is above the autoignition temperature, typically exceeding $700K$, it can spontaneously ignite even without an ignition source.

2.1.1 Lower Flammability Limit

The lower flammability limit defines the minimum combustion gas fraction needed in the fuel-air mixture for the mixture to be flammable. If the fraction is lower than the LFL for the gas, an ignition can not occur. This means that at the LFL the combustion gas fraction is the limiting factor for the ignition reaction. As an example methane-air mixture at $20°C$ has a LFL of 5% [4], so once the methane molar fraction reaches 5%, an ignition can occur if introduced to a source of ignition.

2.1.2 Upper Flammability Limit

The upper flammability limit defines the upper limit of combustion gas fraction for which an ignition can happen. The limiting factor here is the oxygen present in the mixture, which is also the reason that oxygen rich mixtures have wider flammability ranges. If the combustion gas fraction is raised above the UFL, the mixture will become too rich to burn. In the case of methane-air mixture at $20°C$ it has a UFL of 15%, so if the fraction is above this limit the gas will not ignite.

2.2 Properties Affecting Flammability Limits

This section will examine different properties, that have been found in literature to have an effect on the flammability limits of combustible gases.

2.2.1 Temperature and Pressure

It is known from literature that the flammability limits depend on the initial temperature and initial pressure.

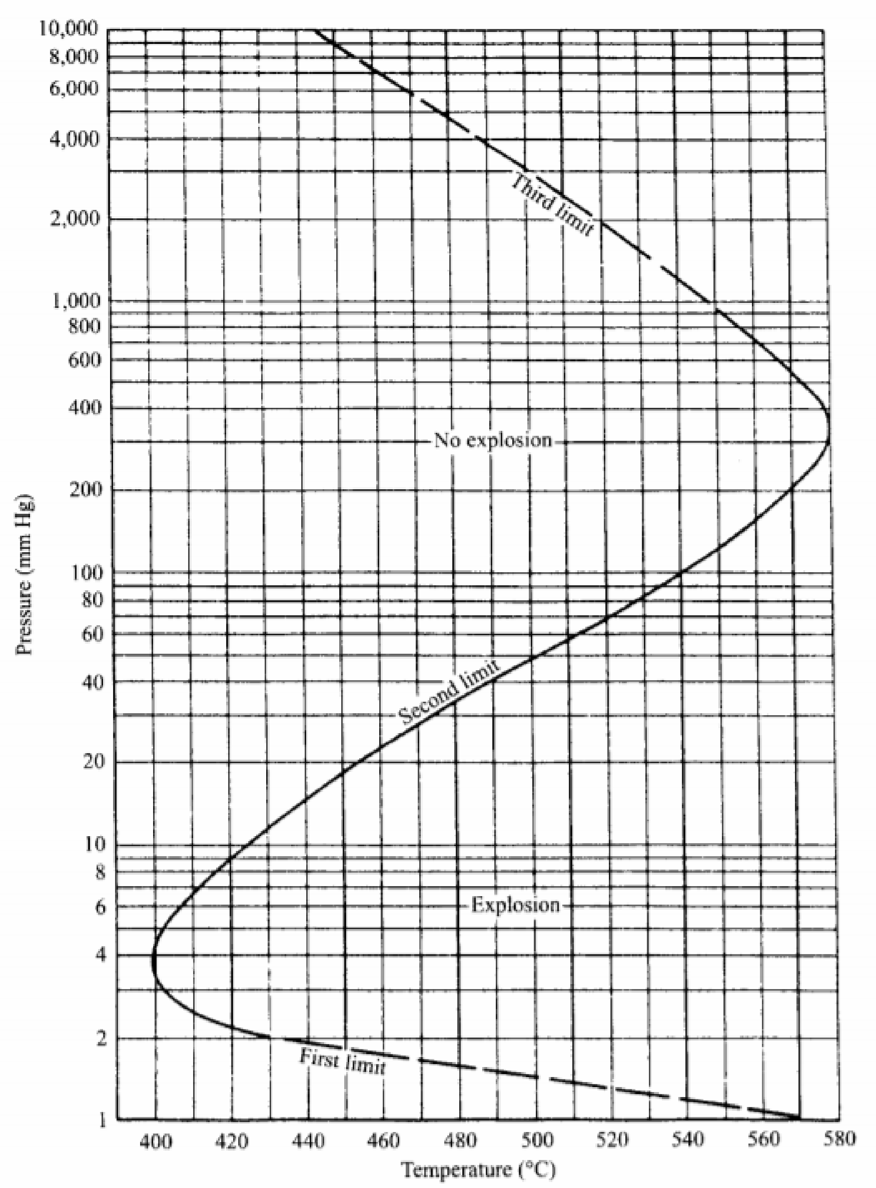

Figure 2.2: Explosion limits for a stoichiometric hydrogen-oxygen mixture in a spherical vessel [5].

Figure 2.2 from Turns shows explosion limits for a stoichiometric hydrogen-oxygen mixture. There are regions of temperature and pressure combinations, where the mixture will and will not explode. The initial temperature is observed to have a linear relation with the flammability limits, where an increase in temperature also increases the range of the limits as seen in figure 2.3 from Vanderstraeten et al. [6, 7, 8, 9].

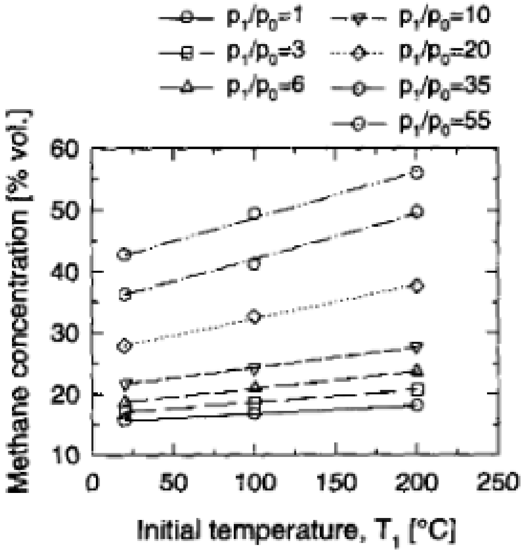

Figure 2.3: Temperature dependence of the UFL of methane-air mixture at different initial pressure levels [7].

Similar to the temperature, an increase in initial pressure widens the flammability limit range, however, instead of being linear, the relation is exponential as seen in figure 2.4 from Vanderstraeten et al. [7, 10].

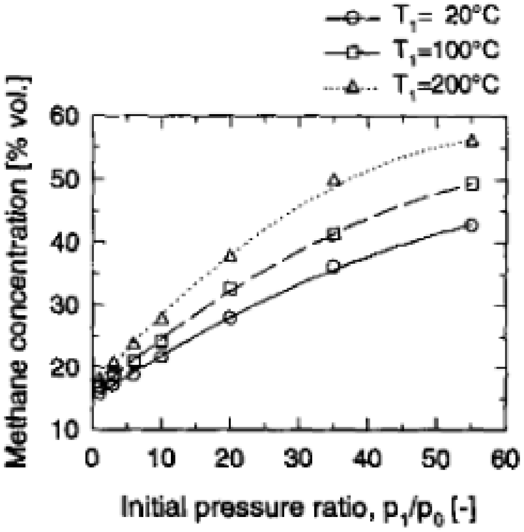

Figure 2.4: Pressure dependence of the UFL of methane-air mixture at different initial temperature levels [7].

Knowing that temperature and pressure have an effect on the flammability limits, it is important to keep these properties constant, when performing tests for flammability limits. Typically tests are performed in room temperature at atmospheric pressure, as these values are the most common of interest.

2.2.2 Oxygen Concentration

Oxygen is one of the most important components when flammability is considered. As mentioned before, having a medium with higher oxygen concentration increases the range of the flammability limits. A minimum oxygen concentration is required, in order for a flame to propagate. This means that reducing the oxygen fraction can be used as a means to prevent fires and explosions from flammable gases. A common method used to reduce the oxygen concentration is diluting the mixture with an inert gas.

2.3 Inert Gas Dilution

As the flammability limits define the range of concentration for which a gas can ignite, it is desired to be able to have the gas outside the flammability limits. One method is to use inert gas dilution, as adding inert gas to a combustion gas will reduce the range of the flammability limits [11, 12]. As the inert gas concentration is increased, the trend for combustion gases and mixtures shows that the UFL is reduced, while the LFL is almost unchanged only increasing slightly as inert gas is added [11, 13, 14]. Eventually the UFL and LFL converge at a point called the fuel inertization point (FIP) or limiting oxygen concentration (LOC), where the mixture is no longer flammable, as there is not enough oxygen for a combustion reaction to happen. Being able to predict the LOC for a gas mixture is very helpful, in order to secure the gas from exploding.
On figure 2.5 from Kuchta [15] the flammability limit curves for various alkane-air-nitrogen mixtures is seen. The figure shows that the flammability limits for the different gas mixtures are quite different, and they also have different LOC.

Inert gases commonly used for this purpose are CO_2 and N_2, where the work of Zabetakis [6] shows that CO_2 has stronger inerting effect than N_2. It is explained that the ratio of inert gas volume percent at inerting point for these two inert gases is approximately inversely proportional to the ratio of their heat capacities at the temperature, at which combustion occurs.
In practice inerting is done by first purging the combustion vessel with inert gas to bring the oxygen concentration below the LOC. Typically the used control point is 4% below the LOC [2]. As an example, if the LOC for a gas is 10%, inert gas must be added until the fraction is 6%, before the flammable gas is charged. Then a control system should be used, to keep the oxygen fraction on a safe level.

2.4 Natural Gas Composition

If the flammability limits for a gas mixture is to be predicted, it is first and foremost important to know the composition of the said mixture. The composition of natural gas from oil rigs depends on the reservoir, it is extracted from. In table 2.1 the composition of Danish natural gas from Energinet is shown, the numbers are taken from January 2019, as it updates monthly [16].

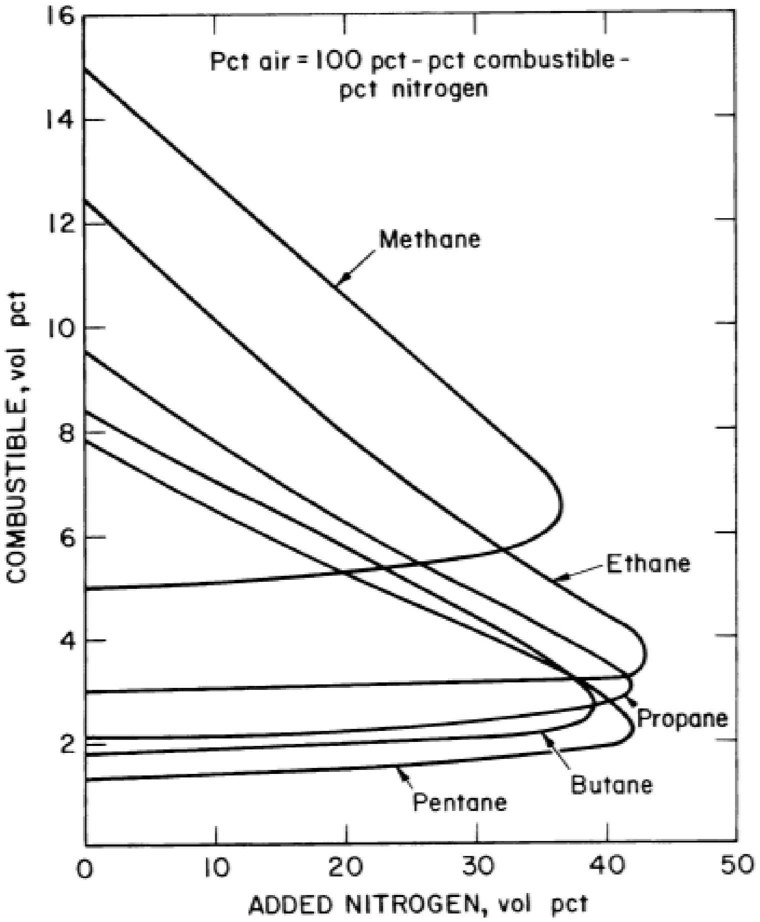

Figure 2.5: Flammability limits of alkane-air-nitrogen mixtures at 25°C and 1 atm.

Table 2.1: Natural gas composition table from Energinet January 2019 given in mole %.

Component	Chemical formula	Average	Range
Methane	CH_4	89.15	86.56-91.62
Ethane	C_2H_6	5.83	5-6.93
Propane	C_3H_8	2.42	1.64-3.17
I-butane	C_4H_{10}	0.39	0.33-0.42
N-butane	C_4H_{10}	0.63	0.48-0.75
I-pentane	C_5H_{12}	0.14	0.11-0.17
N-pentane	C_5H_{12}	0.10	0.07-0.14
Hexane and higher	C_6+	0.06	0.04-0.09
Nitrogen	N_2	0.30	0.26-0.79
Carbondioxide	CO_2	0.97	0.28-1.75

It is evident that the natural gas consists mostly of methane, almost 90% on average, which is also the case for many other reservoirs around the world. The hydrocarbons with more than three carbon atoms make out less than one percent of the composition. It should therefore be considered which hydrocarbons to include when creating a model to predict flammability limits.

2.5 Methods To Determine Flammability Limits

2.5.1 Le Chatelier

The flammability limits of a mixture can be calculated by using Le Chatelier's mixing rule [2]

$$LFL_{mix} = \frac{1}{\sum_i \frac{x_i}{LFL_i}} \tag{2.1}$$

With x_i being the molar fraction of the combustible. Similarly for the upper flammability limit:

$$UFL_{mix} = \frac{1}{\sum_i \frac{x_i}{UFL_i}} \tag{2.2}$$

The standard Le Chatelier's rule does not account for any inerting effect from diluent gases, therefore, in order to calculate flammability limits for mixtures of fuel and inert gas.

In the work by Kondo et al. [12] they modified the Le Chatelier's rule, while considering a mix of one fuel component and one inert component. At the lower flammability limit, since the heat of combustion is zero for the inert gas, the heat of combustion for the mixture can be given as:

$$Q = c_1 Q_1 \tag{2.3}$$

Where c_1 is the fuel gas fraction, Q is the heat of combustion per mole of the mixture and Q_1 is the heat of combustion per mole of the fuel gas. Assuming the heat of combustion per mole of lower flammability limit mixture is the same for the component fuel and the mixture, the following can be written:

$$Q_1 LFL_1 = Q\ LFL = k \tag{2.4}$$

Where LFL_1 is the lower flammability limit of the fuel component and LFL is for the mixture. Substituting this equation into equation 2.3 the following equation is obtained:

$$c_1 LFL = LFL_1 = LFL_{fuel} \tag{2.5}$$

At the upper flammability limit the combustion reaction will no longer be stoichiometric, as fuel is abundant with deficient oxygen. Kondo et al. assumes that the heat of combustion per mole of fuel is constant in the upper flammability limit region of mixtures containing inert gas. They define the oxygen concentration at the upper limit to be $0.21(100 - UFL_1)$ percent. These assumptions give the following equation:

$$Q_1 \frac{0.21(100 - UFL_1)}{n_1} = Q \frac{0.21(100 - UFL)}{n} = k' \tag{2.6}$$

$$Q = \frac{k'n}{0.21(100 - UFL)}; Q_1 = \frac{k'n_1}{0.21(100 - UFL_1)} \tag{2.7}$$

Where n_1 is the moles oxygen consumed by combustion of one mole fuel gas, and n is moles oxygen consumed by combustion of one mole mixture gas. UFL_1 is the upper flammability limit of the fuel component and UFL is for the mixture. Substituting this into equation 2.3 gives:

$$\frac{n}{(100 - UFL)} = \frac{c_1 n_1}{(100 - UFL_1)} \tag{2.8}$$

n can be estimated as $c_1 n_1$, so the upper flammability limit can be calculated as:

$$c_1 UFL = c_1 UFL_1 = UFL_{fuel} \tag{2.9}$$

When comparing the calculated results using equation 2.5 and 2.9 with observed values, it was found that the LFL results had a deviation of 2.5 percent while the UFL had a deviation of 35.1 percent. As the modified rule was not able to accurately predict the UFL, a correction term was made to account for the dilution effect of individual inert gases. The LFL equation added a linear term as the deviation was not too high:

$$\frac{c_1}{LFL_{fuel}} = \frac{c_1}{LFL_1} + pc_{in} \tag{2.10}$$

Where c_{in} is the fraction of inert gas in the mixture and p is a parameter to be experimentally determined. As for the UFL the following expression was developed:

$$\frac{c_1 n_1}{100 - (\frac{UFL_{fuel}}{c_1})} = \frac{c_1 n_1}{100 - UFL_1} + qc_{in} + rc_{in}^2 + sc_{in}^3 \tag{2.11}$$

With q, r, and s being parameters to be determined experimentally as well. Using these two equations compared to observed values showed a deviation in 1.2 percent and 1.1 percent for LFL and UFL respectively. This suggest that an extended Le Chatelier's rule could be used, to predict the flammability limits for mixtures of hydrocarbons and inert gases.

In the work by Zhao and Mannan [14] another modification of Le Chatelier's rule was tested on binary hydrocarbon mixtures with nitrogen as inert gas. The mixtures tested were methane and propane, ethane and propane, methane and ethylene, and ethylene and propylene at molar ratios of 20%/80%, 40%/60%, 60%/40%, and 80%/20%. Using the modified rule the minimum inerting concentration, (MIC), was found for these mixtures, which is the same as the limiting oxygen concentration.
The modification of the rule with dilution of inert gas was done by introducing an inert gas dilution coefficient $\gamma^{L,inert}$ for LFL and $\gamma^{U,inert}$ for UFL. These coefficient are defined as the ratio of change in LFL to the addition of inert gas as volume concentration ΔX:

$$\gamma^{L,inert} = \frac{\Delta LFL}{\Delta X}; \gamma^{U,inert} = \frac{\Delta UFL}{\Delta X} \tag{2.12}$$

Applying the dilution coefficient, the LFL for a hydrocarbon gas mixture with nitrogen as inert gas can be calculated as:

$$LFL_m^{N_2} = LFL_m + \gamma_m^{L,N_2} X_{N_2} \tag{2.13}$$

Where

$$\frac{1}{LFL_m} = \frac{x_1}{LFL_1} + \frac{x_2}{LFL_2} \tag{2.14}$$

And

$$\frac{1}{\gamma_m^{L,N_2}} = \frac{x_1}{\gamma_1^{L,N_2}} + \frac{x_2}{\gamma_2^{L,N_2}} \tag{2.15}$$

$LFL_m^{N_2}$ is the LFL of the fuel mixture with nitrogen and LFL_m is without nitrogen. LFL_1 and LFL_2 are the LFL of the individual fuel gases in the mixture. γ_1^{L,N_2}, γ_2^{L,N_2}, and γ_m^{L,N_2} are nitrogen dilution coefficients on the LFLs for the fuels and mixture. Lastly x_1 and x_2 are the molar fractions of the fuels.
Similarly for UFL the dilution coefficient was introduced, the difference here is the use of molar fraction adjusting factors:

$$\frac{1}{UFL_m} = \frac{x_1^{\alpha_1}}{UFL1} + \frac{x_2^{\alpha_2}}{UFL_2} \tag{2.16}$$

And

$$\frac{1}{\gamma_m^{U,N_2}} = \frac{x_1^{\kappa_1}}{\gamma_1^{U,N_2}} + \frac{x_2^{\kappa_2}}{\gamma_2^{U,N_2}} \tag{2.17}$$

α_1 and α_2 are molar fraction adjusting factors, where $\alpha_1 = \alpha_2 = 1$ when the mixture contains only saturated hydrocarbons. If the mixture contains at least one unsaturated hydrocarbon, the molar fraction adjusting factors will be different from 1. Likewise κ_1 and κ_2 are also molar fraction adjusting factors, that need to be determined experimentally. For the binary hydrocarbon mixtures in the study the factors κ_1 and κ_2 could be simplified to 1.
These adjustments to the Le Chatelier's mixing rule assumes a linear relation between added nitrogen and the LFL and UFL. While this is generally applicable to most hydrocarbons, ethylene showed a non-linear relation in its UFL, so a modification was made:

$$\sqrt{UFL_m^{N_2}} = \sqrt{UFL_m} + \gamma_m^{\sqrt{U},N_2} X_{N_2} \tag{2.18}$$

The minimum inerting concentration, MIC, of the mixtures without ethylene can be found as:

$$MIC_{N_2} = \frac{LFL_m - UFL_m}{\gamma_m^{U,N_2}} \tag{2.19}$$

While the MIC of the mixtures with a significant ratio of ethylene can be found as:

$$MIC_{N_2} = \frac{\sqrt{LFL_m} - \sqrt{UFL_m}}{\gamma_m^{\sqrt{U},N_2}} \tag{2.20}$$

When the results were compared to experimental data, the deviation in MIC for the mixtures without ethylene was < 3%. So a modified Le Chatelier's mixing rule is a good predictor of MIC for saturated hydrocarbon mixtures with nitrogen as inert gas.

3 Method

In this chapter a description of the method, that is used to obtain a model for predicting flammability limits, is presented.

3.1 Model Description

The method used to create this model is a simple combustor. Figure 3.1 shows the setup for the model.

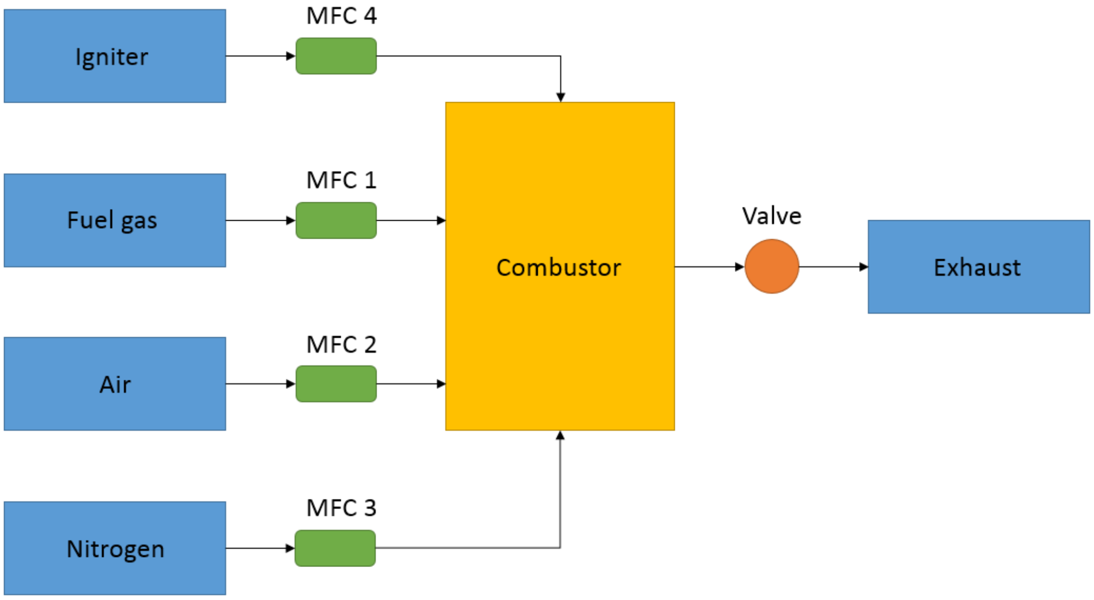

Figure 3.1: Visualisation of the model setup.

The model starts with four different reservoirs, which each holds a different input gas. These gases are the fuel gas, which is the gas whose flammability limits are of interest, the atmospheric air, nitrogen acting as the inerting gas and the igniter gas, which is H atoms.

Each of the input gases are controlled by a mass flow controller (MFC). The first MFC controls how big a percentage of the mixture consists of the fuel gas. The second MFC controls how big a percentage of the mixture is air. The third MFC controls the amount of nitrogen added to the mixture. The fourth and last MFC sends a short pulse of H atoms, this is used to ignite the mixture, as the radicals will react with the oxygen and release a high amount of energy, this energy can then cause the mixture to ignite, if it is within the flammable range.

The next step in the model is the combustor. This is where the gases are mixed in ratios dependent on how the mass flow controllers are configured. The gas mixture is burned in the combustor once the pulse of H atoms is introduced, if the fuel gas is within its flammable range.

Lastly, after the combustor is a valve which is used to keep the pressure constant in the combustor, this is important as the flammability can change with a change in pressure. After the valve is an exhaust, where the gas is let out to complete the process.

When using Cantera the first thing to do is to create an object representing some phase of matter. Since the model uses gases the following object is made:

$$gas = ct.Solution('gri30.cti') \tag{3.1}$$

This creates an object that uses the thermodynamic states, reaction rates and transport properties from the components included in the reaction mechanism (gri30).
This object can then be used to set the states of the gas wanted:

$$gas.TPX = 300, 101325, 'CH4 : 1.0' \tag{3.2}$$

The TPX function sets the temperature, pressure and composition of the gas, in this case the gas is methane at $300K$ and $1atm$. This gas can then be used in any object created, for example a reactor:

$$combustor = ct.IdealGasReactor(gas, volume = 1.0) \tag{3.3}$$

This creates a reactor filled with the chosen gas and sets the volume to one.
The model is set up by creating reservoirs with each input gas respectively. The mass flow controllers take the gas from the reservoirs, and inputs it to the reactor at specified rates. After the reactor the mixture is output to an exhaust reservoir through a valve.
The reaction mechanism used in this model is the gri30 mechanism. This one is chosen, as it is sufficient, when small hydrocarbons are used. Cantera uses this reaction mechanism when solving thermodynamic, kinetics and transport equations for different gases and mixtures as it contains properties used in these equations. The gri30 mechanism contains thermodynamic and transport properties for methane, ethane and propane along with a number of other gases present in combustion processes such as nitrogen, oxygen, hydrogen etc.
The pressure chosen is atmospheric pressure, and this is kept constant throughout the combustion process by using the valve. The initial temperature is set to ambient temperature of $300K$.

The model is used by modifying the inputs in the equations used by the mass flow controllers. The first MFC controlling the fuel gas has the following equation:

$$\dot{m}_{fuel} = n_{total} \cdot x_{fuel} \cdot MW_{fuel} \tag{3.4}$$

Where $\dot{m}_{fuel}$ is the mass flow of the fuel that the controller sends into the combustor, n_{total} is the total amount of moles in the fuel-air-nitrogen mixture, x_{fuel} is the molar fraction of fuel in the mixture and MW_{fuel} is the molecular weight of the fuel gas.
The second MFC controlling the air has the equation:

$$\dot{m}_{air} = (n_{total} - n_{fuel} - n_{N_2}) \cdot MW_{air} \tag{3.5}$$

Here $\dot{m}_{air}$ is the mass flow of air sent to the combustor, n_{fuel} is the moles of fuel in the mixture, n_{N_2} is the moles of nitrogen in the mixture and MW_{air} is the molecular weight of air.
The third MFC controlling the nitrogen added has a similar equation to the first:

$$\dot{m}_{N_2} = n_{total} \cdot x_{N_2} \cdot MW_{N_2} \tag{3.6}$$

Where $\dot{m}_{N_2}$ is the mass flow of nitrogen sent to the combustor, x_{N_2} is the molar fraction of added nitrogen in the mixture and MW_{N_2} is the molecular weight of N_2.

The last MFC uses a gaussian function to supply a short pulse of H atoms to the combustor:

$$\dot{m}_{igniter} = \lambda(t) = A \cdot e^{-\left(\frac{(t-t_0)^2 \cdot 4 \cdot ln(2)}{W^2}\right)} \tag{3.7}$$

$\dot{m}_{igniter}$ is the mass flow of the H atom pulse, A is the amplitude of the pulse, t_0 is the offset time at which the pulse is sent, W is the full width half max value of the pulse. This equation is taken from a Cantera example of a combustor model, as it is not possible to run a Gaussian function in the Cantera version used.

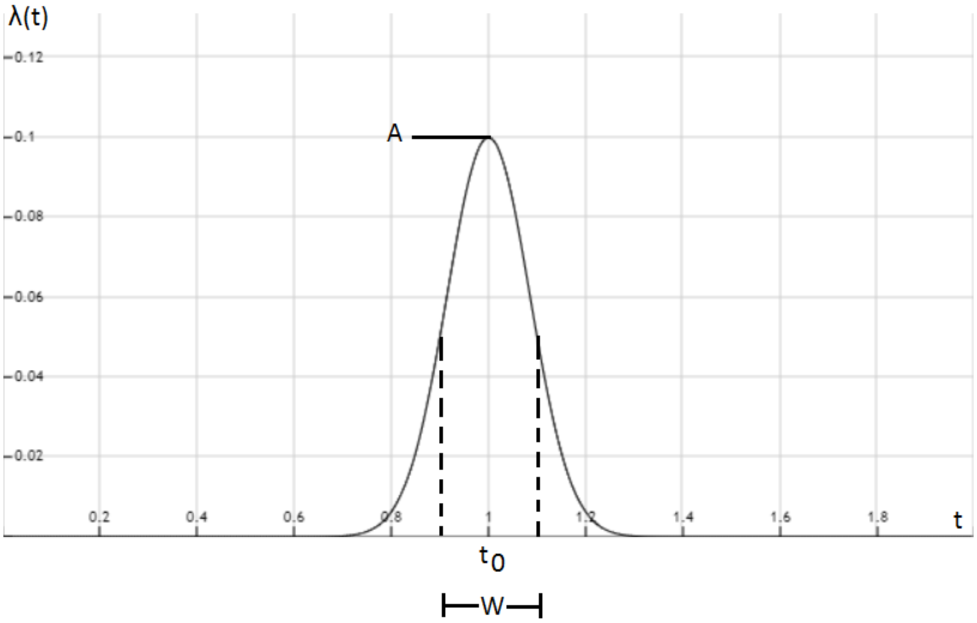

Figure 3.2: Gaussian function used in the model.

Figure 3.2 shows the gaussian function used in the model. It is seen that the igniter will open somewhere around $0.7s$ and reach its peak at t_0 with a value of 0.1 which is the amplitude.

Now the model has all of the inputs for the gases in the combustor. To simulate the combustion it runs a while loop:

$$while\ t_{now} < t_{final} \tag{3.8}$$

Where t_{final} is set to 6 seconds. It sets the temperature to be the temperature in the combustor for the new step. Inside the while loop there is an if condition:

$$if\ |(T_{now} - T_{prev})| > 1.0\ or\ t_{now} - t_{prev} > 2e - 2: \tag{3.9}$$

$$t_{prev} = t_{now} \tag{3.10}$$

$$T_{prev} = T_{now} \tag{3.11}$$

Which says if the difference in temperature or time between the present and previous step are above the given values, the two previous values are set as the new. This is done to set new values for time and temperature for the next step in the while loop.

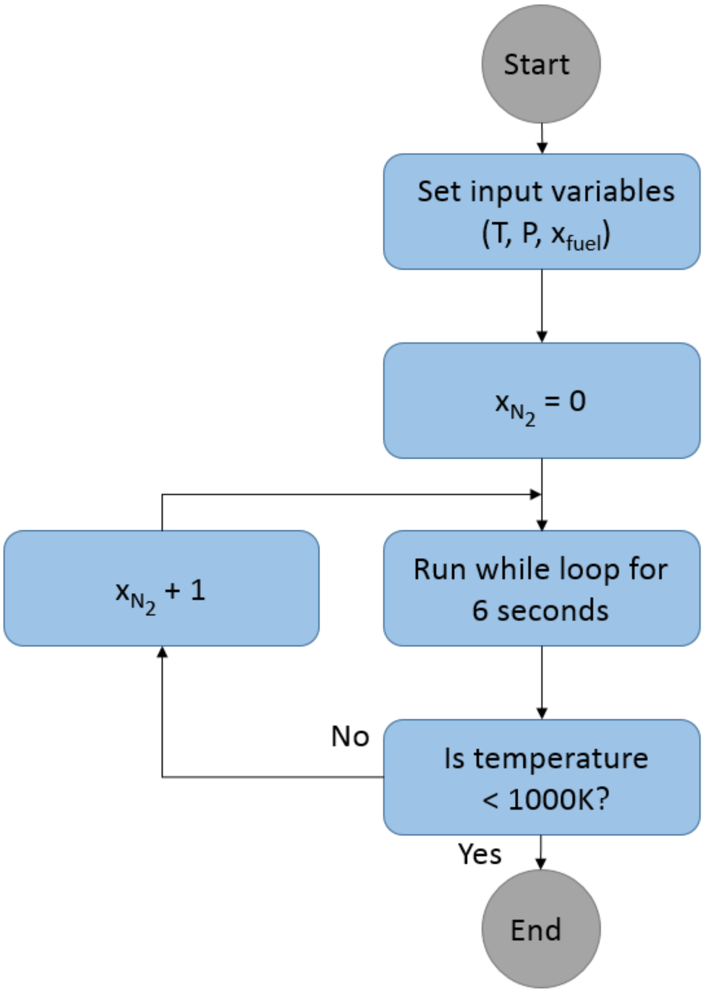

Figure 3.3: Model simulation algorithm.

Figure 3.3 shows how the model simulation is performed. Once the input variables are set, the nitrogen molar fraction starts at zero. The while loop simulating the combustion process is run for 6 seconds. At the end of the while loop the model checks if the temperature is below $1000K$, if it is the simulation stops, if not the nitrogen molar fraction is increased by 1% every step, until the temperature is below $1000K$.

3.2 Test of model

Before using the model to gather flammability data it would be good to verify how the model works with a test. The first test to run is to see if the model can simulate the ignition of the fuel gas. This is tested by using methane as the fuel gas in a methane-air mixture at $300K$ and $1atm$ pressure. The methane fraction is set to 10%, as this should be well within the flammable range according to literature. No diluting nitrogen is added in the first test, since the ignition process is being tested.

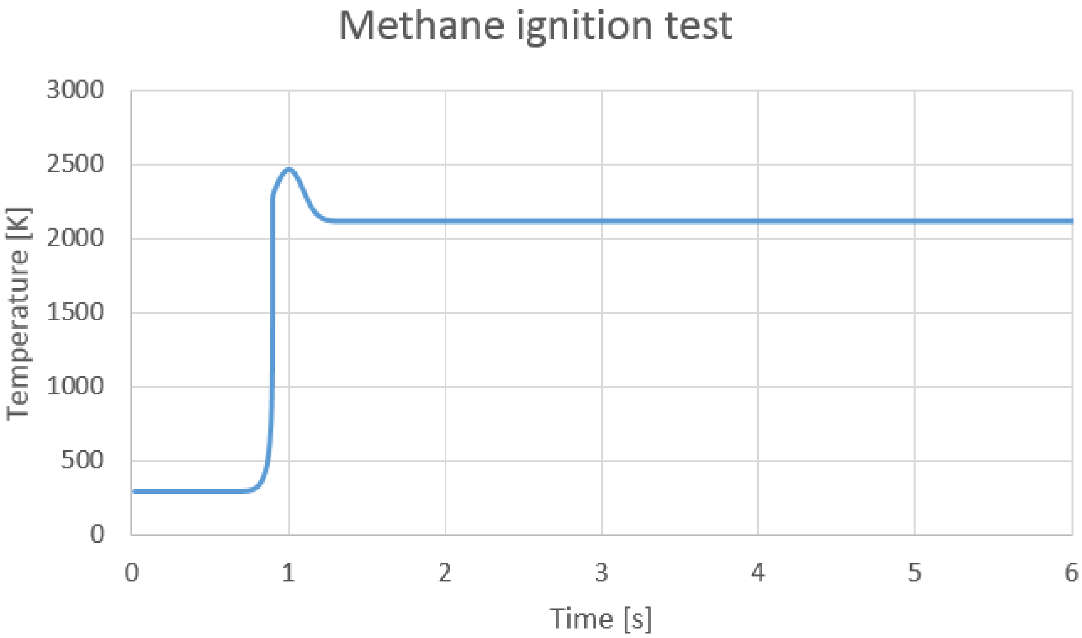

Figure 3.4: Test of methane-air mixture ignition at 10% molar fraction, $300K$ and $1atm$.

Figure 3.4 shows the temperature plot of the combustion process. It starts at the given temperature $300K$ and at the one second mark is where the igniter pulse is introduced, as the t_0 was set to one second. It is seen that the temperature falls a little after the igniter pulse and reaches a steady state at $2120K$, therefore the mixture has ignited, and the test is successful.

The second test to run is to check if the mixture can be inerted by adding nitrogen. This is done, as mentioned in the description of the model, by iterating the nitrogen molar fraction starting from zero, and stopping once the final temperature is below $1000K$. Again the same values will be used for the methane molar fraction, temperature and pressure as in the first test.

Table 3.1: Methane inerting test, temperature and nitrogen molar fraction results.

Nitrogen molar fraction [%]	Temperature [K]
1	2120
2	2077
3	2047
4	2004
5	1987
6	1972
7	1959
8	1946
9	1935
10	1924
11	1914
12	1904
13	1894
14	1885
15	1876
16	1867
17	1858
18	1848
19	1838
20	1827
21	1813
22	1795
23	300

As shown in table 3.1 the inerting value for methane at 10% molar fraction is somewhere between 22% and 23% added nitrogen. This is the case, since the igniter pulse is not able to ignite the inert mixture, so the temperature falls back down to the initial value of $300K$ as is seen in figure 3.5. This shows that the model is also able to simulate the inerting effect of nitrogen on a fuel gas.

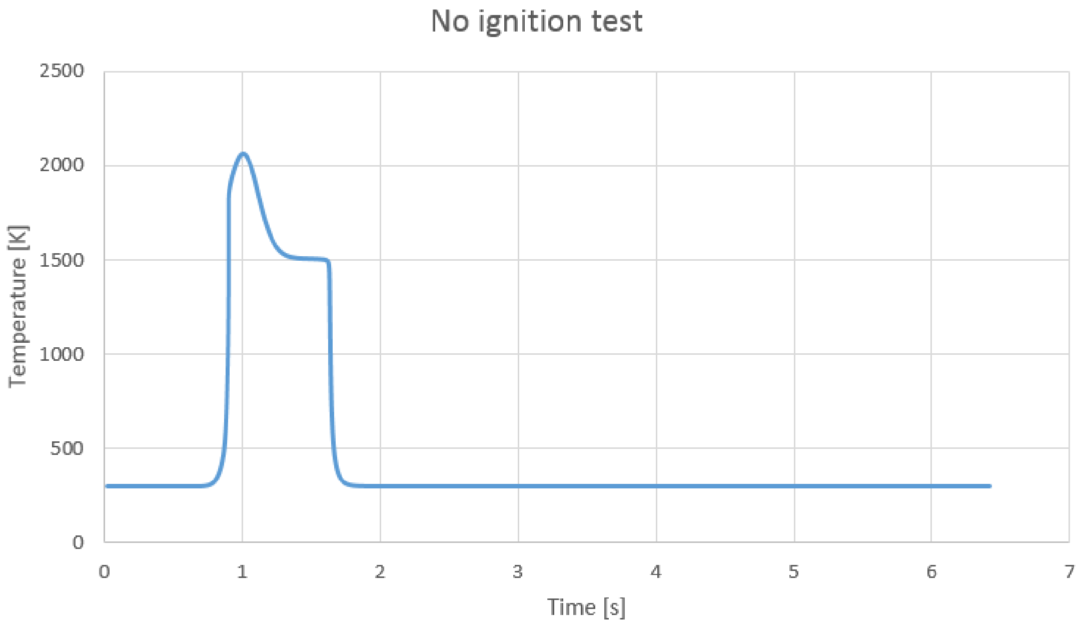

Figure 3.5: Test of methane-air mixture ignition at 10% molar fraction, $300K$, $1atm$ and 23% added nitrogen.

Flammability data is obtained from the model, by manually iterating the fuel molar fraction. A possible further development is making the model able to iterate automatically and produce flammability plots on its own.

4 Results

4.1 Methane

Before testing the models ability to predict flammability limits for mixture fuel gases, it is used to predict the flammability limits for methane in air mixed with nitrogen. This acts as a way to verify the precision on the model compared to existing data. The resulting flammability limit plot for methane in air mixed with nitrogen is seen in figure 4.1.

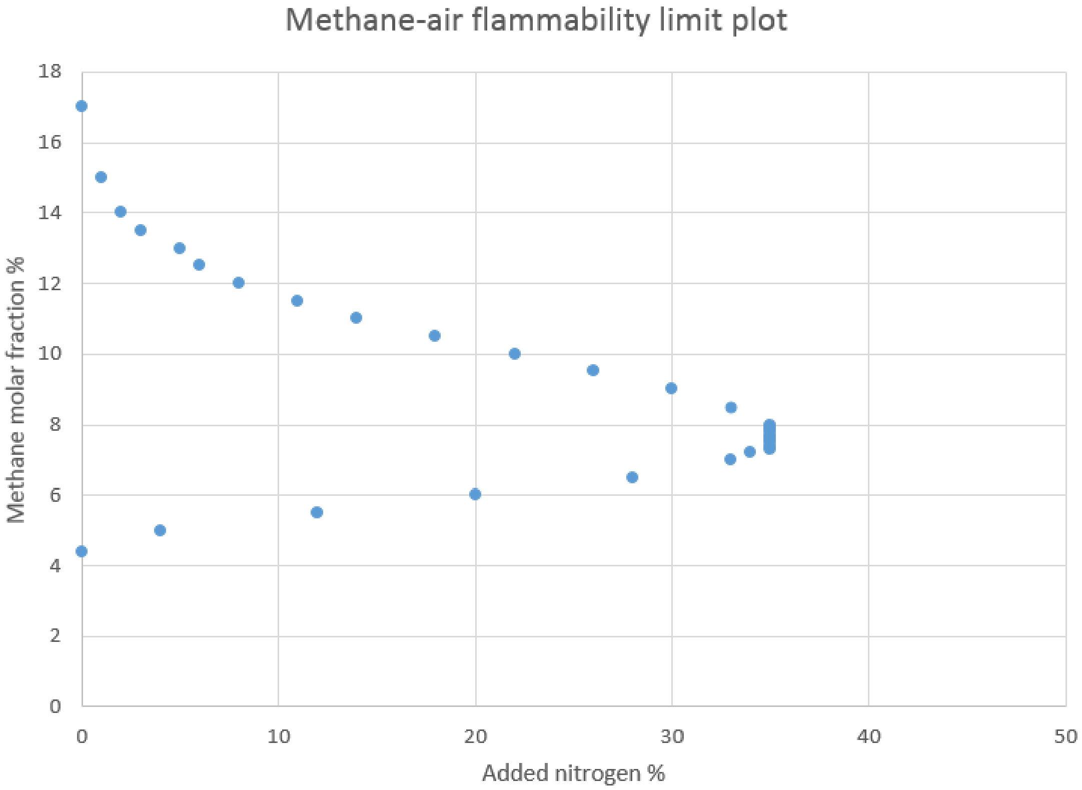

Figure 4.1: Flammability limits for methane-air-nitrogen mixtures at $300K$ and $1atm$.

From figure 4.1 it is seen that when no nitrogen is added to the methane-air mixture, the lower flammability limit is 4.4% and the upper flammability limit is 17% methane molar fraction. The limiting oxygen concentration lies somewhere between seven and eight percent. The reason the tip of the graph looks cut off, is because the model iterates over integers, if the LOC is to be represented more precisely a smaller iteration step is needed at the tip.
To check the models precision, it is compared to another flammability limit plot, figure 2.5 from Kuchta [15].
Figure 4.2 shows the flammability limits of methane from Kuchta and the model plotted together for comparison.

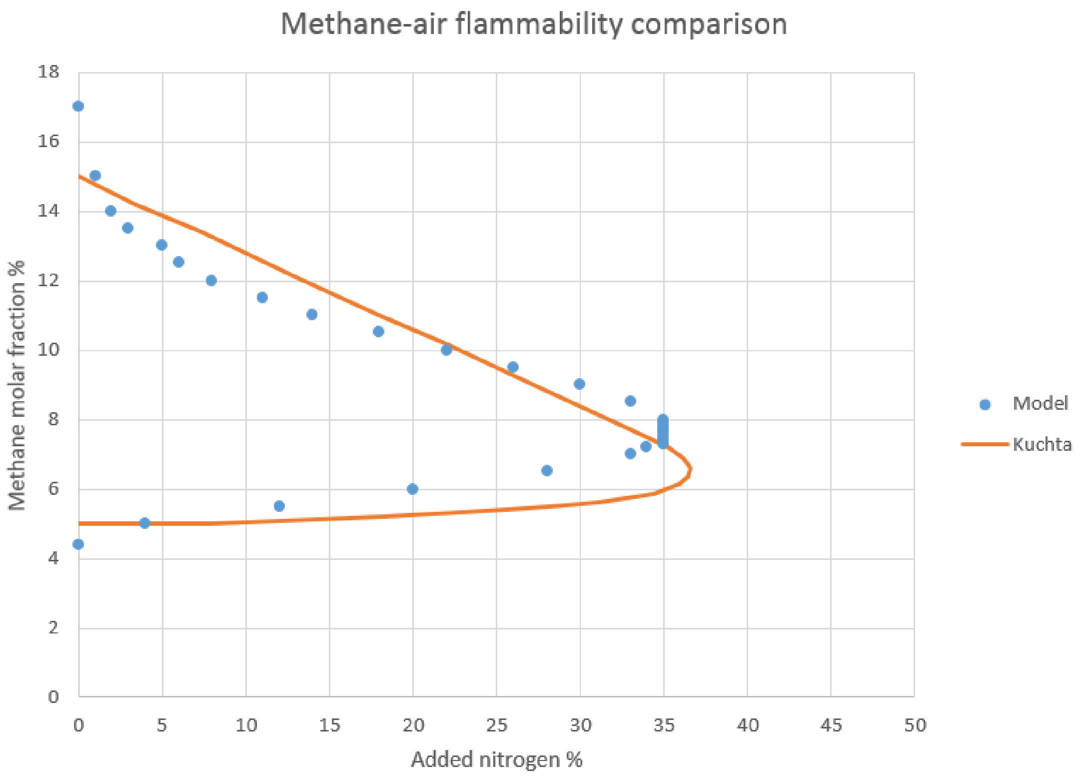

Figure 4.2: Flammability limit plot comparison of methane from Kuchta and the model.

The overall tendency of the plots are similar, where the UFL is the one changing the most and the LOC being around 36% added nitrogen. One thing to note is the flammability limits at no added nitrogen. The LFL from the model is a bit lower at 4.4% compared to Kuchta at 5%. The UFL from the model was 17% where from Kuchta it is 15%. Next thing to note is the point of limiting oxygen concentration. Where the model has a LOC between 7% and 8% methane molar fraction, the plot from Kuchta has a LOC a bit above 6%. The change in the lower flammability limit seems to be higher for the model, when compared to Kuchta.

4.2 Ethane

As the model has shown the capability of producing flammability plots for methane, it is of interest, to check whether it can do the same for larger hydrocarbons. The next fuel gas tested is ethane, where the results from the model are shown and compared to Kuchta in figure 4.3.

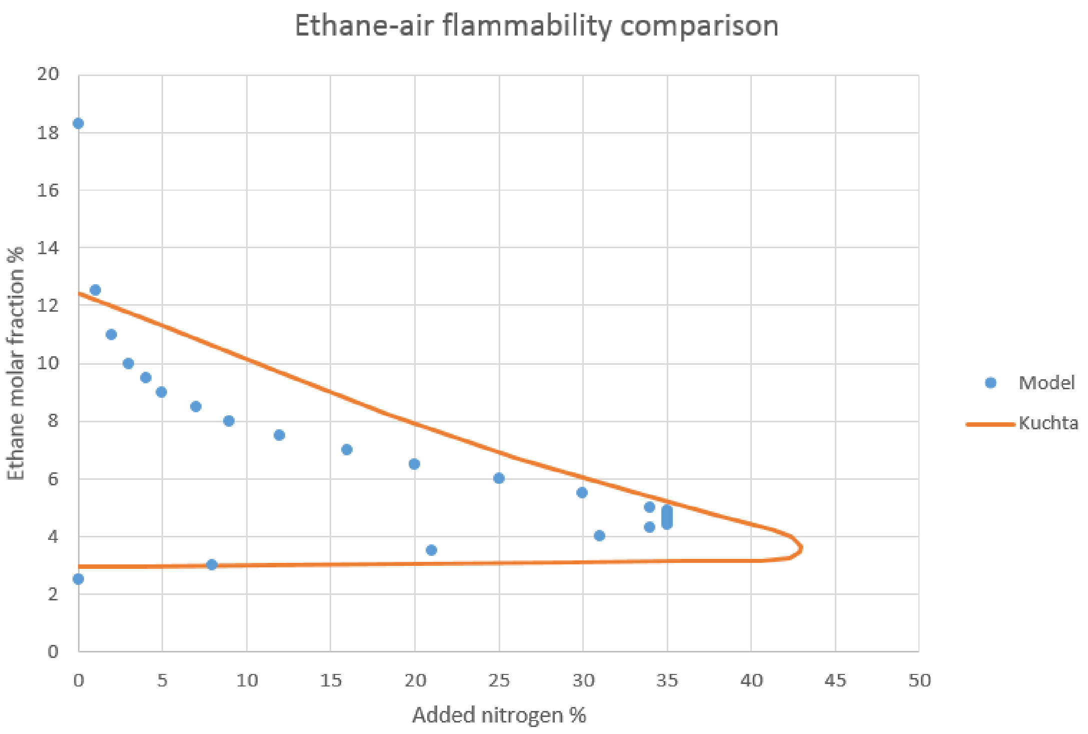

Figure 4.3: Flammability limit plot comparison of ethane from Kuchta and the model.

The flammability plot of ethane from the model has a LFL of 2.5% and a UFL of 18.3%. The LOC seems to be about the same as the models plot for methane around 35% – 36% added nitrogen at a fuel concentration of 4.5%.
The model seems to struggle more with predicting flammability limits for ethane, when compared to methane. The most obvious observation being the UFL of ethane from the model going much higher, than what is found in Kuchta. The LFL, however, are very close when no nitrogen is added. The LOC from the model also deviates from Kuchta, where the model is around 35% and Kuchta is 43% added nitrogen. Similarly to methane the fuel molar fraction at LOC is a bit higher for the model at 4.5% while in Kuchta it is 3.7%.

4.3 Propane

As ethane flammability limits from the model shows higher deviation than methane, it is interesting to see, if this is also true for propane. The plot for propane flammability limits is seen in figure 4.4.

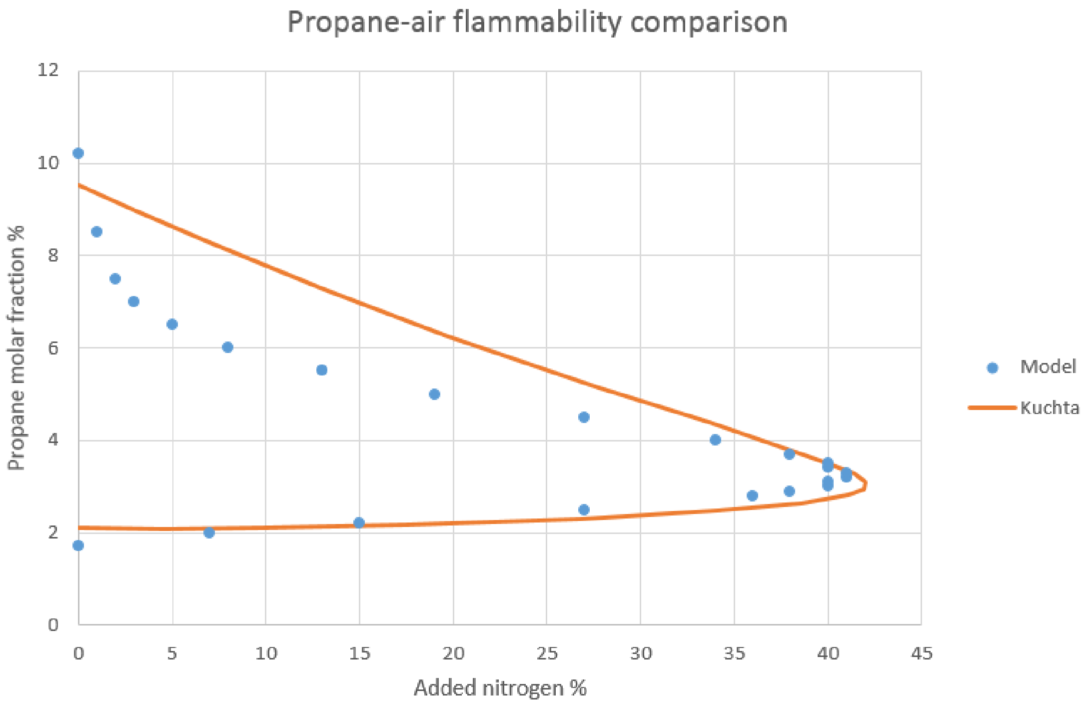

Figure 4.4: Flammability limit plot comparison of propane from Kuchta and the model.

Immediately it is seen, that propane does not have the steep increase in UFL, that ethane has. When no nitrogen is added the LFL here is 1.7% propane, and the UFL is 10.2% propane. The LOC is at 41% added nitrogen with a fuel molar fraction of 3.3%.

The data for the LFL fits very well, but the UFL for the model still fails to capture the linearity shown from Kuchta. The LOC are also very close here with the model being at 41% added nitrogen and 3.3% fuel, and Kuchta being at 42% added nitrogen and 3.1% fuel.

4.4 Binary alkane mixtures

Now that the results for the single fuel gases are presented, it is time to test, how the model handles fuel mixtures. Binary mixtures of methane, ethane and propane are used for this purpose. The mixtures will contain 80% of one component and 20% of another, as these are mixtures that have comparisons in literature.

The first mixture tested is a binary mixture of methane and propane. The fuel mixture ratios tested are 80% methane and 20% propane as well as the opposite ratios. The results from these mixtures are shown in figure 4.5 and 4.6, where the results from the model are compared with experimental results from Zhao [14].

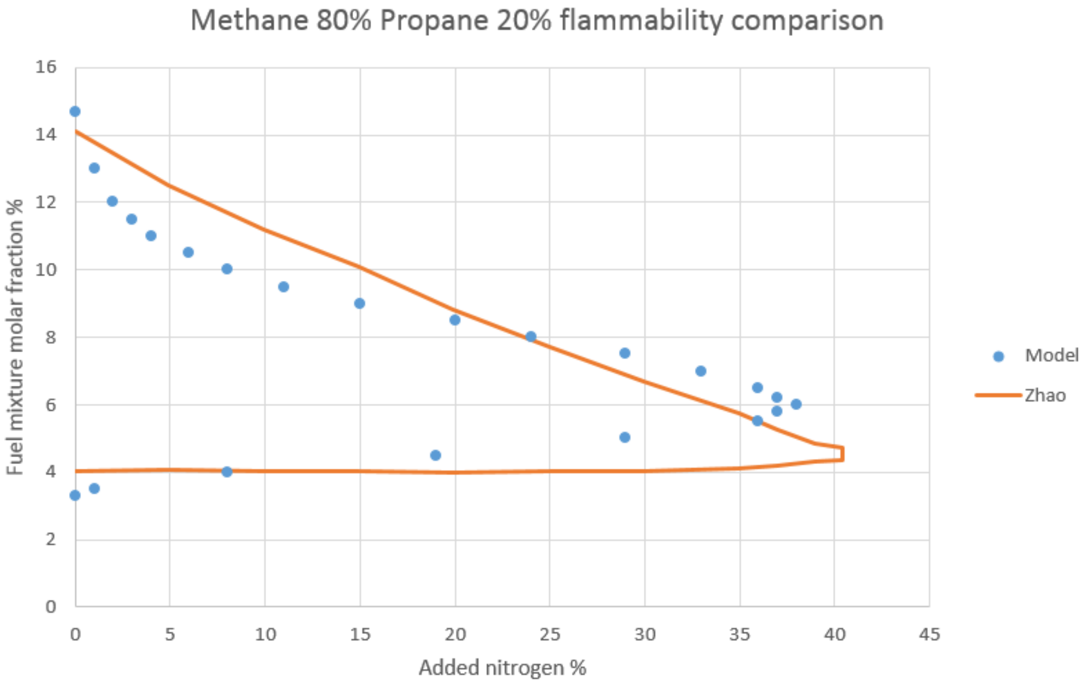

Figure 4.5: Flammability limits for methane80%-propane20%-air-nitrogen mixtures at 300K and 1atm.

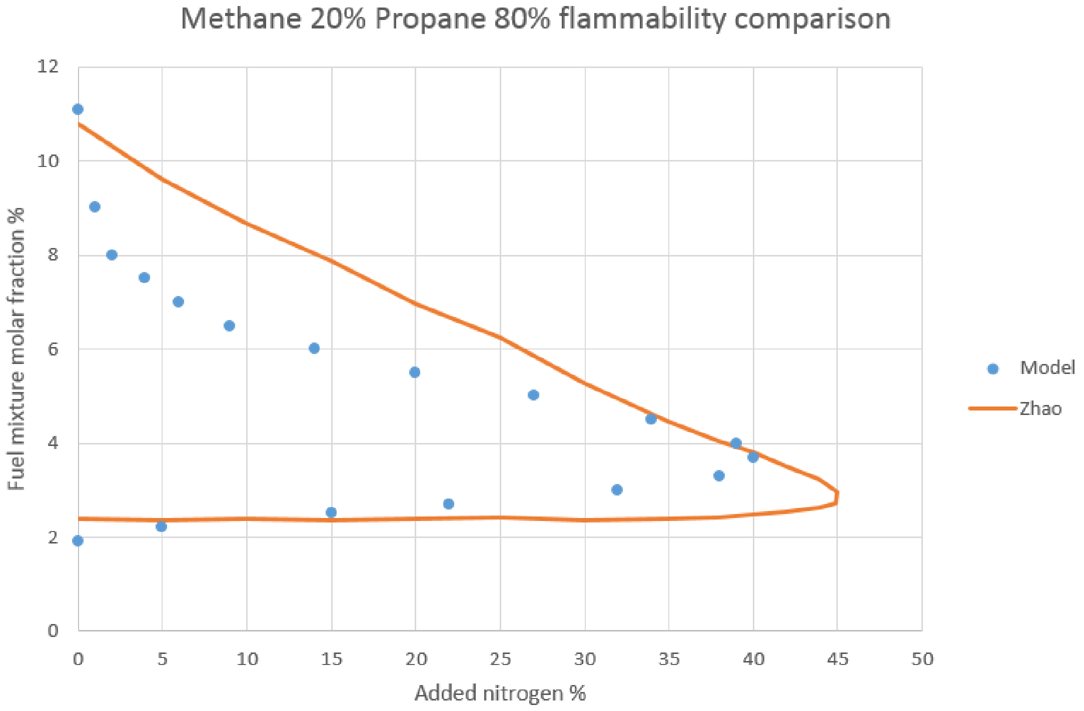

Figure 4.6: Flammability limits for methane20%-propane80%-air-nitrogen mixtures at 300K and 1atm.

From the two figures it is seen, that the flammability limits when no nitrogen is added are fairly close. It still retains the problem from previous tests, where it fails to capture the linearity in UFL. The experimental results from Zhao show almost no change in LFL, until it is close to the LOC, where the model instead shows a linear increase in fuel molar fraction, as nitrogen is added. In both figures the LOC obtained from the model deviates from the experimental data.

The other fuel mixture tested is ethane and propane with the same fuel mixture ratios as methane and propane. The results are once again compared to experimental data from Zhao shown in figure 4.7 and 4.8.

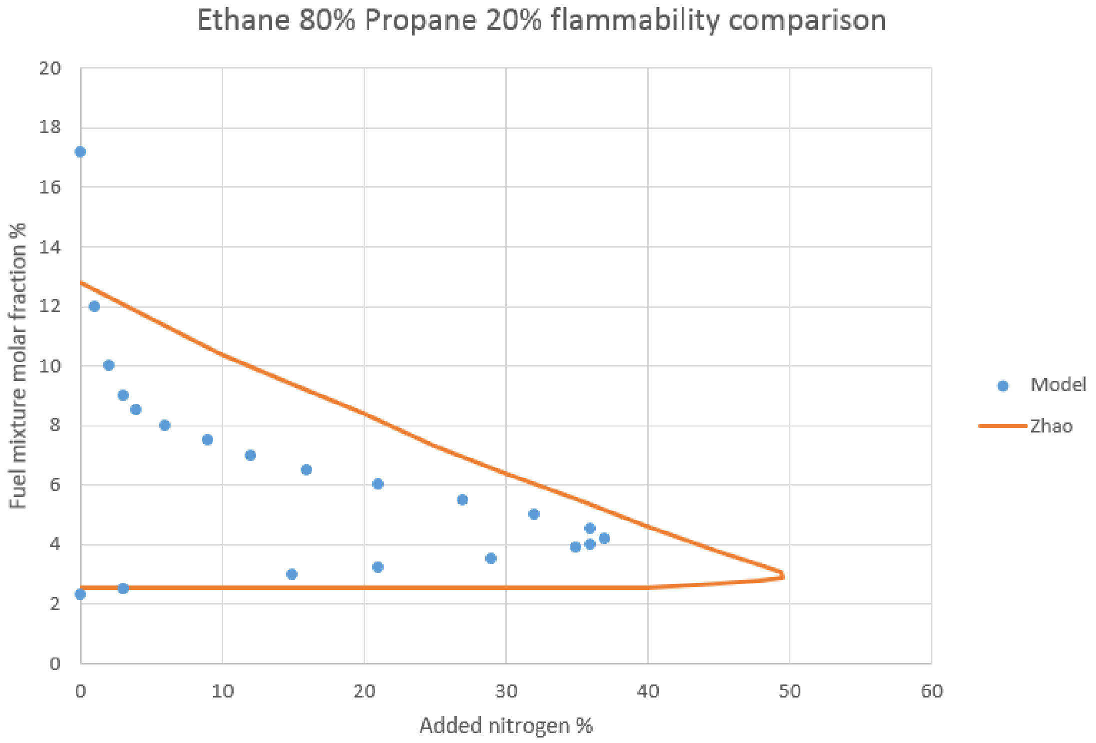

Figure 4.7: Flammability limits for ethane80%-propane20%-air-nitrogen mixtures at 300K and 1atm.

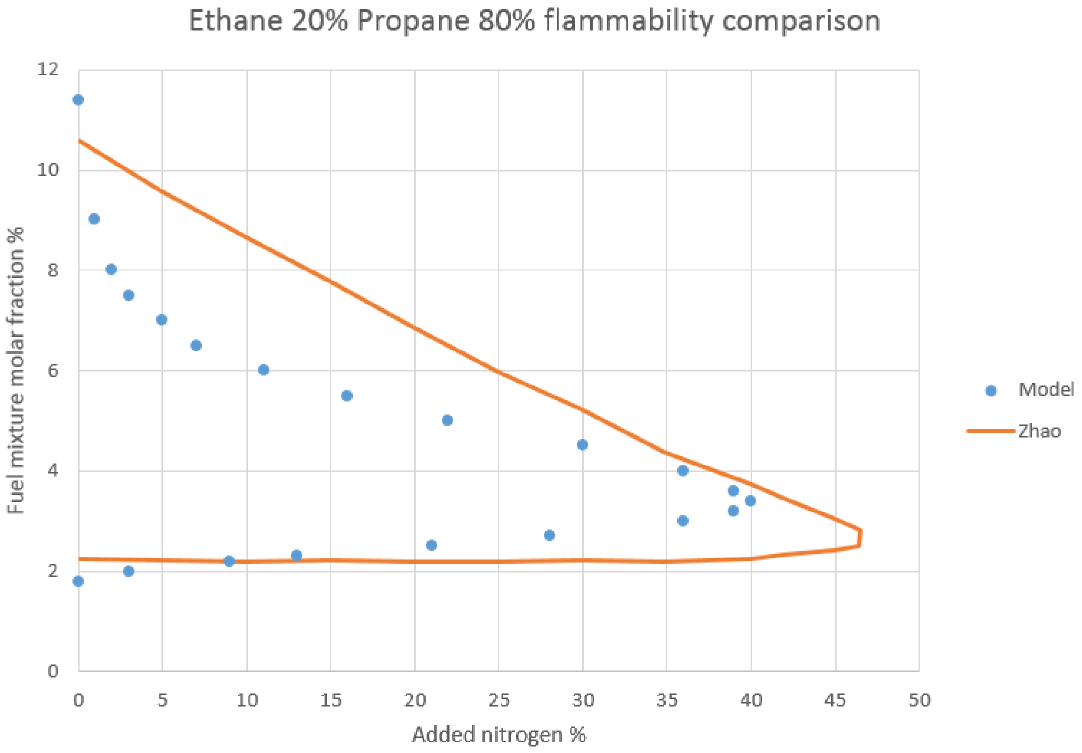

Figure 4.8: Flammability limits for ethane20%-propane80%-air-nitrogen mixtures at $300K$ and $1atm$.

Figure 4.7 shows, as expected, the same faults as in figure 4.3, where the UFL rises much higher than it should, and the LOC remains too low. The results in figure 4.8 have the same tendencies as previous results with non-linearity in the UFL and a linearly increasing LFL. Here the LOC is also lower then experimental data.

Table 4.1: Flammability limits when no inerting nitrogen is added and LOC deviations in molar fraction and % between model results and experimental data for the different fuels.

Fuel gas	Dev. LFL	Dev. UFL	Dev. LOC
Methane	0.6 (12%)	2.0 (13%)	1.6 (4.4%)
Ethane	0.5 (16%)	5.9 (48%)	8.0 (19%)
Propane	0.4 (20%)	0.7 (7.0%)	1.0 (2.4%)
Methane80-Propane20	0.7 (19%)	0.6 (4.3%)	2.4 (6.0%)
Methane20-Propane80	0.5 (21%)	0.3 (2.8%)	5.0 (11%)
Ethane80-Propane20	0.3 (11%)	4.4 (34%)	12.5 (25%)
Ethane20-Propane80	0.4 (20%)	0.8 (7.5%)	6.5 (14%)

Table 4.1 contains the deviations between the model results and existing experimental data. Overall the largest deviations occur in the cases, where ethane is the dominant fuel gas, but only for the UFL and LOC. The binary fuel gas mixtures have a high deviation in LOC. Propane seems to have the lowest overall deviation across the board.

5 Discussion

Using the method described in chapter 3 a model was made to predict flammability limits of hydrocarbons. The results produced by the model showed similar behaviours between the different hydrocarbons and mixtures, with an exception in the case of ethane. When using the model to predict flammability limits for ethane a much higher UFL was found when no nitrogen was added to the mixture. The LOC for ethane was also found to be much lower when compared to existing experimental data from Kuchta and Zhao.

One similarity that all of the results produced by the model shares is the behaviour of the lower and upper flammability limits. The LFL from the model has a small linear increase, where as from experimental data the LFL remains almost constant until shortly before the LOC point is reached. The UFL from the model has a exponential decrease at higher values of fuel molar fraction, and becomes more linear as less fuel is present. The UFL from experimental data on the other hand has a more linear behaviour throughout the data points.

Another shared feature from the model results is having a lower LOC, when compared to experimental data. The point of LOC is also at a higher fuel molar fraction, given the linearly increasing behaviour of the LFL.

Despite these differences in behaviours the model has compared to literature, it is able to closely predict some flammability properties when using methane and propane as fuels, whereas it has difficulties, when it comes to ethane.

It could be of interest to try out different reaction mechanism and see how results from these compare to the results obtained from the gri30 mechanism. Larger reaction mechanisms, such as Aramco, could be used in an attempt to increase the models precision, this would, however, come at the cost of increased computation time. Using other reaction mechanisms could also allow for testing of larger hydrocarbons and mixtures, to see how the model handles these.

Another further development for the model would be to make it iterate automatically over the fuel fraction and have it produce flammability plots simultaneously. This would reduce the manual work required to produce data.

6 Conclusion

The aim of this study was, to develop a model for predicting flammability limits for hydrocarbons and mixtures, with nitrogen as inert gas. A model was made using a simple combustor with mass flow controllers. These control fuel, air and nitrogen molar fractions as well as the pulse of hydrogen radicals used to ignite the mixture. This way it was possible to simulate the ignition of hydrocarbons and mixtures as well as simulating the dilution effect of adding nitrogen to the mixture.

Results obtained form the model were compared to experimental data from Kuchta and Zhao. The model was able to predict flammability limits somewhat precisely for methane and propane, while ethane had some difficulties predicting the upper flammability limit and limiting oxygen concentration. This was also the case when using ethane in a binary mixture with propane.

A method proposed to increase the models precision was to use another reaction mechanism, and see how results from such a method would compare to existing data.

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A Model Python Code

```
import math
import csv
import numpy as np
import cantera as ct
import matplotlib.pyplot as plt

# use reaction mechanism GRI-Mech 3.0

#ReactMech = 'AramcoMech2Chem.cti'
#ReactMech = 'EthaneChem.cti'
ReactMech = 'gri30.cti'
Pressure = 1.0 * ct.one_atm
Temperature = 300.0 # K
gas = ct.Solution(ReactMech)

# create a reservoir for the fuel inlet, and set to pure methane.
gas.TPX = Temperature, Pressure, 'C2H6:1.0'
fuel_in = ct.Reservoir(gas)
fuel_mw = gas.mean_molecular_weight

# use predefined function Air() for the air inlet
air = ct.Solution('air.cti')
air_in = ct.Reservoir(air)
air_mw = air.mean_molecular_weight

# create a reservoir for the nitrogen as inert gas
gas.TPX = Temperature, Pressure, 'N2:1.0'
N2_in = ct.Reservoir(gas)
N2_mw = gas.mean_molecular_weight

# to ignite the fuel/air mixture, we'll introduce a pulse of radicals. The
# steady-state behavior is independent of how we do this, so we'll just use a
# stream of pure atomic hydrogen.
gas.TPX = Temperature, ct.one_atm, 'H:1.0'
igniter = ct.Reservoir(gas)

# create the combustor, and fill it in initially with N2
gas.TPX = Temperature, ct.one_atm, 'N2:1.0'
combustor = ct.IdealGasReactor(gas,volume=1.0)

# create a reservoir for the exhaust
exhaust = ct.Reservoir(gas)

fuel_c = 0.04 #Change this value to set the fuel concentration
#dilution = 23
mol_total = 1

#for fuel_c in range(5, 16, 1):
for dilution in range(0, 61, 1):
    # compute fuel and air mass flow rates
    fuel_mdot = mol_total*(fuel_c)*fuel_mw
    N2_mdot = mol_total*(dilution/100)*N2_mw
    air_mdot = (mol_total-(fuel_c)-(dilution/100))*air_mw

    # create and install the mass flow controllers. Controllers m1 and m2 provide
```

```
    # constant mass flow rates, and m3 provides a short Gaussian pulse only to
    # ignite the mixture
    m1 = ct.MassFlowController(fuel_in, combustor, mdot=fuel_mdot)

    # note that this connects two reactors with different reaction mechanisms and
    # different numbers of species. Downstream and upstream species are matched by
    # name.
    m2 = ct.MassFlowController(air_in, combustor, mdot=air_mdot)

    m3 = ct.MassFlowController(N2_in, combustor, mdot=N2_mdot)

    # The igniter will use a Gaussian time-dependent mass flow rate.
    fwhm = 0.2
    A = 0.1
    t0 = 1.0
    igniter_mdot = lambda t: A * math.exp(-(t-t0)**2 * 4 * math.log(2) / fwhm**2)
    m4 = ct.MassFlowController(igniter, combustor, mdot=igniter_mdot)

    # put a valve on the exhaust line to regulate the pressure
    v = ct.Valve(combustor, exhaust, K=1.0)

    # the simulation only contains one reactor
    sim = ct.ReactorNet([combustor])

    # take single steps to 6 s, writing the results to a CSV file for later
    # plotting.
    tfinal = 6.0
    tnow = 0.0
    Tprev = combustor.T
    tprev = tnow
    #states = ct.SolutionArray(gas, extra=['t','tres'])
    states = ct.SolutionArray(gas, extra=['t','tres','pres'])

    while tnow < tfinal:
        tnow = sim.step()
        tres = combustor.mass/v.mdot(tnow)
        Tnow = combustor.T
        pres = combustor.thermo.P
        if abs(Tnow - Tprev) > 1.0 or tnow-tprev > 2e-2:
            tprev = tnow
            Tprev = Tnow
    #        states.append(gas.state, t=tnow, tres=tres,Pres=p)
    #        states.append(gas.state, t=tnow, tres=tres)
            states.append(gas.state, t=tnow, tres=tres, pres=pres)
    if Tnow < 1000:
        break

    states.write_csv('combustorTC.csv', cols=('t','T','pres','tres','X'))
    print(Tnow,dilution)

print(fuel_c, dilution)
```