The Influence of Magnetic Properties and Electronic Structure of Molecules on Motor Fuel Operating Characteristics by Example of n-Alkanes

Dezortsev Sergey Vladislavovich* and Podyacheva Ksenia Igorevna

Department of oil and gas technology, Ufa state petroleum technical university, Kosmonavtov Str. 1, Ufa 450062, Russian Federation

Abstract: The influence of magnetic properties and electronic structure of hydrocarbons on such operational properties of motor petrol as octane numbers, defined by motor and research methods, saturation vapor pressure, flash temperature, is shown by the single-factor analysis of correlations by the example of n-alkanes C_1-C_{10} . It is shown, that detonation phenomenon in internal-combustion engine, probably, have a critical state nature. Magnetic properties of hydrocarbons are connected with their electronic structure. First ionization potential, assignable by photoelectron spectroscopy, may be recommended as information parameter for the calculation of petrol operating characteristics. Studying of electronic structure of substances is promoting the creation of products with given physical-chemical properties and operating characteristics.

Key words: Octane number, saturation vapor pressure, flash temperature, self-ignition temperature, operating characteristics, specific magnetic susceptibility, electronic structure, first ionization potential, n-alkanes, motor fuel.

1. Introduction

High-quality motor fuels must correspond to the list of standard parameters. One can make an analogy between manufacturing materials with given properties and motor fuels with restricted by standards operating characteristics. For example, values of ON (octane numbers), SVP (saturation vapor pressure), flash temperature and self-ignition temperature for motor petrol are restricted, and today are estimated by standard methods [1, 2]. As a matter of fact, for more than ninety years history of development and perfection standard methods for operating characteristics estimation have no change practically

and could not answer the questions, connected with the nature of the detonation phenomenon in internal combustion engine [3, 4]. It is not possible to give correct physical-chemical description by standard parameters of the processes, which are taking place during manufacturing, transportation and storage of motor fuels.

If one will examine motor petrol as multi component system with complex type and chemical content (more than 200 individual chemical substances, including hydrocarbons and heteroatomic molecules) [5], it is necessary to take into account complex nature of intermolecular interactions. In this case modeling of motor petrol operating characteristics becomes an intricate problem. To our opinion, the search of integral physical-chemical parameter, having reliable correlations with basic operating characteristics will be preferable decision. Some researchers of the time examine dipole moment as such parameter [6, 7]. But, at the same time orbital control for hydrocarbons reactivity in homogeneous organic systems is not taken

Corresponding author: Dezortsev Sergey Vladislavovich, doctor, research fields: Physical chemistry, theory of matter structure, complex multi component organic and biological systems, products and materials with given properties, absorption spectroscopy, rheology, oil dispersed systems, chemical and petrochemical technology, oil refining; materials: organic materials and products on the base of multiring hydrocarbons (semiconductors), bitumen, bitum-polymers, organic compounds, fuels (as products and materials with given properties). E-mail: dezortsev@rambler.ru.

into account [8]. Also it is known, that at the ON proximate analysis electromagnetic methods have the best accuracy [9].

Previous author's research [10-14] exposed non-linear character of interconnections between electronic structure of hydrocarbons (by example of n-alkanes) and their basic physical-chemical (including magnetic) and thermodynamic properties (PCP), which can be described by dependences:

$$\begin{aligned} Z &= \alpha_1 \cdot e^{\beta_1 \cdot E_{HOMO}} \\ Z &= \alpha_2 \cdot e^{\beta_2 \cdot E_{LUMO}} \\ Z &= \alpha_3 \cdot e^{\beta_3 \cdot \Delta E} \end{aligned} \quad (1)$$

where α_i and β_i , empirical coefficients; Z , one of the basic PCPs; E_{HOMO} and E_{LUMO} , calculated values of the highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}) energies, eV; ΔE , forbidden gap (difference between the HOMO and LUMO values), eV.

For individual molecular substances the equation (1) can be expressed by a polynomial of the second-third degree:

$$\begin{aligned} Z &= \alpha_1 + \beta_1 \cdot E_{HOMO} + \gamma_1 \cdot (E_{HOMO})^2 \\ Z &= \alpha_2 + \beta_2 \cdot E_{LUMO} + \gamma_2 \cdot (E_{LUMO})^2 \\ Z &= \alpha_3 + \beta_3 \cdot \Delta E + \gamma_3 \cdot (\Delta E)^2 \end{aligned} \quad (2)$$

where α_i , β_i and γ_i , relevant empirical coefficients.

The Eq. (2) follows from Eq. (1) after expansion Eq. (1) into the Taylor series.

The purpose of this work is to study the influence of

electromagnetic properties and molecular electronic structure on motor fuel operating characteristics. The task of this work is the investigation of SMS (specific magnetic susceptibility), energies of the highest occupied molecular orbital (E_{HOMO}) and first IP (ionization potentials) of n-alkanes influence for their operating characteristics.

2. Experiments

The n-alkanes C_1 - C_{10} selection as test subjects are determined, firstly, by the simplicity of their chemical structure and, secondly, by mostly full and accurate supplemental information about their physical-chemical properties and operating characteristics. Such operating characteristics as octane numbers, saturation vapor pressure, flash temperature, self-ignition temperature were examined. Data on electromagnetic properties and operating characteristics of n-alkanes were taken from database directory [15-17]. Values of E_{HOMO} were computed by ab-initio RHF 6-31**G method [18-20]. Values of the first ionization potentials (IP) of n-alkanes were taken from [21]. Reduced thermodynamic parameters were obtained by dividing current value on the first term value of the homologous series. Correlations between operating characteristics, SMS, E_{HOMO} and IP were studied by the least-squares standard method for polynomial dependencies. The profile of the test subjects is given in Table 1.

Table 1 The profile of n-alkanes C_1 - C_{10} [15-17, 20, 21].

n-alkanes C_1 - C_{10}	Electromagnetic properties				Operating characteristics			
	Specific magnetic susceptibility, $\times 10^{-6}$, 1/g	Energy of the highest occupied molecular orbital, eV	First ionization potential, eV	Research octane number (RON)	Motor octane number (MON)	Flash temperature, °C	Self-ignition temperature, °C	Saturation vapor pressure, 20 °C, kPa
methan, CH_4	0.7606	14.79	12.99	107.5	110	-	595	3,896.14
ethane, C_2H_6	0.8920	13.27	11.65	107.1	104	-	-	3,770.49
propane, C_3H_8	0.8754	12.69	11.21	105.7	100	-96	470	844.08
n- butane, C_4H_{10}	0.8642	12.18	10.8	93.6	92	-69	365	207.42
n- pentane, C_5H_{12}	0.8600	11.84	10.55	61.7	61	-35	285	55.81
n- hexane, C_6H_{14}	0.8586	11.59	10.48	24.8	25	-22	240	15.95
n- heptane, C_7H_{16}	0.8512	11.41	10.35	0	0	-4	215	4.66
n- octane, C_8H_{18}	0.8459	11.32	10.24	-	-17	14	215	1.38
n-nonane, C_9H_{20}	0.8443	11.3	10.21	-	-45	-	-	0.41
n-decane, $C_{10}H_{22}$	0.8398	11.25	10.19	-	-	-	-	0.12

During data analysis of magnetic properties and operating characteristics of n-alkanes it turns out, that methan is an exception from common trend. So, for the specific magnetic susceptibility and operating characteristics it makes sense to examine the homologous series of n-alkanes C₂-C₁₀.

3. Experimental Results

The quantitative correlations between operating characteristics of n-alkanes C₁-C₁₀ and their magnetic properties, values of E_{HOMO} and IP were tested by polynomial function of the second-third degree [10]:

$$\begin{aligned} Z &= \alpha_1 + \beta_1 \cdot \chi + \gamma_1 \cdot (\chi)^2 \\ Z &= \alpha_2 + \beta_2 \cdot E_{HOMO} + \gamma_2 \cdot (E_{HOMO})^2 \\ Z &= \alpha_3 + \beta_3 \cdot IP + \gamma_3 \cdot (IP)^2 \end{aligned} \quad (3)$$

where α_i , β_i and γ_i , relevant empirical coefficients; Z, any operating characteristic from the Tables 1 and 2; χ , specific magnetic susceptibility, 10⁻⁶, 1/g; E_{HOMO}, calculated value of the highest occupied molecular orbital energy, eV; IP, first ionization potential, eV.

Calculated values of empirical coefficients for the second degree polynomial dependences are represented in Table 2. The correlation coefficients values are from 0.92 to 1.0. The values of the relative deviation are from 1.0% to 5.9%.

For n-alkanes C₂-C₁₀ SMS and operating characteristics correlation coefficient for Eq. (3) vary in

interval R = 0.89 ÷ 0.99 (Table 2). The increase of ON, self-ignition temperature and saturation vapor pressure, also decrease of flash temperature is promoted by the SMS growth. I.e. light hydrocarbons are mostly recommended as components of motor petrol. From the values of correlation coefficients one can draw a conclusion, that magnetic properties of n-alkanes are closely connected with operating characteristics, and their investigation have practical importance.

Electronic structure have maximum influence on n-alkanes operating characteristics (Table 2). Diagrams, connecting operating characteristics under study with heist occupied molecular orbital energies calculated values of relevant n-alkanes are presented on Fig. 1-5.

Correlation coefficients for dependences of operating characteristics from E_{HOMO} calculated values for n-alkanes C₂-C₁₀ are higher, than in the case of SMS (R = 0.99 ÷ 1.0; Table 2). In consideration of available data on dipole moment [6, 7] one can make preliminary conclusion about conclusive (but not total) contribution of hydrocarbons electromagnetic properties into motor fuels operating characteristics.

In fact, the case in question is about reactivity of n-alkanes in reaction of combustion. It is necessary to mark, that than lower is E_{HOMO} value, than higher is the reactivity of hydrocarbons in oxygen combustion reactions. The drawn conclusion is in complete agreement

Table 2 Empirical coefficients of polynomial correlation dependences of n-alkanes C₁-C₁₀ operating characteristics from specific magnetic susceptibility, E_{HOMO} and IP.

Operating characteristics	Coefficients of single-factor empirical correlation dependences (3)											
	Specific magnetic susceptibility, × 10 ⁻⁶ , 1/g				Energy of the heist occupied molecular orbital, eV				First ionization potential, eV			
	a ₀	a ₁	a ₂	Correlation coefficient	a ₀	a ₁	a ₂	Correlation coefficient	a ₀	a ₁	a ₂	Correlation coefficient
Research octane number (C ₂ -C ₇)	-97,818	221,991	-125,797	0.96	-8,822	1,390.1	-54.062	1.0	-5,318.1	900.76	-37.21	0.92
Motor octane number (C ₂ -C ₉)	-74,724	169,291	-95,743	0.97	-10,157	1,605.3	-62.732	0.99	-6,355	1,073.6	-44.386	0.94
Flash temperature °C (C ₃ -C ₈)	1,129.3	1,183.9	-2,955	0.98	4,242.5	-638.49	23.373	0.99	9,670.9	-1,698.5	73.787	1.0
Self-ignition temperature, °C (C ₃ -C ₈)	615,940	-10 ⁶	851,204	0.98	4,090.3	-822.46	42.349	1.0	36,199	-7,114.6	351.56	0.99
Saturation vapor pressure, 20 °C, kPa (C ₂ -C ₁₀)	2·10 ⁶	-4·10 ⁶	2·10 ⁶	0.99	215,457	-36,806	1,570.5	0.99	313,194	-59,669	2,840.7	0.99

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Fig. 1 The dependence of RON from E_{HOMO} for n-alkanes C_2 - C_7 .

Fig. 2 The dependence of MON from E_{HOMO} of n-alkanes C_2 - C_9 .

Fig. 3 The dependence of the flash temperature from E_{HOMO} for n-alkanes C_3 - C_8 .

with Fukui conception, which allows the estimation the reactivity of organic molecular by the values of boundary molecular orbital energies [22, 23].

Fig. 4 The dependence of self-ignition temperature from E_{HOMO} for n-alkanes C_3 - C_8 .

Fig. 5 The dependence of saturation vapor pressure from E_{HOMO} for n-alkanes C_2 - C_{10} .

So, for the practical realization of obtained result integral performance index is needed, which can take into account E_{HOMO} effective value for multi component system and, properly, reactivity of motor fuel during direct measurement. Reactivity of the substance may be estimated in line with famous Coopmans theorem [24] by the value of the first ionization potential, which linearly depends on E_{HOMO} .

Analysis of obtained single-factor correlation dependences (Table 2) shows, that connections between operating characteristics of n-alkanes and their first IP, defined by photoelectron spectroscopy method [25, 26], have non-linear character and also can be described by polynomial approximation of the second degree with correlation coefficient $R = 0.92 \div 1.0$.

So, operating characteristics of n-alkanes can be defined by the way of calculating methods using measured values of SMS or first IP as data parameters with respective correction coefficients. And by E_{HOMO} calculated value it is possible to forecast properties of fuel additives, for example, antiknock agents.

The detonation phenomenon in internal-combustion engine is preceded by compression of combustible mixture, which with strong possibility passes across near-critical area and critical point. Connections between reduced critical pressures of n-alkanes and E_{HOMO} calculated values are presented in Fig. 6 [11].

The connection of critical pressures of n-alkanes (Fig. 6) with E_{HOMO} calculated values can be described by quadratic polynomial dependence $P_{\text{cr}} = -18.281 \cdot (E_{\text{HOMO}})^2 + 34.308 \cdot (E_{\text{HOMO}}) - 15.025$ with correlation coefficient $R \approx 0,99$.

After comparison with each other Fig. 1, 2 and 6, it can be determined, that operating characteristics of n-alkanes are connected with their critical pressures. Using phenomenological approach, one can do substantiated assumption about connection of hydrocarbons operating characteristics with their reactivity, assignable by integral electromagnetic and quantum-chemical characteristics.

So, the question about the level of magnetic (spin) properties of n-alkanes influence on their E_{HOMO} values naturally arises.

The SMS influence on E_{HOMO} values for n-alkanes can be described by linear correlation single-factor dependence $\text{SMS} = 0.0229 \cdot (E_{\text{HOMO}}) + 0.5869$ with correlation coefficient $R \approx 0.98$ (Fig. 7).

So, operating characteristics of n-alkanes $\text{C}_2\text{-C}_{10}$ are connected with their electromagnetic and thermodynamic properties, as well as electronic structure.

From all aforesaid one can draw next basic conclusions about operating characteristics of n-alkanes as components of motor petrol.

In spite of the long history of motor fuel operating characteristics studying, one can state, that their

physical-chemical nature is studied insufficiently. To study this question phenomenological approach can be used properly.

Using quality standard measures gives no answers for many questions on the molecular level of research. Petrol operating characteristics estimation (as multi component systems) must be done on the base of integral indexes, which are taking into account nature of intermolecular interactions of the components and their reactivity, specifically, electromagnetic properties and electronic structure.

First ionization potential, assignable by photoelectron spectroscopy method, may be used as data parameter for petrol operating characteristics estimation. Studying of electromagnetic properties and electronic structure of motor fuels and their components is conducive to manufacture products with

Fig. 6 The dependence of critical pressure from E_{HOMO} calculated values for n-alkanes $\text{C}_1\text{-C}_{10}$ [11].

Fig. 7 The dependence of SMS from E_{HOMO} for n-alkanes $\text{C}_2\text{-C}_{10}$ [13, 14].

given operating characteristics.

Another serious conclusion, which follows from presented data, is that macroscopic thermodynamic properties are connected with electromagnetic physical properties and electronic structure on the microlevel of the substance.

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