Density theory of flame propagation for evaluating flammability limits

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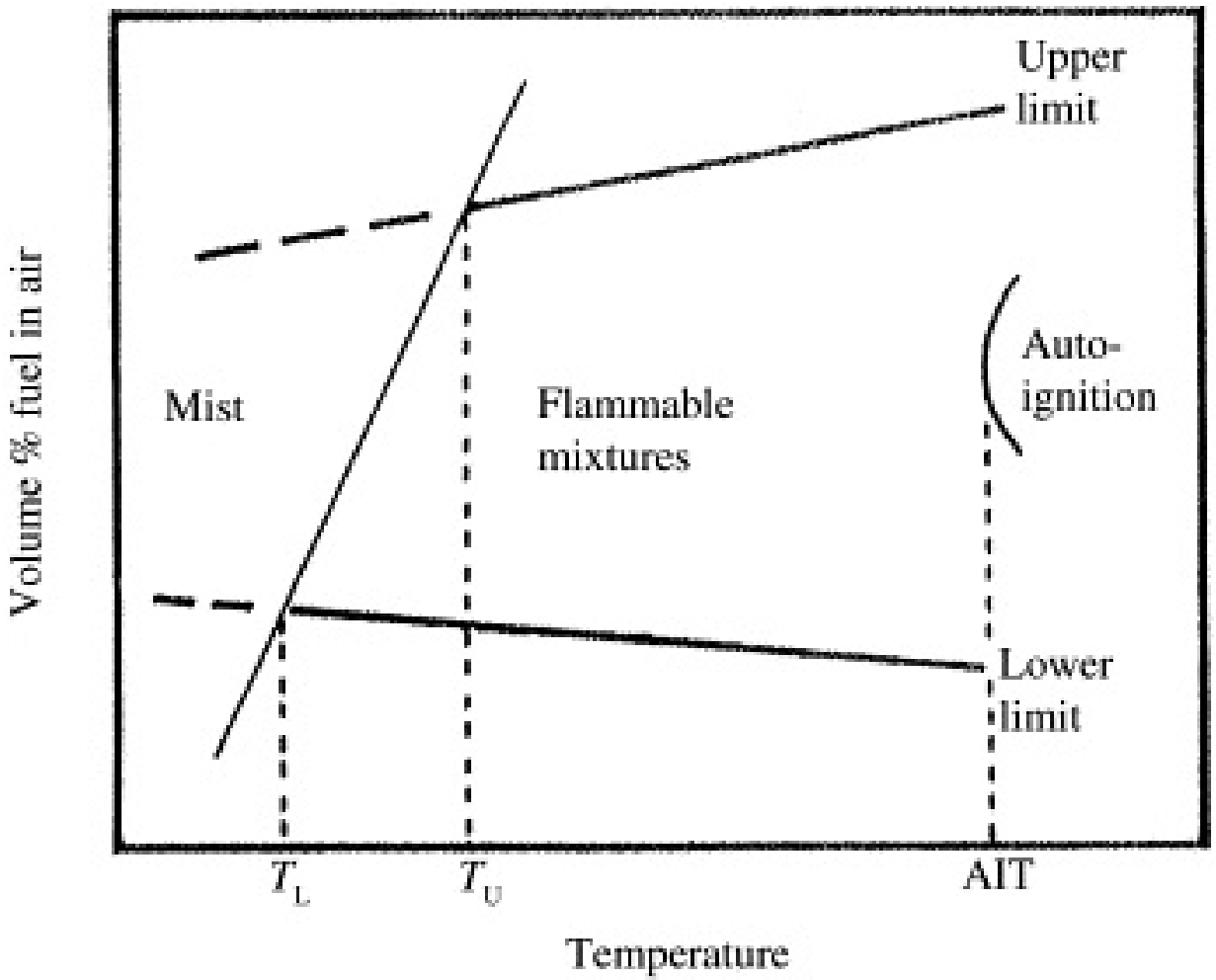
Introduction

- In a fuel/oxidant mixture:
- 1 - Greatest fuel concentration enabling flame propagation is called upper explosive limit (UEL).
- 2 - Least fuel concentration enabling flame propagation is called lower explosive limit (LEL).
- LEL and UEL depend on temperature, pressure and on measurement conditions.
- Measurement and tabulation of LEL and UEL data for all fuels over the whole relevant P and T range is impractical.

Introduction



- Credit to J. Arnaldos, J. Casal, E. Planas-Cuchi.

Why should you care

- Mine safety
- Industrial process safety
- Reactivity controlled compression ignition and the more general case of homogeneous charge compression ignition (HCCI) internal combustion engines. HCCI combines characteristics of conventional gasoline engine and diesel engines. Gasoline engines combine homogeneous charge (HC) with spark ignition (SI), abbreviated as HCSI. Diesel engines combine stratified charge (SC) with compression ignition (CI), abbreviated as SCCI.
- Thermobaric weapons

Background

- Thermal theory suggest a threshold temperature above which a flame can propagate.
- General version of thermal theory implicitly assumes similar rate determining steps for ignition of various fuels at the explosive limit.
- Ignition is a fast reaction thus it can be approximated as adiabatic.
- Therefore a threshold to flame temperature is equivalent to a threshold to adiabatic flame temperature (AFT).
- Density factor (DF) is the ratio of before ignition density of the fuel-oxidizer mixture to after ignition density of the ignition product mixture. DF is equivalent to the expansion ratio (E).
- Density theory suggest a threshold density factor above which a flame can propagate.

Model

- $DF = \frac{\rho_{fuel-oxidant}}{\rho_{products}} = \frac{4.773 l_s \rho_{air} + \phi \rho_f}{(4.773 l_s + \phi)\rho_p} = \frac{T_f}{T_i}\left[\frac{4.773 l_s M_{air} + \phi M_f}{(4.773 l_s + \phi) M_p}\right]$
- $\phi \mathrm{C}_i\mathrm{H}_j\mathrm{O}_k N_m + 4.773 l_s$ dry air $\rightarrow$ combustion products
- dry air $= 0.7808\mathrm{N}_2 + 0.2095\mathrm{O}_2 + 0.0093\mathrm{Ar} + 0.0031\mathrm{CO}_2$.
- The stoichiometric oxygen requirement for each fuel molecule, $l_s = (2i + \frac{j}{2} - k)/2$.
- The equivalence ratio ϕ is the ratio of fuel to oxygen over the stoichiometric ratio of fuel to oxygen.

Method

- Reactions among CH_4, CO, CO_2, H_2, H_2O, NH_3, N_2, C(gr), H, OH, NO, O_2, O and other species are considered.
- Equilibrium composition and conditions for fuel-air mixtures at various values of ϕ are calculated.
- Adiabatic flame temperature vs. ϕ and density factor vs. ϕ are graphed.
- Values of AFT and DF corresponding to each explosive limit are derived by interpolation of the above mentioned graph and tabulated.

Method

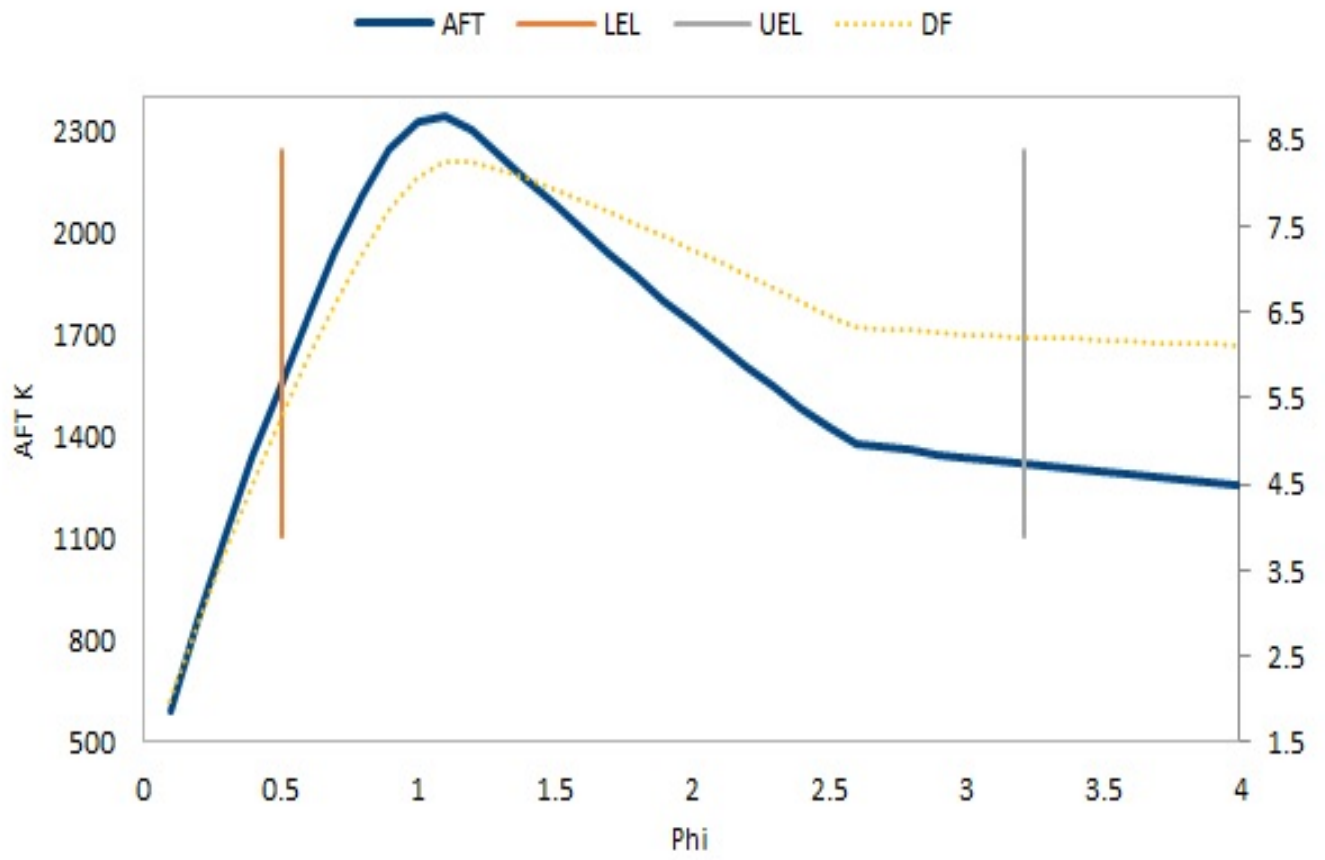


Figure: Adiabatic flame temperature (left vertical axis) and density factor (right vertical axis) vs. equivalence ratio computed for toluene. ϕ_{LEL} and ϕ_{UEL} are marked by vertical bars on the graph.

Flammable gas	LEL vol.%	UEL vol.%	LLFT [K]	ULFT [K]	LLDF [-]	ULDF [-]	SMD LFT [K]	SMD LDF [-]
1,3-Butadiene	2.0	12.0	1671	1448	5.68	6.94	257	1.04
1-Butene	1.6	10.0	1480	1211	5.06	6.05	171	0.47
2,2-Dimethylpropane	1.4	7.5	1585	1051	5.45	5.38	317	1.12
2-Butanone (Methyl Ethyl Ketone)	1.90	10.0	1539	1153	5.29	5.83	170	0.51
3-Methyl-1-Butene	1.50	9.1	1633	1142	5.58	5.89	275	0.75
Acetaldehyde di-ethyl acetal (Acetal)	1.6	10	1821	979	6.43	6.00	626	1.49
Acetone	2.6	13.0	1543	1201	5.33	5.93	126	0.45
Acetylene*	2.5	100	1271	2848	4.23	10.40	1794	5.11
Acrylonitrile*	3.0	17	1762	1772	5.94	7.97	672	2.32
Allene*	1.5	11.5	1157	1891	3.89	8.04	951	3.09
Allyl alcohol (2-propen-1-ol)	2.5	18.0	1563	1081	5.36	6.05	265	0.36
Ammonia	15.0	28.0	1632	1823	5.70	6.93	593	1.04
Benzene (100 C)	1.3	7.9	1500	1411	5.09	6.41	127	0.28
Butane	1.8	8.4	1641	1147	5.67	5.71	277	1.01

Butyl Acetate (butyl ethanoate)	1.4	8.0	1588	1002	5.53	5.54	369	1.05
Carbon Monoxide*	12.5	74	1391	1266	4.39	4.02	206	3.18
Cis-2-Butene	1.7	9.7	1539	1209	5.27	6.00	115	0.32
Cumene (iso-propylbenzene)	0.9	6.5	1583	1183	5.32	5.91	183	0.45
Cyanogen*	6.6	32	2236	2955	7.55	11.42	2329	7.38
Cyclohexane	1.3	7.8	1645	1062	5.69	5.54	367	1.20
Cyclopropane	2.4	10.4	1642	1598	5.60	7.16	378	1.18
Decane	0.7	5.0	1585	1033	5.40	5.61	335	0.84
Deuterium*	4.9	75	708	1167	2.30	3.70	988	5.58
Dimethyl Ether	3.4	27.0	1567	974	5.42	5.81	376	0.66
Ethane	3.0	12.4	1535	1407	5.25	6.22	88	0.12
Ethanol	3.3	19.0 (60C)	1493	1036	5.19	5.52	333	0.87
Ethyl Acetate (ethyl ethanoate)	2.2	11.0	1572	1095	5.42	5.72	260	0.75
Ethyl Benzene (100 C)	1.0	6.7	1560	1248	5.33	6.13	96	0.25
Ethylene	2.7	36	1372	1217	4.62	6.08	273	0.88
Ethylene Oxide (oxirane)*	3.6	100	1553	1060	5.32	10.01	276	3.75
Heptane	1.05	6.7	1623	1033	5.64	5.60	374	1.09

Hexane	1.20	7.4	1610	1037	5.59	5.55	356	1.09
Hydrogen*	4.0	75	628	1159	2.07	3.71	1075	5.80
Hydrogen Cyanide*	5.6	40	1402	2235	4.66	8.47	1049	2.77
Isobutane	1.80	8.4	1638	1134	5.66	5.64	288	1.07
Isobutylene (2-methylpropene)	1.80	9.6	1596	1197	5.47	5.93	182	0.59
Methane	5.0	15.0	1463	1797	4.93	6.75	550	0.77
Methanol	6.7	36 (60 C)	1543	1042	5.33	5.48	285	0.90
ethylamine	3.5	14.0	1802	1235	6.29	6.28	351	1.06
methylamine	4.9	20.7	1636	1361	5.67	6.63	135	0.71
n-Butanol	1.7	12.0	1507	991	5.21	5.54	363	0.83
Nonane	0.80	6	1589	1016	5.48	5.67	356	0.87
Octane	0.92	6.5	1618	1019	5.58	5.62	382	1.01
Pentane	1.40	7.8	1592	1055	5.51	5.49	320	1.07
Propane	2.1	9.5	1530	1331	5.26	6.18	17	0.14
Propene (Propylene)	2.4	11.0	1622	1442	5.53	6.61	202	0.56
Propylene Oxide (epoxypropane)	2.8	37	1682	1098	5.82	6.50	368	0.74
Propyne (Methylacetylene)*	1.70	11.7	1257	1856	4.20	7.96	815	2.71
Styrene	1.10	6.1	1638	1455	5.58	6.75	231	0.75

Toluene (100 C)	1.20	7.1	1597	1316	5.44	6.23	65	0.27
Trans-2-Butene	1.7	9.7	1539	1203	5.23	5.93	120	0.42
Trimethylamine	2.0	12.0	1567	1104	5.42	6.07	246	0.40

Table: These data relate to room temperature and atmospheric pressure except when another temperature is mentioned in the table. They are measured using a 2 inch tube with a spark ignition test setting. Values of LLFT and ULFT, (LLDF and ULDF) are derived using interpolation in the graph of the AFT (DF) vs. ϕ and expressed in Kelvin for LFTs and dimensionless units for LDFs. The penultimate (last) column contains sum of mean deviation for the LFTs (LDFs).
* Excluded from TTFU

Result

		LLFT	ULFT	LLDF	ULDF
All 105	Average	1546	1235	5.31	6.20
studied	Std	187	327	0.67	1.08
fuels	Std/Avg	0.121	0.265	0.126	0.175
	Min	628	717	2.07	3.70
	Max	2236	2955	7.55	11.42
	Range	1608	2238	5.47	7.72
TTFU	Ave	1586	1198	5.46	6.00
	Std	79	205	0.31	0.44
	Std/Avg	0.050	0.171	0.057	0.073
	Max	1821	1823	6.43	7.16
	Min	1372	974	4.62	5.38
	Range	449	848	1.81	1.79

Table: Average values and standard deviations of adiabatic flame temperature and density factor at both explosive limits for all studied fuels and for the thermal theory fuel universe.

Conclusion

- Thermal theory would suggest aggregation of AFTs around their mean.
- While, judging by the ratio of standard deviation over the average, AFT at the LEL shows some aggregation around the mean it is hard to claim considerable aggregation around the mean for AFT at the UEL.
- We have introduced DF (expansion ratio) to achieve better aggregation around the mean at ELs.
- Compounds whose AFT at ELs have greatest deviations from the mean (main culprits) are, respectively, cyanogen, acetylene, hydrogen cyanide, allene, hydrogen, propyne, deuterium, acrylonitrile and ammonia.

Conclusion

- Compounds whose DF at ELs have greatest deviations from the mean (main culprits) are, respectively, cyanogen, hydrogen, deuterium, acetylene, ethylene oxide, allene , carbon monoxide, hydrogen cyanide, propyne, and acrylonitrile.
- Thermal theory fuel universe (TTFU) is defined by excluding hydrogen, compounds with triple or adjacent double bounds and unstable compounds (UEL=100%).
- In TTFU AFT is approximately constant at LEL while DF is approximately constant at both LEL and UEL in TTFU.
- To estimate LEL of a fuel in TTFU we graph AFT vs. ϕ and interpolate the value of ϕ corresponding to the mean AFT at LEL.
- To estimate UEL of a fuel in TTFU we graph DF vs. ϕ and interpolate the value of ϕ corresponding to the mean DF at UEL. When DF is always greater than the mean DF we assume the inflection point in the DF vs. ϕ graph to correspond to the UEL.

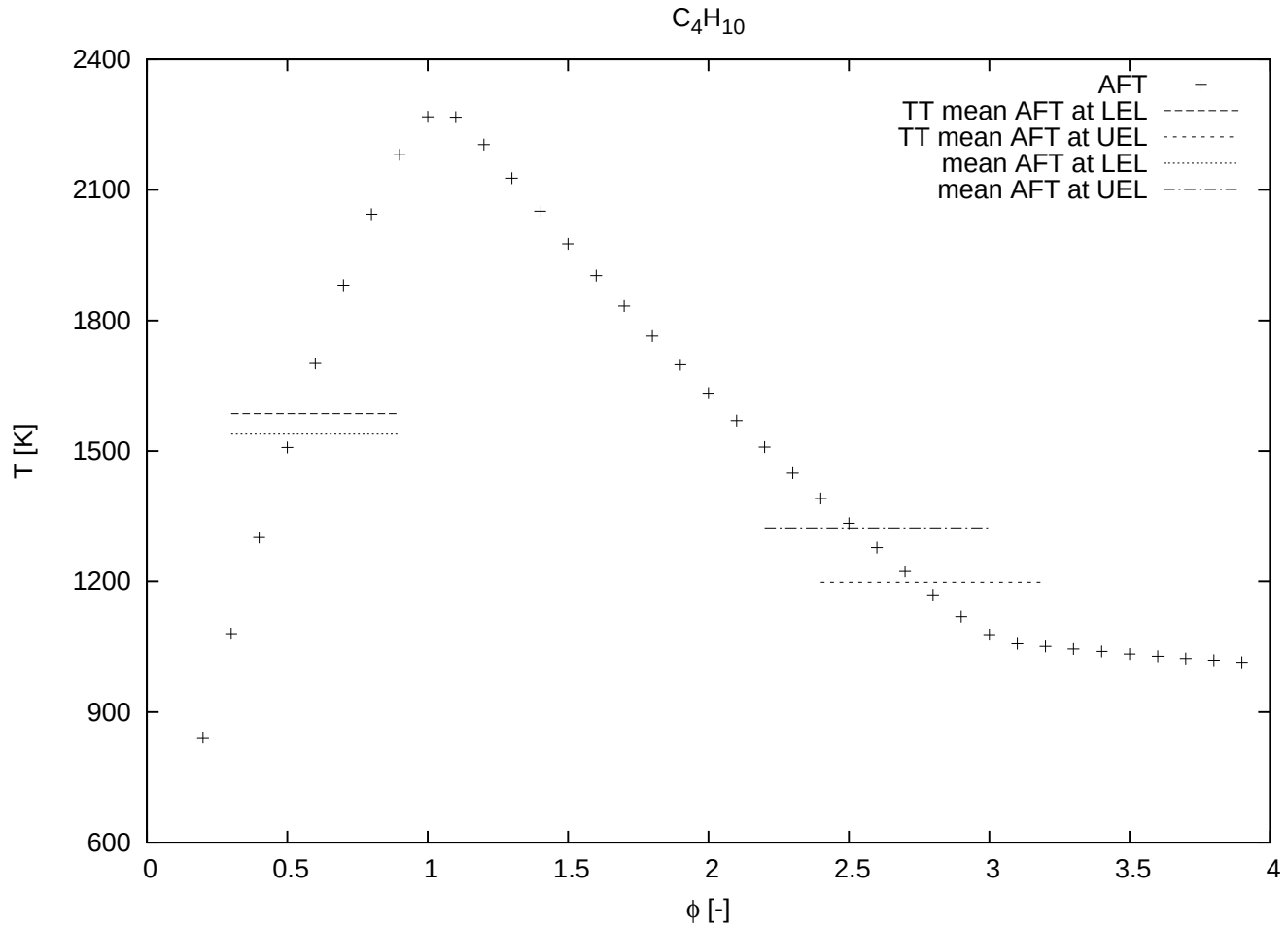


Figure: Adiabatic flame temperature vs. equivalence ratio computed for Butane. The mean values of adiabatic flame temperature (AFT) at the lower explosive limit (LEL) and at the upper explosive limit (UEL) are marked by horizontal bars on the graph.

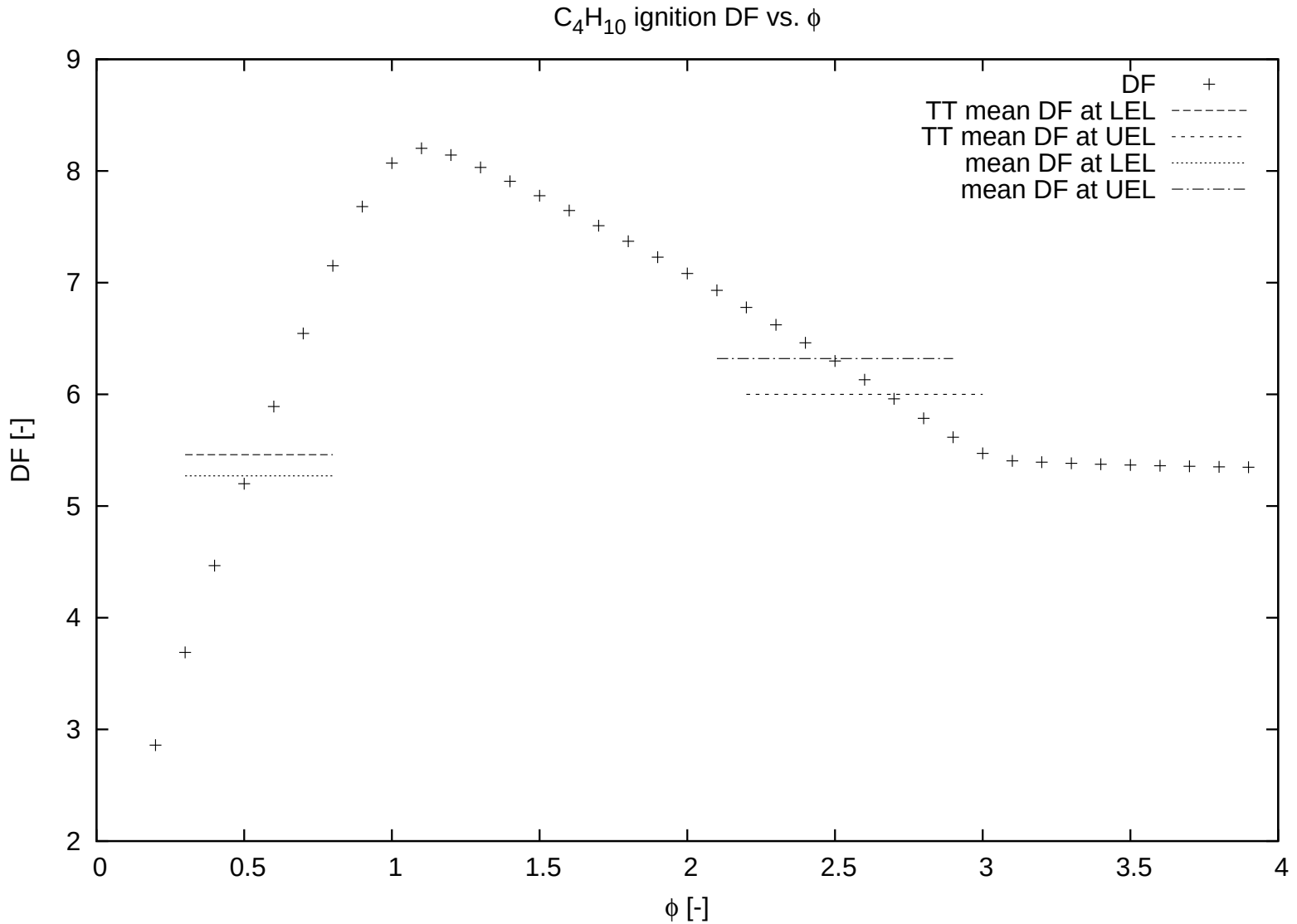


Figure: Density factor vs. equivalence ratio computed for Butane. The mean values of density factor (DF) at the lower explosive limit (LEL) and at the upper explosive limit (UEL) are marked by horizontal bars on the graph.

Flammable	LEL	UEL	LEL P AFT TT	UEL P AFT TT	LEL P DF TT	UEL P DF TT	LEL P AFT	UEL P AFT	LEL P DF	UEL P DF
1,3-Butadiene	2.00	12.00	1.85	38.28	1.89	10.86†	1.77	21.03	1.79	10.86†
1-Butene	1.60	10.00	1.77	10.40	1.78	10.83	1.69	8.88	1.69	8.98
2,2-Dimethylpropane	1.40	7.50	1.40	6.60	1.40	6.42	1.34	6.09	1.33	5.99
2-Butanone (Methyl Ethyl Ketone)	1.90	10.00	1.99	9.72	1.99	9.67	1.90	8.95	1.89	9.02
3-Methyl-1-Butene	1.50	9.10	1.44	7.70	1.45	7.67	1.37	7.06	1.38	7.14
Acetaldehyde diethyl acetal (Acetal)	1.60	10.00	1.29	6.7	1.26	7.4	1.23	6.1	1.20	6.9
Acetone	2.60	13.00	2.71	13.0	2.69	12.8	2.59	12.00	2.55	11.96
Acetylene*	2.50	100.0	3.43		3.63		3.29		3.45	
Acrylonitrile*	3.00	17.0	2.57		2.66	12.65†	2.47		2.53	12.65†
Allene*	1.50	11.50	2.38	12.39	2.49	12.39†	2.28	12.39	2.36	12.39†
Allyl alcohol (2-propen-1-ol)	2.50	18.00	2.55	15.28	2.57	16.59†	2.45	14.03	2.44	15.40
Ammonia	15.00	28.00	14.34	43.2	14.09	37.1	13.73	40.0	13.40	34.11
Benzene	1.30	7.90	1.4	17.6	1.44	19.3†	1.3	11.0	1.4	9

Butyl Acetate (butyl ethanoate)	1.40	8.00	1.71	8.09	1.68	8.38	1.64	7.44	1.60	7.83
Carbon Monoxide*	12.50	74.00	14.99	76.00	17.53	51.78	14.36	72.3	16.60	47.74
Cis-2-Butene	1.70	9.70	1.8	10.04	1.8	9.44	1.7	8.8	1.7	8.8
Cumene (isopropylbenzene)	0.90	6.50	0.90	6.2	0.94	5.4	0.86	4.41	0.89	4.25
Cyanogen*	6.60	32.00	3.99	17.32	4.12		3.83	17.32	3.92	
Cyclohexane	1.30	7.80	1.23	6.02	1.23	5.91	1.18	5.6	1.16	5.5
Cyclopropane	2.40	10.40	2.28	21.27	2.31	21.93†	2.18	13.83	2.20	21.93†
Decane	0.72	5.00	0.72	3.58	0.73	3.57	0.69	3.3	0.70	3.3
Deuterium*	4.90	75.00	16.39	74.03	19.56	46.91	15.74	70.11	18.53	42.21
Dimethyl Ether	3.40	27.00	3.5	18.95	3.4	20.58	3.3	17.3	3.27	19.1
Ethanal	4.00	60.00	3.46	18.37	3.50	17.99	3.31	16.87	3.33	16.71
Ethane	3.00	12.40	3.15	14.13	3.18	13.01	3.01	13.09	3.02	12.10
Ethanol	3.30	19.00	3.62	16.93	3.55	17.14	3.45	15.53	3.37	15.94
Ethyl Acetate (ethyl ethanoate)	2.20	11.00	2.23	10.25	2.23	10.36	2.13	9.39	2.11	9.61
Ethyl Benzene	1.00	6.70	1.03	7.88	1.04	9.32	0.98	5.26	0.98	5.00
Ethylene	2.70	36.00	3.33	29.84	3.44	48.70†	3.19	24.78	3.27	21.53
Ethylene Oxide (oxirane)*	3.60	100.0	3.71	33.62	3.73	29.50†	3.55	27.54	3.55	29.50†
Heptane	1.05	6.70	1.01	4.98	1.00	5.01	0.97	4.59	0.95	4.69

Isobutane	1.80	8.40	1.72	8.06	1.71	7.84	1.64	7.45	1.62	7.32
Isobutylene (2-methylpropene)	1.80	9.60	1.78	9.56	1.79	9.33	1.70	8.72	1.70	8.71
Methane	5.00	15.00	5.52	21.64	5.70	18.08	5.28	20.13	5.41	16.69
Methanol	6.70	36.00	6.86	31.71	6.74	31.76	6.54	28.99	6.40	29.35
Monoethylamine	3.50	14.00	2.88	14.34	2.86	14.83	2.76	13.18	2.72	13.86
Monomethylamine	4.90	20.70	4.68	23.16	4.64	23.88	4.46	21.26	4.41	22.29
n-Butanol	1.70	12.00	1.84	9.02	1.82	9.28	1.75	8.28	1.73	8.66
Nonane (Affen)	0.80	6.00	0.80	3.95	0.80	3.99	0.76	3.64	0.76	3.74
Octane (Affen)	0.92	6.50	0.89	4.41	0.89	4.43	0.85	4.06	0.85	4.14
Pentane	1.40	7.80	1.39	6.71	1.38	6.65	1.33	6.20	1.31	6.22
Propane	2.10	9.50	2.22	10.33	2.22	9.88	2.12	9.55	2.10	9.21
Propene (Propylene)	2.40	11.00	2.32	15.60	2.36	14.96	2.22	11.87	2.24	11.75
Propylene Oxide (epoxypropane)	2.80	37.00	2.51	16.22	2.50	16.96†	2.40	14.86	2.38	16.96†
Propyne (Methylacetylene)*	1.70	11.70	2.38	12.39	2.48	12.39†	2.28	12.39	2.36	12.39†
Styrene	1.10	6.10	1.05	18.76	1.07	8.80†	1.00	10.82	1.01	8.80†
Toluene	1.20	7.10	1.19	10.52	1.21	11.66	1.14	6.92	1.14	6.02
Trans-2-Butene	1.70	9.70	1.78	9.85	1.81	9.36	1.70	8.78	1.72	8.74
Trimethylamine	2.00	12.00	2.04	11.09	2.02	12.23†	1.95	10.18	1.92	11.21

Prediction method	T AFT P LL	T AFT P UL	T DF P LL	T DF P UL	AFT P LL	AFT P UL	DF P LL	DF P UL
all fuels	19	31	23	25.5	18.5	24.5	22	24
all fuels no inflection point	19	32	23	20	18.5	25.5	22	21
TTFU	5	33.5	5.5	25	6	25.5	6.5	23
TTFU no inflection point	5	33	6	19	6	26	7	20

Table: Average of absolute relative error in predicted values of flammability limits (%)

Specific version of thermal and density theory

- There is a threshold temperature dependent on the chemical nature of flammable material above which flame can propagate.
- There is a threshold density factor dependent on the chemical nature of flammable material above which flame can propagate.
- Group contribution methods are used for predicting various material properties, e.g., enthalpy of formation, flash point.
- Group contribution methods are based on the additive principle.

Specific version of thermal and density theory

- To compare specific versions of thermal theory and density theory of flame propagation we use GC to estimate LFL, DF at LFL and AFT at LFL; also we use GC to estimate UFL, DF at UFL and AFT at UFL.
- Use the values of DF at LFL and AFT at LFL to estimate LFL; also use the values of DF at UFL and AFT at UFL to estimate UFL.
- Comparing FL values estimated through DF with directly estimated FL values is a judgment on the specific version of density theory.
- Comparing FL values estimated through AFT with directly estimated FL values is a judgment on the specific version of thermal theory.
- Comparing FL values estimated through AFT with FL values estimated through DF enable us to compare thermal and density theories of flame propagation.

Specific version of thermal and density theory

- 154 compounds are used including 46 test compounds and 108 used for estimating 27 parameters.
- LLDF $= \alpha + n_1 MW + n_2 C_0 + n_3 C_1 + n_4 C_2 + n_5 C_3 + n_6 C_4 + n_7 H + n_8 CO + n_9 COO + + n_{10} O + n_{11} OH + n_{12} Cl + \cdots$

Estimation method	average relative error at the LFL	average relative error at the LFL
GC thorough DF	0.071	0.111
GC thorough AFT	0.10	0.134
GC	0.513	0.258

Table: Average relative error for estimation of flammability limit.

Future work

- Demonstrate the use of this method in calculating explosive limit dependence on T and P.
- Generalize this method to calculation of explosive limits in a fuel-oxidant-diluent mixture.
- Generalize this method to calculation of explosive limits in a fuel-oxidant-fuel mixture.
- Devise a statistical mechanical model for calculating auto-ignition temperature.