Experimental measurement and numerical analysis of binary hydrocarbon mixture flammability limits

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Abstract:

In this report we try to extend the Le Chatelier formula for upper flammability limits which deviates largely from experimental results.

To modify the Le Chatelier's Law powering the percentage concentrations of fuels from maximum R-square values gave empirical modification which increased the prediction accuracy.

We can also fit the experimental data using various curve fitting methods.

Introduction:

Flammability limits are established through experimental means by identifying the composition of mixtures between those that can ignite and those that cannot.

Theoretically, flammability limits are obtained from Le Chatelier's Law. Results from this law is well consistent with LFL's, whereas it is limited to certain fuel mixtures for UFL's. At lower levels of fuel concentration where molecules are more spread out, these assumptions align better with actual scenarios. Consequently, Le Chatelier's Law offers a more accurate estimate of the lower flammability limits for fuel mixtures. However, at concentrations approaching the upper flammability limits, the model's assumptions deviate significantly from real conditions, leading to less reliable estimations.

So, we need to modify the Le Chatelier's Law for UFL's by powering the percentage concentrations of fuels from maximum R-square values. This empirical modification significantly increases the prediction accuracy.

Flammability limits or explosion limits is defined as the volume percentage concentration range of gas or vapor in air at specified temperature and pressure that will burn if ignited.

We have two flammability limits:

(i) the upper flammable limit (UFL) above which the fuel concentration is too rich to burn.

(ii) the lower flammability limit (LFL) below which the fuel concentration becomes too low to be ignited.

Flammability limits has various applications in chemical processing such as preventing explosions and designing safe processes, Efficient combustion, Material selections etc.

Let's say Efficient combustion:

In processes where combustion is desired, operating within the flammability limits ensures efficient and controlled burning of the fuel. This is important for processes such as combustion engines.

By extending Le Chatelier for concentrations approaching the upper flammability limits of fuel mixture, we can accurately define these limits.

Methods used in the past:

1. Visual Identification: This method is based on the criteria that if a gas propagates halfway from its point of ignition (or to a well-defined distance) is declared to be flammable.

Limitations:

(i) As it relies on human observation precise data cannot be obtained which can lead to variation in the determination of flammability limits.

(ii) It is not sensitive enough to determine lower flammability limits.

2. Pressure Variations:

Here, the detection criterion is the relative pressure increase in a reaction vessel resulting from combustion.

Advantages:

(i) Precise determination of flammable limits and high sensitivity.

Limitations:

(ii) It may also fail in detecting lower flammability limits in situations where concentrations are close to the lower detection threshold of the measurement system.

3. Counterflow burners:

Here, two nozzles release premixed fuel and oxidizer facing each other ignites to generate two planar flames simultaneously.

The exit velocity of the gas, or stretch rate, is measured across different concentration values and extrapolated to determine the intercept, which represents the flammability limit.

The flammability apparatus used in this research was developed by Wong (2006) at Texas A&M University.

The apparatus consists of:

(i) Reaction vessel.

(ii) Gas feeding system.

(iii) Gas mixer.

(iv) Gas mixture ignition system.

(v) Data acquisition system.

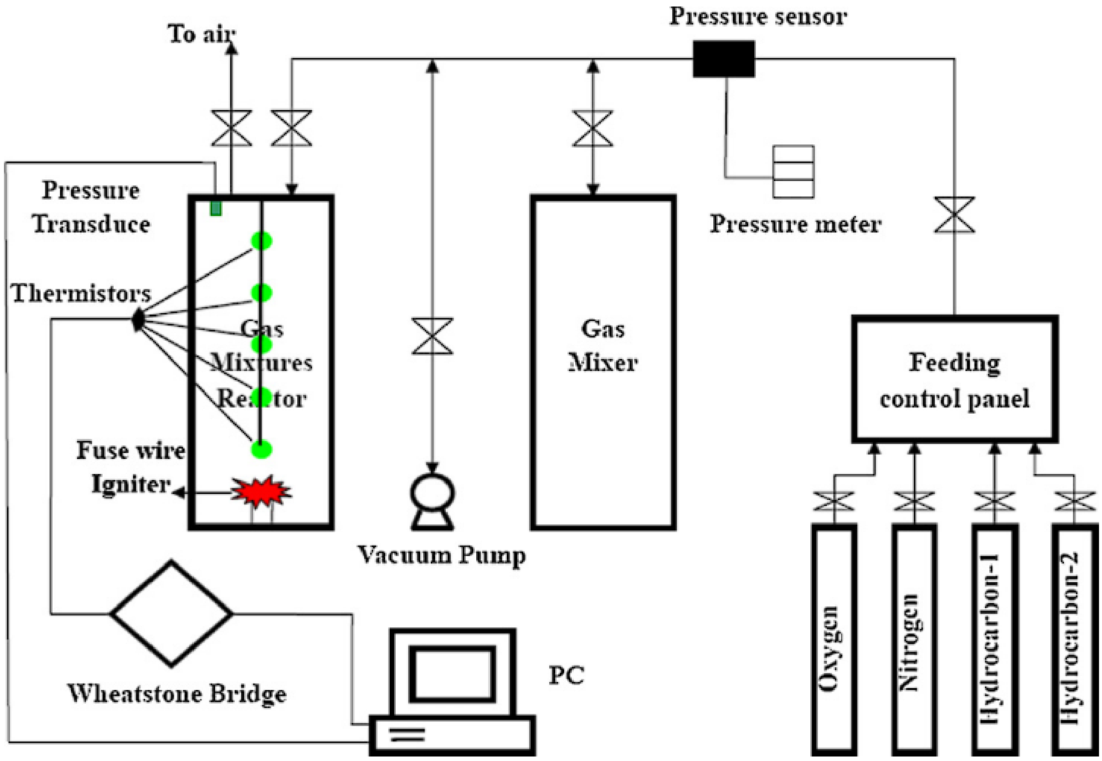


Fig. 1 – Flammability experimental apparatus.

In the reaction vessel,

There are 5 thermistors which are capable of real-time flame front detection and determining the distance of self-sustained flame propagation when fuel/air mixtures ignite and combust in an upward direction.

A dynamic pressure transducer mounted inside the cylinder measures pressure variation when fuel mixture burns.

A special desktop computer is utilized for data acquisition, measuring the differential voltages from both the thermistors and the pressure transducer. The collected data on temperature and pressure profiles were then acquired and analysed.

Based on this data, various assessments were conducted at different concentrations. The propagation probabilities were graphed against different fuel concentrations, and through regression analysis, a linear function was derived. This function identified the concentration at which there was a 0.5 or 50% probability of continuous flame propagation, determining it as the lower flammability limit.

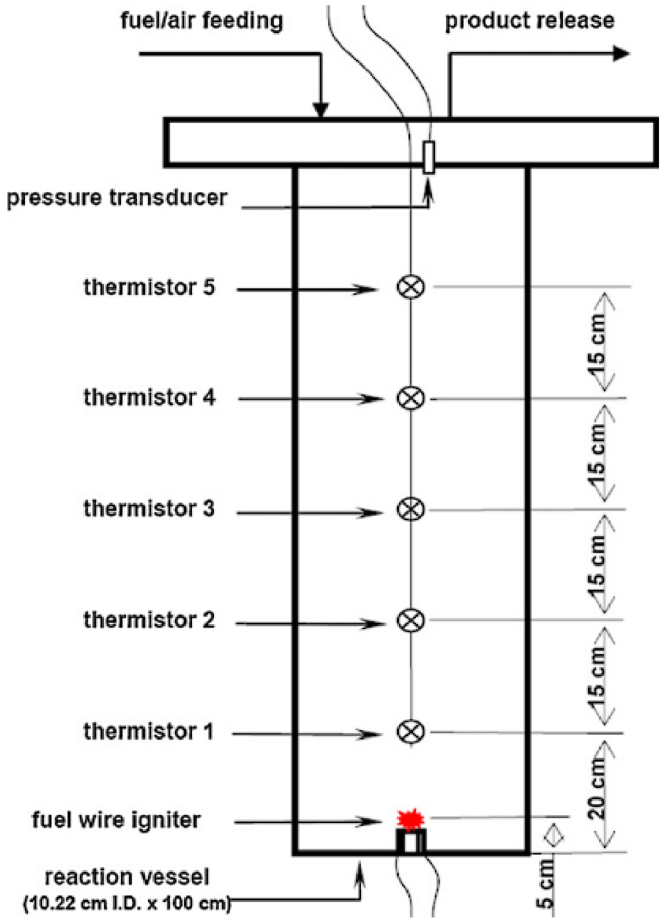


Fig. 2 – Reaction vessel.

Problem Formulation:

The lower flammability limit can be estimated by averaging the lowest fuel concentration with flame propagation and the highest concentration in which flame will not propagate, and vice versa for the upper flammability limit.

$$LFL_{T,P} = \frac{1}{2}\left(C_{g,n} + C_{l,f}\right) \quad \textbf{(1)}$$

$$UFL_{T,P} = \frac{1}{2}\left(C_{g,f} + C_{l,n}\right) \quad \textbf{(2)}$$

$LFL_{T,P}$, $UFL_{T,P}$ are lower flammability limit and upper flammability limit at a specific temperature and pressure.

$C_{l,n}$, $C_{g,n}$ the greatest concentration and the least concentration of a fuel in an oxidant that are non-flammable.

$C_{l,f}$, $C_{g,f}$, are the greatest concentration and the least concentration of a fuel in an oxidant that are flammable.

For fuel mixtures:

$$LFL_{mix} = \frac{1}{\Sigma_{i=1}^{N}(y_i/LFL_i)} \quad \textbf{(3)}$$

$$UFL_{mix} = \frac{1}{\Sigma_{i=1}^{N}(y_i/UFL_i)} \quad \textbf{(4)}$$

where y_i is the mole fraction of the ith component considering only the combustible species.

LFL_i, UFL_i are the lower and upper flammability limit of the ith component in volume percent.

Modification of Le Chatelier's Law is required to predict upper flammability limits for some binary hydrocarbon mixtures. So, based on maximum R-square values, a simple way was applied to modify Le Chatelier's Law by powering the fuel percentage concentrations. This empirical modification significantly increases the prediction.

Modified formulas varies with type of mixture components, some modified formulas in the paper are:

$$\frac{1}{UFLmethane/ethylene} = \frac{x^\wedge 1.3}{UFLmethane} + \frac{(1-x)^\wedge 0.6}{UFLethylene} \quad \textbf{(5)}$$

$$\frac{1}{UFLmethane/acetylene} = \frac{x^\wedge 2.1}{UFLmethane} + \frac{(1-x)^\wedge 0.3}{UFLacetylene} \quad \textbf{(6)}$$

Numerical Approach:

Theoretical values were calculated form the code using function regression and formula mentioned above, linear values using linear regression, Interpolation using newton's divided difference method, the graphs have been made by using theoretical data obtained from the code. All the readings were given at 25 C and 1atm.

For saturated mix (methane and n-butane):

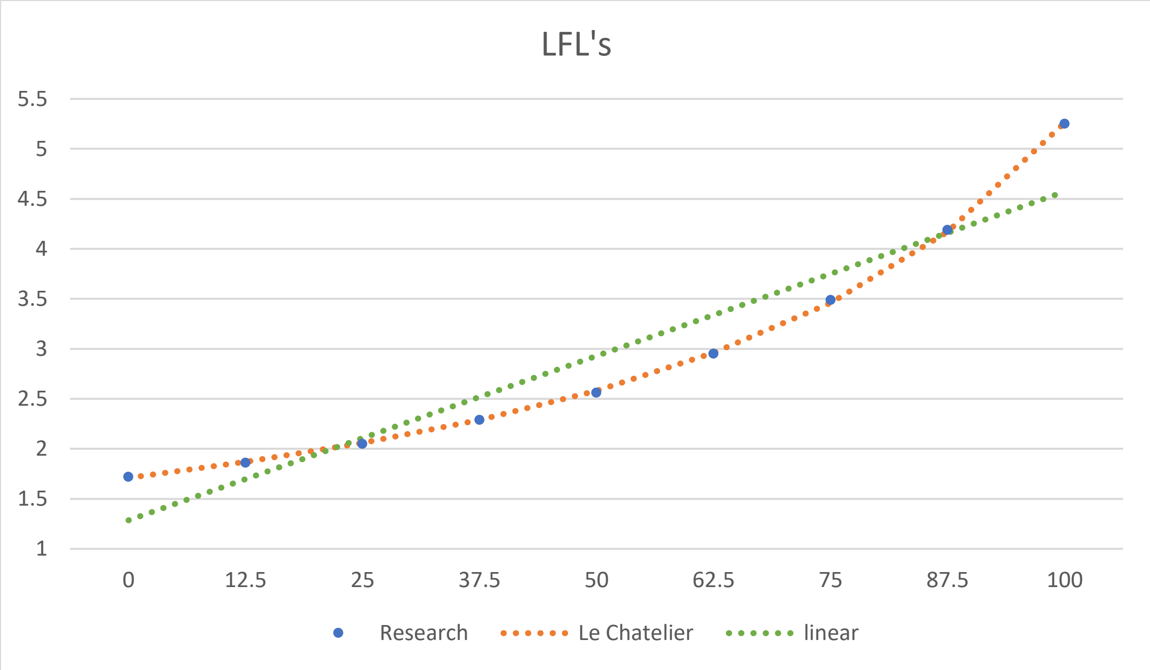
Used Equations (3) and (4) to get theoretical values.

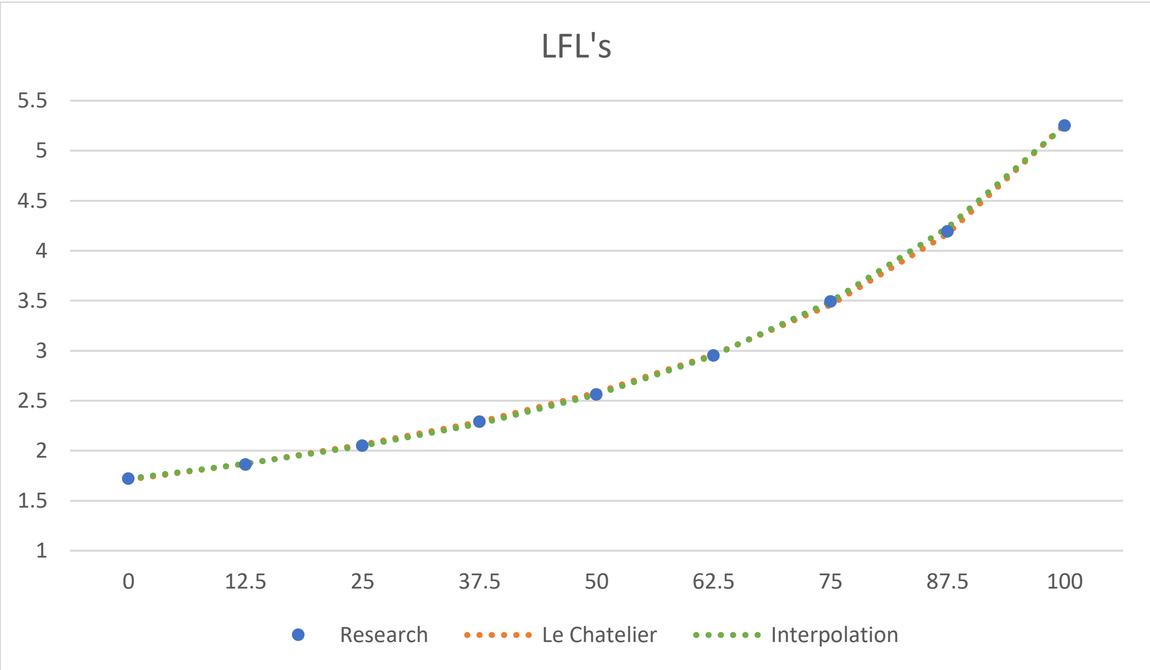
X(CH_4 % Mole fraction)	Experimental LFL values	Le Chatelier Values (Theoretical)	Linear	Interpolation
0	1.72	1.71	1.28556	1.72
12.5	1.86	1.87	1.69639	1.87
25	2.05	2.06	2.10722	2.05
37.5	2.29	2.29	2.51806	2.27
50	2.56	2.58	2.92889	2.56
62.5	2.95	2.96	3.33972	2.95
75	3.49	3.46	3.75056	3.49
87.5	4.19	4.17	4.16139	4.23
100	5.25	5.26	4.57222	5.25

Estimated LFL value of CH4 used = 5.256

Estimated LFL value of n butane used = 1.709

Plot:





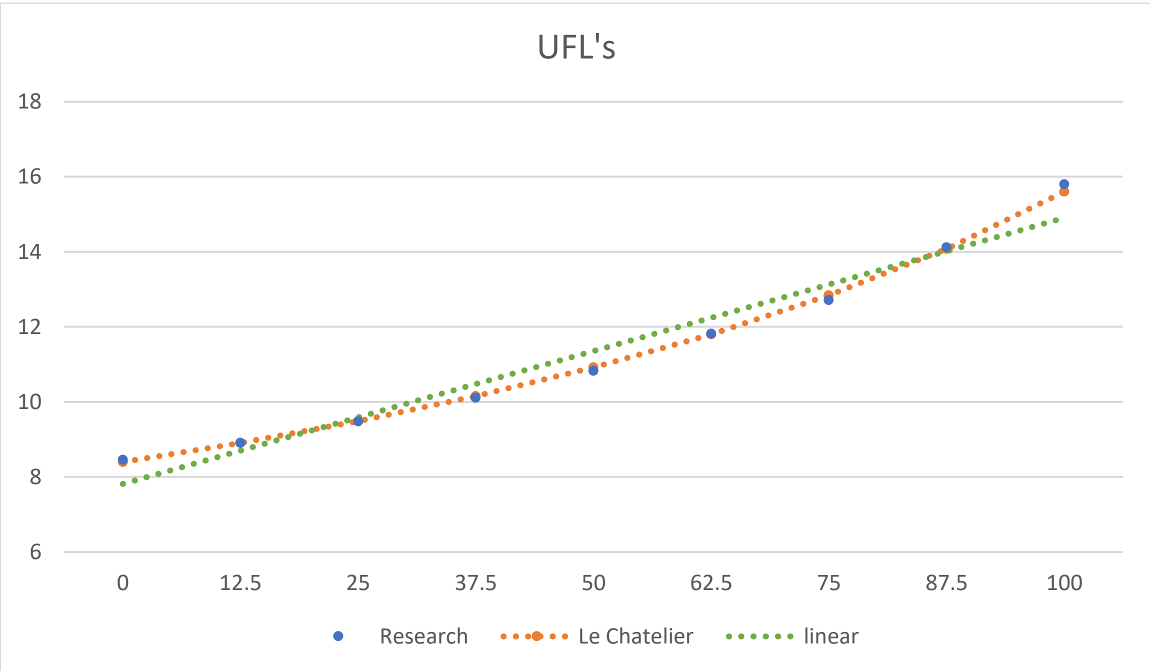
X(CH_4 % Mole fraction)	Experimental UFL values	Le Chatelier Values (Theoretical)	Linear	Interpolation
0	8.46	8.4	7.816	8.46
12.5	8.91	8.91	8.702	8.92
25	9.48	9.49	9.588	9.48

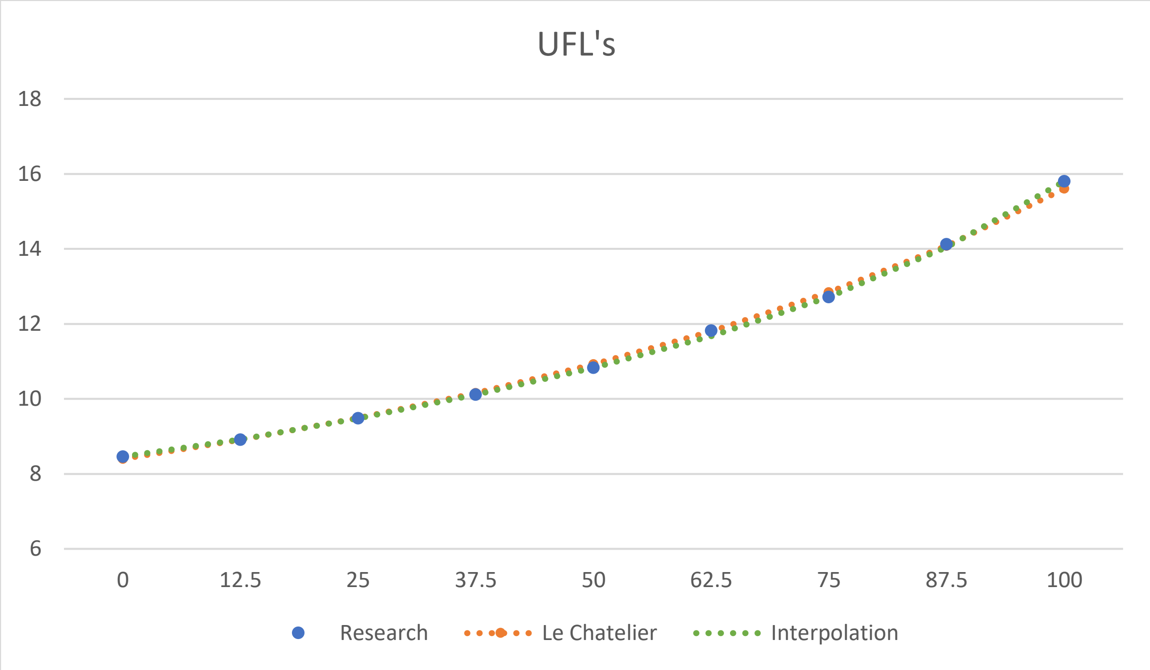
37.5	10.11	10.15	10.474	10.11
50	10.83	10.92	11.36	10.83
62.5	11.82	11.8	12.246	11.67
75	12.71	12.84	13.132	12.71
87.5	14.12	14.08	14.018	14.04
100	15.80	15.6	14.904	15.8

Estimated UFL value of CH_4 used = 15.585

Estimated UFL value of n butane used = 8.398

Plot:





For fuel mixture containing unsaturated component (methane and ethylene):

Used Equations (3) and (4) to get theoretical values.

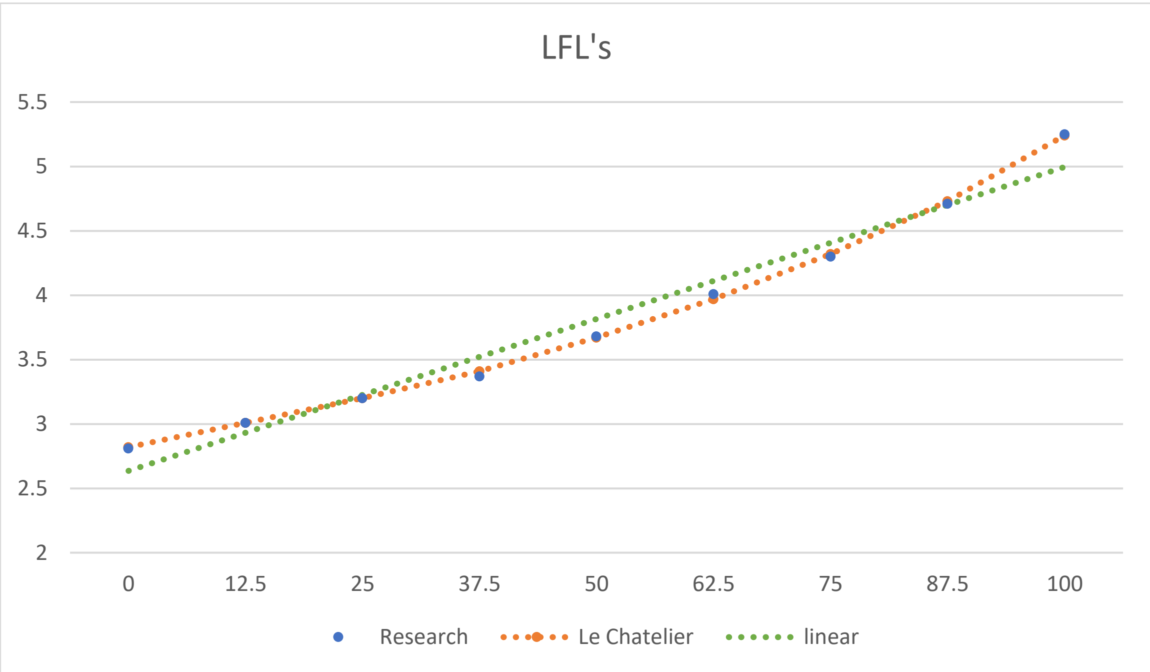
X(CH_4 % Mole fraction)	Experimental LFL values	Le Chatelier Values (Theoretical)	Linear	Interpolation
0	2.81	2.82	2.63556	2.81
12.5	3.01	3.01	2.93056	2.99
25	3.20	3.20	3.22556	3.2
37.5	3.37	3.41	3.52056	3.43
50	3.68	3.67	3.81556	3.68

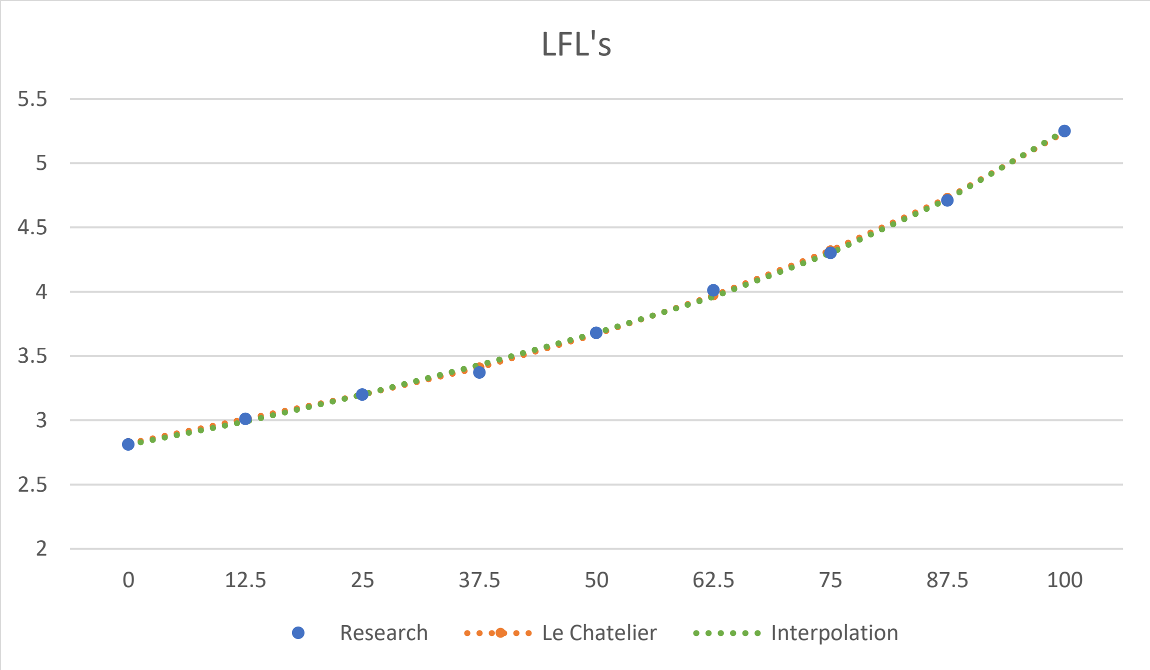
62.5	4.01	3.97	4.11056	3.96
75	4.3	4.32	4.40556	4.3
87.5	4.71	4.73	4.70056	4.72
100	5.25	5.24	4.99556	5.25

Estimated LFL value of CH4 used = 5.243

Estimated LFL value of ethylene used = 2.821

Plot:



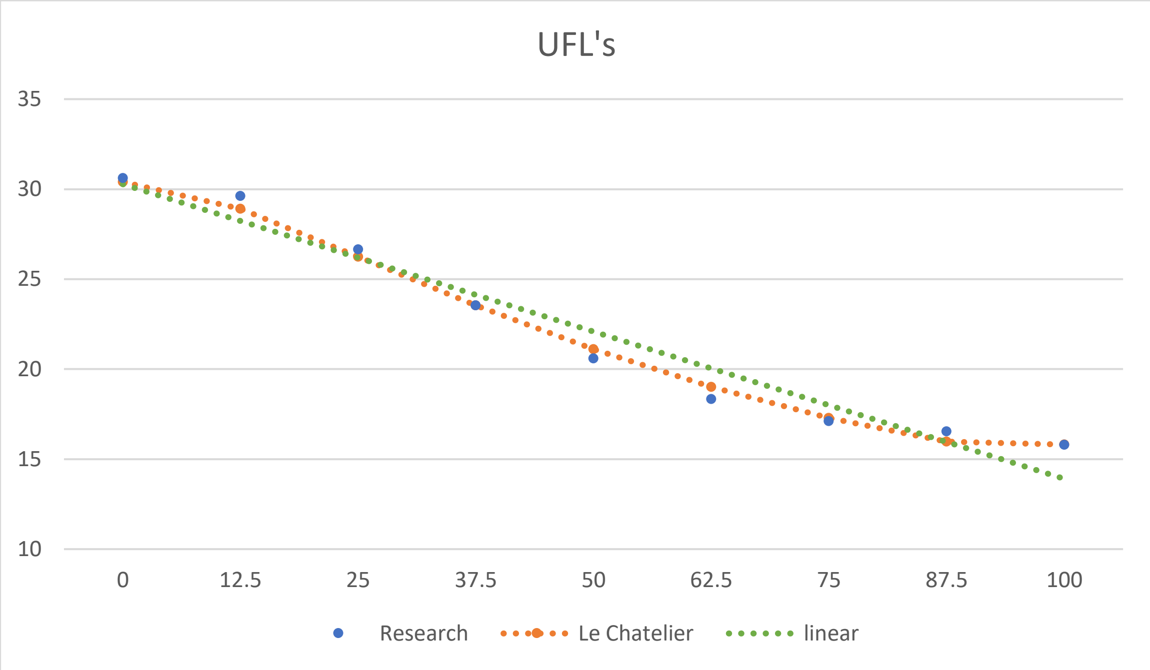


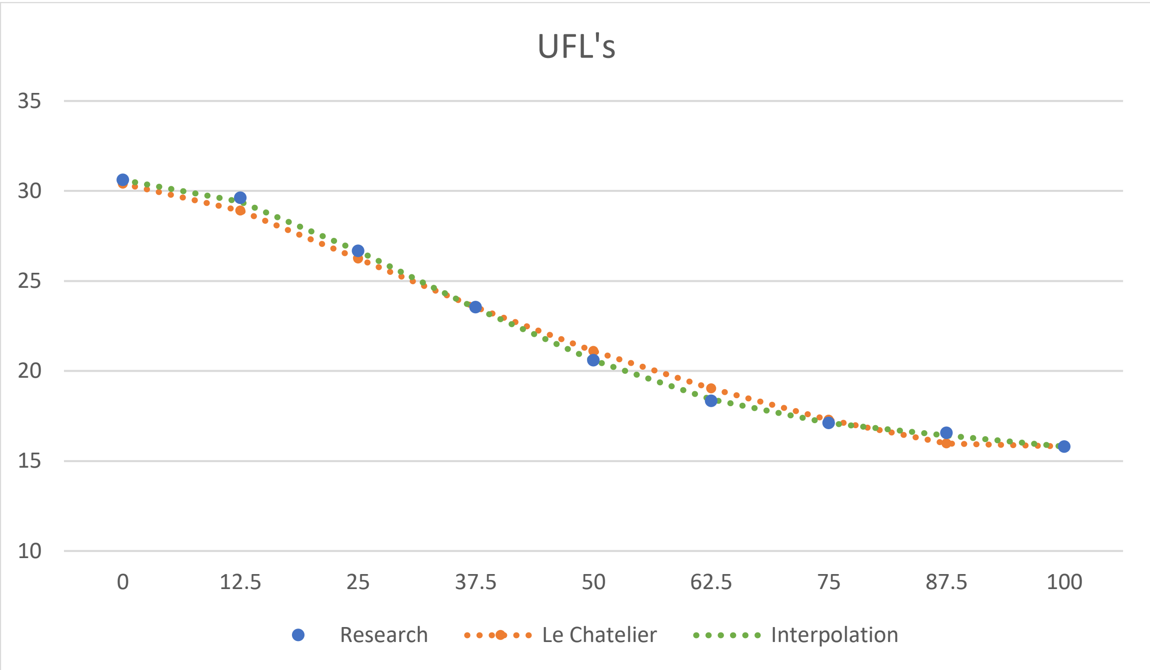
Now used equations (5) to get theoretical values.

X(CH_4 % Mole fraction)	Experimental UFL values	Le Chatelier Values (Theoretical)	Linear	Interpolation
0	30.61	30.40	30.2744	30.61
12.5	29.62	28.91	28.2286	29.4
25	26.66	26.24	26.1828	26.66
37.5	23.54	23.54	24.1369	23.48
50	20.59	21.10	22.0911	20.59
62.5	18.34	19.02	20.0453	18.43
75	17.11	17.29	17.9994	17.11
87.5	16.55	15.97	15.9536	16.41
100	15.80	15.81	13.9078	15.80

Estimated UFL value of CH4 used = 15.371

Estimated UFL value of ethylene used = 32.393





For fuel mixture containing unsaturated component (methane and acetylene):

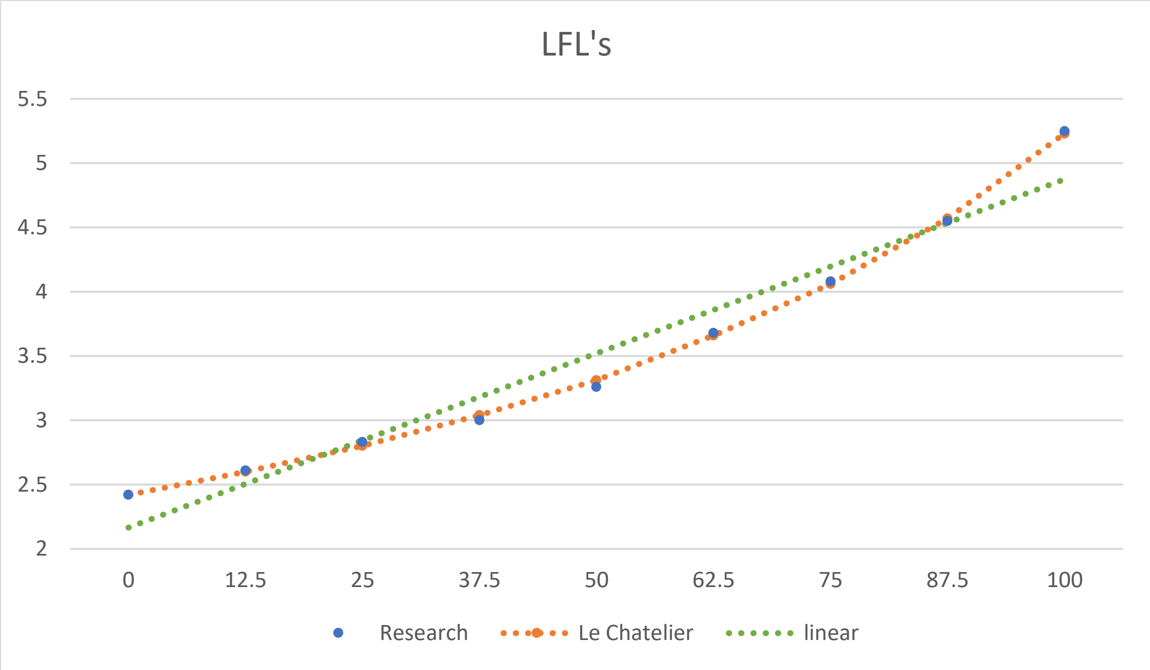
Used Equations (3) and (4) to get theoretical values.

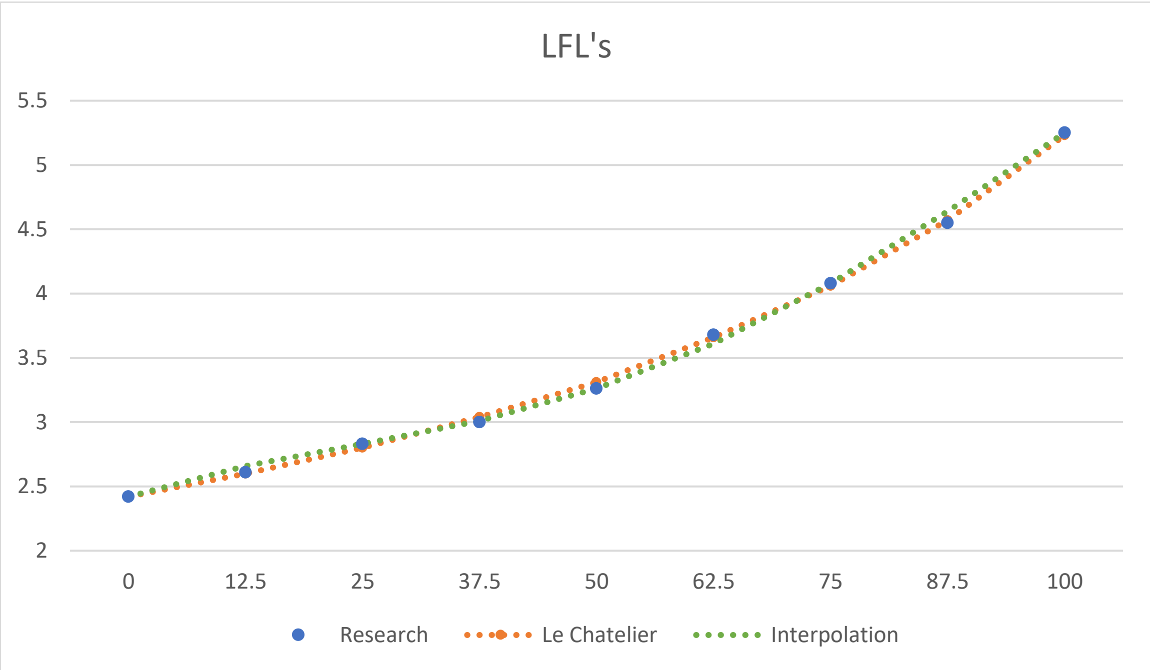
X(CH_4 % Mole fraction)	Experimental LFL values	Le Chatelier Values (Theoretical)	Linear	Interpolation
0	2.42	2.42	2.16533	2.42
12.5	2.61	2.60	2.504	2.66
25	2.83	2.8	2.84267	2.83
37.5	3.00	3.04	3.18133	3.01
50	3.26	3.31	3.52	3.26
62.5	3.68	3.66	3.85867	3.61
75	4.08	4.06	4.19733	4.08
87.5	4.55	4.57	4.536	4.64
100	5.25	5.23	4.87467	5.25

Estimated LFL value of CH4 used = 5.228

Estimated LFL value of acetylene used = 2.424

Plot:





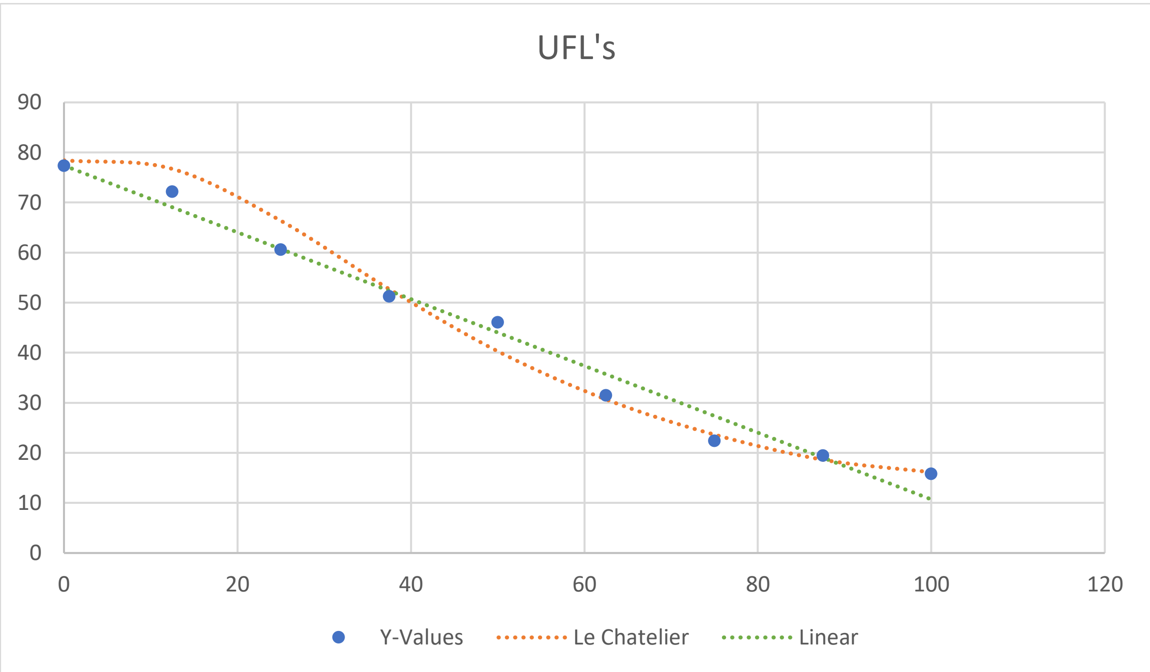
Now used equations (6) to get theoretical values.

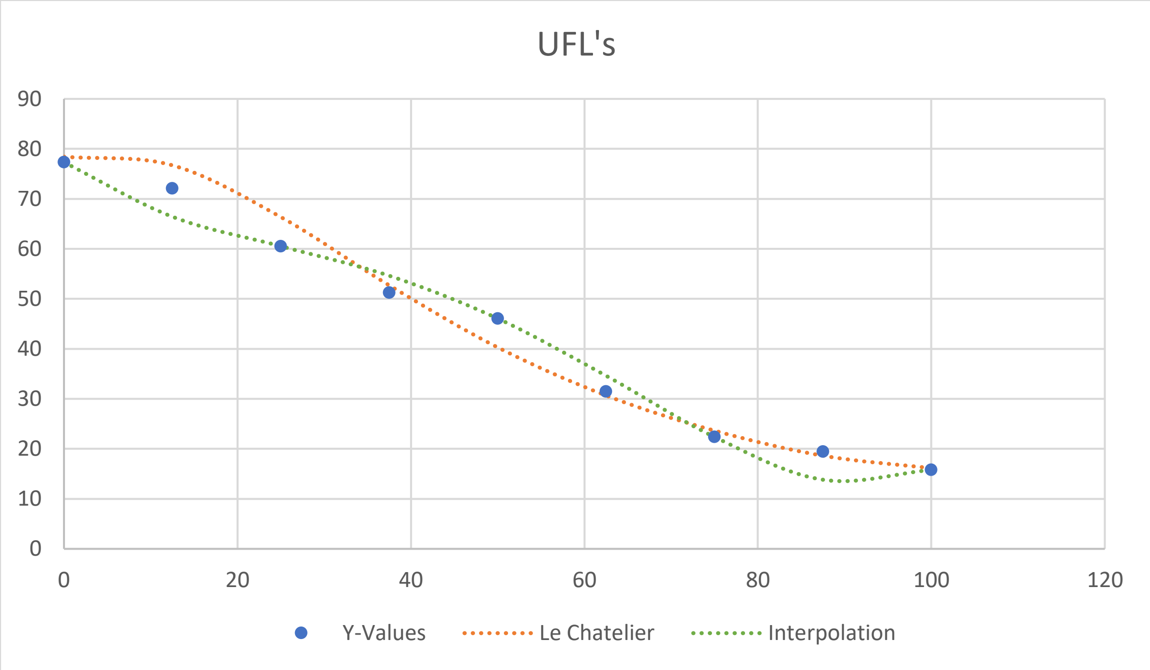
X(CH_4 % Mole fraction)	Experimental UFL values	Le Chatelier Values (Theoretical)	Interpolation	Linear
0	77.31	78.43	77.31	77.3807
12.5	72.12	76.71	66.428	69.0455

25	60.53	66.36	60.53	60.7103
37.5	51.24	52.7	54.6199	52.3752
50	46.07	40.3	46.07	44.04
62.5	31.45	30.67	34.6205	35.7048
75	22.38	23.64	22.38	27.3697
87.5	19.46	18.63	13.8249	19.0345
100	15.80	16.13	15.8	10.6993

Estimated UFL value of CH_4 used = 16.129

Estimated UFL value of acetylene used = 78.432





Results and Discussion:

We have used experimental data and made plot using three methods – (1) Functional regression, (2) Linear regression, (3) Newton's Divided Difference Method. Linear regression fits roughly whereas plots with Functional regression and Newton's Divided Difference fits well with given data. For UFL values of unsaturated mix we have used the equations (5) and (6) which were provided in journal.

For saturated mix (methane and n-butane):

Estimated LFL value of CH4 used = 5.256

Estimated LFL value of n butane used = 1.709

Estimated UFL value of CH4 used = 15.585

Estimated UFL value of n butane used = 8.398

The above values are obtained using **functional regression** by using equations **(3)** and **(4)**,

CH4 mole fraction is taken as X values and 1/ (LFL's or UFL's) as Y values. By estimating these values then we plotted our graph which is represented as Le Chatelier.

$$\frac{1}{UFLmix} = \frac{x}{UFLc_1}\frac{+(1-x)}{UFLc_2}$$

$$\frac{1}{UFLmix} = \frac{1}{UFLc_2} + x\left(\frac{1}{UFLc_1} - \frac{1}{UFLc_2}\right)$$

$$Y = a0 + a1*X$$

Plots obtained are shown below data table.

We also plotted data using **linear regression** took CH4% mole fraction as x values and LFL's or UFL's as y values. It roughly predicts the values as shown in table represented as linear (research).

Then we try to interpolate the data using **Newton's divided difference method** to get better plot with less deviation.

For fuel mixture containing unsaturated component (methane and ethylene):

Estimated LFL value of CH4 used = 5.243

Estimated LFL value of ethylene used = 2.821

Estimated UFL value of CH4 used = 15.371

Estimated UFL value of ethylene used = 32.393

LFL values are obtained using **functional regression** by using equations **(3).**

For UFL values we used equation **(5)** and estimated the values using **non-linear regression**.

$$\frac{1}{UFLmethane/ethylene} = \frac{x\text{^}1.3}{UFLmethane} + \frac{(1-x)\text{^}0.6}{UFLethylene}$$

$Y = a*x^{1.3} + b*(1-x)^{0.6}$

Linear regression and Interpolation are done same as mentioned above.

For fuel mixture containing unsaturated component (methane and acetylene):

Estimated LFL value of CH4 used = 5.228

Estimated LFL value of acetylene used = 2.424

Estimated UFL value of CH4 used = 16.129

Estimated UFL value of acetylene used = 78.432

LFL values are obtained using **functional regression** by using equations **(3).**

For UFL values we used equation **(6)** and estimated the values using **non-linear regression**.

$$\frac{1}{UFLmethane/acetylene} = \frac{x\hat{}2.1}{UFLmethane} + \frac{(1-x)\hat{}0.3}{UFLacetylene}$$

$Y = a*x^{2.1} + b*(1\text{-}x)^{0.3}$

Linear regression and Interpolation are done same as mentioned above.

Conclusion:

In this research we have estimated the UFL's/LFL's values of individual component used in the binary mixture with data given in journal using functional regression and non-linear regression. We have plotted the results we got from functional regression, linear regression, non-linear regression, and newton's divided difference methods and compared them with experimental values, where we found out that functional regression, non-linear regression, and newton's divided differences data fits well, but non-linear regression needs modified equation of unsaturated mixtures whereas interpolation using newton's divided difference method does not require any modified equation. One can interpolate experimental data using newton's divided difference method and find out UFL values of mix at different compositions.

Self-Assessment:

We examined the research paper and identified the potential for utilizing the data within the journal to derive results. We learned new terms that we came across and understood the basic mechanism of the experimental setup. Subsequently, we devised a strategy to use our existing knowledge for improved outcomes. Our progression included making linear regression code, non-linear regression, functional regression code that aligns with the formula provided in the research paper. We generated graphs using experimental data and observed that interpolation could yield results with fewer deviations. To achieve this, we incorporated plots utilizing Newton's divided difference method and again included the data table for Interpolation. It also developed our interest in learning new method for curve fitting. Overall, this term paper has been a valuable as we came to know the application of numerical methods learned in class on real world research papers. We believe that we got results with the best of our knowledge.

References:

Zhao, F.; Rogers, W. J.; Sam Mannan, M. Experimental measurement and numerical analysis of binary hydrocarbon mixture flammability limits. Process Saf. Environ. Prot. 2009, 87, 94 – 104, DOI: 10.1016/j.psep.2008.06.003 [Crossref], [CAS], Google Scholar

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