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**“Explosion Pressure”:
The program for calculation of maximum pressure of
explosion for chemical equilibrium conditions**

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Report

“Explosion Pressure”: The program for calculation of maximum pressure of explosion for chemical equilibrium conditions.

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1. Introduction

The program „**Explosion Pressure**” calculates the theoretical maximum explosion pressure for gaseous fuel-oxidiser mixtures in a closed volume. It is designed as a simple tool to make quick estimates. The program works under Windows 98, 2000 and Windows XP systems. Calculation of the maximum pressure is based on the assumption of chemical equilibrium and combustion in constant volume. It uses the minimum free energy method to calculate the composition and properties of products. At this stage of the project adiabatic combustion is assumed. Convection and wall effects are neglected. Numerical procedures needed for chemical equilibrium calculation are written in FORTRAN and are built as a dynamic link library (dll). Graphical interface is written in C++ and it calls the FORTRAN library. Thermodynamic data of used species are stored in a file compatible with Chemkin thermodynamic data format.

2. Mathematical model

The numerical procedure used in the program is based on the free energy minimizing method. This approach is often applied in many procedures calculating chemical equilibrium. The most known programs are Stanjan, CEC, and GasEQ. The method is well known and described in a large number of references [1-4], hence in this report there is no need for a detailed description.

The method used here is simplified as compared to Stanjan or CEC because of a smaller range of problems that needs to be solved by “Explosion Pressure”. It is assumed that:

- only one (mixed) gas phase and one condensed phase are allowed, this holds both for reactants and for products
- loss of energy and other transport phenomena are not taken into consideration.

The problem to be solved is formulated in the following equations of which the first part is derived from element balance equations

$$a_j = \sum_{i=1}^I n_i A_{i,j}, \quad \text{Eq. 1}$$

where:

a_j – moles of j-th element (atom),

n_i – moles of i-th species,

$A_{i,j}$ – number of j-th element in i-th species.

The free energy (Helmholtz function) of the system F is equal to

$$F = \sum_{i=1}^I n_i f_i, \quad \text{Eq. 2}$$

where:

f_i – free energy of i-th species.

Minimizing of F by the method of Lagrange multipliers leads to the set of equations

$$f_i = \sum_{j=1}^J \lambda_j A_{i,j}. \quad \text{Eq. 3}$$

Free energy f_i is calculated from equation (Eq. 4) for an assumed temperature T .

$$f_i = g_i^o + RT \ln x_i + RT \ln \frac{RT}{V}. \quad \text{Eq. 4}$$

where:

$x_i = n_i/n$ – molar fraction of i-th species.

The starting temperature for the iteration loop is set to 3000K. This value is proper for all available fuel-air mixtures. Function g_i^o for i-th species is calculated on the base of its thermodynamic properties.

$$g_i^o(T) = \Delta H_{f_i}^o(T^o) + \{h_i(T) - h_i^o(T^o)\} - Ts_i^o(T). \quad \text{Eq. 5}$$

Substituting Eq. 4 and Eq. 1 to Eq. 3 and using constraints for x_i

$$\sum_{i=1}^I x_i = 1, \quad \text{Eq. 6}$$

we obtain a set of final equations

$$a_j = n \sum_{i=1}^I A_{i,j} \exp\left(-g_i^o + \frac{1}{RT} \sum_{j=1}^J \lambda_j A_{i,j} - RT \ln \frac{RT}{V}\right) \quad j = 1, 2, 3, \dots, J, \quad \text{Eq. 7}$$

$$1 = \sum_{i=1}^I \exp\left(-g_i^o + \frac{1}{RT} \sum_{j=1}^J \lambda_j A_{i,j} - RT \ln \frac{RT}{V}\right) .$$

This set of non-linear equations (Eq. 7) is solved by the use of the Newton-Raphson method. Known values of λ_i allow calculating the composition of the product x_i . Next the temperature T is adjusted to fulfil the energy conservation law (Eq.8)

$$U_{\text{substrates}} = U_{\text{products}} . \quad \text{Eq. 8}$$

More detailed descriptions of the method can be found in references [1-5].

3. Reactants and products

The program was designed for the calculation of explosion of any combustible mixture of ten species, which are divided into two groups: fuel (5 components) and oxidiser (also 5 components). The user can specify the composition of the fuel and oxidiser and mole fraction of fuel in the whole mixture (fuel + oxidiser). The division is made for user's convenience and has no impact on calculation. The program treats the reactants as single mixture. If there are reactants of different phase the mixture is divided into two phases: gas and condensed phase (liquids and solids). Both phases have the same temperature. A list of available fuels is shown below. New fuels (and other species) can be added by the user (see next section: 5.8).

Table 1. The list of available fuels.

No	Name	Formula
1	hydrogen	H ₂
2	methane	CH ₄
3	ethane	C ₂ H ₆
4	propane	C ₃ H ₈
5	butane	C ₄ H ₁₀
6	pentane	C ₅ H ₁₂
7	hexane	C ₆ H ₁₄
8	heptane	C ₇ H ₁₆
9	octane	C ₈ H ₁₈
10	nonane	C ₉ H ₂₀
11	decane	C ₁₀ H ₂₂
12	benzene	C ₆ H ₆
13	toluene	C ₆ H ₅ CH ₃
14	ethene etc.	C ₂ H ₄ etc.

As an oxidiser can be used a mixture of oxygen and any other species e.g. N₂, Ar, He, Ne, CO₂ ...

The full list of products contains 26 species (Table 2). The species were chosen by means of an analysis of the influence of given species on the burnt mixture properties.¹ The current list of products (for given fuel and oxidiser) is automatically prepared by adding species present in the fuel and oxidiser and eliminating species which contain atoms not present in the initial mixture. The product mixture is also divided into two phases if necessary.

Table 2. The full list of available products.

No	Formula	No	Formula
1	H	14	HCN
2	H ₂	15	NO
3	O	16	N ₂ O
4	O ₂	17	NO ₂
5	HO ₂	18	CH ₂ CO
6	H ₂ O	19	NH ₂
7	H ₂ O ₂	20	HNO
8	OH	21	C ₂ N ₂
9	CO	22	NH ₃
10	CO ₂	23	N ₂
11	CHO	24	CH ₃ OH
12	CH ₃	25	C ₂ H ₄
13	CH ₂ O	26	C _{solid}

The list of products (Table 2) is stored in the file "products.lst". It can be changed by the user. Properties of the species used in the calculation are stored in Chemkin format in "THERMO.DAT". Details of the input files will be discussed in section 5.8.

The program can handle the calculation with 100 species (with 4 kinds of atoms in each), 2 phases, 20 elements (in the whole mixture)

4. Installation

The program is installed by unpacking the file: "ExplPress.zip" to a destination directory.

Note: Use of the programme with MS Office 97 and lower may cause loss of certain functions such as the HELP.

5. Using the program

5.1. Overview

The program has a graphical interface (Fig. 1). The input data are:

- composition of fuel (up to 5 species),

¹ This analysis was carried out by Prof. M. Braithwaite (personal correspondence).

- composition of oxidiser (up to 5 species),
- molar percent of fuel in mixture [%],
- initial temperature [K],
- initial pressure [bar].
- single \ loop mode of calculation
- name of results file

Output data are displayed on screen and saved in a results file:

- final temperature [K],
- final pressure [bar],
- overall composition of reactants [mole %].
- composition of products (displayed in descending order) [mole %].

The calculation is done after the CALCULATE button is pressed.

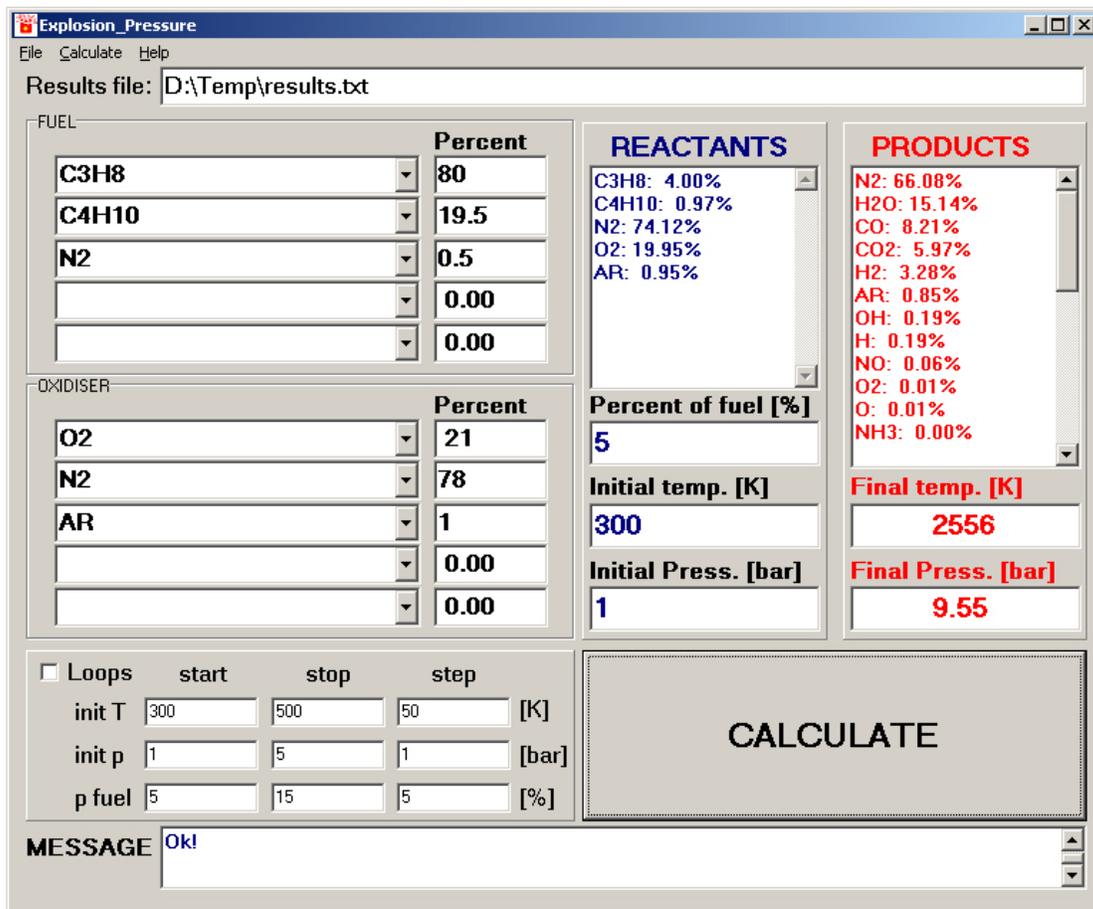


Fig. 1. Graphical interface of the program.

5.2. Menu bar

File

- **Open result file** – opens the text file where the results of calculation are stored,
- **Exit** – closes the program and all files.

Calculate – executes the calculation.

Help

- **Description** – displays the manual,
- **About** – brief information about the program.

5.3. Reactants composition

Composition of the fuel is set in the FUEL panel. User can choose the species from a list expanded under each slot. The list is read from "THERMO.DAT" file. The mole fraction of each specie must be written in the "Percent" box (right hand side of the name slot). The last box (fifth) shows the difference between the sum of specified species and 100%. Non-zero percentage is not acceptable for empty slots (except last one).

Composition of the oxidiser is set in the OXIDISER panel. The method is exactly the same as for the fuel.

Overall composition of the reactants is defined by "percent of fuel" in the whole mixture in the REACTANTS panel. It is expressed as the mole fraction. The "percent of fuel" can be also defined in the Loop panel if loop mode of calculation is chosen: "p fuel" (see subsection 5.6 Loop calculation).

The REACTANTS panel shows also species present in fuel and oxidiser together. After calculation the window displays overall mole composition of the initial mixture.

Note:

Division of reactants into fuel and oxidiser is not strict. Both of them can have any composition including products (e.g. products from a previous reaction can be the reactants in a next one, recirculation, etc.).

5.4. Initial conditions

Initial pressure and temperature is set in the REACTANTS panel in bars and kelvins respectively. They can be also defined in the Loop panel in the loop mode of calculation "init T", "init p" (see subsection Loop calculation).

5.5. Calculation

When the composition of fuel and oxidiser, and the initial conditions are set the program is ready for calculation. The calculation is started by pressing CALCULATE button. If the result file has not be opened before the "Open result file" dialog window will occur. While calculation are finished the results are displayed in the PRODUCTS panel. The first window shows the composition of the products from the most important down to the smallest fraction.

Note: Use the scroll bar to see all products.

The two text windows below show the final temperature in kelvins and pressure in bars.

The whole set of results is saved in the result file to be opened by user. Information about the calculation process, warnings and errors are displayed in the MESSAGE window and saved in theLog.txt file. The file is erased at each run of the program.

5.6. Loop calculation

Calculation can be also done in loops (percent of fuel, temperature, pressure) while the check box “Loops” is checked. The structure of the loops is as below:

- main loop - fuel loop: $pf = \text{from } pf_s \text{ to } pf_e \text{ step } pf_d$
 - sub loop - pressure loop: $p = \text{from } p_s \text{ to } p_e \text{ step } p_d$
 - lowest sub loop- temperature loop: $T = \text{from } T_s \text{ to } T_e \text{ step } T_d$

The initial parameters and results are displayed in the interface for every step respectively.

5.7. MESSAGE window

The MESSAGE window displays the information about the course of a run of the program. It shows:

- current list of reactants,
- case No. (number of current calculation counted from the last run),
- path of results file,
- warnings (e.g. skipped species)
- errors (e.g. bad data format)

The messages for the last run are also stored in the Log.txt file.

5.8. Input files

The program uses two input files: “THERMO.DAT” and “products.lst”.

“THERMO.DAT” includes the thermodynamic data for species in Chemkin format [6]. Lines starting with “!” contain comments and they are skipped by the program.

Listing 1. Data format in THERMO.DAT

```
!FUELS - comment
H2          RUS 78H  2  0  0  0  OG  200.000  6000.000  1000.          1
 0.29328305E+01 0.82659802E-03-0.14640057E-06 0.15409851E-10-0.68879615E-15  2
-0.81305582E+03-0.10243164E+01 0.23443029E+01 0.79804248E-02-0.19477917E-04  3
 0.20156967E-07-0.73760289E-11-0.91792413E+03 0.68300218E+00          4
CH4         J 5/61C  1H  4  0  0G  300.000  5000.000  1000.          1
 0.23594046E 01 0.87309405E-02-0.28397053E-05 0.40459835E-09-0.20527095E-13  2
-0.10288820E 05 0.60290012E 01 0.29283962E 01 0.25691092E-02 0.78437060E-05  3
-0.49102979E-08 0.20380030E-12-0.10054172E 05 0.46342220E 01          4
```

Compared to the Chemkin format there is a minor modification. Optionally at the end part of the file there are stored densities (g/cm^3) of liquid and solid species (Listing 2):

Listing 2. Condensed phase definition

```
CONDENSED          |A8
! DENSITY OF SOLIDS G/CM^3 |comment
C(S)              2.700 |A8 2X F10.5
! DENSITY OF LIQUIDS G/CM^3 |comment
H2O(L)           1.000 |A8 2X F10.5
C7H16(L)         0.68375 |A8 2X F10.5
C8H18(L)         0.70267 |A8 2X F10.5
```

```

C9H20(L)  0.71772          |A8 2X F10.5
.....   .....          |A8 2X F10.5
C6H6(L)   0.8789         |A8 2X F10.5
END                               |A3

```

The data start with “CONDENSED” statement. Next lines contain: name of the specie and its density. The field is finished with “END” statement. If this is not defined the program assumes that volume of condensed species is zero. This does not almost affect results for typical situations where volume of liquids on solids is very small compared to gas phase

Note: The program can take into calculation up to 100 species! If more species are defined in the file an error will occur.

“**products.lst**” – contains the list of names of species which are potential products. The names must exactly match the names in THERMO.DAT file. The names are stored in single line and are separated by blanks. Firstly the program corrects the list in order to remove species which contain elements not present in the reactants e.g. CO₂ when H₂ is burnt in air. Next the program skips the species which are not included in THERMO.DAT file. The skipped product is shown in MESSAGE window and Log.txt file.

5.9. Output files

The program uses two output files: results file and Log.txt file.

The user opens the **results file** by clicking **File>Open result file** menu or just before a calculation if not opened earlier. An example of the listing of the file is printed here at the next page (Listing 3). Below the structure of the output is described:

1st line: Case number
2nd line: Fuel species
3rd line: Mol fraction of fuel species (in fuel)
4th line: Oxidiser species
5th line: Mol fraction of oxidiser species (in oxidiser)
6th line: List of variables with their units (SI)
7th line: Values of variables.
8th... nth line: Values of variables for each iteration in the loop mode (if loops box is checked).

The variables are:

thermodynamic properties:

- R: -denotes reactant mixture initial property values
- fuel -mol fraction of fuel mixture
- p_0[bar] -initial pressure
- T_0[K] -initial temperature
- v_0[m³/kg] -initial specific volume
- u_0[J/kg] -initial specific internal energy
- h_0[J/kg] -initial specific enthalpy
- s_0[J/kgK] -initial specific entropy
- a_0[m/s] -initial sound speed

- mw_0[kg/kmol] -initial mole weight
- P: -denotes product mixture final property values
- p_f[bar] -final pressure
- T_f[K] -final temperature
- v_f[m³/kg] -final specific volume
- u_f[J/kg] -final specific internal energy
- h_f[J/kg] -final specific enthalpy
- s_f[J/kgK] -final specific entropy
- a_f[m/s] -final sound speed
- mw_f[kg/kmol] -final mole weight

compositions:

- R: - denotes reactant composition, in mole fraction (0...1)
- H2
- ...
- O2
- N2 -last specie in reactants
- P: -denotes product composition, in mole fraction (0...1)
- H2
- O2
- N2
- H
- O
- ...
- HO2
- H2O
- OH
- NO -last specie in products

Note: It is recommended to use programs like MS Excel, or Grapher for post-processing. The Grapher can read the file directly. If Excel is used the file should be opened as type "Text file" with space as a column separator. Column width can be Auto-adapted. If MS Notepad is used uncheck "folding lines" or "word wrap" in Format menu.

Log.txt stores messages generated by the program during the last run. It is a copy of the MESSAGE window of the program interface. The file can be useful in case errors or malfunctions occur.

6. Examples of results

The program was used to carry out some calculation for several fuels. The first graph (Fig. 2) shows the maximum pressure as a function of the amount of fuel. In the next graph (Fig. 3) the maximum pressure vs. initial temperature of a mixture is depicted. Also the dependence of explosion temperature and composition of the mixture can be easily studied (Fig. 4). The last graph (Fig. 5) shows the oxygen fraction in the products as a function of initial composition.

Listing 3. Shortened sample of the result file.

```
Case: 1
Fuel: CH4
Mol%: 100.00
Oxidiser: Air
Mol%: 100.00
R: fuel  p_0[bar] T_0[K] ... mw_0[kg/kmol] P: p_f[bar] T_f[K] ... R: CH4      ... P: CH4      O2      ... CH3OH      C2H4      C(S)
R: 0.1000 2.00    400    ... 27.679    P: 13.59    2662    ... R: 1.0000e-01 ... P: 3.9612e-14 3.8569e-03 ... 5.8333e-15 1.1780e-21 0.0000e+00

Case: 2
Fuel: CH4
Mol%: 100.00
Oxidiser: Air
Mol%: 100.00
R: fuel  p_0[bar] T_0[K] ... mw_0[kg/kmol] P: p_f[bar] T_f[K] ... R: CH4      ... P: CH4      O2      ... CH3OH      C2H4      C(S)
R: 0.0500 2.00    400    ... 28.325    P: 9.39     1879    ... R: 5.0000e-02 ... P: 3.1931e-24 9.7565e-02 ... 2.1202e-23 1.3216e-37 0.0000e+00
R: 0.0600 2.00    400    ... 28.196    P: 10.53    2105    ... R: 6.0000e-02 ... P: 2.4085e-21 7.4141e-02 ... 6.1891e-21 5.7931e-33 0.0000e+00
R: 0.0700 2.00    400    ... 28.067    P: 11.56    2308    ... R: 7.0000e-02 ... P: 4.5413e-19 5.1144e-02 ... 5.3777e-19 2.5650e-29 0.0000e+00
R: 0.0800 2.00    400    ... 27.937    P: 12.46    2480    ... R: 8.0000e-02 ... P: 3.4034e-17 3.0116e-02 ... 2.0337e-17 2.3996e-26 0.0000e+00
R: 0.0900 2.00    400    ... 27.808    P: 13.17    2606    ... R: 9.0000e-02 ... P: 1.3840e-15 1.3539e-02 ... 4.2452e-16 7.5988e-24 0.0000e+00
R: 0.1000 2.00    400    ... 27.679    P: 13.59    2662    ... R: 1.0000e-01 ... P: 3.9612e-14 3.8569e-03 ... 5.8333e-15 1.1780e-21 0.0000e+00
R: 0.1100 2.00    400    ... 27.550    P: 13.66    2633    ... R: 1.1000e-01 ... P: 8.1056e-13 6.5622e-04 ... 5.2543e-14 9.1287e-20 0.0000e+00
R: 0.1200 2.00    400    ... 27.420    P: 13.49    2551    ... R: 1.2000e-01 ... P: 9.5035e-12 9.3485e-05 ... 2.7812e-13 2.7764e-18 0.0000e+00
R: 0.1300 2.00    400    ... 27.291    P: 13.22    2451    ... R: 1.3000e-01 ... P: 6.7383e-11 1.3991e-05 ... 9.6174e-13 3.8929e-17 0.0000e+00
R: 0.1400 2.00    400    ... 27.162    P: 12.91    2347    ... R: 1.4000e-01 ... P: 3.4342e-10 2.2141e-06 ... 2.5355e-12 3.3296e-16 0.0000e+00
R: 0.1500 2.00    400    ... 27.032    P: 12.58    2242    ... R: 1.5000e-01 ... P: 1.4323e-09 3.5439e-07 ... 5.6512e-12 2.1077e-15 0.0000e+00
```

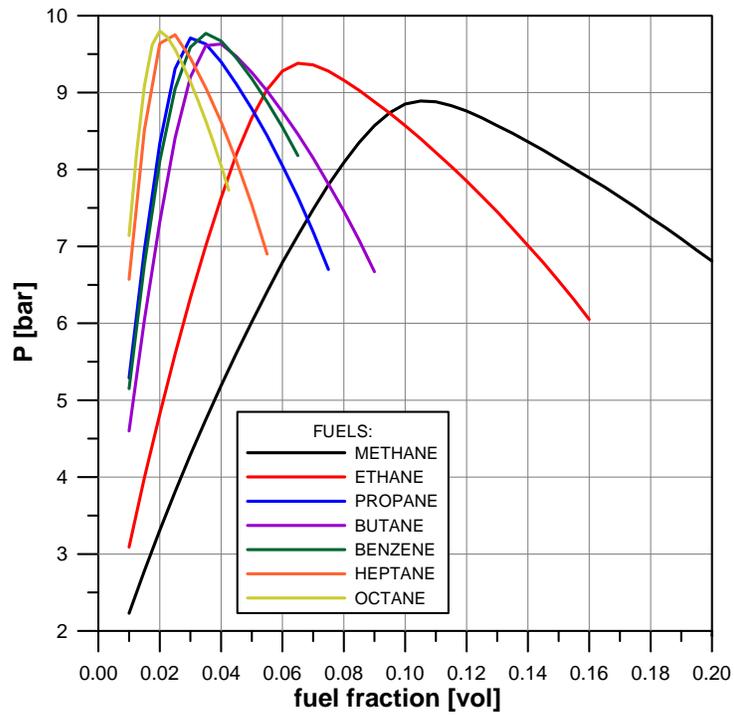


Fig. 2. Maximum pressure vs. volume fraction of fuel (oxidiser: air).

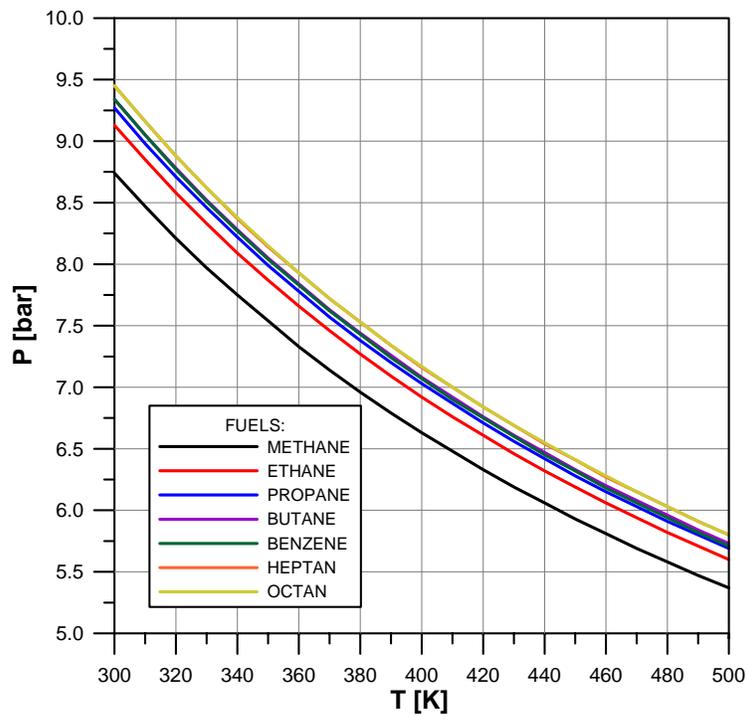


Fig. 3. Maximum pressure vs. initial temperature of stoichiometric mixture (oxidiser: air).

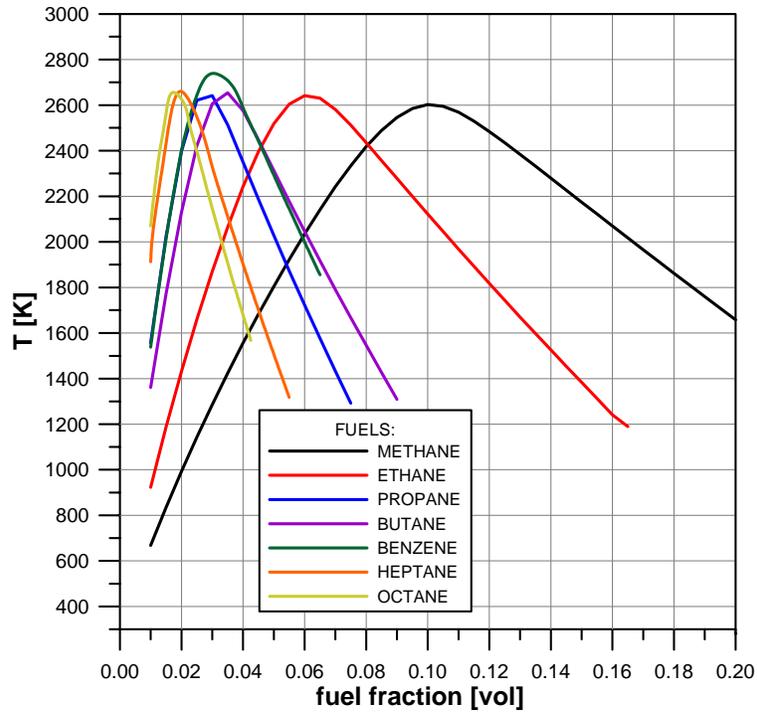


Fig. 4. Maximum temperature vs. volume fraction of fuel (oxidiser: air).

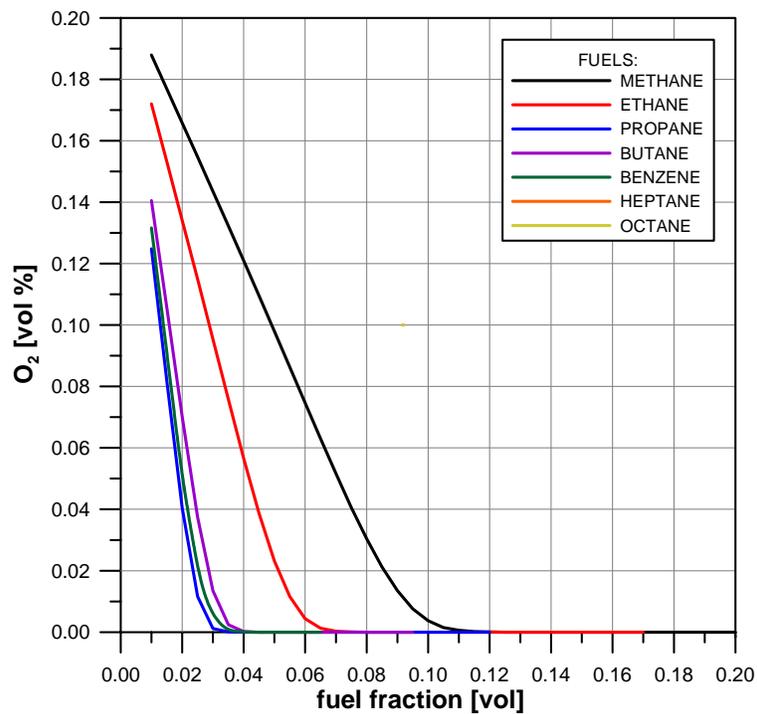


Fig. 5. Concentration of O_2 in products of explosion vs. volume fraction of fuel (oxidiser: air).

7. Conclusions

The program "Explosion Pressure" is a simple tool, which estimates the maximum explosion pressure for basic cases of combustion in a constant volume. A graphical user interface and a small number of necessary input data make it accessible even for a person not familiar with combustion science.

It is important to be aware of the limitations of the program. The limitations are related to the assumptions of chemical equilibrium and adiabatic combustion. The results of the calculation for cases where heat loss is significant will lead to overestimation. In practice significant heat losses will occur when getting closer to the flammability limits (FL). Therefore near the FL the pressure values the programme provides will become far too high.

8. References

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