

# USING THE ENTROPY PRODUCTION TO EVALUATE THE COMBUSTION EFFICIENCY OF A GAS MIXTURE

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**Rezumat.** O metodă de evaluare a eficienței combustiei pentru amestecurile obișnuite de gaze o reprezintă determinarea entropiei produse. Combustibilul și oxidantul sunt amestecate anterior. Este luată în considerare influența presiunii. Poluantul vizat este NO. Aplicațiile iau în considerare atât instalațiile casnice de încălzire în combinație cu cogenerarea electricității, cât și utilizarea gazului pentru motoarele autovehiculelor. Sunt evidențiate metode de îmbunătățire a performanțelor instalațiilor prin cuantificarea entropiei generate.

**Cuvinte cheie:** unde Chapman-Jouguet, control de masă, poluare.

**Abstract.** An evaluation method of the combustion efficiency for usual gas mixtures is done by calculating the entropy production. The fuel and the oxidizer are premixed. The influence of pressure is also considered. The expected pollutant is NO. The applications take into account the home heating installations eventually in combination with electrical power cogeneration, as well as with using gas for vehicle engines. By using the entropy production suggestions to obtain a performable installation are obtained.

**Keywords:** Chapman-Jouguet waves, mass rate control, pollution.

## Notations

$R_u$  – universal gas constant (8.31451 J/molK);  $R$  – gas constant (J/kgK);

$p$  – pressure (bar);

$T$  – temperature (K);

$\Delta T_{\text{dim}}$  – temperature interval (K) used to obtain dimensionless temperature  $\theta$ ;

$\theta$  – dimensionless temperature;  $\theta_{\text{ref}} = 0.29815$ , the reference temperature;

$F_{ci}(\theta), F_{hi}(\theta), F_{si}(\theta), i = 1, 2$  – dimensionless temperature functions for specific heats, enthalpy and entropy, respectively;

$I_1 = [0.2; 1]; I_2 = [1; 6]$  – intervals of dimensionless temperature.

## 1. INTRODUCTION

Using gas for domestic purposes as heating, electrical power cogeneration or for vehicle engines is a largely alternative due to its low cost and commodity. The highest heat quantity per unit mass is released at stoichiometric composition. One considers hydrocarbons as fuel and air as oxidant premixed in a mixing chamber. In this case the burning is concentrated in a combustion (deflagration) wave. The air can be in excess. The following fuels are studied: 1) methane (CH<sub>4</sub>); 2) propane (C<sub>3</sub>H<sub>8</sub>); 3) butane (C<sub>4</sub>H<sub>10</sub>); 4) gas of deposit (CH<sub>4</sub>+CO<sub>2</sub>); 5) liquefied oil gas (GPL). The combustion reaction is considered irreversible. One admits the formation of NO as the main pollutant. The viscous and thermal effects are concentrated in the combustion (deflagration) wave. Such installation to improve the gas combustion are presented in [3; 6; 9].

## 2. THE BURNING INSTALLATION

The burning installation is presented in Figure 1. The fuel and the air are premixed in a mixing chamber. The speed of the combustible mixture is then adjusted in a nozzle. The combustion is initiated by a spark plug and a deflagration wave is formed at subsonic speed.

The proposed strategy recommends the using of premixed fuel and oxidizer, a deflagration wave rather than diffusion flame, the burning efficiency being from start with at least 5% better. To this aim the mixture velocity has to be adjusted by the nozzle in combination with the air mass rate.

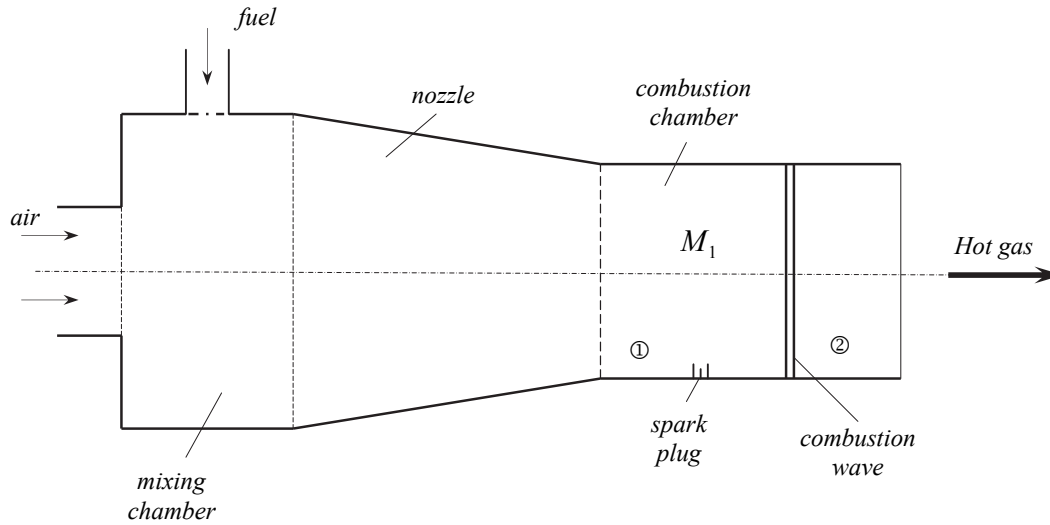


Fig. 1 – The burning installation.

## 3. THE GOVERNING EQUATIONS OF THE REACTING FLOW

The governing equations at the wave are [1; 5 ]:

$$\rho_1 v_1 = \rho_2 v_2 = m' \quad (\text{mass conservation}) \quad (3.1-a)$$

$$p_1 + \rho_1 v_1^2 = p_2 + \rho_2 v_2^2 \quad (\text{momentum}) \quad (3.1-b)$$

$$h_1(T_1) + \frac{1}{2} v_1^2 = h_2(T_2) + \frac{1}{2} v_2^2 \quad (\text{energy}) \quad (3.1-c)$$

where  $v_j, \rho_j, p_j, T_j, j=(1;2)$  are velocities, densities, pressures and temperatures respectively.

The enthalpy  $h$  of an ideal gas is a function of the temperature  $T$  only, and can be written as:

$$h(T) = h(T_{ref}) + \int_{T_{ref}}^T c_p(T) dT \quad (3.2)$$

$T_{ref} = 298.15$  K being a reference temperature and  $c_p(T)$  - the specific heat at constant pressure. The specific heat released by reaction, denoted by  $q$ , is the enthalpy difference:

$$q = h_1(T_1) - h_2(T_1) \quad (3.3)$$

Now one introduces an average specific heat  $c_{pm}^{(2)}(T_1, T_2)$  defined by:

$$c_{pm}^{(2)}(T_1, T_2) = \frac{1}{T_2 - T_1} \int_{T_1}^{T_2} c_p^{(2)}(T) dT; \quad (3.4)$$

The energy equation can then be written in the form:

$$c_{pm}^{(2)} T_1 + \frac{1}{2} v_1^2 + q(T_1) = c_{pm}^{(2)} T_2 + \frac{1}{2} v_2^2. \quad (3.5)$$

After some algebra one can eliminate the velocity from the above equations, to obtain:

$$\begin{aligned} p_r = 1 + \bar{m}(1 - \tau_r); p_r = p_2 / p_1; \tau_r = \rho_1 / \rho_2; \\ T_r = \frac{R_1}{R_2} p_r \tau_r; T_r = T_2 / T_1; \bar{m} = \frac{m^2}{p_1 \rho_1}. \end{aligned} \quad (3.6)$$

The specific volume ratio  $\tau_r$  is given by the equation:

$$\frac{\bar{m}(1 + k_{m2})}{2k_{m2}} \tau_r^2 - (1 + \bar{m}) \tau_r + \frac{R_2}{R_1} (1 + q) + \frac{\bar{m}}{2k_{m2}} (k_{m2} - 1) = 0 \quad (3.7)$$

Further one introduces the dimensionless temperature,  $\theta$ , the dimensionless specific heat at constant pressure,  $\overline{c_p(T)}$  and the dimensionless specific enthalpy,  $\overline{h(T)}$ , as follows:

$$\theta = \frac{T}{\Delta T_{\text{dim}}}; \overline{c_p(T)} = \frac{c_p(T)}{R}; \overline{h(T)} = \frac{h(T)}{R \Delta T_{\text{dim}}}, \quad (3.8)$$

$R$  being the gas constant and  $\Delta T_{\text{dim}}$  a temperature interval. We take  $\Delta T_{\text{dim}} = 1000$  K. The ratios of specific heats,  $k$ , for various states and  $\bar{m}$  are then:

$$k_1 = \frac{\overline{c_p^{(1)}(\theta_1)}}{c_p^{(1)}(\theta_1) - 1}; k_{m2} = \frac{\overline{c_{pm}^{(2)}(\theta_1, \theta_2)}}{c_{pm}^{(2)}(\theta_1, \theta_2) - 1}; \bar{m} = k_1 M_1^2 \quad (3.9)$$

Because the equation (3.7) has two solutions, two states are theoretically possible: a strong wave and a weak wave. The most probable state, met experimentally, corresponds however to the case when the two states coincide: this is the **Chapman – Jouguet wave (CJ)**. The solution is:

$$\begin{aligned} \tau_{rCJ} = \frac{k_{m2}(1 + \bar{m}_{CJ})}{(1 + k_{m2})\bar{m}_{CJ}}; p_{rCJ} = \frac{k_{m2}(1 + \bar{m}_{CJ})}{(1 + k_{m2})}; \\ T_{rCJ} = \frac{R_1}{R_2} p_{rCJ} \tau_{rCJ} \end{aligned} \quad (3.10)$$

The mass flow rate corresponding to a CJ wave is obtained by equating to zero the discriminant of the eq.(3.7). This condition leads again to an equation of second degree having the following two solutions:

$$\frac{\bar{m}_{CJ}}{k_{m2}} = \left( \frac{R_2}{R_1} - 1 \right) k_{m2} + \frac{R_2}{R_1} + \alpha \frac{k_{m2}^2 - 1}{k_{m2}} \pm \sqrt{\delta}, \quad (3.11)$$

$\delta$  being given by the expression:

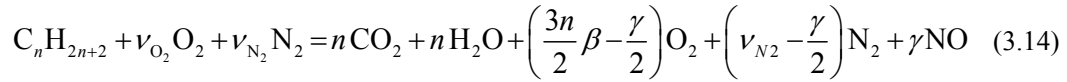
$$\delta = \left( \left( \frac{R_2}{R_1} - 1 \right) k_{m2} + \frac{R_2}{R_1} + \alpha \frac{k_{m2}^2 - 1}{k_{m2}} \right)^2 - 1; \alpha = \frac{q}{R_1 T_1}. \quad (3.12)$$

The sign ( + ) in (3.11) corresponds to **detonation wave** ( $M_1 > 1$ ); the sign ( - ) corresponds to **deflagration wave** ( $M_1 < 1$ ). The Mach number after the wave is in both cases:

$$M_2 = \sqrt{\frac{k_{m2}}{k_2}} > 1; M_{2e} = M_2 \sqrt{\frac{k_2}{k_{m2}}} = 1, \quad (3.13)$$

$M_{2e}$  being the **equivalent Mach number**. Therefore the state after the CJ waves considering the variation of the specific heats with temperature is critical only in terms of the equivalent Mach number.

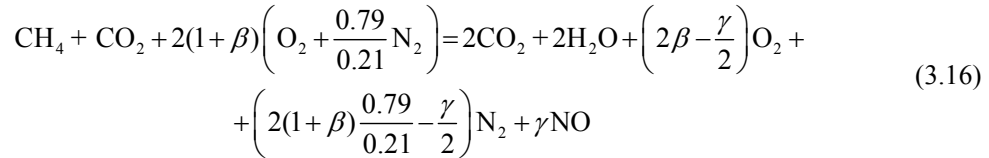
The chemical (irreversible) reactions for a hydrocarbon  $C_nH_{(2n+2)}$  – alkane – are written in the form:



where: 
$$\nu_{O_2} = 3n(1 + \beta) / 2; \nu_{N_2} = 0.79 / 0.21 \nu_{O_2}. \quad (3.15)$$

$\beta$  is the coefficient of the air excess and  $\gamma$  the admitted coefficient for the pollutant *NO*. One has:  $n = 1$  for methane;  $n = 3$  for propane;  $n = 4$  for butane. For the liquefied oil gas (GPL) one takes equal masses of propane and butane.

For the gas of deposit ( $CH_4 + CO_2$ ) one writes the reaction:



$\beta$  and  $\gamma$  having the same meaning as above.

#### 4. THE CALCULATION OF SPECIFIC HEATS, ENTHALPIES AND ENTROPY

The variation of specific heats, enthalpies and entropy with temperature is taken into account using NASA data [1;4]. In addition one introduces a dimensionless temperature,  $\theta$ , defined by:

$$\theta = \frac{T}{\Delta T_{dim}}; \Delta T_{dim} = 1000K. \quad (4.1)$$

Then the dimensionless specific heat at constant pressure is given by:

$$\frac{C_p(\theta)}{R_u} \equiv \overline{C_p}(\theta) = F_c(\theta) = \begin{cases} F_{c1}(\theta), & \text{if } \theta \in I_1 = [0.2; 1]; \\ F_{c2}(\theta), & \text{if } \theta \in I_2 = [1; 6]; \end{cases} \quad (4.2)$$

where: 
$$F_{ci}(\theta) = \sum_{j=1}^7 \alpha_{ji} \theta^{j-3}, j=1; \overline{7}, i=1;2, \quad (4.3)$$

the NASA dimensionless  $\alpha_{ji}$  being given [1;5].

The dimensionless enthalpies are:

$$\bar{H}(\theta) = \frac{H(\theta)}{R_u(\Delta T_{\text{dim}})} = \begin{cases} \bar{b}_{h1}(\theta_{\text{ref}}) + F_{h1}(\theta), & \text{if } \theta \in I_1 = [0.2; 1]; \\ \bar{b}_{h2}(\theta_{\text{ref}}) + F_{h2}(\theta), & \text{if } \theta \in I_2 = [1; 6]; \end{cases} \quad (4.4)$$

where  $F_{hi}(\theta), i = \overline{1; 2}$  are the *enthalpy functions on intervals*, given by the relations:

$$F_{hi}(\theta) = \sum_{j \neq 2} \frac{\alpha_{ji}}{j-2} \theta^{j-2} + \alpha_{2i} \ln \theta, \quad (4.5)$$

$$j = \overline{1; 7}, i = \begin{cases} 1, & \text{if } \theta \in I_1 = [0.2; 1]; \\ 2, & \text{if } \theta \in I_2 = [1; 6]; \end{cases}$$

The dimensionless coefficients  $\bar{b}_{hi}(\theta_{\text{ref}}), i = \overline{1; 2}$ , are given.

$$\bar{b}_{h1}(\theta_{\text{ref}}) = \bar{H}(\theta_{\text{ref}}) - F_{h1}(\theta_{\text{ref}}); \quad \bar{b}_{h2}(\theta_{\text{ref}}) = \bar{b}_{h1}(\theta_{\text{ref}}) + F_{h1}(1) - F_{h2}(1); \quad (4.6)$$

As regards the molar gas entropy,  $S(\theta, p)$ , this is a function of both temperature and pressure for any gas [1;5]. For the molar entropy variation,  $S(\theta, p)$  and for its dimensionless correspondent,  $\bar{S}(\theta, p)$  one writes:

$$\frac{S(\theta, p)}{R_u} \equiv \bar{S}(\theta, p) = \bar{S}(\theta_{\text{ref}}, p_{\text{ref}}) + \int_{\theta_{\text{ref}}}^{\theta} \frac{\bar{C}_p(\theta) d\theta}{\theta} - \ln \left( \frac{p}{p_{\text{ref}}} \right), \quad (4.7)$$

where  $p$  is the pressure. The reference pressure  $p_{\text{ref}}$  is usually 1 bar. The entropy  $S(\theta_{\text{ref}}, p_{\text{ref}})$  is given. The calculation formulas are:

$$\begin{aligned} \bar{S}(\theta, p_{\text{ref}}) &= \bar{S}(\theta_{\text{ref}}, p_{\text{ref}}) - F_s(\theta_{\text{ref}}) + F_s(\theta) = \\ &= \bar{b}_s(\theta_{\text{ref}}, p_{\text{ref}}) + F_s(\theta); \quad (4.8) \\ \bar{b}_s(\theta_{\text{ref}}, p_{\text{ref}}) &\equiv \bar{S}(\theta_{\text{ref}}, p_{\text{ref}}) - F_s(\theta_{\text{ref}}), \end{aligned}$$

the dimensionless entropy constant,  $\bar{b}_s(\theta_{\text{ref}}, p_{\text{ref}})$ , being calculated once for ever (and given) for every gas.  $\bar{b}_s(\theta_{\text{ref}}, p_{\text{ref}})$  and  $F_s(\theta)$  are interval functions. One writes:

$$F_s(\theta) = \begin{cases} F_{s1}(\theta), & \text{if } \theta \in I_1 = [0.2; 1]; \\ F_{s2}(\theta), & \text{if } \theta \in I_2 = [1; 6]; \end{cases} \quad (4.9)$$

with: 
$$F_{si}(\theta) = \sum_{j \neq 3} \frac{\alpha_{ji}}{j-3} \theta^{j-3} + \alpha_{3i} \ln \theta, j = \overline{1; 7}, i = \overline{1; 3}; \quad (4.9\text{-a})$$

$$\begin{aligned}\overline{b}_{s1}(\theta_{ref}, p_{ref}) &= \overline{S}(\theta_{ref}, p_{ref}) - F_{s1}(\theta_{ref}); \\ \overline{b}_{s2}(\theta_{ref}, p_{ref}) &= \overline{b}_{s1}(\theta_{ref}, p_{ref}) + F_{s1}(1) - F_{s2}(1);\end{aligned}\quad (4.9-b)$$

The coefficients  $\overline{b}_{si}(\theta_{ref}, p_{ref}), i=1,2$ , are also given in [1;4]. One obtains for the total dimensionless entropy,  $\overline{S}(\theta, p)$ , at arbitrary temperature and pressure, the final expression:

$$\overline{S}(\theta, p) = \overline{b}_s(\theta_{ref}, p_{ref}) + F_s(\theta) - \ln\left(\frac{p}{p_{ref}}\right), \quad (4.10)$$

**The case of the gas mixture.** In this case, one needs first to define the gas composition. Let  $r=1; \overline{N}_a$  be the index indicating a component of a gas mixture of  $N_a$  components. We consider two possibilities:

a) The molar fractions  $x_r, r=1; \overline{N}_a$ , are given. Then we first calculate the mixture coefficients  $\alpha_{jia}, j=1; 7; i=1; 3$ , and the mixture reference constants,  $\overline{b}_{hia}, \overline{b}_{hia}, i=1; 2$ , from the corresponding component coefficients, as follows:

$$\begin{aligned}\alpha_{jia} &= \sum_{r=1}^{N_a} x_r \alpha_{jir}; j=1; 7, i=1; 2; \\ \overline{b}_{hia} &= \sum_{r=1}^{N_a} x_r \overline{b}_{hir}; \overline{b}_{sia} = \sum_{r=1}^{N_a} x_r \overline{b}_{sir}, i=1; 2;\end{aligned}\quad (4.11)$$

Then one computes the molar mass and the gas constant for gas mixture:

$$M_a = \sum_{r=1}^{N_a} x_r M_r; R_a = R_u / M_a. \quad (4.11-a)$$

by using the given molar fractions. In this way the problem was reduced to the one component case.

Finally one calculates the dimensionless thermodynamic functions  $C_{pa}(\theta); \overline{H}_a(\theta); \overline{S}_a(\theta, p)$  etc.

As regards the entropy, one more term has to be added, namely *the entropy of mixing*, as a result of the pressure modification after mixing for each component  $r, r=1; \overline{N}_a$ . The entropy of mixing,  $S_x(\theta, p)$  and its corresponding dimensionless quantity,  $\overline{S}_x(\theta, p)$ , are given by [1;4]:

$$\frac{S_x(\theta, p)}{R_u} = \overline{S}_x(\theta, p) = - \sum_{r=1}^{N_a} x_r \ln x_r. \quad (4.12)$$

The dimensionless mixture total entropy will be:

$$\overline{S}_a(\theta, p) = - \sum_{r=1}^{N_a} x_r \ln x_r - \ln\left(\frac{p}{p_{ref}}\right) + \begin{cases} \overline{b}_{s1a}(\theta_{ref}, p_{ref}) + F_{s1a}(\theta), & \text{if } \theta \in I_1 = [0.2; 1]; \\ \overline{b}_{s2a}(\theta_{ref}, p_{ref}) + F_{s2a}(\theta), & \text{if } \theta \in I_2 = [1; 6]; \end{cases} \quad (4.13)$$

## 5. RESULTS. CONCLUSIONS

The results of calculations for different fuels, air excesses and possible *NO* formation are given in Tables 5.1, 5.2, 5.3 and 5.4:

Table 1

**Methane (CH<sub>4</sub>):**  $\theta_1 = 0.3$ ;  $p_1 = 1$  bar

$\beta$	$\gamma$	$\theta_f$	$10^2 \bar{m}_{CJ}$	$p_{rCJ}$	$10^{-1} \tau_{rCJ}$	$M_1$	$10^{-6} q$	$10^3 \Delta ent / q$
0.00	0.00	2.1094	3.820	0.4595	1.5301	0.1660	2.7982	0.9672
0.20	0.00	1.8489	4.367	0.4561	1.3512	0.1773	2.3436	1.0647
0.50	0.00	1.5786	5.165	0.4549	1.1568	0.1927	1.8840	1.1093
0.50	0.10	1.5645	5.216	0.4593	1.1462	0.1937	1.8631	1.2038

Table 2

**Propane (C<sub>3</sub>H<sub>8</sub>):**  $\theta_1 = 0.3$ ;  $p_1 = 1$  bar

$\beta$	$\gamma$	$\theta_f$	$10^2 \bar{m}_{CJ}$	$p_{rCJ}$	$10^{-1} \tau_{rCJ}$	$M_1$	$10^{-6} q$	$10^3 \Delta ent / q$
0.00	0.00	1.2617	6.2551	0.4386	0.9975	0.2088	1.2115	1.2800
0.20	0.00	1.0650	7.6540	0.4442	0.8261	0.2230	0.9718	1.6085
0.50	0.00	0.8823	9.6450	0.4525	0.6676	0.2579	0.7512	1.3824
0.50	0.10	0.8753	9.7388	0.4528	0.6618	0.2592	0.7424	1.4082

Table 3

**Butane (C<sub>4</sub>H<sub>10</sub>):**  $\theta_1 = 0.3$ ;  $p_1 = 1$  bar

$\beta$	$\gamma$	$\theta_f$	$10^2 \bar{m}_{CJ}$	$p_{rCJ}$	$10^{-1} \tau_{rCJ}$	$M_1$	$10^{-6} q$	$10^3 \Delta ent / q$
0.00	0.00	1.233	6.348	0.4392	0.8148	0.2100	1.1391	0.9954
0.20	0.00	1.030	7.883	0.4411	0.8089	0.2333	0.9055	1.3550
0.50	0.00	0.8477	9.645	0.4525	0.6676	0.2625	0.6951	1.1320
0.50	0.10	0.8421	1.0130	0.4512	0.6418	0.2636	0.6883	1.1508

Table 4

**Gas of deposit (CH<sub>4</sub> + CO<sub>2</sub>) and CH<sub>4</sub>:**  $\theta_1 = 0.45$ ;  $p_1 = 7$  bar

$\beta$	$\gamma$	$\theta_f$	$10^2 \bar{m}_{CJ}$	$p_{rCJ}$	$10^{-1} \tau_{rCJ}$	$M_1$	$10^{-6} q$	$10^3 \Delta ent / q$
0.00	0.00	1.9410	6.4857	3.3004	0.9143	0.2191	2.4237	0.8519
0.20	0.00	1.7444	7.7159	3.2969	0.8372	0.2300	2.0765	0.9310
0.50	0.00	1.5756	8.2260	3.3027	0.7421	0.2456	1.7091	1.0265
0.50	0.10	1.5635	8.3006	3.3041	0.7361	0.2469	1.6894	1.0384
CH <sub>4</sub> – stoic.	$\beta = 0.0$ $\gamma = 0.0$	2.2291	5.6546	3.3045	1.0492	0.2034	2.8040	0.8346

The highest wave temperature and released heat per unit mass correspond to the stoichiometric reaction of methane ( $\beta = 0$ ;  $\gamma = 0$ , Table 1). This also gives the smallest entropy increasing per combustion heat ( $\Delta ent / q$ ). The applications are made at  $p_1 = 1$  bar and  $\theta_1 = 0.3$  (Tables 1,2,3;) as

well as at  $p_1 = 7\text{bar}$  and  $\theta_1 = 0.45$  (Table 4). Both the air in excess and the formation of  $NO$  increase the ratio  $\Delta ent / q$ . The propane has the largest entropy increasing as compared to  $CH_4$  and butane under similar conditions. One notes a maximum entropy of propane and butane at smaller air excess values ( $\beta = 0.2$ ) then decreasing with  $\beta$ . For methane and gas of deposit there is a constant increasing with  $\beta$ . Also one can see an entropy rise with pollutant coefficient  $\gamma$ .

The liquefied oil gas (GPL) considered as a combination of propane and butane in equal mass parts has intermediate properties between the two.

The pressure rise studied for methane and gas of deposit has a positive effect leading to diminution of the ratio  $\Delta ent / q$ .

In the Chapman – Jouguet deflagration wave the initial Mach number  $M_1$  lies in the interval (0.166-0.2625) whereas the equivalent Mach number after combustion  $M_{2e} = 1$  (sonic regime), the gas being accelerated by introducing heat at subsonic speed. Then a supplementary amount of energy in kinetic form is at hand. The corresponding stagnation temperature is with 14-18 % larger than the deflagration temperature. A system using a convergent nozzle and the adjustment of the oxidant mass rate are necessary to control this advantageous burning installation able to reduce the entropy generation up to 2 times, in combination with the rising of pressure. A large installation can use turbo-engines of aviation with finished resource making possible the pressure increasing.

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