Correlation of Flammability Limits to Laminar Burning Velocity

Matthew Pletcher

Purdue University, Chemical Engineering – CHE 411 Research

Mentored by: Dr. Ray Mentzer, Silvio Esterellas (ExxonMobil), &

Zhiyan Wang (ExxonMobil)

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Executive Summary

This research report examines the correlation of lower flammability limits (LFLs) to the adiabatic flame speed of fuel-air mixtures. 16 species were evaluated at ambient pressure, and 3 species were evaluated at elevated pressure. Flame speeds and compositions were found using a Python program known as Cantera, with various mechanisms to model the combustion of different fuel mixtures.

The model was first validated by generating flame speed graphs and comparing them to empirical correlations found in literature. Model data was found to have low deviation from literature correlations, especially at the lower end of the flammability graph. Since the LFL correlations occur at low flame speeds, the model suggests high accuracy at this range of data.

Flame speeds of 0 cm/s, 2 cm/s, 4 cm/s, and 5 cm/s were selected as options for ideal flame speed, and the compositions for each fuel-air mixture were determined at these speeds for each species studied. These values were then compared to the chemical's LFLs, and the percent deviation from the LFLs were calculated. These deviations were averaged to yield a percent deviation per chemical species, and the flame speed with the lowest deviation became the choice for ideal flame speed.

At ambient pressure, the ideal flame speed was chosen to be 5 cm/s with an average deviation of 9.22%. This choice also yielded conservative estimates with low overprediction. At elevated pressure, the 5 cm/s flame speed yielded high error and overprediction, leading to the ideal selection of 0 cm/s with an average deviation of 19.78%. This means that increases in pressure cause a decrease in the ideal flame speed for the model, a trend that should be examined in future study.

Further research should evaluate more species at ambient and elevated pressure, and at different pressures in between 1 and 10 bar. Adding inert chemicals or changing the oxidizer may also yield promising conclusions. However, these avenues are limited by the empirical data needed to gain reliable LFLs to cross-reference model data.

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Introduction/Methods

As more in-depth research has developed regarding process safety, combustion has consistently been an important topic of discussion. Since combustion is highly exothermic, there is a high energy yield that can be used in many applications. However, this causes fuel mixtures to rapidly jump temperatures to up to around 2,000 ° C when using air as an oxidizer[1], presenting safety concerns that must be predicted and planned for. The speed at which the flame propagates (also known as the laminar flame speed) can range from 1 to 10 cm/s[2] and is an important metric for analyzing the characteristics of a flame traveling by combustion.

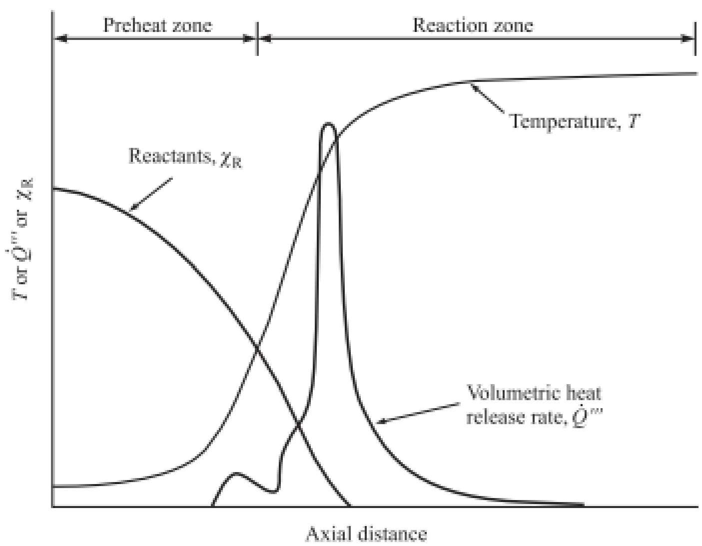

Figure 1. Diagram of a Laminar Flame Structure[2]

Seen above is a typical graph of a laminar flame. There are two distinct zones: the preheat zone and the reaction zone[2]. The preheat zone represents where reactants first come into contact with the flame and are supplied with initial heat to start the combustion reaction. Once a threshold of energy is reached, the temperature of the mixture rapidly increases as combustion occurs, beginning the reaction zone[2]. This threshold is considered to be the flame front, representing a very thin part of the reaction zone with very fast chemistry occurring[2]. Assuming that the flame is laminar and traveling 1-dimensionally, there is a characteristic velocity of this flame front, representing the speed at which the flame moves through space. This is known as the laminar flame speed.

Laminar flame speed is known to be a function of temperature, pressure, and composition of the fuel mixture[2]. However, the relationship between pressure and laminar flame speed currently does not hold much research or discussion. Additionally, the lower flammability limit (LFL), being similarly a function of temperature and pressure[3], contains a small amount of data for certain species. There have been past studies that suggest a correlation between the lower flammability limit and the laminar burning velocity of similar mixtures of fuel and air[4]. From this suggestion, it is possible to use estimated laminar flame speeds to predict LFLs at different conditions. Since the temperature dependence has been previously studied and documented, the pressure dependence of flame speed and LFL will be examined in this report.

In order to bridge the connection between flame speed and LFL, a replicable method of analysis must be developed. For this research, a Python computer program created by ExxonMobil was used to convert composition, temperature, and pressure inputs into an estimation of the laminar flame speed at the given conditions. The model uses published combustion data and mechanisms through a framework known as Cantera. Cantera allows for multiple different mechanisms, which evaluate different species depending on which mechanism is used[5]. For example, the GRI30 mechanism is focused solely on the combustion of methane using empirical kinetic, transport, and thermodynamic data. For this research, GRI30, H2O2, and USCII were used to simulate all the species used, with GRI30 and H2O2 being built in mechanisms and USCII being external[6]. Chosen mechanisms were used to create flame speed curves of laminar flame speed vs equivalence ratio (representing the actual fuel/air ratio divided by the stoichiometric fuel/air ratio). These results were compared with literature-built curves to determine if the program model was accurate.

Following the verification of model accuracy and proper operation, a strategy was developed to correlate estimated flame speed values to lower flammability limits. With some extra lines of code added, the program could function in reverse, determining composition from an estimated flame speed input. The composition given could then be compared to empirical values for LFLs found in literature, first at ambient pressure, then at elevated pressure. Values for ideal flame speeds were selected for estimation of LFLs, and the changes exhibited as pressure increased were documented.

Results and Discussion

In order to validate the Cantera model, flame speed curves were plotted using model data and cross-referenced with empirical correlations for the same fuel. An example of this is shown for methane below in Figure 2.

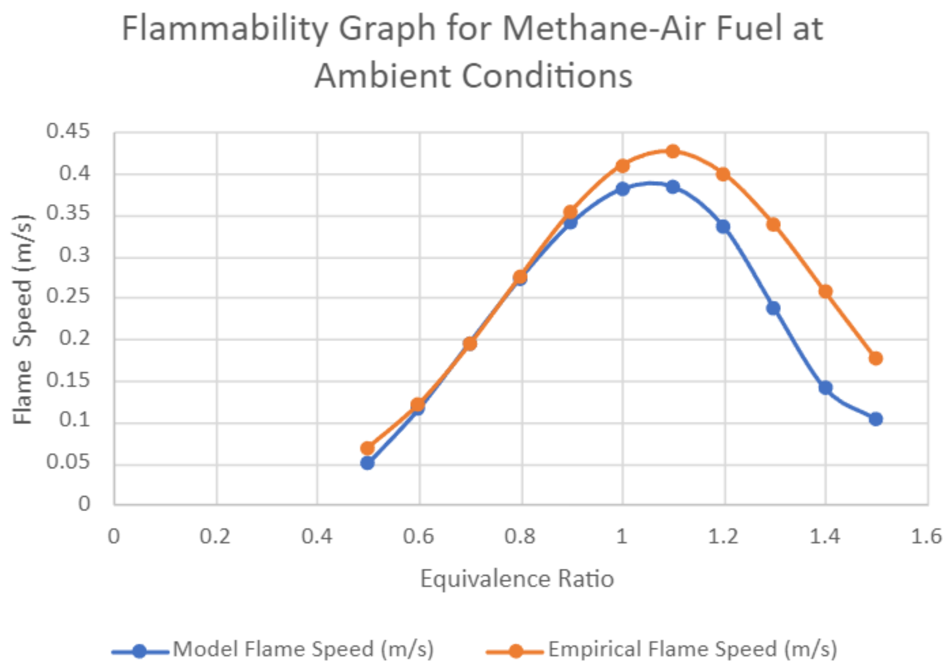

Figure 2. Flammability Graph for Methane Comparing Model to Empirical Flame Speeds[7].

In general, deviation of the model was less than 30% for the majority of the curve, suggesting close correlation to empirical data[7]. The model seemed to undershoot the flame speeds at higher equivalence ratios, however since LFLs will be the main focus of this research, these equivalence ratios will not be used. The high accuracy at lower equivalence ratios (roughly 5%) ensures proper functioning of the model and utility in analyzing the LFLs of various fuel mixtures.

Analysis at Ambient Conditions

At ambient pressure, the comparison of laminar flame speed composition and LFL is relatively simple due to the amount of LFL data available. Continuing with Methane-air mixtures, the program can be run in reverse, given inputs of flame speed. For ambient pressure, values of 0 cm/s (the model predicted LFL), 2 cm/s, 4 cm/s, and 5 cm/s were selected for evaluation. Thus, the equivalence ratio was determined from the model to find the composition for these 4 values. Each of these were then converted to a volume percentage for easier comparison to LFLs. The results for methane-air mixtures at ambient conditions are shown below in Table 1.

Table 1. LFL Comparison for Methane at Ambient Conditions

US LFL (Methane[3])	Volume % at 0 cm/s (model LFL)	Vol % at 2 cm/s	Vol % at 4 cm/s	Vol % at 5 cm/s
5	4.223	4.517	5.063	5.267

Based on the individual results for methane, the 4 cm/s flame speed provides the closest estimate of the true LFL, at a value of 5.063 % by volume. However, the value for ideal flame speed is intended to encompass a good estimate of many species, and thus the same method was conducted on many species. These results are shown below in Table 2.

Table 2. LFL Comparison for Multiple Fuels at Ambient Conditions

Fuel	LFL value[3]	Flame speed at LFL (m/s)	Vol % at 2 cm/s	Deviation at 2 cm/s (%)	Vol % at 4 cm/s	Deviation at 4 cm/s (%)	Vol % at 5 cm/s	Deviation at 5 cm/s (%)
Methane	5	0.049	4.622	-7.56	5.095	1.9	5.267	5.34
Methanol	7.5	0.082	5.831	-22.25	6.534	-12.88	6.797	-9.37
Acetylene	2.5	0.059	2.192	-12.32	2.361	-5.56	2.439	-2.44
Formaldehyde	7	0.024	6.727	-3.9	7.790	11.29	8.147	16.39
Ethane	3	0.104	2.341	-21.97	2.581	-13.97	2.660	-9.97
Ethylene	2.7	0.036	2.581	6.33	2.820	-4.04	2.914	-9.22
Propane	2.1	0.079	1.744	-16.95	1.891	-9.95	1.967	-6.45
Propylene	2.4	0.086	1.821	-24.13	2.031	-15.38	2.123	-11
Isobutane	1.8	0.075	1.374	-23.67	1.519	-15.61	1.591	-11.58
Ammonia	15	0.102	12.232	-18.45	13.543	-9.71	14.20	-5.34
1,3-Butadiene	2	0.094	1.414	-27.45	1.549	-17.9	1.611	-13.13
1-Butene	1.6	0.089	1.401	-12.44	1.523	-4.81	1.589	-1
n-Butane	1.8	0.095	1.302	-28.17	1.432	-19.22	1.485	-14.75
Propyne	2.1	0.052	1.934	-7.48	2.106	0.048	2.179	-3.81
Hydrogen	4	0	13.63	240.8	13.89	247.25	14.28	257
Acetaldehyde	1.6	0	3.337	108.6	3.668	129.3	3.807	137.9
			Avg	16.64	Avg	10.63	Avg	9.22

Once volume percentages were determined from each flame speed value, the deviation from the empirical LFL was estimated on a percentage basis. A positive sign in the deviation indicates that the model overpredicted the LFL, while a negative sign indicates that the model underpredicted the LFL. From the results given, even in the largest flame speed choice of 5 cm/s, many species still underpredict the LFL within the context of the model. However, this is largely preferred compared to consistent overprediction. Since the LFL is such a critical value, having too high of a prediction may cause resulting research or operation to occur above the true LFL, presenting clear safety concerns. For this reason, deviation should be below the LFL rather than above. Further research should exercise caution if further increasing the ideal flame speed past 5 cm/s, as positive error may occur more often, indicating overprediction.

At the current maximum, acetaldehyde and hydrogen have notable overpredictions of the LFL. There are multiple possible reasons for this. Firstly, the mechanism simulating many of these species (USCII) may have inaccurate modeling of acetaldehyde combustion. Another possible explanation is that acetaldehyde and hydrogen are improperly modeled using Cantera's combustion programming. Due to their inaccurate modeling, acetaldehyde and hydrogen will be treated as an outlier in the deviation analysis and deviation totals will not include this species.

The effectiveness of each flame speed at predicting LFLs in total was evaluated through taking the absolute value of all error for each individual species and summing them up for each flame speed. This value was then divided by the number of species being studied to yield an average deviation per species. Shown in Table _, 2 cm/s yielded an average deviation of 16.64, 4 cm/s yielded a deviation of 10.63, and 5 cm/s yielded a deviation of 9.22. Since the ideal flame speed requires the closest estimate to empirical data, the lowest error represented by 5 cm/s makes it the best choice. Furthermore, this choice also presents low visual deviation, as shown in Figure _.

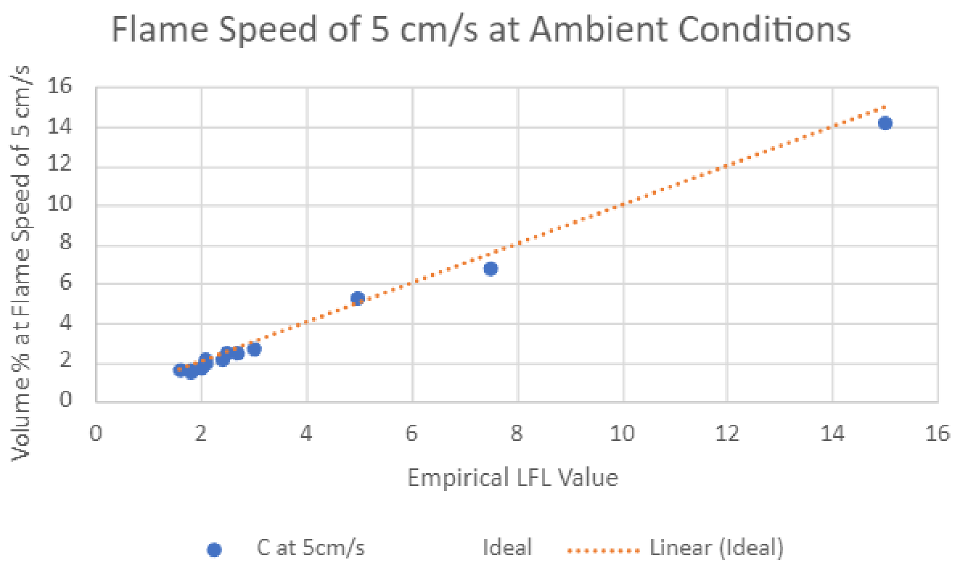

Figure 3. Correlation of Flame Speed at 5 cm/s to LFLs at Ambient Conditions[3]

This is combined with the consideration that 5 cm/s does not have a high amount of overprediction, also shown in Figure 3, making it also a safe choice for ideal flame speed. For these reasons, at ambient conditions, 5 cm/s is the ideal flame speed for the Python model being used.

Analysis at Elevated Pressure

Now that an ideal flame speed has been chosen, it is important to evaluate if this choice retains its effectiveness at elevated pressures. Thus, a similar analysis has been conducted using the same Python model on a smaller scale of species. Since flammability data is less available at elevated pressures, LFLs were found for methane, ethane, and propane for subsequent model analysis. All three of these used pressure values of 10 bar. The model results contrasted with the experimental LFLs are shown below in Table 3.

Table 3. LFL Comparison for Multiple Fuels at Elevated Pressure

Fuel	LFL value[8,9]	Vol % at 0 cm/s	Dev at 0 cm/s (%)	Vol % at 2 cm/s	Dev at 2 cm/s (%)	Vol % at 4 cm/s	Dev at 4 cm/s (%)	Vol % at 5 cm/s	Dev at 5 cm/s (%)
Methane	4.22	3.428	-18.76	5.869	39.08	6.81	61.37	7.178	70.09
Ethane	2.25	3.089	37.29	5.045	124.2	5.603	149.02	5.819	158.6
Propane	1.25	1.291	3.28	2.131	70.48	2.393	91.44	2.499	99.92
		Avg	19.78	Avg	77.93	Avg	100.6	Avg	109.5

Flame speed effectiveness was evaluated using the same method as ambient conditions, with deviation being added and divided by the number of species to yield an average deviation. Shown in Table _, 0 cm/s yielded an average deviation of 19.78%, 2 cm/s yielded a deviation of 77.93%, 4 cm/s yielded a deviation of 100.6%, and 5 cm/s yielded a deviation of 109.5. In general, the deviation of elevated data is significantly higher than ambient data. This is mainly due to significant overestimation of the LFL in most concentrations. The deviation occurs in the 0 cm/s section, with ethane and propane still overpredicting the empirical LFLs. This is a stark difference from the ambient data (which suggested lowest deviation in 5 cm/s). Thus, the ideal flame speed choice of 5 cm/s will not be accurate for estimation of LFLs at elevated pressure. Instead, a lower flame speed is needed. At 10 bar, the deviation analysis suggests that the model predicted LFL (flame speed of 0 cm/s) is the most accurate predictor of empirical LFLs.

In the future, further analysis can be conducted on more species based on data available. Currently, elevated LFL data on other species are difficult to find and highly limited. However, this method presents high repeatability, as Cantera and all used mechanisms are open source. As more data becomes available, a larger table of species can be built over time, increasing accuracy of evaluation of the method. At pressures lower than 10 bar, ideal flame speeds will likely fall in between 0 cm/s and 5 cm/s, requiring further analysis to determine the most appropriate choice. However, since the model overpredicts values at 10 bar, further raising the pressure will lead to unusable data from the model, as overpredictions will be even higher. This would lead to unsafe predictions of LFLs.

Conclusion and Recommendations

To conclude, flame speed has been accurately calculated using the Cantera combustion framework in Python[5]. This model was validated by comparing generated flammability curves to empirical data. Fuel-air compositions were then found for chosen flame speeds and deviations from the LFL values were calculated. These deviations were averaged to find an overall error per species of the model at given flame speeds. At ambient pressure, a flame speed of 5 cm/s could be used to estimate the LFL with an error of 10%. At elevated pressure, this flame speed choice becomes ineffective, causing high overpredictions of LFL values. Thus, a flame speed of 0 m/s should be used to estimate the LFL with an error of 20%. These recommendations are not applicable to hydrogen and acetaldehyde, for which a better kinetic model is required for the purpose of this application. These results offer the conclusion that increasing the pressure will lead to a lower ideal flame speed being needed to gain accurate predictions with the model. While the elevated data reflected a pressure of 10 bar, lower pressure values will likely need further analysis to determine ideal flame speeds, while higher pressure values will likely not be usable with the model.

There are many possibilities to move forward with this research that will aid in its utility. A primary example is further establishment of a database of LFL comparisons. Ideal flame speeds above 5 cm/s can be researched with the consideration of overprediction. Additional species can be added to the tables of ambient and elevated conditions to assess if ideal flame speed is affected. Furthermore, since most of the flammability data was calculated with the USCII mechanism[6], these results can be compared to those of other mechanisms, and further evaluation of which mechanism is more accurate can be conducted. Since there can be a high degree of variance between mechanisms, this could be a crucial step in increasing model accuracy. Additionally, further examination of elevated pressure could yield useful information. Ideal flame speeds should be calculated at pressures between 1 and 10 bar to show how the correlation between flame speed and LFL shifts on the axis of pressure. Finally, additional fuel mixtures should be studied. Examples could include the mixture of an inert into the fuel, or use of a different oxidizer other than oxygen. However, the limiting factor will likely remain the low amount of available data in the near future. There is currently not enough essential data to properly assess mixtures of fuel with oxidizers other than air, and inert mixtures are highly difficult to find. As more comprehensive data on other fuels are released, this research will remain an important topic of discussion in the process safety considerations of combustion.

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