

**"USING THE EXPLOSION HAZARD
CRITERIA OF PROGRAM 'CHETAH'
TO PREDICT THE FLAMMABILITY LIMITS
OF VAPOUR FUELS IN AIR"**

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SUMMARY

More than twenty years ago, the ASTM designed a computer program named CHETAH, to predictively evaluate the thermal explosion hazard of a compound or a mixture. CHETAH, which is still in use in the chemical industry, generates four hazard criteria based on some easily available or estimated thermochemical and structural data.

We propose to extend the use of these explosion hazard criteria to the evaluation of gas phase flammability, in order to estimate the flammability limits of organic fuels in air. Statistics on over two hundred compounds show that some of the explosion criteria computed by CHETAH can be used as flammability criteria, even if some care must be exercised regarding the domain of validity of this extension.

The estimation method that we propose applies to lower flammability limits in air, at atmospheric pressure and ambient temperature, of hydrocarbons and their oxygen and nitrogen derivatives. It is predictive in most cases, and very easy to use. In more than 2 cases over 3, its precision is of the same order that experimental determinations, that is typically ± 0.2 mole percent. The domain of validity of the method is described precisely, and the major exceptions are reported.

CHETAH COMPUTER PROGRAM

Statistics published by the American Society for Testing Material showed that the sensitivity of an explosive material is strongly correlated to the maximum energy it is potentially able to release while decomposing [1]. The maximum energy potential calculation is quite easy, provided that some thermochemical properties of the compound are known. In most cases, required data can be estimated accurately using the group contribution method described by Benson [2].

The Chemical Thermodynamics and Energy Hazard Evaluation Program (CHETAH) was designed to perform these calculations on a computer. It contains in its data bank many group contributions and thermochemical data necessary to obtain the maximum energy potential from the only developed chemical formulae of the reactants. CHETAH then generates four criteria to determine whether the compound, or mixture, presents a 'low', a 'medium' or a 'high' explosion hazard.

Explosion hazard criteria

The four hazard criteria used by CHETAH are briefly explained in the following. For reasons of homogeneity with other authors, we express all thermodynamic values in calories. Conversion to SI units is made on the basis of 4.184 Joules per calory exactly.

First criterion: C1

For the first criterion, CHETAH defines those products which could be formed from the reaction mixture and which would release the maximum amount of energy: ΔH_{\max} . The program lists the energy hazard potential as 'low' if ΔH_{\max} is more positive than -0.3 kcal.g^{-1} , as 'medium' if it is between -0.3 and -0.7 kcal.g^{-1} , and as 'high' if it is equal or more negative than -0.7 kcal.g^{-1} .

Second criterion: C2

The second criterion is based on the idea that a compound containing enough oxygen to convert itself into its oxidation products is more hazardous than one which does not. Therefore, this criterion compares the difference between the heat of combustion of the compounds and the maximum heat of decomposition, $\Delta H_c - \Delta H_{\max}$, to ΔH_{\max} itself.

Third criterion: C3

The third criterion is based on the oxygen balance, given by:

$$C3 = \left(n_O - 2n_C - \frac{n_H}{2} \right) \frac{16}{M} \times 100\%$$

where n_O , n_C and n_H stand for the numbers of oxygen, carbon and hydrogen gramme-atoms present in M grammes of the mixture.

If the oxygen balance is greater than +160% or less than -240%, the energy hazard potential is rated as 'low'; if it is between -240 and -120%, or between +80 and +160%, the energy hazard potential is rated as 'medium'; if it is between -120 and +80%, the energy hazard potential is rated as 'high'.

Fourth criterion: C4

The fourth criterion is represented by the following equation:

$$C4 = 10 \Delta H_{\max}^2 \frac{M}{n}$$

where ΔH_{\max} is the maximum energy of decomposition defined for criterion C1, and n the number of gramme-atoms contained is the mass M of the mixture. The energy hazard potential is rated as 'high' if $C4$ is less than 30, as 'medium' if it is between 30 and 110, and as 'high' if it is greater than 110.

Principle

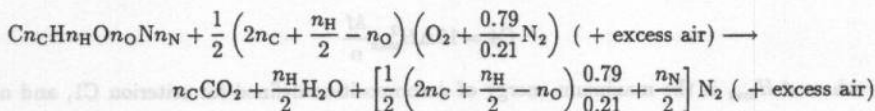
For each one of its four criteria, CHETAH assumes that the transitions from 'low' to 'medium', and from 'medium' to 'high' hazard potentials are characterized by unique values, independently of the nature of the reactants. These transition values were chosen once for all by an ASTM task group, on the basis of statistical results [1].

Let us now consider mixtures of a gaseous fuel with air at increasing concentrations, from pure air to stoichiometry. There is a particular concentration, named the lower flammability limit, that marks the frontier between non flammable and flammable atmospheres. CHETAH hazard criteria grow while the risk of inflammation increases, and this transition is characterized by a particular value of each criterion. Provided that these values are either independent of the fuel or correlated to some easily available property of it, this would result in a precise and predictive method of estimation of flammability limits. The objective of our work was to verify this hypothesis, and to develop and optimise such an estimation method.

Computing the hazard criteria

We consider the case of fuel-air mixtures in which the oxidizer is in excess. The most exothermic reaction that can take place is the total combustion of the fuel, and the hazard criteria calculation is thus very simple. Let the chemical formula of the fuel be: $Cn_C Hn_H On_O Nn_N$. Its molecular weight is: $M_F = 12 \times n_C + n_H + 16 \times n_O + 14 \times n_N$, and it contains $n_F = n_C + n_H + n_O + n_N$ gramme-atoms per mole. We assume that air is composed of 21% of oxygen and 79% of nitrogen, have a molecular weight $M_A = 0.21 \times 32 + 0.79 \times 28 = 28.84 \text{ g.mol}^{-1}$, and contains $n_A = 2$ gramme-atoms per mole.

The reaction we consider is the ideal combustion at 298 K:



The enthalpy of combustion per mole of fuel is given by:

$$\Delta H_c^\circ = n_C \Delta H_f^\circ(CO_2) + \frac{n_H}{2} \Delta H_f^\circ(H_2O) - \Delta H_f^\circ(F)$$

The standard enthalpies of formation of carbon dioxide and water in the gaseous state are: $\Delta H_f^\circ(\text{CO}_2) = -94,045 \text{ kcal.mol}^{-1}$ and $\Delta H_f^\circ(\text{H}_2\text{O}) = -57.798 \text{ kcal.mol}^{-1}$ at 298 K. $\Delta H_f^\circ(F)$ is the standard molar enthalpy of formation of the fuel in the gaseous state at 298 K. When not available in the thermodynamic tables, it can be estimated by the Benson's group contribution method.

Notice that in the case of lean fuel-air mixtures, criterion C2 has no meaning because the combustion is the most exothermic possible reaction (C2 would always be equal to 0). If x is the molar fraction of fuel in the mixture, the three remaining criteria are given by:

$$C1 = \frac{x\Delta H_c^\circ}{xM_F + (1-x)M_A} \quad (1)$$

$$C3 = \left(0.42(1-x) + xn_O - 2xn_C - \frac{xn_H}{2} \right) \frac{1600}{xM_F + (1-x)M_A} \quad (2)$$

$$C4 = \frac{10(x\Delta H_c^\circ)^2}{(xM_F + (1-x)M_A)(xn_F + (1-x)n_A)} \quad (3)$$

STATISTICAL ANALYSIS

Experimental data

The major difficulty, while selecting flammability data, is that experimental results are strongly influenced by the operational conditions used to obtain them. As the standard measurement methods that exist are quite recent, it is usual to find wide discrepancies between different sources. We retained preferably the data from Coward and Jones [3], who mentioned systematically the type of apparatus and the experimental conditions. Two other sources were also used: the Sax's Dangerous Properties of Industrial Materials [4], and the Hazardous Chemical Data Book [5].

In addition, we determined several flammability limits using an improved version of the apparatus described by Coward and Jones, designed at the laboratory [6, 7].

A total of 216 test molecules were finally selected, all belonging to hydrocarbons, or oxygen and nitrogen hydrocarbon derivatives. One third approximately are hydrocarbons, mostly alkanes, cycloalkanes and aromatics, plus a few alkenes and alkynes. About one half are oxygenated hydrocarbons, mainly alcohols, ethers, ketones and aldehydes, plus some acids and anhydrides. The remainder are nitrogen compounds, such as amines, azides, amides and others. The exhaustive list of the test fuels was published elsewhere [6].

Table 1: Hazard rating of just flammable fuel-air mixtures: statistics on 216 test fuels

Criterion	C1	C3	C4
Mean	-0.362	10.82	17.86
Standard deviation	0.046	1.70	4.39
Minimum	-0.237	15.82	7.63
Maximum	-0.477	6.55	30.12
Domain of definition	$-\infty$	-800	0
	0	+100	$+\infty$

Hazard rating of just flammable mixtures

In order to determine whether the explosion hazard criteria are representative of flammability, we examined the hazard rating of 'just flammable' mixtures, that is, those mixtures in which the fuel concentration is just sufficient to allow flame propagation. Accordingly, we computed the criteria for fuel-air mixtures at the limit concentration, for each one of the 216 test fuels. The results are synthetically reported in table 1, and graphically in figures 1-A and 1-B, which show the proportion of flammable compositions as functions of C1 and C3. Similar observations could be done with C4, but this criterion has no direct physical meaning and is therefore less interesting for illustrative purposes. The domain of definition of each criterion appears divided into three zones:

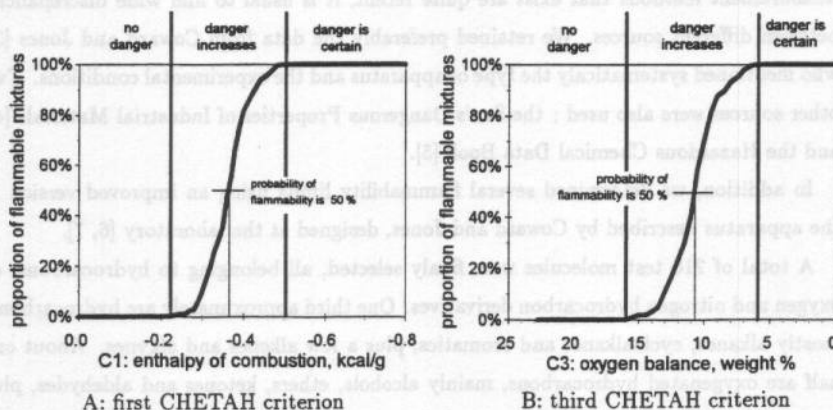


Figure 1: Distribution of flammable mixtures as a function of hazard criteria values

One 'safe' zone: any mixture that release less than 0.237 kilocalory per gramme while burning is non flammable. Also, any mixture that contains more than 15.8 weight percent oxygen in excess is not flammable.

One definitely 'dangerous' zone: 100% of the mixtures that release more than 0.477 kilocalory per gramme, or contain less than 6.6 % excess oxygen, are flammable.

One 'fuzzy' zone: the transition from safety to definite danger is not marked by a unique, well defined value of the criterion. Instead, the probability of flammability grows rapidly from 0 to 100 %, within a relatively narrow portion of the domain of variations. These domains of uncertainty are roughly centered on the mean values of table 1. Hence, a mixture having an enthalpy of combustion equal to $-0.362 \text{ kcal.mol}^{-1}$, or an oxygen balance equal to 10.82%, has a probability of approximately 50% to be flammable.

The major conclusion of this preliminary study is that no satisfying corelation with the nature of the fuel could be found. The values of criteria that mark the transition between flammable and non flammable mixtures does not depend on the chemical family to which the fuel belongs. They can no more be clearly corelated to any thermodynamic property of the fuel, nor to its degree of insaturation, elemental composition, molecular mass, nor to any simple molecular property. Only a slight influence of the chain branching of the carbon skeleton was evidenced [6], leading to a kinetic interpretation. The study of the influence of kinetics would be far beyond the scope of this work, and would result in much more complex calculations. To keep simplicity and predictivity, we prefer to consider that:

For each criterion C1, C3 or C4, there is a value C1*, C3* or C4*, caracterising the frontier between non flammable and flammable compositions, with an uncertainty that cannot be explained by simple corelations.

THE ESTIMATION METHOD

Assuming these transition values C_i^* are determined, estimating a flammability limit consists in finding the composition so that $C_i = C_i^*$. Therefore, our objective was to determine the optimal values for C_i^* , that is, those values that minimize the errors of estimation. For each fuel, there are three estimations, corresponding to the three criteria:

First criterion:

We want to find the molar percentage x so that $C1 = C1^*$. Relation 1 gives:

$$x = \frac{C1^*M_A}{\Delta H_c^\circ - C1^*(M_F - M_A)}$$

Third criterion:

As a result of relation 2, the third CHETAH criterion equals $C3^*$ when:

$$x = \frac{1600 \times 0.42 - C3^*M_A}{C3^*(M_F - M_A) - 1600(n_O - 2n_C - \frac{n_H}{2} - 0.42)}$$

Fourth criterion:

Relation 3 gives:

$$x^2 \left[(M_F - M_A)(n_F - n_A) - 10 \frac{\Delta H_c^\circ}{C4^*} \right] + x [n_A(M_F - M_A) + M_A(n_F - n_A)] + M_A n_A = 0$$

The positive root of this equation is the mole fraction of the fuel so that $C4 = C4^*$.

Optimisation

Finding the optima for $C1^*$, $C3^*$ and $C4^*$ required the following iterative process:

- 1) Choosing one initial value C_i^* ; we choosed the mean values reported in table 1.
- 2) Computing the 216 estimated lower flammability limits with this value.
- 3) Computing the standard error of these estimations, given by:

$$\left(\frac{1}{215} \right)^{1/2} \left(\sum_{216} Err^2 - \frac{\left(\sum_{216} Err \right)^2}{216} \right)^{1/2}$$

where *Err* stands for the estimation error: estimated limit minus experimental limit.

- 4) Checking for minimum.
- 5) Adjusting C_i^* and going back to step 2.

The results are reported in table 2. The first column contains the optimal values found for $C1^*$, $C3^*$ and $C4^*$. The second column contains statistics on the absolute estimation errors: the standard range of error (mean \pm standard deviation), followed by the extreme errors observed among the 216 test molecules. The third column contains the same statistics for relative errors. Criteria $C1$ and $C4$ give quite similar results: estimation

Table 2: Estimation results: statistics on absolute and relative estimation errors

Criterion	Absolute, mol. %		Relative, % of experimental value	
	standard	extreme	standard	extreme
C1* = -0.345	-0.08±0.28 %	-1.15...+1.00 %	-3.2±13.4 %	-28.4...+48.4 %
C3* = 11.2	-0.03±0.48 %	-3.84...+2.87 %	-1.1±15.1 %	-28.9...+61.6 %
C4* = 15.1	-0.13±0.28 %	-1.23...+0.94 %	-6.2±13.1 %	-30.6...+44.6 %

errors are typically comprised between -0.4 and +0.2 mole percent approximately. With criterion C3, the standard and extreme errors are much greater. Concerning relative errors, C1 and C4 are still very similar. Estimations obtained with C4 are generally lower than those obtained with C1; with these two criteria, the dispersion of estimates is comparable, while C3 gives more dispersed results.

Figure 2 shows the distribution of absolute errors for the three series of estimations. In over 60% of the cases, the estimation is exact to ±0.2 mole% (to ±0.6% in more than 9 cases over 10). C3 gives the greatest number of very good, but also the greatest number of very bad estimates. C4 gives the smallest number of very good, and the smallest number of very bad estimates. It also gives more slightly underestimated limits ($-0.6 < Err < -0.2\%$), and fewer overestimated limits ($Err > 0.2\%$) than the other criteria. Besides these few differences, the three series of estimates seem quite similar, and some reflexion on the reliability of flammability data will help to make a choice.

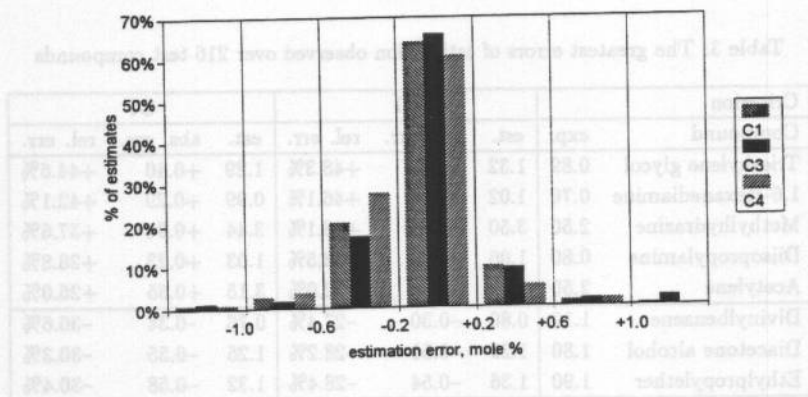


Figure 2: Estimation results: distribution of absolute estimation errors

Precision versus reliability: what is the best criterion for flammability evaluation?

It is usual to judge an estimation method on its precision. But when safety is concerned, not only the amplitude, but also the direction of the error must be taken into account. When negative, errors on lower flammability limits lead to consider flammable mixtures that are not, with no dangerous consequences. On the other hand, large positive errors lead to point as secure mixtures that are strongly flammable, with dramatic potential consequences. Accordingly, estimations obtained with C1 and C4 are more exact and more reliable than those obtained with C3. Besides, estimations obtained with C1 are slightly more exact, while those obtained with C4 are more reliable in terms of safety.

Domain of application and exceptions

The method that we propose is intended to evaluate the lower flammability limits in air, of fuels in the stable gaz phase, excluding droplets or dust clouds. All the experimental values retained for statistics were measured at atmospheric pressure, and temperatures from ambient to 100°C. As flammability limits vary slightly with pressure and temperature, it is recommended to be very careful while extrapolating estimation results.

The method applies to hydrocarbons and oxygen or nitrogen substituted hydrocarbons. The precision is generally better with hydrocarbons, but the majority of the oxygen and nitrogen derivatives tested gave good or acceptable results. Major exceptions are reported in table 3: five compounds present a positive error greater than 25% relative. Notice that

Table 3: The greatest errors of estimation observed over 216 test compounds

Criterion		C1			C4		
Compound	exp.	est.	abs. err.	rel. err.	est.	abs. err.	rel. err.
Triethylene glycol	0.89	1.32	+0.43	+48.3%	1.29	+0.40	+44.6%
1,6-Hexanediamine	0.70	1.02	+0.32	+46.1%	0.99	+0.29	+42.1%
Methylhydrazine	2.50	3.50	+1.00	+40.1%	3.44	+0.94	+37.6%
Diisopropylamine	0.80	1.06	+0.26	+32.5%	1.03	+0.23	+28.8%
Acetylene	2.50	3.30	+0.80	+32.0%	3.15	+0.65	+26.0%
Divinylbenzene	1.10	0.80	-0.30	-27.4%	0.76	-0.34	-30.6%
Diacetone alcohol	1.80	1.29	-0.51	-28.2%	1.25	-0.55	-30.3%
Ethylpropylether	1.90	1.36	-0.54	-28.4%	1.32	-0.58	-30.4%

for these fuels, C1 gives much more erroneous results than C4. The three compounds presenting estimation errors more negative than -30% are also reported. We cannot propose any satisfactory explanation to these exceptions. Since we could not verify experimentally all the values collected, we can even not exclude the possibility of erroneous data.

The method does not apply to non hydrocarbons such as hydrogen or carbon monoxide, or to compounds containing other elements than the four cited above. Attempts to apply the method to halogenated hydrocarbons resulted in strongly erroneous estimations. No other classes of fuel have been tested yet. Thus, it is recommended to limit the usage of the method to its clearly identified domain of validity.

CONCLUSION

A statistical study was conducted. Two of the four CHETAH explosion hazard criteria may be extended to flammability evaluation, with a precision sufficient to allow flammability limit estimation. The method proposed here has an acceptable precision in most cases, considering that the precision of experimental limits is generally not better than one tenth of a mole percent. It is predictive, requires only simple computations, and applies to a great variety of fuels.

Such a method is not intended to totally replace experiments. However, as a predictive approximation tool, it may help saving many expensive and time consuming tests.

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for these fuels CI gives much more erroneous results than CI. The three compounds pre-
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A statistical study was conducted on the four CHEETAH explosion hazard criteria
 may be extended to flammability evaluation, with a precision sufficient to allow hazard-
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