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DETERMINATION OF COMBUSTION HEAT OF DIESEL FUEL COMPOSITIONS USING THE METHODS OF QUANTUM CHEMISTRY

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Abstract

In this paper, we calculated the average values of the formation enthalpies and calorific values of hydrocarbon groups using quantum chemical methods of calculation. The dependence of the calorific value of diesel fuel compositions on the group composition at the operating parameters of the diesel engine was studied. The calorific values of five diesel fuel compositions having a different hydrocarbon composition were calculated, and the dependence of the calorific value of diesel fuel on the group and fractional composition was established.

Keywords: *diesel fuel compositions; hydrocarbons; enthalpies; the calorific value; quantum chemical methods.*

1. Introduction

In the conditions of a new strategy of economic development in Russia increasing attention is given to the processes of deep petroleum refining for the production of high quality motor fuels. The problem is becoming now becoming even more relevant because of the increase in the demand for diesel fuels of winter and arctic grades, which is due to reclaiming north and arctic regions [1-2]. For this reason, production of low-freezing diesel fuels is a topical issue for Russia, having large north territories [3]. Meanwhile, fuel compositions must meet specifications to operation in the conditions of low temperature, ignition quality as well as they must have the maximum calorific capacity. These properties include cold filter plugging point, cetane number and combustion heat of volume unit (energy output) [4].

As far as the production of diesel fuel is performed by the mixing petroleum fractions, which consist of paraffinic, olefinic, naphthenic and aromatic hydrocarbons, the obtained mixtures are complex multi-component systems, which properties are determined both by the ratios between them and molecular interactions [5]. These explain the main complexity of their determination. As far as the determination of low-temperature properties and cetane number is performed mainly by experimental methods, the calculation of heat effects of fuel combustion in laboratory conditions is a challenging task.

The fuels combustion heat is determined by calorific values of the components, which contents depend on hydrocarbon compositions of mixing fractions. The last depends on feedstock composition, technological conditions and catalyst activity in the processes of production of these fractions [6] and the ratio between mixing fractions at the stage of production of diesel fuels.

Thus, this work aimed to determine combustion heat of diesel fuel compositions using the calculation methods of quantum chemistry and to evaluate the influence of different hydrocarbon groups on the value of combustion heat for prediction of their heat capacity.

2. Research object and methods

The objects of research are diesel fuel compositions, obtained by the mixing of diesel fractions of the following boiling ranges: 150-310°C, 180-240°C, 200-360°C; and denormalization process product (the fraction, purified from paraffinic hydrocarbons). Table 1 shows hydrocarbon compositions and physical properties of fractions, involved in the process of diesel fuel production.

Table 1. Hydrocarbon composition and properties of fractions, involved in the process of diesel fuel production

Hydrocarbon composition and properties of fractions	Petroleum fractions					
	Fr.1	Fr.2	Fr.3	Fr. 4	Fr.5	DN
N-Paraffins, wt.%	30.7	29.5	19.0	19.3	19.9	23.0
I-Paraffins, wt.%	23.0	24.1	33.1	32.9	32.4	29.6
Naphthenes, wt.%	13.6	14.2	19.0	18.9	18.6	17.1
Aromatic hydrocarbons, wt.%	32.6	32.2	28.9	29.0	29.2	30.2
Boiling temperature of 50 %, °C	184	191	283	281	267	253
Density at 20°C, kg/m^3	794	799	838	837	835	823
Molecular weight, g/mol	92.5	98.1	171.7	170.1	158.9	147.7

Fr.1 (boiling between 180-240ºC, composition 1); Fr. 2(boiling between 180-240ºC; composition 2); Fr. 3(boiling between 200-360ºC, composition 1); Fr. 4(boiling between 200-360ºC; composition 2); Fr. 5 (boiling between 150-310ºC); DN (Denormalization process product)

In order to calculate molecular weights of fractions the following formulae were used [7-8]:
$M = 0.4448.T_{Rankine} - 273.56$
$T_{Rankine} = (T_{50°C} + 273.15).9/5$, where $T_{50\%}$ – the boiling temperature of 50% fraction.

3. Results and discussion

Because combustion heat of diesel fuel compositions depends on the calorific value of the components, constituting the composition, as was mentioned above, at the first stage of the research the enthalpies of formation of hydrocarbon groups, oxygen, and products of combustion (carbon dioxide and water steam) were calculated at operating parameters of diesel engine: the temperature in the combustion zone is 2273 K, the pressure is 110 atm. Using the calculation methods of quantum chemistry. Further, according to the Hess law the reaction heat effects of the combustion of individual hydrocarbons, constituting diesel fuel compositions, were calculated and their average values were determined for the following homological groups: n-paraffins, i-paraffins, naphthenes, aromatic hydrocarbons (Table 2).

Table 2. The combustion reaction of the different hydrocarbon group

Hydrocarbon group	General reaction of combustion
N-Paraffins	$C_nH_{(2\cdot n+2)}+(1,5\cdot n+0,5)\cdot O_2 \rightarrow n\cdot CO_2+(n+1)\cdot H_2O$
I-Paraffins	$C_nH_{(2\cdot n+2)}+(1,5\cdot n+0,5)\cdot O_2 \rightarrow n\cdot CO_2+(n+1)\cdot H_2O$
Naphthenes	$C_nH_{2\cdot n}+1,5\cdot n\cdot O_2 \rightarrow n\cdot CO_2+n\cdot H_2O$
Aromatic hydrocarbons	$C_nH_{(2\cdot n-6)}+(1,5\cdot n-1,5)\cdot O_2 \rightarrow n\cdot CO_2+\frac{(2\cdot n-6)}{2}\cdot H_2O$

In order to calculate enthalpies of hydrocarbons Gaussian software, which implements the methods of quantum chemistry, was applied. The models of substances, taking part in reactions, were created in GaussView software. The Density Functional Theory (DFT) was applied for calculations. The advantage of this method lies in that DFT takes into account the effect of electron correlation, i.e. the fact that electrons in molecule bounce off as a result of interaction between them. The method DFT is accurate enough for the calculation of hydro-carbons of diesel boiling range [9-11]. The theoretical approximation was the model B3LYP [12-14].
Table 3 shows the average values of enthalpies of formation and heat effects (combustion heat) of combustion reactions for each group of hydrocarbons of diesel fuel compositions.

Table 3. The average enthalpies of formation and combustion heats of hydrocarbon groups

	Enthalpy of formation $\Delta_r H_f$, MJ/mol	Combustion heat $Q=-\Delta_r H$, MJ/mol
Hydrocarbon group		
N-Paraffins	−1438.66	10.29
I-Paraffins	−1592.48	11.37
Naphthenes	−692.18	4.87
Aromatic hydrocarbons	−708.54	4.53
Components of the combustion reaction		
O_2	−392.4	–
CO_2	−492.4	–
H_2O	−199.4	–

**Q* – combustion heat, MJ/mol; $\Delta_r H$ – heat effect of combustion reaction of a hydrocarbon group, MJ/mol.*

Thus, in series "n-paraffins" – "i-paraffins" – "naphthenes" – "aromatic hydrocarbons" the enthalpies of formation and combustion heats decrease, which is due to increase in the ratio (C:H) in the molecule. Because the combustion heat of hydrogen is much higher than combustion heat of carbon (143 MJ/kg and 32 MJ/kg [15]), the increase in the ratio (C:H) in diesel fuel corresponds to decrease in the heat effects of combustion reactions.

According to the calculated values of combustion heats of different hydrocarbon groups, the heats of combustion reactions of diesel fuel compositions, obtained by mixing the fractions presented in Table 1 in different ratios, were determined (Table 4).

Table 4. The content of different fractions at the stage of diesel fuel compositions production (vol.%)

Fractions, vol.%	Compositions				
	1	2	3	4	5
Fraction boiling between180-240ºC, Composition 1	10	–	26	75	85
Fraction boiling between180-240ºC, Composition 2	–	85	–	–	–
Fraction boiling between 200-360ºC, Composition 1	85	–	55	25	15
Fraction boiling between 200-360ºC, Composition 2	–	10	–	–	–
Fraction boiling between 150-31 ºC	5	5	–	–	–
Denormalization process product	–	–	19	–	–
Density at 20°C, kg/m^3	834	805	824	805	801

Table 5 shows the compositions of diesel fuels in wt.% and calculates the molecular weight.

Table 5. The content of different fractions at the stage of diesel fuel compositions production (wt.%)

Fractions, wt.%	Compositions				
	1	2	3	4	5
Fractions, vol.%	9.5 –	– 84.4	25.0 –	74.0 –	84.3 –
Fraction boiling between180-240 ºC, Composition 1	85.5	–	56.0	26.0	15.7
Fraction boiling between180-240 ºC, Composition 2	–	10.4	–	–	–
Fraction boiling between200-360 ºC, Composition 1	5.0	5.2	–	–	–
Fraction boiling between200-360 ºC, Composition 2	–	–	19.0	–	–
Molecular weight, kg/mol	0.164	0.109	0.147	0.113	0.105

For the obtained diesel fuel compositions (1-5), according to the rule of additivity, the thermal performance (combustion heat), and hydrocarbon composition were determined. The combustion heat effects were determined at the conditions of the internal combustion engine (temperature in the combustion zone is 2273 K, the pressure is 110 atm.). Calculation results are presented in Table 6.

Table 6. Hydrocarbon composition and thermal performance of diesel fuel compositions

	Compositions				
	1	2	3	4	5
N-Paraffins, wt.%	20.1	27.9	22.7	27.7	28.9
I-Paraffins, wt.%	32.1	25.4	29.9	25.7	24.6
Naphthenes, wt.%	18.4	14.9	17.3	15.0	14.5
Aromatic hydrocarbons, wt.%	29.3	31.7	30.1	31.7	32.0
(N-Paraffins+I-Paraffins), wt.%	52.2	53.3	52.6	53.4	53.5
(Naphthenes+Aromatichydrocarbons), wt.%	47.7	46.6	47.4	46.7	46.5
Density at 20 °C, kg/m^3	834	805	824	805	801
Molecular weight, kg/mol	0.164	0.109	0.147	0.113	0.105
Combustion heat, MJ/mol	7.94	7.92	7.94	7.94	7.93
Combustion heat, MJ/kg	48.42	72.67	54.02	70.26	75.49
Combustion heat, MJ/m^3	40372	58463	44514	56577	60461

As can be seen from Table 6, the lighter the composition (lower molecular weight and density), the higher the heat of fuel combustion. For example, for fuel composition 2, 4 and 5, which have the lowest molecular weights (0.109, 0.113 and 0.105 kg/mol) and densities (805, 804 and 801 kg/m^3), the calculated values of combustion heat are maximum (58463, 56577 and 600461 MJ/m^3). This is due to the speciality of hydrocarbon composition. Namely, the contents of n-paraffins and i-paraffins in diesel fuel compositions 2, 4 and 5 is the highest (53.3, 53.4 and 53.5 wt.%). These hydrocarbons have the highest combustion heats in comparison to naphthenes and aromatic compounds. Contrariwise, compositions 2 and 3 have the lowest combustion heats (40347 and 44514 MJ/m^3). These compositions are heavier (the molecular weights are 0.164, and 0.147 kg/mol and densities are 834 and 824 kg/m^3). They also have the highest contents of naphthenes and aromatic hydrocarbons (47.7 and 47.4 wt.%).

The obtained regularities of dependency of diesel fuels composition combustion heats on the hydrocarbon composition are explained by different contents of carbon and hydrogen, which are characterized by different calorific values (hydrogen has much higher calorific value), as well as by the structure of the molecules. That is why the more the content of saturated hydrocarbons and lower the content of unsaturated hydrocarbons in fuel composition, the higher its calorific value. Herewith, while developing optimal diesel fuel compositions, the contribution of different hydrocarbons in low-temperature properties and cetane number should be taken into account.

4. Conclusions

1. Using the methods of quantum chemistry the average values of enthalpies of combustion and combustion heats of hydrocarbon groups, constituting diesel fuel composition, were calculated at the conditions of their combustion in an internal combustion engine (temperature in the combustion zone is 2273 K, the pressure is 110 atm.). Combustion heats constitute for n-paraffins and i-paraffins 10.29 and 11.37 MJ/mol, for naphthenes 4.87 MJ/mol, for aromatic hydrocarbons 4.53 MJ/mol.

2. It was established, that increase in the ratio C:H in diesel fuel in series "n-paraffins" – "i-paraffins" – "naphthenes" – "aromatic hydrocarbons" the enthalpies of formation and combustion heats decrease, which is due to higher combustion heat of hydrogen than combustion heat of carbon.

3. The combustion heats of five diesel fuel compositions, which have different hydrocarbon composition, were calculated. It was shown, that their value comprises from 32000 to 49500 MJ/mol, which influences much on the power efficiency of the internal combustion engine.

4. The influence of hydrocarbon composition of diesel fuel on the combustion heat at the conditions of combustion inside the internal combustion engine was shown: the higher the ratio between saturated and unsaturated hydrocarbons, the higher the calorific value of the fuel. It was also established, that the lighter the fuel compositions (lower molecular weight and density), the higher the combustion heat. Thus, compositions 2, 4 and 5, which are characterized by the lowest molecular weights (0.109, 0.113 and 0.105 kg/mol) and densities (805, 804 and 801 kg/m^3), have maximum combustion heats (58463, 56577 and 60461 MJ/m^3). Contrariwise, compositions 1 and 3, which are heavier (molecular weights are 0.164 and 0.147 kg/mol, densities are 834 and 824 kg/m^3) and are characterized by higher content of naphthenic and aromatic hydrocarbons (47.8 and 47.4 wt.%), have the lowest combustion heats (40347 and 44514 MJ/m^3).

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