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Thermal and Physical Properties of Methane Family Hydrocarbon and Oxygen Combustion Products in State-of-the-Art Arc Steel Furnace

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Abstract. The work deals with the particular combustion characteristics of methane family hydrocarbons (methane, ethane, propane, butane) and wet natural gas with process oxygen at carbon dioxide and water steam dissociation in a state-of-the-art arc steelmaking furnace. An algorithm is developed to calculate chemistry, the amount and concentration of combustion products at carbon dioxide and hydrogen dissociation, their physical and thermophysical parameters; heating power, balance and actual temperature, heat and pyrometric factors are evaluated considering heat transfer by radiation into unbounded medium. Based on the calculation results the recommendations are given for development of cold charge material heating conditions in order to minimize dusting, carbon oxide and hydrogen and charge material loss.

1. Introduction

Finished and semi-finished steel making in a state-of-the-art arc steel furnace is related to employment of practically all iron containing materials [1], including scrap of various form and dimensions, frequently containing non-ferrous metal additions (copper, tin, lead, stibium, etc.). Charge material composition and structure changes require development of heating conditions with the use of various thermal energy sources, ensuring rapid heating of cold charge materials. Charging is generally arranged into two baskets. The second basket may be fed only after the charge materials of the first basket settle. It is expedient to heat the first basket charge materials to the temperature of 1300 °C with the minimum power consumption, if possible. The heating conditions corresponding to this melting period shall be developed considering the minimum formation of carbon oxide (CO) and hydrogen, charge material wastes and dust. It is expedient to manufacture semi-finished steel in state-of-the-art furnaces following scrap and scrap and coke method with the use of an additional cheap energy carrier – natural gas (NG). However, in some cases natural gas combustion with process oxygen results in local charge material overheating and scars on the lining. Design analysis of natural gas and oxygen combustion conditions allows mitigation of possible negative results of the furnace operation. NG combustion analysis is related to three objectives: determination of the oxidizer consumption, in our case it is the process oxygen [2, 3, 4, 5, 6], component concentration in the combustion products, their quantity and temperature.

Let's consider combustion of natural gas with the chemistry containing methane family hydrocarbons C_nH_{2n+2} (methane CH_4 , ethane C_2H_6 , propane C_3H_8 , butane C_4H_{10}).

Boundary parameters include the following combustion conditions.

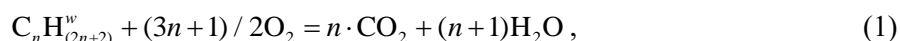


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1. Initial stoichiometric mixture of fuel and oxidizer thoroughly mixed beforehand with the oxygen flow coefficient of $\alpha_o = 1.0$. Initial temperature and sensible heat of natural gas are $t_g = 0$ °C, $Q_h^g = 0$ kJ and of oxygen – $t_o = 0$ °C, $Q_h^o = 0$ kJ. The volume of the initial mixture and combustion products has a shape of a sphere. The mixture ignites in its center at the pressure of $P = 101325$ Pa.
2. The mixture kinetic combustion takes place by a chain mechanism in the static volume.
3. Internal heat exchange is related to transition of ionized atoms (particles) to combustion product molecules without changing their weight.
4. External heat exchange of combustion products takes place only due to CO_2 and H_2O radiation into the free and unlimited open air volume.

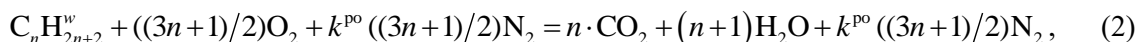
Stoichiometric combustion equation of wet NG is as follows:

- in pure oxygen by stoichiometric ratio:



where n – number of carbon atoms in hydrocarbon, integral;

- in process oxygen:



where $k^{po} = \text{N}_2^o / \text{O}_2^o = (100 - \text{O}_2^o) / \text{O}_2^o$ – nitrogen factor of process oxygen; N_2^o , O_2^o – nitrogen and oxygen concentrations in process oxygen, correspondingly, vol. %.

Stoichiometric (pure) oxygen consumption

$$V_{\text{O}_2} = 0.01 \cdot \left[\sum \left(\frac{3n+1}{2} \right) \cdot \text{C}_n\text{H}_{(2n+2)}^w - \text{O}_2^w \right], \text{m}^3 / \text{m}^3 \quad (3)$$

where O_2^w - oxygen concentration in wet NG, vol. %.

Process oxygen consumption:

$$V_{\text{O}_2}^{po} = (1 + k^{po}) \cdot V_{\text{O}_2}, \text{m}^3 / \text{m}^3 \quad (4)$$

Actual process oxygen consumption at $\alpha_o > 1.0$:

$$V_{\alpha}^{po} = \alpha_o \cdot V_{\text{O}_2}^{po}, \text{m}^3 / \text{m}^3 \quad (5)$$

where α_o – process oxygen consumption factor.

The amount and concentration of the NG combustion product components at $\alpha_o > 1.0$ exclusively of CO_2 and H_2O dissociation:

$$V_{\text{CO}_2} = 0.01 \left(\text{CO}_2^w + n \text{C}_n\text{H} \sum_{2n+2}^w \right), \text{m}^3 / \text{m}^3 \quad (6)$$

$$V_{\text{H}_2\text{O}} = 0.01 \left[\text{H}_2\text{O}^w + (n+1) \text{C}_n\text{H} \sum_{2n+2}^w \right], \text{m}^3 / \text{m}^3 \quad (7)$$

$$V_{\text{N}_2} = 0.01 \cdot \text{N}_2^w + \alpha_o k^{po} V_{\text{O}_2}, \text{m}^3 / \text{m}^3 \quad (8)$$

$$V_{\text{O}_2^e} = (\alpha_o - 1) \cdot V_{\text{O}_2}, \text{m}^3 / \text{m}^3 \quad (9)$$

where O_2^e – excess oxygen.

Total amount of NG combustion products:

$$V_{\alpha} = V_{\text{CO}_2} + V_{\text{H}_2\text{O}} + V_{\text{N}_2} + V_{\text{O}_2^e}, \text{m}^3 / \text{m}^3 \quad (10)$$

Component concentration in NG combustion products:

$$x_i = V_i/V_\alpha \cdot 100 \text{ vol. \%}; \sum x_i = 100 \text{ vol. \%} \quad (11)$$

Let's review temperature computation for C_nH_{2n+2} hydrocarbon combustion products with initial and boundary conditions introduced so that the obtained results could be used to compare thermal and physical characteristics of the fuel components, generation of heat energy (enthalpy), quality of fuel combustion (Q_3 incomplete combustion), process (H_2) and environmental (CO) parameters when developing temperature and heating conditions of the furnace operation.

To compare heat energy generation of fuel and various composition natural gas combustible components the heating power parameter is used which describes heat content (enthalpy) of combustion products.

Balance equation of hydrocarbon combustion with oxygen will take the following form when estimating the heating power:

$$t_{\alpha=1}^h = Q_{lowest}^{op.} / (0.01 \cdot V_{\alpha=1}^{h \sum c_i} \cdot c_i^{t_{\alpha=1}^h}), \text{ } ^\circ\text{C} \quad (12)$$

where $t_{\alpha=1}^h$ – combustion product heating power, $^\circ\text{C}$; $V_{\alpha=1}^h$ – stoichiometric volume of hydrocarbon combustion products, m^3/m^3 ; c_i – i-th component concentration, vol. %; $c_i^{t_{\alpha=1}^h}$ – i-th component heat capacity at the temperature of $t_{\alpha=1}^h$, $\text{kJ}/\text{m}^3 \cdot ^\circ\text{C}$.

Physical and thermophysical parameter calculation results are shown in Table 1.

Table 1. C_nH_{2n+2} Hydrocarbon Combustion Product Properties at $\alpha_o = 1.0$, $t_y = 0 \text{ } ^\circ\text{C}$, $t_o = 0 \text{ } ^\circ\text{C}$ and $P = 101325\text{Pa}$ exclusive of CO_2 и H_2O dissociation.

Substance	$Q_{lowest}^{op.}$, kJ/m^3	$V_{\alpha=1}^h$, m^3/m^3	CO_2 , $\text{m}^3/\text{m}^3/\text{vol.}\%$	H_2O , $\text{m}^3/\text{m}^3/\text{vol.}\%$	$c_{\text{CO}_2}^{t_{\alpha=1}^h}$, $\text{kJ}/\text{m}^3 \cdot ^\circ\text{C}$	$c_{\text{H}_2\text{O}}^{t_{\alpha=1}^h}$, $\text{kJ}/\text{m}^3 \cdot ^\circ\text{C}$	$t_{\alpha=1}^h$, $^\circ\text{C}$
CH ₄	35797	3.356	1/29.79	2/59.69	3.534	3.027	3553
C ₂ H ₆	64351	5.624	2/35.56	3/53.45	3.593	3.092	3697
C ₃ H ₈	93573	7.891	3/38.02	4/50.8	3.624	3.127	3774
C ₄ H ₁₀	123552	10.337	4/39.38	5/49.33	3.648	3.142	3833

It is known [7, 8, 9, 10] that CO_2 and H_2O dissociation occurs at the temperature of over $1500 \text{ } ^\circ\text{C}$. Thermal dissociation refers to internal heat exchanger related to structural change of the combustion product component molecules and occurrence of new molecules (substances) with the initial weight retained. Dissociation degree is the ratio of the dissociated molecule weight to the total molecule weight of the substance (CO_2 and H_2O); it depends on the temperature and concentration of the concerned components [11].

Water steam dissociation in NG combustion products results in additional oxygen and hydrogen:

$$V_{\text{O}_2}^{\text{H}_2\text{O}} = 4.775 \cdot 10^{-5} \cdot a_d \cdot \text{H}_2\text{O}^d \cdot V_{\alpha_o}, \text{ m}^3 / \text{m}^3 \quad (13)$$

$$V_{\text{H}_2}^{\text{H}_2\text{O}} = 9.57 \cdot 10^{-5} \cdot a_d \cdot \text{H}_2\text{O}^d \cdot V_{\alpha_o}, \text{ m}^3 / \text{m}^3 \quad (14)$$

Total volume of the combustion products including the non-dissociated water steam, hydrogen and oxygen is

$$V_{\text{H}_2\text{O}}' = (1 - 0.01 \cdot a) \cdot V_\alpha \cdot \text{H}_2\text{O}^d \cdot 0.01 + V_{\text{H}_2}^{\text{H}_2\text{O}} + V_{\text{O}_2}^{\text{H}_2\text{O}}, \text{ m}^3 / \text{m}^3 \quad (11)$$

CO_2 dissociation in the combustion products results in free oxygen and carbon oxide formation. Oxygen and carbon oxide volumes are:

$$V_{\text{O}_2}^{\text{CO}_2} = 5.03 \cdot 10^{-5} \cdot b_d \cdot \text{CO}_2^d \cdot V_\alpha, \text{ m}^3 / \text{m}^3 \quad (16)$$

$$V_{\text{CO}_2}^{\text{CO}_2} = 10.06 \cdot 10^{-5} \cdot b_d \cdot \text{CO}_2^d \cdot V_\alpha, \text{ m}^3 / \text{ m}^3 \quad (17)$$

The volume of the combustion products including the non-dissociated carbon dioxide, carbon oxide and oxygen, is:

$$V_{\text{CO}_2}' = (1 - 0.01 \cdot b) \cdot V_\alpha \cdot \text{CO}_2^d \cdot 0.01 + V_{\text{O}_2}^{\text{CO}_2} + V_{\text{CO}}^{\text{CO}_2}, \text{ m}^3 / \text{ m}^3 \quad (18)$$

where b and a are the dissociation degrees of carbon dioxide and water steam, correspondingly.

The total volume and composition of NG combustion products with due account for water steam (H_2O) and carbon dioxide (CO_2) dissociation is:

$$V_\alpha^{\text{dis.}} = V_{\text{H}_2\text{O}}' + V_{\text{H}_2}^{\text{H}_2\text{O}} + V_{\text{O}_2}^{\text{H}_2\text{O}} + V_{\text{CO}_2}' + V_{\text{O}_2}^{\text{CO}_2} + V_{\text{CO}}^{\text{CO}_2} + V_{\text{N}_2} + V_{\text{O}_2}, \text{ m}^3 / \text{ m}^3 \quad (19)$$

Component concentrations of natural gas and process oxygen combustion products with due account for H_2O and CO_2 dissociation are:

$$\text{CO}_2' = (1 - 0.01 \cdot b) \cdot V_{\alpha_o}^w \cdot \text{CO}_{2d} / V_\alpha^{\text{dis.}}, \text{ vol. \%} \quad (20)$$

$$\text{H}_2\text{O}' = (1 - 0.01 \cdot a) \cdot V_{\alpha_o}^w \cdot \text{H}_2\text{O}_d / V_\alpha^{\text{dis.}}, \text{ vol. \%} \quad (21)$$

$$\text{N}_2' = (0.01 \cdot \text{N}_2^w + k^{\text{po}} \cdot \alpha_o \cdot V_{\text{O}_2}^o) / V_\alpha^{\text{dis.}}, \text{ vol. \%} \quad (22)$$

where N_2^w – nitrogen concentration in wet NG, vol.%; α_o – process oxygen consumption factor;

$$\text{O}_2' = ((\alpha_o - 1)V_{\text{O}_2}^o + V_{\text{O}_2}^{\text{CO}_2} + V_{\text{O}_2}^{\text{H}_2\text{O}}) \cdot 100 / V_\alpha^{\text{dis.}}, \text{ vol. \%} \quad (23)$$

$$\text{CO}' = V_{\text{CO}}^{\text{CO}_2} \cdot 100 / V_\alpha^{\text{dis.}}, \text{ vol. \%} \quad (24)$$

$$\text{H}_2' = V_{\text{H}_2}^{\text{H}_2\text{O}} \cdot 100 / V_\alpha^{\text{dis.}}, \text{ vol. \%} \quad (25)$$

Balance equation for combustion product temperature computation with due account for incomplete combustion caused by H_2O and CO_2 dissociation will take the form of:

$$t_{\alpha_o=1}^b = (Q_{\text{lowest}}^{\text{op.}} - Q_3^{\text{dis.}}) / (0.01 \cdot V_{\alpha=1}^{\text{dis.}} \cdot \sum c_i \cdot c_i^{t_{\alpha=1}^b}), \text{ }^\circ\text{C} \quad (26)$$

where $Q_3^{\text{dis.}} = 0.01 \cdot V_{\alpha_o=1}^{\text{dis.}} (Q_{\text{CO}} \cdot \text{CO}' + Q_{\text{H}_2} \cdot \text{H}_2')$ is incomplete combustion resulting from H_2O and CO_2 dissociation at the temperature of $t_{\alpha=1}^h$

Table 2 shows the computation results of physical and thermophysical properties of methane family hydrocarbon combustion products at $\alpha_o=1.0$.

It is known [14, 15], that diatomic gasses with symmetrical molecules, such as N_2 , O_2 , H_2 , do not absorb or emit heat energy. The absorption and emission properties are characteristic of triatomic gasses, such as CO_2 and H_2O [4, 7, 12, 15, 16]. Emissivity factor of combustion product layer depends on the combustion product temperature and on product of the radiating gas concentration and the effective path length:

$$\varepsilon_{\text{cpr}} = \varepsilon_{\text{CO}_2} \cdot (T_\alpha^b \cdot 0.01 \cdot S_{\text{ef}}^{\text{sph}} \cdot \text{CO}_2') + \beta \cdot \varepsilon_{\text{H}_2\text{O}} \cdot (T_\alpha^b \cdot 0.01 \cdot S_{\text{ef}}^{\text{sph}} \cdot \text{H}_2\text{O}'), \quad (28)$$

where $S_{\text{ef}}^{\text{sph}} = \eta_{\text{ef}} \cdot 4V_{\text{sph}} / F_{\text{sph}}$ is effective path length in a spherical volume of combustion products provided that $V_{\text{sph}} = 4/3 \pi R_{\text{sph}}^3 = V_{\alpha=1}^{\text{dis.}}$ m³; T_α^b is balance temperature of combustion products, K; β – correction factor, inclusive of higher impact of water steam concentration on H_2O emissivity factor [4, 7] as compared to S_{ef} ; η_{ef} is a gas volume radiation efficiency factor corresponding to the heat energy share reaching the sphere reference surface [8].

Table 2. C_nH_{2n+2} Hydrocarbon Combustion Product Properties with Due Account for CO_2 and H_2O Dissociation at $\alpha_o = 1.0$ and Temperature of $t_{\alpha=1.0}^h$.

Sub stance	$a, \%$ $H_2O^{dis.}$	$b, \%$ $CO_2^{dis.}$	$V_{H_2O}^{H_2O}$ m^3/m^3 /vol. %	$V_{O_2}^{H_2O}$ m^3/m^3 /vol. %	$V_{H_2O}^{non\ dis.}$ m^3/m^3 /vol. %	$V_{CO}^{CO_2}$ m^3/m^3 /vol. %	$V_{O_2}^{CO_2}$ m^3/m^3 /vol. %	$V_{CO_2}^{non\ dis.}$ m^3/m^3 /vol. %	$V_{O_2}^{dis.}$ m^3/m^3 /vol. %	$Q_3^{dis.}$ kJ/m^3 /%	$t_{\alpha=1}^b$ $^{\circ}C$
CH_4	19.84	62.50	0.38/ 9.89	0.204/ 5.3	1.61/ 41.75	0.63/ 16.34	0.31/ 8.05	0.37/ 9.75	0.514/ 13.4	12051 /33.67	2692
C_2H_6	25.44	62.34	0.73/ 11.1	0.394/ 5.98	2.24/ 34.01	1.25/ 19.03	0.63/ 9.56	0.75 /11.43	1.024/ 15.5	23751 /36.91	2703
C_3H_8	27.06	63.54	1.04/ 11.12	0.562/ 6.02	2.92/ 31.33	1.92/ 20.55	0.96/ 10.29	1.09/ 11.72	1.522/ 16.3	35439 /37.87	2728
C_4H_{10}	28.3	65.13	1.36/ 11.22	0.68/ 5.62	3.59/ 29.67	2.62/ 21.65	1.31/ 10.82	1.39/ 11.53	1.99/ 16.4	47771 /38.66	2746

Thermal ray efficient length in the spherical volume is:

$$S_{ef.}^{sph.} = \eta_{ef.} \cdot 4V_{sph.} / F_{sph.} = 1.333 \cdot \eta_{ef.} \cdot R_{sph.}, \text{ m.} \quad (29)$$

Sphere radius equivalent to the stoichiometric volume of combustion products is:

$$R_{sph.} = \sqrt[3]{V_{\alpha=1}^{dis.} \cdot 3 / (4\pi)} = 0.621 \cdot \sqrt[3]{V_{\alpha=1}^{dis.}}, \text{ m.} \quad (30)$$

$$S_{ef.}^{sph.} = 1.333 \cdot 0.621 \cdot \eta_{ef.} \cdot \sqrt[3]{V_{\alpha=1}^{dis.}} = 0,828 \cdot \eta_{ef.} \cdot \sqrt[3]{V_{\alpha=1}^{dis.}} \text{ m.} \quad (31)$$

The emissivity factor of the combustion product stoichiometric volume components can be determined using the interpolatory equation and table data [7].

Actual emissivity factor of the combustion product volume is $\varepsilon_{cpr.}^a = \varepsilon_{CO_2} + \beta \varepsilon_{H_2O}$. Based on this amount a correction $\delta = \varepsilon_{CO_2} \cdot \varepsilon_{H_2O}$, related to coincidence of some radiation bands within CO_2 and H_2 spectrum, is calculated, then $\varepsilon_{cpr.}^d = \varepsilon_{cpr.}^a - \delta = \varepsilon_{cpr.}^a - \varepsilon_{CO_2} \cdot \varepsilon_{H_2O}$.

Actual balance temperature of hydrocarbon combustion products, considering heat energy output from radiation into the unbounded open space is:

$$t_{\alpha=1}^d = (Q_{lowest}^{op.} - Q_3^{dis.} - Q_l) / (0.01 \cdot V_{\alpha=1}^{dis.} \cdot \sum c_i \cdot c_i^{t_{\alpha=1}^d}) \text{ } ^{\circ}C, \quad (32)$$

where Q_1 – the amount of heat from combustion products released to atmosphere due to CO_2 and H_2O radiation at the temperature of $t_{\alpha=1}^d$, kJ; $c_i^{t_{\alpha=1}^d}$ – CO_2 and H_2O heat capacity at the actual temperature of $t_{\alpha=1}^d$, kJ/(m \cdot $^{\circ}C$).

Following the recommendations of S. S. Kutateladze [15]

$$Q_l = 4.9 \left[\varepsilon_{cpr.}^d \left(T_{\alpha=1}^b / 100 \right)^4 - a_w \left(T_0 / 100 \right)^4 \right] \text{ kJ,} \quad (33)$$

where a_w is a unit value atmosphere absorption degree; T_0 is thermodynamic temperature of 273.15K.

Heat pyrometric factor is

$$\eta_{pyr.}^{heat} = (1 - Q_l / (V_g \cdot Q_{lowest}^{op.})) 100\%, \quad (34)$$

where V_g – the amount of initial gas, m 3 .

Temperature pyrometric factor of combustion products may be estimated for the selected initial and boundary conditions:

$$\eta_{pyr.}^{heat} = T_d / T_{\alpha=1}^b = \sqrt[4]{1 - \varepsilon_{cpr.}} \quad (35)$$

Table 3 shows computation results of hydrocarbon combustion product properties at $t_{\alpha=1}^b$ and radiation heat transfer to unbounded medium.

Table 3. C_nH_{2n+2} Hydrocarbon Combustion Product Properties at the Temperature of $t_{\alpha=1}^d$.

Sub stance	$V_{\alpha=1}^{dis.}$, m^3/m^3	$V_{spr.}^{dis.}$ m^3	$F_{sph.}^{dis.}$ m^2	$R_{sph.}^{dis.}$ m	$S_{ef.}$ m	$0.01S_{ef.}$ $H_2O^{dis.}, \mathcal{M}$	$0.01S_{ef.}$ $CO_2^{dis.}, \mathcal{M}$	Q_1 , kJ	$\eta_{pyr.}^{heat}$ %	t_d , °C	$\eta_{pyr.}^{heat}$, %
CH ₄	3.81	3.81	1.23	0.97	1.23	0.53	0.13	1277.38	96.43	2654	98.61
C ₂ H ₆	6.55	6.55	1.47	1.16	1.47	0.51	0.18	1559.05	97.58	2678	99.09
C ₃ H ₈	9.28	9.28	1.65	1.31	1.65	0.53	0.20	1793.11	98.08	2708	99.28
C ₄ H ₁₀	12.2	12.2	1.81	1.43	1.81	0.55	0.22	1987.85	98.39	2729	99.65

2. Conclusion

Using the proposed procedure a chemistry and actual temperature computation program was developed for combustion products of methane family hydrocarbons (methane, ethane, propane, butane) with industrial oxygen in Microsoft Excel with due account for dissociation (of water steam and carbon dioxide) and radiation heat transfer to unbounded medium.

Hydrogen in the amount of 9.89 vol.% to 11.22 vol.% and carbon oxide in the amount of 16.34 vol.% to 21.65 vol.% are generated in combustion products with due account for the water steam and carbon dioxide dissociation what results in incomplete combustion [17, 18, 19, 20] of 33.67% to 38.66% based on these parameters. Thus preliminary kinetic combustion of natural gas with oxygen causes combustion in a layer of charge materials of not initial fuel mixture with oxygen but H₂O and CO₂ dissociation products with free oxygen (O₂ vol. %), which content varies within 13.4 vol. % – 16.4 vol. %.

Design heat output, balance and actual temperatures describe the possible (maximum) level and shall be used to compare gaseous medium temperature condition in the furnace work space.

Heat and temperature pyrometric factors significantly dependent on the fuel combustion conditions and boundary heat exchange conditions shall be used in computation as a first approximation.

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