CALCULATION OF THE COMBUSTION HEATS
OF HYDROCARBONS OF THE HOMOLOGOUS
SERIES OF METHANE

V. V. Sagadeev, E. V. Sagadeev,
R. A. Kafiatullin, and V. I. Sagadeev

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A new empirical method of calculation of the combustion heats of organic compounds according to the additive scheme on the basis of their chemical structure has been proposed.

Combustion heat (calorific value) is the most important characteristic of both an organic fuel and its constituent individual components. As applied to the latter, the term "combustion enthalpy" that is usually related to standard conditions is used instead of the term "combustion heat" in thermochemistry [1]. In thermochemistry, it is agreed that the heat absorbed by a system has a positive value while the heat released by a system has a negative value [2].

TABLE 1. Experimental and Calculated Enthalpies of Combustion and Vaporization of Hydrocarbons of the Methane Series

Compound	Standard combustion enthalpy, kJ/mole		Standard enthalpy of vaporization, kJ/mole		Standard enthalpy of combustion in the gas phase, kJ/mole	
	experiment	calculation	experiment	calculation	experiment	calculation
Methane	−890.4[a]	−	−	−	−890.4[a]	−890.4
Ethane	−1559.8[a]	−1559.8	−	−	−1559.8[a]	−1559.8
Propane	−2220.0[a]	−2212.1	−	−	−2220.0[a]	−2212.1
Butane	−2876.7[a]	−2864.4	−	−	−2876.7[a]	−2864.4
i-Butane	−2868.7[a]	−2858.1	−	−	−2868.7[a]	−2858.1
Pentane	−3511.9[b]	−3516.7	26.7[c]	27.0	−3536.1[d]	−3543.7
u-Pentane	−3507.4[e]	−3510.4	25.2[c]	25.0	−3531.2[b]	−3535.4
Hexane	−4163.1[d]	−4168.9	31.5[c]	31.8	−4194.8[d]	−4200.7
Heptane	−4816.9[d]	−4821.2	36.6[c]	36.6	−4853.5[d]	−4857.8
Octane	−5470.7[d]	−5473.5	41.5[c]	41.3	−5512.2[d]	−5514.8
Nonane	−6124.0[a]	−6125.8	46.4[f]	46.1	−6171.0[g]	−6171.9
Decane	−6777.8[a]	−6778.1	51.4[f]	50.9	−6829.7[g]	−6829.0
Undecane	−7431.5[a]	−7430.4	56.3[f]	55.7	−7488.4[g]	−7486.0
Dodecane	−8085.3[a]	−8082.7	61.3[f]	60.4	−8147.2[g]	−8143.1
Tridecane	−8739.0[a]	−8734.9	66.2[h]	65.2	−8805.9[g]	−8800.1
Tetradecane	−9392.8[a]	−9387.2	71.2[h]	70.0	−9464.7[g]	−9457.2
Pentadecane	−10046.5[a]	−10039.5	74.0[h]	74.7	−10123.4[g]	−10114.2
Hexadecane	−10700.3[a]	−10691.8	80.4[f]	79.5	−10782.2[g]	−10771.3
Heptadecane	−11354.0[a]	−11344.1	85.6[h]	84.3	−11440.9[g]	−11428.4
Octadecane	−12007.8[a]	−11996.4	90.8[h]	89.0	−12099.6[g]	−12085.4
Nonadecane	−12661.5[a]	−12648.7	95.8[h]	93.8	−12758.4[g]	−12742.5
Eicosane	−13315.3[a]	−13300.9	100.8[h]	98.6	−13417.1[g]	−13399.5

Note: a) data of [2], b) [7], c) [6], d) [8], e) [9], f) [10], g) [11], and h) [12].

TABLE 2. Experimental and Calculated Calorific Values of Hydrocarbons of the Methane Series

Compound	Net calorific value			
	kJ/m^3		kJ/kg	
	experiment	calculation	experiment	calculation
Methane	35807.0[a]	35826.0	50031.0[b]	50031.0
Ethane	63727.0[b]	63750.0	47503.0[b]	47489.0
Propane	91211.0[a]	90909.0	46366.0[b]	46176.0
Butane	118595.0[a]	118068.0	45735.0[b]	45504.0
Pentane	146022.0[a]	146433.0	45406.0[b]	45462.0
Hexane	173636.0[b]	173805.0	44769.0[b]	45176.0
Heptane	200260.0[b]	201176.0	44769.0[b]	44974.0
Octane	228028.0[b]	228548.0	44769.0[b]	44817.0
Nonane	256341.0[b]	255920.0	44769.0[b]	44695.0
Decane	283675.0[b]	283291.0	44610.0[b]	44600.0
Pentadecane	418400.0[b]	420150.0	44338.0[b]	44305.0
Octadecane	503892.0[b]	502265.0	–	44207.0
Eicosane	552288.0[b]	557008.0	44217.0[b]	44158.0

Note: a) data of [13] and b) [14].

Therefore, the standard combustion enthalpies of compounds appearing in what follows have a negative value. In heat engineering, conversely, it is agreed that the calorific values of compounds are positive [1].

Solution of the problem of calculation of the combustion enthalpies of organic compounds in general form (rigorously and not empirically) is rather difficult [3]. But, as shown in practice, the thermochemical characteristics of individual organic compounds can safely be calculated with the use of the additivity rule [4, 5]. The construction of the additive scheme is based on the assumption that the value of a thermochemical characteristic can be represented in the form of a sum of partial contributions (increments) which account for individual fragments of a molecule. This principle has been used to calculate the combustion enthalpies of hydrocarbons of the methane series. The method of group contributions (scheme by atoms with allowance for the nearest environment) that enables one to take into account most of the available intramolecular electronic effects was used, which provides the possibility of using it for different classes of organic compounds [6]. From the experimental literature data given in Table 1, we calculated for the first time the set of carbon-containing group contributions to the standard combustion enthalpy. The notation for the increments is introduced according to Benson and Buss [4, 5]. The value of each group contribution is constant without regard to the molecule (linear, branched, or cyclic) in which a given group is found. Using the contributions obtained, we calculated the standard combustion enthalpies of hydrocarbons of different structure (Table 1).

In practice, when individual compounds are utilized as fuels, one uses the term "gross or net calorific value" instead of the term "combustion enthalpy" [1]. From the calculated values of the combustion enthalpies of hydrocarbons in the gas phase, we calculated the calorific values of hydrocarbons in kilojoules per cubic meter, taking into account the Avogadro law [2], and in kilojoules per kilogram, taking into account their molecular weight (Table 2). Good agreement between the experimental and calculated calorific values was established for all the considered compounds.

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