Ivan VITÁZEK[*], Juraj HAVELKA[**]

THERMODYNAMICS OF COMBUSTION GASES FROM LPG PROPANE-BUTANE

TERMODYNAMIKA SPALÍN Z LPG PROPÁN-BUTÁNU

Abstract

Liquefied LPG is a mixture of good quality hydrocarbons, propane and butane without inert gases. In their paper the authors would like to present the methodology for derivation of all necessary thermodynamic parameters of combustion gases of LPG and relations for modelling and control evaluation of LPG combustion in a specific appliance. Two computer programs in Q-Basic have been made to carry out these calculations.

Abstrakt

Skvapalnený LPG je zmes kvalitných uhľovodíkov, propánu a butánu, bez inertných plynov. Autori vo svojej práci predkladajú metodiku pre odvodenie všetkých potrebných termodynamických parametrov LPG, pre odvodenie termodynamických parametrov spalín z LPG a vzťahy pre modelovanie a kontrolné vyhodnotenie spaľovania LPG v určitom zariadení. Vypracované boli dva výpočtové programy v Q-Basicu pre realizáciu týchto výpočtov.

1 INTRODUCTION

Basic data about LPG can be found e.g. on the internet, but only in minimal volume. In the paper we present LPG combustion dynamics at constant pressure. LPG is supplied as liquefied gas. Its extra advantage is that it contains only liquefied hydrocarbons; no inert gases as nitrogen and carbon dioxide. For this reason, in STN (Slovak Technical Norm) its composition in mass concentrations is considered – mass %. All calculations are carried out in SI units. These are the simplest relations that are possible.

Combustion gases and air are a mixture of several gases with partly different qualities. For this reason analyses and computations have been made for gas mixtures. Thermal balances are stated in accordance with STN and are related to ambient temperature. In the paper we present the derivation of LPG thermodynamic parameters, thermodynamics of LPG combustion at constant pressure, methodology of modeling and evaluation of a specific combustion process.

2 MATERIALS AND METHODS

LPG (Liquefied Petroleum Gas) is a mixture of liquefied hydrocarbons. The supplier – the Slovak Propane-Butane Company has introduced the following compositions:

LPG in summer: propane 40 mass%, butane 60mass%, propylene 3-5 mass%

LPG in winter: propane 60 mass%, butane 40 mass%, propylene 3-5 mass %
In Ražnjevič tables [2] the following parametres can be found:

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[*] doc., Ing., CSc., Slovak University of Agriculture in Nitra, Faculty of Engineering, Department of Transport and Handling, Tr.A. Hlinku 2, Nitra, tel. (+421) 37 6414756, e-mail ivan.vitazek@uniag.sk
[**] doc., Ing., CSc., Slovak University of Agriculture in Nitra, Faculty of Engineering, Department of Transport and Handling, Tr.A. Hlinku 2, Nitra, tel. (+421) 37 7721033, e-mail juraj.havelka@gmail.com

Propane	C_3H_8	M = 44.09	q_n = 46348 kJ.kg^{-1}
Butane	C_4H_{10}	M = 58.12	q_n = 45657 kJ.kg^{-1}
Propylene	C_3H_6	M = 34.08	q_n = 46055 kJ.kg^{-1}

As oxygen source for LPG oxidation – combustion atmospheric air is used. Chyský [1] introduces the following composition:

Nitrogen	N_2	σ_{N2} = 0.75524	M_{N2} = 28.016
Oxygen	O_2	σ_{O2} = 0.23144	M_{O2} = 32.000
Argon+	Ar	σ_{Ar} = 0.0005	M_{Ar} = 40.000
Carbon dioxide	CO_2	σ_{CO2} = 0.01282	M_{CO2} = 44.01
Water vapour	H_2O		M_W = 18.016
Air			M_V = 28.96

2.1 Thermodynamic parameters of LPG

LPG composition is usually introduced by means of individual mass concentrations σ_{gi}. Molar mass of LPG – mixture of ideal gases is:

$$M_g = \frac{m_g}{n_g} = \frac{m_g}{\sum \dfrac{m_{gi}}{M_i}} = \frac{1}{\sum \dfrac{\sigma_{gi}}{M_i}}, \qquad [\text{kg.mol}^{-1}] \qquad (1)$$

Specific gas constant:

$$r_g = 8314.4 / M_g, \qquad [\text{J.kg}^{-1}.\text{K}^{-1}] \qquad (2)$$

LPG density at standard conditions t = 15 ^{o}C, p = 101.325 kPa:

$$\rho_g = \frac{p}{r_g.T} = \frac{101325}{r_g(273.15+15)}, \qquad [\text{kg.m}^{-3}] \qquad (3)$$

LPG standard relative density in comparison with air:

$$d_g = \frac{\rho_g}{\rho_a} = \frac{M_g}{M_a} = \frac{M_g}{28.96}, \qquad (4)$$

LPG – gas mixture heat value according to STN:

$$q_n = \sum q_{ni}.\sigma_{gi}, \qquad [\text{kJ.kg}^{-1}] \qquad (5)$$

LPG – gas mixture combustion heat value according to STN:

$$q_s = q_n + \Delta m_W.2500, \qquad [\text{kJ.kg}^{-1}] \qquad (6)$$

Wobbe number – criterion of fuel gas interchangeability – related to heat value:

$$W_n = \frac{q_n}{\sqrt{d_g}}, \qquad [\text{kJ.m}^{-3}.\text{K}^{-1}] \qquad (7)$$

Wobbe number – criterion of fuel gas interchangeability – related to combustion heat value:

$$W_s = \frac{q_s}{\sqrt{d_g}} \,, \qquad\qquad\qquad [\text{kJ.m}^{-3}.\text{K}^{-1}] \qquad (8)$$

2.2 Stechiometric relations

Composition of individual gases is given by a chemical formula. Mass concentrations of carbon C and hydrogen H combustibles in these gases are calculated as follows:

carbon C $\qquad\qquad\qquad \sigma_{iC} = \dfrac{n_C . M_C}{M_i} \qquad\qquad\qquad (9)$

hydrogen H $\qquad\qquad\qquad \sigma_{iH} = \dfrac{n_H . M_H}{M_i} \qquad\qquad\qquad (10)$

From that C, H mass ratios in LPG gas mixture are:

carbon C $\qquad\qquad\qquad c = \sum \sigma_{iC} . \sigma_{gi} \qquad\qquad\qquad (11)$

hydrogen H $\qquad\qquad\qquad h = \sum \sigma_{iH} . \sigma_{gi} \qquad\qquad\qquad (12)$

Stechiometric – ideal mass balance of combustibles oxidation is:

$$1kg\,C + 2.6642kg\,O_2 = 3.6642kg\,CO_2 \qquad\qquad (13)$$

$$1kg\,H_2 + 7.9365kg\,O_2 = 8.9365kg\,H_2O \qquad\qquad (14)$$

Stechiometric – ideal amount of oxygen to combust 1 kg of LPG is:

$$m_{O2i} = 2.6641.c + 7.9362.h \,, \qquad [\text{kg}] \qquad (15)$$

Stechiometric – ideal amount of dry air to combust 1 kg of LPG is:

$$m_{Vi} = m_{O2} / \sigma_{aO2} = m_{O2} / 0.23144 \,, \qquad [\text{kg}] \qquad (16)$$

On combustion of 1 kg of LPG new gases are released:

carbon dioxide CO_2 $\qquad \Delta m_{CO2} = 3.6641.c \,, \qquad\qquad [\text{kg}] \qquad (17)$

water vapour H_2O $\qquad \Delta m_W = 8.9362.h \,, \qquad\qquad [\text{kg}] \qquad (18)$

3 RESULTS

3.1 LPG combustion at constant pressure

Mass balance

A gas burner scheme showing the mass flows is in Fig.1. Combustion gases m_3 represent a mixture of stechiometric combustion gases m_2 and additional air m_p.

Overall aspirated atmospheric air m_0 is:

$$m_{OC} = m_{Vi}(1+x_0) + m_p(1+x_0) = m_{Vi}(1+x_0).\alpha \,, \qquad (19)$$

where air excess coefficient is: $\alpha = \dfrac{m_{Vi} + m_p}{m_{Vi}}$ (20)

Overall mass of stechiometric mixture m_{1C} is:

$$m_{1C} = m_{OC} + m_g = m_{Vi}(1 + x_0) + m_g , \quad [\text{kg}]$$ (21)

its dry fraction: $m_{1S} = m_{Vi} + m_g ,$ [kg] (22)

its moist fraction: $m_{1W} = m_{Vi} . x_0 ,$ [kg] (23)

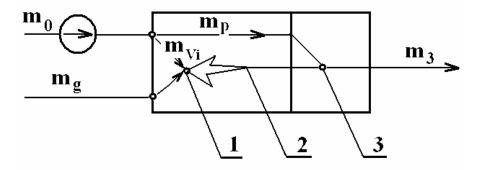specific moisture: $x_1 = m_{1W} / m_{1S} ,$ [kg.kg^{-1}] (24)

Fig. 1 Scheme of mass flows in a combustion appliance

Overall mass of stechiometric combustion gases:

$$m_{2C} \equiv m_{1C} ,$$ (25)

its dry fraction: $m_{2S} = m_{Vi} - m_{O2} + \Delta m_{CO2} ,$ [kg] (26)

its moist fraction: $m_{2W} = m_{Vi} . x_0 + \Delta m_W ,$ [kg] (27)

Overall mass of combustion gases m_{3C} produced by the burner is:

$$m_{3C} = m_{2C} + m_{pC} = m_{Vi}(1 + x_0) . \alpha + m_g ,$$ (28)

its dry fraction m_{3S}: $m_{3S} = m_{Vi} . \alpha - m_{O2} + \Delta m_{CO2} ,$ [kg] (29)

its moist fraction m_{3W}: $m_{3W} = m_{Vi} . \alpha . x_0 + \Delta m_W ,$ [kg] (30)

Chemical composition - mass flows – are:

$$m_{3N2} = m_{Vi} . \alpha . \sigma_{aN2} ,$$ [kg] (31)

$$m_{3O2} = m_{Vi} . (\alpha - 1) . \sigma_{aO2} ,$$ [kg] (32)

$$m_{3Ar} = m_{Vi} . \alpha . \sigma_{aAr} ,$$ [kg] (33)

$$m_{3CO2} = m_{Vi} \cdot \alpha \cdot \sigma_{aCO2} + \Delta m_{CO2}, \qquad \text{[kg]} \qquad (34)$$

$$m_{3W} = m_{Vi} \cdot \alpha \cdot x_0 + \Delta m_W, \qquad \text{[kg]} \qquad (35)$$

Molar mass:
$$M_3 = \frac{1}{\sum \dfrac{\sigma_{3i}}{M_i}} = \frac{m_{3C}}{\sum \dfrac{m_{3i}}{M_i}}, \qquad \text{[kg.mol}^{-1}\text{]} \qquad (36)$$

Thermal balance

On combustion of 1 kg of LPG reaction heat is released – heat value q_n and enthalpy of combustion gases compared to ambient increase by:

$$\Delta I_3 = m_g \cdot q_n \cdot \eta_h = 1 \cdot q_n \cdot \eta_h, \qquad \text{[kJ]} \qquad (37)$$

Ražnjevič tables for gas enthalpy are composed in such a manner that values $i_i = 0$ are assigned to $t = 0$ °C. When using these tables, it is necessary to add a conversion amendment that represents the residual difference of enthalpy between temperatures 0 °C and t_0

$$\Delta I_{30} = \sum m_{3i} \cdot i_{3i} = \sum m_{3i} \cdot c_{pi} \cdot t_0, \qquad \text{[kJ]} \qquad (38)$$

Enthalpy of combustion gases to 0 °C is then:

$$I_3 = \Delta I_3 + \Delta I_{30}, \qquad \text{[kJ]} \qquad (39)$$

and specific enthalpy:
$$i_3 = I_3 / m_{3C}, \qquad \text{[kJ.kg}^{-1}\text{]} \qquad (40)$$

By means of linear regression we have obtained linear regression relations from Ražnjevič tables [2] for temperature range 1000 °C – 2400 °C with satisfactory value of regression coefficient r as follows:

$$i_i = b_i \cdot t + a_i, \qquad \text{[kJ.kg}^{-1}\text{]} \qquad (41)$$

Specific enthalpy of combustion gases to base 0 °C:

$$i_3 = \sum \sigma_{3i} \cdot i_{3i} = \frac{\sum \sigma_{3i} (b_i \cdot t_3 - a_i)}{m_{3C}}, \qquad \text{[kJ.kg}^{-1}\text{]} \qquad (42)$$

from where the following relation for temperature t_3 has been derived:

$$t_3 = \frac{i_3 \cdot m_{3C} - \sum m_{3i} \cdot a_i}{\sum m_{3i} \cdot b_i}, \qquad \text{[°C]} \qquad (43)$$

3.2 Operation of an appliance with LPG

Let us consider the operation of a given appliance with LPG combusted at constant pressure. Burner efficiency η_h is given, LPG consumption V_g [m³.h⁻¹] is measured, volume fraction of oxygen O_2 in combustion gases x_{O2} is also measured.

As evaluation base it is necessary to find the instantaneous value of air excess coefficient α.

The measured value:
$$x_{O2} = \sigma_{3O2} \frac{M_3}{M_{O2}}$$
(44)

is customized by substitution for σ_{3O2} a M_3:

$$x_{O2} = \frac{m_{3O2}}{M_{O2} \sum \frac{m_{3i}}{M_i}}$$
(45)

By customizing other relations and substitution we obtain a relation for α:

$$\alpha = \frac{m_{Vi} . \sigma_{aO2} + x_{O2} . M_{O2} . B}{m_{Vi} (\sigma_{aO2} - x_{O2} . M_{O2} . A)} \ ,$$
(46)

where:
$$A = \sum \frac{\sigma_{ai}}{M_i} \ ,$$
(47)

$$B = \frac{m_{CO2}}{M_{CO2}} + \frac{\Delta m_W}{M_W} - \frac{m_{Vi} . \sigma_{aO2}}{M_{O2}}$$
(48)

Volume flow of consumed LPG:
$$\dot{V}_g = V_g / 3600 \ ,$$
$[\text{m}^3.\text{s}^{-1}]$
(49)

Mass flow of consumed LPG:
$$\dot{m}_g = \dot{V}_g . \rho_g \ ,$$
$[\text{kg}.\text{s}^{-1}]$
(50)

Thermal power of the burner:
$$P = \dot{m}_g . q_n . \eta_h \ ,$$
$[\text{kW}]$
(51)

Volume flow of aspirated air with temperature t_0 and pressure p_0:
$$\dot{V}_0 = \frac{m_{Vi} . (1 + x_0) . \alpha . m_g . r_a . (273.15 + t_0)}{p_0} \ ,$$
$[\text{m}^3.\text{s}^{-1}]$ (52)

Volume flow of hot combustion gases with temperature t_3 and pressure p_0:
$$\dot{V}_3 = \frac{m_{3C} . m_g . r_3 . (273.15 + t_3)}{p_0} \ ,$$
$[\text{m}^3.\text{s}^{-1}]$ (53)

Volume fraction of oxygen O_2 in combustion gases (is calculated on modelling):
$$x_{O2} = \sigma_{3O2} \frac{M_3}{M_{O2}} 100 = \frac{m_{3O2}}{m_{3C}} \frac{M_3}{M_{O2}} 100 \ ,$$
$[\%]$
(54)

Volume fraction of carbon dioxide CO_2 in combustion gases:

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$$x_{CO2} = \sigma_{3CO2} \frac{M_3}{M_{CO2}} 100 = \frac{m_{3CO2}}{m_{3C}} \frac{M_3}{M_{CO2}} 100, \quad [\%] \quad (55)$$

Volume flows of individual gases in combustion gases:

$$\dot{m}_{3i} = m_{3i} . \dot{m}_g, \quad [kg.s^{-1}] \quad (56)$$

Emission factor – criterion of CO_2 production – is a ratio of CO_2 mass released on combustion of 1 kg of LPG and heat value

$$e_{fCO2} = \frac{\Delta m_{CO2}}{q_n}, \quad [kg_{CO2}.GJ^{-1}] \quad (57)$$

3.3 Program of calculations in Q-Basic

The above calculation methodology and necessary thermodynamic table values have been concentrated in the calculation program in Q-Basic.

The program consists of three parts:

1. Entering basic data about the appliance and LPG
2. Calculation program
3. A report including all basic information and a unique range of calculated values

Due to limited length, the program is not part of the paper, it will be included in the presentation.

4 DISCUSSION

All calculations have been made in basic SI units and for gas masses in kg. These are the simplest relations that are possible. The qualities of all gases – enthalpies – change in dependence on temperature. They can be found in thermal tables, e.g. Ražnjevič [2].

Thermal balances have been made in accordance with STN, due to ambient temperature as a base. Thermal tables Ražnjevič [2] for gas enthalpies in i are published in such a manner that zero values $i_1 = 0$ are assigned to basic temperature $0\,^{o}C$. For the sake of using these tables, we have introduced a transformation value ΔI for the difference between $0\,^{o}C$ and ambient temperature t_0.

As part of the solution to the above problem, we have derived relatively complex relations for the temperature of combustion gases t_3 and for air excess α from the measured value x_{O2}.

5 CONCLUSION

The above methodology can be implemented in two alternatives:

1. Mathematical modelling of a selected LPG combustion process
2. Detailed evaluation of control measurement in a specific appliance

Calculations presented in the methodology are relatively simple, but extensive. We have made two calculation programs that enable the user to carry out fast and precise calculations without methodology study and retrieving data from thermal tables.

In our future work we would like to apply the above methodology to other heating gases, to processes with combustion at constant volume, to modelling and control of appliances where these gases are used.

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