DEVELOPMENT OF COMPUTATION TECHNIQUES AND DATA GENERALIZATION ON BURNING VELOCITY OF DRY AND HUMIDIFIED INFLAMMABLE GAS FUEL-OXIDANT MIXTURES

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Three various approaches to calculation of the laminar (normal) burning velocity $u_n$ of fuel mixtures of different compositions based on two-parametric semiempiric generalization (TPG) and upon a chemical kinetics mechanism have been developed and verified. The first technique (TPG 1) is related to $u_n$ definition for mixtures of low-calorific gases and their mixtures with methane as well as to hydrocarbon combustion velocities. The second method (TPG 2) uses the correction factor, for taking into account the preheating mixture temperature and initial pressure (introducing the two simplexes in form of a power law: $(T_{in}/T_0)^n (P_{in}/P_0)\gamma$. Oxidants used were air and oxygen-enriched air, both of dry and humidified composition. By our approach an application of GRI-Mech 3.0 combustion mechanism has been modernized and improved proven to make the most universal procedure. Validation of our computed data by a set of predicted $u_n$ has been performed regarding measured values and appropriate literature sources.

KEY WORDS: adiabatic combustion temperature, ballasted fuel, combustion mechanism, humidified oxidant, laminar burning velocity, low-calorific (LCV) gases, mixture fraction, natural gas, oxy–fuel combustion, preheating temperature

1. INTRODUCTION

In our earlier paper (Soroka, 2009) the methodology has been developed for determining the normal (laminar) flame propagation velocity $u_n$ of gas fuel mixtures of different compositions based upon a basic version of two-parametric semiempiric generalization (TPG) proposed in a paper by Fossum and Hustad (2002). There are three methods of calculating the laminar burning velocity $u_n$ of gas fuels under various initial conditions. Temperature $T_{in}$ and pressure $P_{in}$ for different types of
Fuel–oxidant mixtures have been advanced by our team. The oxidants used were air and oxygen-enriched air, both of dry and humidified composition.

Two of the mentioned techniques are related to various approaches for the laminar burning velocity calculation of fuel mixtures of different compositions based upon two-parametric generalization (TPG) have been developed at the Gas Institute. The first technique, TPG 1, is related to laminar burning velocity for mixtures of low-calorific gases and their mixtures with methane as well as to hydrocarbon combustion velocities. The calculation equation in this case could be represented as a semiempirical function of two parameters: the mixture fraction ($M_F$) and adiabatic (theoretical) combustion temperature $T_T$ of fuel–oxidant mixture, mentioned for the correction factor $\nu_{arb}$:

$$u_n = u_{n,0} \nu_{arb} = f[(1 - Z_{st})^m, \exp(-E/RT_T)] \nu_1 \nu_2,$$

where the function $f$ is related to a fuel–air mixture at standard conditions ($T_0, P_0$); $u_{n,0}$ is the normal flame propagation (burning) velocity for combustion processes.

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**NOMENCLATURE**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>O$_2$ content in oxidizer, vol. %</td>
</tr>
<tr>
<td>$E$</td>
<td>activation energy, J/mol</td>
</tr>
<tr>
<td>$n$</td>
<td>exponent of a power for temperature influence</td>
</tr>
<tr>
<td>$P$</td>
<td>pressure, MPa</td>
</tr>
<tr>
<td>$Q_{high}$</td>
<td>high calorific value, MJ/Nm$^3$</td>
</tr>
<tr>
<td>$Q_{low}$</td>
<td>low calorific value, MJ/Nm$^3$</td>
</tr>
<tr>
<td>$R$</td>
<td>universal gas constant, J/mol-K</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature, K</td>
</tr>
<tr>
<td>$u_n$</td>
<td>normal (laminar) flame propagation velocity, cm/s</td>
</tr>
<tr>
<td>$W_r$</td>
<td>reaction rate, mol/m$^3$-s</td>
</tr>
<tr>
<td>$Z_{st}$</td>
<td>stoichiometric mixture fraction value</td>
</tr>
</tbody>
</table>

**Subscripts and Superscripts**

- $un$ normal (laminar) flame propagation velocity, cm/s
- $calc$ calculation results
- $cor$ correction case
- $exp$ experimental data
- $in$ initial conditions (pressure $P_{in}$; temperature $T_{in}$)
- $ox$ enriched oxidizer (oxidant)
- $T$ at theoretical combustion temperature
- $T_T$ for zero reference values of thermodynamic parameters and properties, at standard conditions ($P_0 = 0.1013$ MPa; $T_0 = 298$ K)

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**Greek symbols**

- $\gamma$ exponent of a power for pressure influence
- $\lambda$ oxidizer excess factor (ratio), particularly combustion air excess factor
- $\nu_{arb}$ correction factor by $u_n$ computation for the case under consideration (arbitrary conditions)
under cold (standard) initial conditions ($T_{10} = T_0 = 298$ K, $P_{10} = P_0 = 0.1013$ MPa); $Z_{st} = (1 + \lambda \Omega)^{-1}$ is the stoichiometric MF value for $\lambda \gtrapprox 1.0$, the mass fraction of fuel in the mixture with oxidant; $E$ and $R$ are the activation energy and universal gas constant, respectively; $\nu_1$ is the correction factor to account for the reagent composition; and $\nu_2$ is the correction factor to account for the initial reagent temperature.

By use of dry cold air application as an oxidant, the simplified equation (1) can be used by recognition of the correction factors $\nu_1 = \nu_2 = 1.0$; $\nu_{arb} = \nu_1 \nu_2 = 1.0$. In the last case, the result coincides with the basic TPG version.

It must be taken into account that the basic TPG version is related only to a traditional oxidant for boilers and engines, i.e., to cold air, while the current trend for industrial applications is to use oxy–fuel combustion (process furnaces) (Atreya and Everest, 2003; Lantz et al., 2009) and humidified oxidants (engines, combustion chambers of turbines, boilers) (Schlemmer-Kelling and Ratenstrauch, 2001; von Scheele, 2009). In many cases, the combustion process is performed under enhanced initial temperatures and pressures of the inflammable mixture, the parameters of which are out of consideration in the development of the basic version of the TPG procedure.

The case of application of the humidified and preheated air in an oxidizer has been preliminarily extracted from recovery facilities by the Maisotsenko cycle (M-cycle) and is of particular interest as promising a lot of power efficiency and environmental advantages (Maisotsenko et al., 2010; Gillan, 2008; Miyazaki et al., 2010).

The M-cycle combines the processes of heat abstraction of product air flow and heat transfer to working air flow accompanied by mass (water vapor) transportation. The humidification consists of the working air flow along with preheating of the last while cooling the "dry" product flow to "dew-point" temperature, i.e., providing maximum efficiency of the system under 100% humidity (saturation) of preheated working air flow (Maisotsenko et al., 2010; Gillan, 2008; Miyazaki et al., 2010).

The range of M-cycle utilization is ample and permanently widening: from cold, power, drinking water production to the creation of innovative solar systems (Miyazaki et al., 2010). But in the context of the present paper, the main purpose and area of application involves heat recovery for furnace efficiency increases and reducing the formation of harmful substances in the flue gases of combustion chambers (gas turbines, engines).

Thus the basic TPG technique needs further advancement.

2. ESTIMATION OF CURRENT METHOD BY DETERMINATION OF THE $u_n$ VALUE UNDER COMBUSTION OF THE TEST BALLASTED MIXTURES

Most of the data used when receiving TPG (Fossum and Hustad, 2002) refers to the multicomponent fuel gases of high ballast (inert components) content. In the
cases analyzed the combustibles make the fuels for which definition of un is especially complicated. The main burning components make the fuel mixtures of CH₄, CO, and H₂ strongly diluted with N₂ and CO₂. There are indications that the nitrogen fraction ([N]₂) in the tested fuels usually corresponds to a 45–55%, [CO₂] 10–20 vol. %, while total content of the inert components in average represents a range of 50–60 vol. %. The adiabatic (theoretical) combustion temperature is around 1700 K (Fossum and Beyer, 1998).

Below are presented the results of our calculations of uₙ values for combustion of various flammable gases in a mixture with an air oxidant under stoichiometric conditions (air excess factor λ = 1.0), along with the cases of depletion of the burning mixture composition (λ > 1.0). The characteristics of low-calorific-value (LCV) combustible gases were used for measurements of uₙ by data generalization in a paper by Fossum and Hustad (2009) and are given in Table 1. In addition, for verification of the proposed procedure the mixtures of LCV gases with methane were used, the characteristics being summarized in the Table 2. Let us consider, first of all, the impact of replacement of the inert ingredient, nitrogen (N₂), in the LCV gas (mixtures) by fuel gas. As has been described in a survey (Fossum and Beyer, 1998) prepared by the same authors (Fossum and Hustad, 2002), the LCV gases make the products of air conversion for the lean fuels (biomass gasification). This is confirmed by a significant fraction of N₂ in the gas composition and by a low calorific value Qₜ₉₀ = 4–6 MJ/Nm³ (Fossum and Beyer, 1998).

**TABLE 1:** Characteristic of LCV gases for calculation of the normal combustion velocity uₙ LCV air mixtures (stoichiometric λ = 1.0) (Fossum and Hustad, 2002)

<table>
<thead>
<tr>
<th>No.</th>
<th>CH₄ (%)</th>
<th>CO (%)</th>
<th>H₂ (%)</th>
<th>N₂/CO₂ (%)</th>
<th>LHV (MJ/Nm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>15</td>
<td>10</td>
<td>74</td>
<td>3.29</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>15</td>
<td>10</td>
<td>72</td>
<td>3.99</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>15</td>
<td>10</td>
<td>70</td>
<td>4.70</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>15</td>
<td>10</td>
<td>67</td>
<td>5.76</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>15</td>
<td>10</td>
<td>65</td>
<td>6.47</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>18</td>
<td>10</td>
<td>71</td>
<td>3.66</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>20</td>
<td>10</td>
<td>69</td>
<td>3.91</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>23</td>
<td>10</td>
<td>66</td>
<td>4.29</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>25</td>
<td>10</td>
<td>64</td>
<td>4.54</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>15</td>
<td>13</td>
<td>71</td>
<td>3.61</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>15</td>
<td>15</td>
<td>69</td>
<td>3.82</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
<td>15</td>
<td>18</td>
<td>66</td>
<td>4.14</td>
</tr>
<tr>
<td>13</td>
<td>1</td>
<td>15</td>
<td>20</td>
<td>64</td>
<td>4.35</td>
</tr>
</tbody>
</table>
In the case of water steam or $O_2$ using gasification products serving as the combustible gases, we have combustion heat $Q_{\text{low}} = 9–13 \text{ MJ/Nm}^3$. A similar combustion heat value would be attained when the generator LCV gas is mixed with the natural gas, the last consisting mainly of $CH_4$.

The dependence of the calculation of the laminar flame propagation velocity proposed in Fossum and Hustad (2002) and used by means of our techniques (Soroka, 2009) gives a good match with the experimental data of Norwegian authors Fossum and Hustad (2002). The last data have been collected under partial substitution of $N_2$ combustible gases: $CH_4$, $CO$, and $H_2$.

Figures 1(a)–1(c) summarize three sets of data by $u_n$. Two of them are predicted results, with experimental data given in the work of Fossum and Hustad (2002). The first is our generalization based on the theory of mixture fraction (MF). Another group of computation data are conformed to the dependencies obtained based on using the software product CHEMKIN related to an eight-stage "reduced" mechanism by Chang and Chen (Fossum and Beyer, 1998). The comparison shows that our calculations have been brought qualitatively and quantitatively enough to conformity with the test data concerning the burning of cold (hereafter within the frame of this work $T = 298 \text{ K}$) stoichiometric mixtures ($\lambda = 1.0$). Thus an influence of the basic parameters — concentration of combustible and that of inert components, relevant theoretical combustion temperatures, air mixtures, and stoichiometric ratio of the fuels — on the real $u_n$ value is reflecting correctly under conditions of zero oxidizer excess ($\lambda = 1$).

The discrepancy of the results of our calculations and of experimental data (Fossum and Hustad, 2002) led to the following values:

- when you change the $[CH_4]$ fraction: $(-7.65 \text{ to } +15.0\%)$;
- if the $[CO]$ fraction is varied: $(-6.85 \text{ to } +10.5\%)$; and

### TABLE 2: Characteristic of gas mixtures of LCV gases with $CH_4$ (D1–D4) for calculation of the normal combustion velocity $u_n$. LCV/$CH_4$–air mixtures under varying the air excess factor in the range $\lambda = 1.0–1.3$ (Fossum and Hustad, 2002)

<table>
<thead>
<tr>
<th>Component (vol. %)</th>
<th>LCV gas (D1)</th>
<th>LCV 75% + 25% CH$_4$ (D2)</th>
<th>50% LCV gas + 50% CH$_4$ (D3)</th>
<th>LCV gas + 75% CH$_4$ (D4)</th>
<th>CH$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$</td>
<td>16</td>
<td>12</td>
<td>8</td>
<td>4</td>
<td>–</td>
</tr>
<tr>
<td>H$_2$</td>
<td>10</td>
<td>7.5</td>
<td>5</td>
<td>2.5</td>
<td>–</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>4</td>
<td>28</td>
<td>52</td>
<td>76</td>
<td>100</td>
</tr>
<tr>
<td>N$_2$</td>
<td>53</td>
<td>39.75</td>
<td>26.5</td>
<td>13.25</td>
<td>–</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>17</td>
<td>12.75</td>
<td>8.5</td>
<td>4.25</td>
<td>–</td>
</tr>
<tr>
<td>$Q_{\text{low}}$, MJ/N·m$^3$</td>
<td>4.54</td>
<td>12.37</td>
<td>20.21</td>
<td>28.04</td>
<td>35.88</td>
</tr>
</tbody>
</table>
if the $[H_2]$ fraction is varied: (–7.0 to –20.9) %; which does not yield the results of the Norwegian authors. In their presentation (Fossum and Hustad, 2002) the authors stipulated within 20% as an acceptable deviation from the experimental data by using the proposed dependence. In the last case, the method of the calculations was obscure.

Consequently, it could be stated that the empirical generalization made by the authors (Fossum and Hustad, 2002) by means of the procedures, being unknown for us on the one hand, and with the approaches proposed by us [including specifying the $Z_{st}$ value according to the technique described in by Soroka (2009)] and the definition of $T_T$ using the code (our original software product "FUEL") on the other hand, give $u_n$ values that do not differ between themselves.

In general, it should be pointed out that our described two-parametric generalization gives estimations of $u_n$ which do not yield an accurate calculated results compared to those obtained with the CHEMKIN II computer code by burning the stoichiometric LCV gas–air mixtures.

FIG. 1: Dependence of normal (laminar) flame propagation velocity $u_n$ on substituting nitrogen ($N_2$) for combustible components $CH_4$ (a), CO (b), $H_2$ (c) for stoichiometric ($\lambda = 1.0$) mixtures of LCV gases. The basic composition of fuel, vol. %: a: $[CO] = 15; [H_2] = 10; [N_2] = 75 — [CH_4]$; b: $[CH_4] = 1; [H_2] = 10; [N_2] = 89 — [CO]$; c: $[CO] = 15; [CH_4] = 1; [N_2] = 84 — [H_2]$. 1 — results of experimental studies (Fossum and Hustad, 2002); 2 — according to our calculations [Eq. (1) under $\nu_1 = \nu_2 = 1.0$]; 3 — estimated dependences (CHEMKIN-II code)
The results of the experimental definition of laminar burning velocity \( u_n \) and of the impact of air excess factor on its change has been shown in the work of Fossum and Hustad (2002) for the case of lean mixtures. The LCV gases of the following composition have been considered (vol %): CO — 16, H\(_2\) — 10, CH\(_4\) — 4, N\(_2\) — 53, CO\(_2\) — 17, the combustion heat \( Q_{\text{low}} = 4.54 \text{ MJ/N\textcdot m}^3 \) (marked D1) as well as the mixtures titled D2: 75% LCV + 25% CH\(_4\); D3: 50% LCV + 50% CH\(_4\); D4: 25% LCV + 75% CH\(_4\) (see Table 2).

The measurement results and calculations by the CHEMKIN code in comparison with our calculations by two-parametric generalization are presented in Figs. 2 and 3.
in the range of $\lambda \{1.0; 1.3\}$ variation. Despite the satisfactory enough coincidence on the whole of the tested and predicted values of $u_n$, one has to give a more successful description of the dependencies $u_n (\lambda)$ by means of computer code CHEMKIN II in comparison with two-parametric generalization. The limit in divergence of the computation values $u_n$ with those accordingly mentioned techniques are of the relative ranges $+(5.4–16.7)\%$ and $–(10.1–20.7)\%$.

But the dependence $u_n (\lambda)$ defined by us with two-parametric generalization gives a more pronounced impact of air excess $\lambda$ on the $u_n$ pattern.

### 3. CALCULATION OF BURNING VELOCITY FOR HYDROCARBONS AND NATURAL GASES OF DIFFERENT FIELDS

Checking of two-parametric MF generalization to calculate $u_n$ for six European natural gases (Table 3) has been conducted in methodological work by Soroka (2009). Good accuracy of the burning velocity definition of stoichiometric ($\lambda = 1.0$) cold air mixtures of natural gases of high ([CH$_4$] $> 80\%$) methane content has been shown.

#### TABLE 3: Comparison of predicted and measured data by $u_n$ value

<table>
<thead>
<tr>
<th>No.</th>
<th>Composition</th>
<th>Types of European natural gas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Parameter</td>
<td>Dimensions</td>
</tr>
<tr>
<td>1</td>
<td>CO$_2$</td>
<td>mol %</td>
</tr>
<tr>
<td>2</td>
<td>N$_2$</td>
<td>mol %</td>
</tr>
<tr>
<td>3</td>
<td>O$_2$</td>
<td>mol %</td>
</tr>
<tr>
<td>4</td>
<td>CH$_4$</td>
<td>mol %</td>
</tr>
<tr>
<td>5</td>
<td>C$_2$H$_6$</td>
<td>mol %</td>
</tr>
<tr>
<td>6</td>
<td>C$_3$H$_8$</td>
<td>mol %</td>
</tr>
<tr>
<td>7</td>
<td>C$<em>4$H$</em>{10}$</td>
<td>mol %</td>
</tr>
<tr>
<td>8</td>
<td>C$<em>5$H$</em>{12}$</td>
<td>mol %</td>
</tr>
<tr>
<td>9</td>
<td>C$_6$+</td>
<td>mol %</td>
</tr>
<tr>
<td>10</td>
<td>$T_f$</td>
<td>K</td>
</tr>
<tr>
<td>11</td>
<td>$u_n^{exp}$</td>
<td>m/s</td>
</tr>
<tr>
<td>12</td>
<td>$n_n^{calc}$</td>
<td>m/s</td>
</tr>
<tr>
<td>13</td>
<td>$\delta u$</td>
<td>%</td>
</tr>
</tbody>
</table>

Note: Types of the natural gases under consideration (Germany) (Erdgas, 2005): NEH — Nordsee-Erdgas H; MEH — Mish Erdgas H; REH — Russ-Erdgas H; HEL — Holland-Erdgas L; VEL — Verbund Erdgas L; WEEL — Weser/Ems Erdgas L. Lines 1–9, 11 — see (Erdgas, 2005), 10, 12, 13 — our computations.
The possibility of using the proposed technique to calculate the burning characteristics of individual hydrocarbons and of natural gases of various fields within the framework of searching the universal approaches is related to the priority tasks by carrying out the applied research in the area of studying fossil fuel combustion.

The comparison of experimental data of $u_n^{\text{exp}}$ with that of $u_n^{\text{calc}}$ according to our calculations for the case of combustion of the air mixtures of the natural gases from different gas fields is shown in Table 3. The discordance $\delta u_n = (1 - u_n^{\text{calc}}/u_n^{\text{exp}}) \times 100\%$ of the German measured data (Erdgas, 2005) and of our predicted values does not exceed 4.75%.

In addition to the applicability of the proposed procedures for the discussed fuel mixtures (LCV gas and European natural gases), verification has been performed of the formulas’ (Fossum and Hustad, 2002) adequacy for clean fuels — methane CH$_4$, propane C$_3$H$_8$, and the mixture of CH$_4$ — with LCV gases as part of our methodology (Soroka, 2009). These calculations have been carried out by varying an air excess factor $\lambda$ beginning with $\lambda = 1.0$ and under $\lambda > 1.0$. A significant portion of the calculations is connected with $u_n$ prediction under $\lambda < 1.0$ (for rich mixtures). Thus widening the range of application of the proposed approach has been tested.

In Fig. 4 is given comparison of $u_n$ data as a function of $\lambda$, both by our computations and according to data by various sources collected in the book by Lewis.

**FIG. 4:** Dependence of normal flame propagation velocity $u_n$ (laminar burning velocity) on air excess factor $\lambda$ by combustion of cold methane–air mixtures: 1 — curve by experimental data of Singer, Grumer, Cook (Lewis and von Elbe, 1961); 2, ○ — experimental data by Yan, Denesis, Huff (Lewis and von Elbe, 1961); 3, ○ — according to our calculations [Eq. (1) under $\nu_1 = \nu_2 = 1.0$]; 4, • — by Odessa University’s (Ukraine) experimental data while natural gas (91.2% CH$_4$) — air mixture burning; 5, ▲ — Gas Institute’s (Kiev, Ukraine) kinetic computations accordingly GRI-Mech 3.0 combustion mechanism.
and von Elbe (1961), and for the case of combustion, the stoichiometric ($\lambda = 1.0$) and nonstoichiometric ($\lambda \geq 1.0$) CH$_4$–air mixtures. It could be stated that a fairly good agreement of comparative $u_n$ values — by our data and accordingly, the experimental data taken from literature — has been attained. The character of impact of $\lambda$ value on $u_n$ under conditions of varying the ratio of "air-oxidizer:combustible gas" is typical for any group of data used. The maximum divergence of $u_n$ values to be compared makes 10% of average value for all data by the sources collected under the drawing of Fig. 4.

In Fig. 5 are given $u_n$ values by two-parametric generalization and under experimental researches of the Combustion Institute, Odessa National University, obtained by natural gas ([CH$_4$] = 91.2%)–air mixture combustion. This comparison confirms the applicability of the proposed computation technique.

In Western Poland and in East Germany, like that in the Netherlands, there are the deposits of natural gases which contain the inert components, typically nitrogen, along with the hydrocarbons (Dobski et al., 2006). The combustion heat of these gases, referred to the group of natural low-calorific ones is, in MJ/Nm$^3$: $Q_{\text{low}} = 29.6$–13.4 and $Q_{\text{high}} = 32.8$–14.4. Nitrogen N$_2$ content in these gases is 17–64.5%.

In connection with the abundance of these gases, combustion of the mixture CH$_4$/N$_2$, low-calorific natural gas (LCNG) (Dobski et al., 2002), with an air-oxidizing agent is of applied interest and was the subject of our analysis.

Figure 6 demonstrates the values of $u_n$ depending on the content of CH$_4$ in fuel gas ($0.25 \leq D_{\text{CH}_4} \leq 1.0$), where $D_{\text{CH}_4}$ presents the CH$_4$ molar or volume fraction,
under varying air excess factor in the range of $0.9 \leq \lambda \leq 1.3$. These data are the result of combustion kinetics calculations (Dobski et al., 2002) [Fig. 6(a)] and our data [Fig. 6(b)].

The results of $u_n$ computation for Polish natural gas ($\text{CH}_4$–hydrocarbons/$\text{N}_2$) mixtures by means of two-parametric dependence (TPG 1) is given in Fig. 7 as a function of the air excess factor $\lambda$. The gas computation and heat values are presented in Table 4, along with the compositions of the natural gases considered in Fig. 7.

Let us consider the possibility of using our methodology for calculations of $u_n$ values for the mixtures of higher hydrocarbons with combustion air.

In this sense, interest represents the work (Ratha Kishore et al., 2007), where the laminar burning velocities are under consideration for the hydrocarbons, known as similar to natural gas (natural-gas-like mixtures), by essence of the alkene mixtures (methane, ethane), including clean $\text{CH}_4$, $\text{C}_2\text{H}_6$, and the mixtures with CO$_2$ (until
**FIG. 7:** Dependence of burning velocity $u_n$ of natural gas–air mixtures on air excess factor $\lambda$. Low-calorific natural gases of Polish gas fields: a: 1, — Niemierzyce; 2, — Mlodarsko; 3, $\Delta$ — Paproc; 4, — Zuchlow; b: 1, — Antonin; 2, — Cychry; 3, $\Delta$ — Wilkow; 4, — Grochwice. Our computations (the calculative curves) have been carried out by means of two-parametric generalization (TPG).

**TABLE 4:** Typical molar (volume) content of low caloric natural gases (Western Poland fields)

<table>
<thead>
<tr>
<th>Gas field</th>
<th>Niemierzyce</th>
<th>Mlodarsko</th>
<th>Paproc</th>
<th>Zuchlow</th>
<th>Antonin</th>
<th>Wilkow</th>
<th>Cychry</th>
<th>Grochwice</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>81.2</td>
<td>75.8</td>
<td>68.5</td>
<td>56.8</td>
<td>42.2</td>
<td>38.1</td>
<td>42</td>
<td>34.6</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>0.59</td>
<td>0.57</td>
<td>0.92</td>
<td>1.37</td>
<td>8.06</td>
<td>0.65</td>
<td>4.61</td>
<td>0.74</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>0.03</td>
<td>0.02</td>
<td>0.05</td>
<td>0.24</td>
<td>3.51</td>
<td>0.08</td>
<td>2.28</td>
<td>0.08</td>
</tr>
<tr>
<td>C$<em>4$H$</em>{10}$</td>
<td>0.48</td>
<td>0.51</td>
<td>0.19</td>
<td>0.27</td>
<td>1.57</td>
<td>0.14</td>
<td>0.55</td>
<td>0.04</td>
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<tr>
<td>N$_2$</td>
<td>17.1</td>
<td>22.5</td>
<td>30</td>
<td>40.9</td>
<td>44.1</td>
<td>60.8</td>
<td>50.5</td>
<td>64.4</td>
</tr>
<tr>
<td>He</td>
<td>0</td>
<td>0</td>
<td>0.03</td>
<td>0</td>
<td>0.01</td>
<td>0</td>
<td>0</td>
<td>0.09</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.39</td>
<td>0.5</td>
<td>0.17</td>
<td>0.15</td>
<td>0.35</td>
<td>0.06</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$Q_{\text{high}}$</td>
<td>MJ/Nm$^3$</td>
<td>32.8</td>
<td>30.5</td>
<td>28</td>
<td>24</td>
<td>27.9</td>
<td>15.8</td>
<td>22.5</td>
</tr>
<tr>
<td>$Q_{\text{low}}$</td>
<td>MJ/Nm$^3$</td>
<td>29.6</td>
<td>27.5</td>
<td>25.2</td>
<td>21.7</td>
<td>25.3</td>
<td>14.3</td>
<td>20.3</td>
</tr>
</tbody>
</table>

Note: $Q_{\text{high}} = \text{HHV}$, $Q_{\text{low}} = \text{LHV}$ — high and low calorific value, respectively.
60% of the last) and with N2 (until 40%). In Fig. 8 verification is given of our \( u_n \) estimations by ethane–air mixtures versus the set of experimental data (Ratha Kishore et al., 2007).

In general we observe a good match of our calculations with experimental data, but the last show a weaker influence of \( u_n(\lambda) \) in the range \( 1.2 < \lambda < 1.4 \).

As a result, the divergence between our estimated \( u_n \) values and average values of the test data is \((4–8)\%\) within stoichiometric mixtures \( (\lambda = 1.0) \), and for the mixtures which provide \( u_n = u_{n,\text{max}} \) (by \( \lambda \approx 0.9–0.95 \)), and/or \((5–9)\%\) for rich mixtures, and \((11–20)\%\) for lean flammable mixtures.

In the mentioned work (Ratha Kishore et al., 2007), the adequacy of calculative definition of the \( u_n \) value by means of GRI-Mech 3.0, in comparison with measured data and computed with PREMIX code was confirmed for the burning velocities of CH4–air and C2H8–air mixtures, including the case of gas dilution with N2 and CO2. Our experience of using the GRI-Mech 3.0 mechanism in comparison with two-parametric generalization (the last approach, without using the kinetic combustion mechanism) has shown an actual agreement between the values of laminar burning velocities by means of both techniques. Thus, the basic dependencies by Zeldovich and Frank-Kamenetsky (Warnatz et al., 2001) for calculation of the laminar burning velocity accounting chemical (integral rate of chemical reaction) and physical (thermal diffusivity coefficient) characteristics of the combustible mixture, have been confirmed grounded upon validation of two-parametric generalization being qualitatively similar to mentioned fundamentals (Ratha Kishore et al., 2007; Williams, 1965).

**FIG. 8:** Dependence of burning velocity of the ethane–air mixtures on air excess factor \( \lambda \). The initial mixture temperature \( T_{in} = 307 \) K, pressure 0.1013 MPa. Solid curve and the points: ● — the results of our calculations by means of two-parametric generalization (TPG); ○ — according to data of preprint (Ratha Kishore et al., 2007) with temperature adjustment: □ — the same without temperature correction. Experimental data (Ratha Kishore et al., 2007): ○ — Konnov \( (T_{in} = T_{0} = 298 \) K); × — Bosschaart \( (T_{in} = T_{0} = 295 \) K); ▲ — Vagelopoulos
GRI-Mech 3.0 represents the optimized kinetic mechanism intended for the modeling of natural gas combustion, including NO formation and the chemistry ("re-burn") of the staged processes. In this connection the main assignment of the mechanism makes calculation of methane burning. As to other alkanes, this mechanism serves only in so far as relevant to inclusions (small fractions) of higher hydrocarbons in the natural gases, i.e., slightly accounting for the presence of auxiliary hydrocarbon components.

Moreover, our practice of application of the GRI-Mech 3.0 provides opportunity for computation of the combustion of separate hydrocarbons.

In our work (Soroka and Sandor, 2009) the patterns of laminar burning velocities of methane–air mixtures are mapped depending on the air excess factor according to a two-parametric model and by using the GRI-Mech 3.0 kinetic mechanism. Two curves are in good agreement between themselves and with the experimental data of different authors and of various sources.

In our calculations of \( u_n \) values the modeling with GRI-Mech 3.0 has been realized by means of the Cantera 1.7.0 program. Python language has been used under a programming procedure of the laminar burning velocity computation (Goodwin, 2003).

The Cantera program package represents open computer code for deciding the tasks in chemical kinetics, thermodynamics, and fluid dynamics. It could be used for modeling the chemical kinetics of a great number of components and reactions for both perfectly stirred (PSR) and plug flow (PFR) reactors.

The Cantera package has advantages of flexibility in comparison with the well-known specialized CHEMKIN code, and modifications of the last version are purposed for chemical kinetics computations of multicomponent reaction systems. Adaptive improvement of the computation grid ensures an option of number and arrangement of the nodes has been defined just in the computation process individually for each under consideration.

4. CALCULATION OF BURNING VELOCITY FOR HYDROCARBONS AND NATURAL GAS COMBUSTION WITH HUMIDIFIED OXIDANTS UNDER PREHEATING AND DIFFERENT PRESSURE CONDITIONS

The separate task makes definition of burning velocities for the fuel oxidant mixtures related to up-to-date trends, methods, and modern combustion facilities characterized by oxy–fuel system applications along with related inflammable mixtures distinguished by humidified and/or a highly preheated oxidizer.

By using the TPG in case of humidified air as an oxidant we are grounded upon the basic equation, taking into account the fundamental dependence for burning velocity estimation (Soroka, 2009):

\[
u_n^{\text{cor}} \sim (W_r^{\text{cor}})^{0.5}, \quad u_n^{\text{base}} \sim (W_r^{\text{base}})^{0.5},
\]  

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where \( W_r^{\text{base}}, \ W_r^{\text{cor}} \) are the chemical reaction rates for a dry methane–air mixture at \( T_0 \) as the initial condition (\( T_{\text{in}} = T_0 \)) and the same for the mixtures, different from "basic" ones by initial temperature (\( T_{\text{in}} \neq T_0 \)) and by oxidant composition.

Using one of the recommended reaction rates (Zhenjun et al., 2010) for "basic" methane–air mixtures, the correction coefficient \( \nu^{\text{arb}} \) has been obtained by use for the case of a combustion \( \text{CH}_4/O_2/N_2/H_2O \) mixture at \( T_{\text{in}} \) as initial temperature:

\[
\nu^{\text{arb}} = \nu_1 \nu_2 = \left( \frac{\text{[CH}_4]^{\text{ox}}}{\text{[CH}_4]^{\text{air}}} \right)^{-0.15} \left( \frac{\text{[O}_2]^{\text{ox}}}{\text{[O}_2]^{\text{air}}} \right)^{0.65} \times \exp \left[ -0.5ER^{-1}(T_T^{-1} - T_{T,0}^{-1}) \right],
\]

where \( E, R \) are the activation energy in the global kinetics equation and the universal gas constant; \( T_T \) is the theoretical combustion temperature of the considered \( \text{CH}_4/O_2/N_2/H_2O \) mixture related to \( T_{\text{in}} \); \( T_{T,0} \) is the same (theoretical combustion temperature) under \( T_{\text{in}} = T_0 \); \( \text{[CH}_4]^{\text{ox}}, \ \text{[O}_2]^{\text{ox}} \) are the \( \text{CH}_4 \) and \( \text{O}_2 \) concentrations, respectively, for the case under consideration at given air excess factor’s value \( \lambda \); and \( \text{[CH}_4]^{\text{air}}, \ \text{[O}_2]^{\text{air}} \) are the same (concentrations) for the case of basic mixture with air as an oxidant by given \( \lambda \). This approach has been titled as TPG 1 approximation.

In Fig. 9 are presented \( u_n \) values by two-parametric generalization, TPG 1 under application of the \( \nu_1 \) correction factor of proper value. Measured and calculated by the TPG 1 procedure, \( u_n \) values are compared with the results of mathematical modeling (GRI-Mech 3.0) performed for a methane–nitrogen–oxygen mixture com-

![FIG. 9: Dependence of the burning velocity \( u_n \) of the dry methane–nitrogen–oxygen mixture under oxygen content in oxidant (molar, volume fraction) \( \Lambda = 40\% \) and by atmospheric pressure: 1 — experimental data by Yan, Denewis, Huff (Lewis and von Elbe, 1961); 2 — by the calculations results according to GRI-Mech 3.0 computations; 3 — according to our calculations [Eq. (1) under \( \nu_1 = \nu_2 = 1.0 \)]; 4 — according to our calculations with account of correction factor \( \nu_1 \) [Eqs. (1) and (3)]](image-url)
bustion. The curves shown in Fig. 9 confirm the applicability of proposed computation technique.

In Fig. 10 are considered the velocities for complicated conditions when methane–oxygen enriched air mixtures are tested and are burning up by some preliminary preheating and humidification. Various fuel/oxidant mixtures (by $\lambda$ value) were tested: both stoichiometric ($\lambda = 1.0$) and nonstoichiometric: rich ($\lambda < 1.0$) and lean ones ($\lambda > 1.0$). The complicated GRI-Mech 3.0 kinetic approach makes the most widely acceptable technique for $u_n$ strict prediction, but sometimes the

**FIG. 10:** Dependence of the burning velocity $u_n$ of the methane-nitrogen-oxygen mixture, $A = 50\%$, under initial temperature $T_{in} = 373$ K and atmospheric pressure on water vapor content in mixture (molar, volume fraction). Oxidizer excess factor: a — $\lambda = 1.0$; b — $\lambda = 0.66$; c — $\lambda = 1.66$: 1 — experimental data by Mazas et al. (2009), 2 — by the calculation results according to GRI-Mech 3.0 computations, 3 — according to our calculations with account of correction factor $\nu_{arb}$ [Eqs. (1) and (3), 4 — according to our calculations [Eq. (1) under $\nu_1 = \nu_2 = 1.0$]
TPG 1 approach gives the necessary accuracy for defining the flame propagation velocity \( u_n \).

The influence of the humidification of reaction mixture (oxidant’s vapor content) on \( u_n \) value is of paramount importance, especially according to modern trends of environmentally benign combustion. The dependence of \( u_n \) on the H\(_2\)O fraction in stoichiometric methane–air mixture under initial temperature \( T_{in} = 473 \) K is shown in Fig. 11.

Another computation approach (TPG 2), providing the second way for obtaining \( u_n \) under variation of the initial parameters impacting the combustion velocity (temperature \( T_{in} \), pressure \( P_{in} \)), has been tested for various fuels and oxidants. The most famous dependence has been proposed for different methane–air mixtures in the form of a power function with two simplexes (Metghalchi and Keck, 1982):

\[
\frac{u_n}{u_{n,0}} = \left( \frac{T_{in}}{T_0} \right)^n \left( \frac{P_{in}}{P_0} \right)^\gamma .
\]

The procedure of accounting for the initial temperatures and pressures by means of the exponents of power in accordance with the TPG 2 approach is widespread, but the numerical values of exponents \( n \) and \( \gamma \) are different by various studies.

The exponent of a power in Eq. (4) is dependent on air excess factor \( \lambda \). By comparison of various power dependencies has been approved the validity of empiric correlations for exponents of a power \( n \) and \( \gamma \) proposed by Chinese authors (Liao et al., 2004):

\[
n = 7.98 - 12.15 \lambda^{-1} + 5.75 + \lambda^{-2} ,
\]

FIG. 11: Dependence of the burning velocity \( u_n \) of stoichiometric (\( \lambda = 1.0 \)) methane–air mixture under initial temperature \( T_{in} = 473 \) K and by atmospheric pressure, on water vapor content in mixture (volume, molar fraction): 1 — experimental data by (Babkin and V’yun (1971), 2 — by the calculations results according to GRI-Mech 3.0 computations, 3 — according to our calculations with account of correction factor \( \nu^{arb} \) [Eqs. (1) and (3)], 4 — according to our calculations [Eq. (1) under \( \nu_1 = \nu_2 = 1.0 \)], 5 — according to our calculations with account of simplexes in the form of a power law: \( (T_{in}/T_0)^n (P_{in}/P_0)^\gamma \) [Eqs. (4)–(6)]
\[
\gamma = -0.925\lambda^{-2} + 2\lambda^{-1} - 1.473 .
\] (6)

Checking the conformity of calculated data to experimental ones by using a power function approach (TPG 2) is demonstrated in Fig. 11 for the methane–air preliminary preheated mixtures as a function of water vapor content.

In the paper by Liao et al. (2004), the \( u_n \) values have been defined by experiments for the dry methane–air mixtures as a function of the initial temperature \( T_{in} \) and pressure \( P_{in} \). The tests have been carried out under conditions of enhanced (\( P_{in} = 0.15 \text{ MPa} \)), atmospheric (\( P_{in} = 0.1013 \text{ MPa} \)), and decreased (\( P_{in} = 0.05 \text{ MPa} \)) pressures. Comparison of relevant experimental data with the predicted values determined according to our computations by means of the TPG 2 approach is demonstrated in Fig. 12 for stoichiometric (\( \lambda = 1.0 \)), enriched (\( \lambda = 0.83 \)), and lean (\( \lambda = 1.2 \)) mixtures. The maximum divergence of \( u_n \) measured and predicted values is (–8.8 to 8.5)% within the range of temperatures and pressures considered in the investigations of Liao et al. (2004).

The experimental results by German authors Lauer and Leuckel (1995) are concerning the laminar burning velocities \( u_n \) for methane–air and coal gasification products×air mixtures in a wide range of initial temperatures and pressures. The experimental parameters of this work were selected following the current burner inlet conditions of stationary high-temperature gas turbines: \( T_{in} = 723 \text{ K} \), \( P_{in} = 1.2–2.0 \text{ MPa} \). The methane–air mixtures were examined with respect to their laminar burning velocity at pressures up to \( P_{in} = 2.0 \text{ MPa} \) and preheating temperature \( T_{in} = 673 \text{ K} \) in a wide composition range.

The laminar burning velocity of methane shows a strong decrease with increasing pressure. Its maximum value under an air excess factor of \( \lambda = 0.95 \) is about \( u_n = 45 \text{ cm/s} \) by \( P_{in} = 0.1013 \text{ MPa} \) and 11 cm/s by \( P_{in} = 20 \text{ MPa} \) (pressure exponent \( \gamma = -0.47 \)). The temperature exponent describing an increase of burning velocity with preheating temperature according to Lauer and Leuckel (1995) makes the value within \( n = 1.9–2.2 \) for any pressure. At \( T_{in} = 723 \text{ K} \) and \( P_{in} = 2.0 \text{ MPa} \) the experimental burning velocity of methane is 56 cm/s. However by using our TPG 2 approach and the \( u_n = 46 \text{ cm/s} \) in accordance with Liao et al. (2004) (see above), the temperature exponent would be assumed \( n = 1.56 \) and the pressure exponent \( \gamma = -0.392 \) for a mentioned \( \lambda = 0.95 \).

Divergence of computed and experimental data could be reduced if the value of \( u_{n,0} \) at standard initial conditions \( T_{in} = T_0 = 298 \text{ K} \), \( P_{in} = P_0 = 0.1013 \text{ MPa} \) makes \( u_n (\lambda = 0.95) = 42 \text{ cm/s} \); accordingly, our calculations and exponents values \( n \) and \( \gamma \) by Lauer and Leuckel (1995) will be taken. Application of a mentioned set of data by using computation equation (4) will bring the laminar burning velocity of \( u_n = 59 \text{ cm/s} \), drawing near to the measured value of 56 cm/s (see above).

An adequacy of \( u_n \) variation trends by the impact of the acting parameters and coincidence of predicted and measured data on changing the \( u_n \) values by variation of the initial temperatures \( T_{in} \) and pressures \( P_{in} \) has been stated by using corresponding exponents of power in each case under consideration.
5. CONCLUSIONS

1. The opportunities of utilizing various approaches to define normal flame propagation velocity $u_n$ (laminar burning velocity $S_L$) of the individual fuels and the gas mixtures of various compositions with different oxidants have
been considered. Significant progress has been achieved in development of the procedures of $u_n$ value calculation for gas fuels of arbitrary types, semiempiric two-parametric generalization (TPG) and the technique of process account by means of application of a detailed chemical kinetics mechanism GRI-Mech 3.0, have been advanced.

2. The range of combustible mixtures which could be considered under $u_n$ calculations in conformity with the opportunity of each tested technique was determined based on original verifications, including comparison with the results of experimental studies and of the calculations by means of other techniques application. The oxidants used were air and oxygen-enriched air, both of dry and humid composition.

3. Two various improvements of the laminar burning velocity calculation of fuel mixtures of different compositions based upon two-parametric generalization (TPG) have been developed. In this case, the physical factor is presented by the MF value while the chemical combustion kinetics is characterized by an exponent included the theoretical combustion temperature $T_T$. The first technique (TPG 1) is related to laminar burning velocity for mixtures of low-calorific (LCV) gases and their mixtures with methane as well as to hydrocarbon combustion velocities and includes some concentration and temperature correction factors. Oxidants used are air and oxygen-enriched air, both of dry and humidified composition. The second method (TPG 2) uses the general correction factor for taking into account the initial temperature and pressure in the form of a power law for two simplexes $(T_{in}/T_0)^n (P_{in}/P_0)\gamma$. In the case of utilization of cold dry air as an oxidant, both techniques bring together the basic TPG procedure.

4. The analysis has confirmed the suitability of the first method for $u_n$ calculation for gas fuels with oxygen-enriched air, under standard conditions, as well as in the case of combustion of humidified mixtures (by water vapor adding in amount of 0.3–0.4 of fuel–oxidant mixture volume) of relatively low initial temperature ($T_{in} = 373$ K). Verification of TPG for calculation of the burning velocities of gas fuels with dry and humidified air–oxidant, depending on the initial temperature $T_{in}$ with application of temperature correction, has been carried out within the framework of the second method. The TPG 2 technique could be recommended for un calculation for both dry and humid gas–air mixtures, depending on the initial mixture temperature $T_{in}$ and pressure $P_{in}$.

5. The measuring of chemical kinetics by application of the GRI-Mech 3.0 mechanism in combination with procedures by the Cantera code provides the best and the widest opportunities for the most accurate prediction of un values for fuels and oxidants of various compositions. Nevertheless, the modernized TPG techniques, TPG 1 and TPG 2, are characterized by much simpler performance procedures in comparison with those under GRI-Mech 3.0 application. These TPG approaches are providing satisfactory accuracy for many
fuel–oxidant mixtures, particularly for complicated cases of using M-cycle facilities for heat recovery by combustion.

REFERENCES


