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Calculation of gasoline octane numbers taking into account the reaction interaction of blend components

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Abstract

A new approach for calculation of gasoline octane numbers was described taking into account the reaction interaction of blend components and the interaction mechanism of antiknock additives with hydrocarbons. It was determined that for octane numbers of alkylates and isomerizates, synergistic effect is observed, and for octane numbers of reformates, antagonistic effect is observed. The computer modeling system «Compounding» for calculation of gasoline octane numbers was designed.

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Keywords: Octane number; non-additivity; blending; composition; isomerizate; alkylate; reformate.

1. Introduction

Today, the world production and consumption of gasoline steadily grow. So, according to the statistics[1] in 2010, 22251.4 thousand barrels per day of gasoline were produced in the world, in 2011 production of gasoline increased to 22298.8 thousand barrels per day. Gasoline consumption has also increased and amounted to 21758.5 and 22069 thousand barrels per day in 2010 and 2011 respectively.

As can be seen from the above data, the production and consumption of gasoline increased, but only insignificantly. This is primarily due to decrease in production and consumption in the US and the EU. So, the production of gasoline in the United States amounted to 9058.6 thousand barrels per day and 9057.6 thousand barrels

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per day in 2010 and 2011 respectively; the consumption of gasoline in the USA was smaller and amounted to 8992.7 thousand barrels per day in 2010, in 2011 – 8752 thousand barrels per day. The same situation is in Europe (gasoline production decreased over a period of 2010-2011 from 2429.9 to 2325.5 consumption – from 3309 to 3112.5 thousand barrels per day).

However, due to the rapid development of the Asian market, especially China, where consumption of motor fuels increased by 173.3 from 1442.6 to 1615.9 thousand barrels per day over the period of 2010 and 2011 years, increase in gasoline demand is expected at least until 2015 year. The situation in Russia in terms of production and consumption is also positive. In 2010 the production and consumption of gasoline amounted to 1710.8 and 731 thousand barrels per day respectively, in 2011 – 1720.1 and 779.6 thousand barrels per day.

Gasoline production technology is specific to each refinery, which is associated with a different set of technological processes in the enterprise, the availability of raw materials and their value in each case. The final process of gasoline production is compounding. Optimization of compounding process is one of the most difficult optimization problems. This is primarily due to the fact that the main characteristic of gasoline – octane number is not subject to the law of additivity. Thereby, hydrocarbon composition of flows, such as reformates, isomerates, alkylates, which are involved in the compounding process, is not constant quantity even for the same processes and is changed depending on the composition of raw material, process conditions and catalyst activity.

Thus, the creation of mathematical models, which allows calculating the octane numbers of flows involved in the compounding process, becomes urgent because motor gasoline demand increases annually.

2. Methods of octane number calculation

Today, many scientists are engaged in the development of methods based on different physicochemical and structural properties of gasoline hydrocarbons and which allows calculating octane numbers.

For example, in the article of Albahri[2] the authors developed a method of calculating the antiknock basic homology groups of hydrocarbons according to the boiling point:

$$RON = a + b(T) + c(T)^2 + d(T)^3 + e(T)^4 \tag{1}$$

$$T = \frac{T_b}{100} \tag{2}$$

where RON – research octane number; T_b – normal boiling temperature; a, b, c, d – empirical coefficients.

For the calculation of high-octane gasoline antiknock characteristics, the authors accepted that the gasoline mixture model consists of four components: n-alkanes, isoalkanes, cycloalkanes and aromatics. The formula for calculating the octane number of gasoline has the following form:

$$RON = x_{NP}(RON)_{NP} + x_{IP}(RON)_{IP} + x_N(RON)_N + x_A(RON)_A \tag{3}$$

where x_{NP}, x_{IP}, x_N, x_A – volume fraction of n-alkanes, isoalkanes, cycloalkanes and aromatics.

In the scientific paper of Twu and Coon[3] an interaction method for predicting the research and motor octane numbers of gasoline blends is presented. The proposed method and correlation has the following characteristics:

- The blended octane number is unchanged when blending identical components.
- The blending equation describes blending behavior throughout the entire composition range.
- The blending correlation works not only for binaries, but also for multicomponents.
- The predicted research and motor octane numbers for a given blend from the correlation is invariant when a component is divided into two or more identical subcomponents.

The authors Paranghooshi, Sadeghi and Shafiei[4] presented a model for the gasoline blending which is beneficial for operation and prediction of gasoline qualities. The developed artificial neural network (ANN) models use the volumetric amount of six most commonly used fractions in gasoline productions multiplied by their octane number as input variables. Results show that ANN model simulated gasoline blending better than regression model as judged by the higher value of correlation coefficient (R2) (0.9812 vs. 0.9495), lower value of mean square error (0.0094 vs. 0.0294), and lower value of average absolute relative error (0.910 vs. 0.1799).

In the article of Ghosh[5] the authors presented a model that predicts the research and motor octane numbers of a wide variety of gasoline process streams and their blends including oxygenates based on detailed composition. The model predicts the octane number within a standard error of 1 number for both the research and motor octane numbers and has the following form:

$$ON = \frac{\sum_{PONA} \upsilon_i \beta_i ON_i + I_P \sum_{P} \upsilon_i \beta_i ON_i}{\sum_{PONA} \upsilon_i \beta_i + I_P (\sum_{P} \upsilon_i \beta_i - \sum_{P} \upsilon_i)} \tag{4}$$

where υ_i – volume fraction of the i-th molecule; β – adjustable parameter; I_p – the period of interaction; *PONA* – paraffin, olefins, naphthenes, and aromatics.

In the research paper of Pasadakis[6] the non-linear method is indicated. This method uses calculable weighting factors, which are specific for each gasoline blend, and shows an excellent agreement with the research octane number values of various refinery isomerizates samples as they are measured in a standard engine.

The other research paper of Albahri[7] shows the method, which is based on a structural group contribution approach and requires no experimental procedure or knowledge of physical or chemical properties. The proposed model is simple and can predict the research and motor octane numbers of more than 200 pure hydrocarbon liquids with an average deviation of 4 and 5.7, respectively. The analysis, carried out by the authors, shows that octane numbers may be predicted by the following equation:

$$ON = a + b\left(\sum_i ON_i\right) + c\left(\sum_i ON_i\right)^2 + d\left(\sum_i ON_i\right)^3 + e\left(\sum_i ON_i\right)^4 + f / \left(\sum_i ON_i\right) \tag{5}$$

where a, b, c, d, e, f – correlation coefficients.

3. Method of octane numbers calculation taking into account the reaction interaction of blend components

At the Department of Fuel Engineering and Chemical Cybernetics of Tomsk Polytechnic University, quantitative regularities between the magnitude of gasoline mixtures components polarity (dipole moment) and nonadditivity of blending octane number were established, according to which the blending octane number can be represented as the sum of two parts – the additive and nonadditive[8-10]:

$$RON_{mix}(MON_{mix}) = \sum_{i=1}^{n} \left[RON_i(MON_i) \cdot C_i \right] + B \tag{6}$$

$$B = \sum_{i=1}^{n-1} \sum_{j=2}^{n} B_i B_j C_i C_j / 100 \tag{7}$$

$$B_i = \alpha \left(D_i / D_{\max} \right)^{\beta} \tag{8}$$

where C_i – concentration of i-th component, rel. units.; B_i, B_j – quantities that characterize the tendency of the i-th molecule to the intermolecular interaction with j-th molecule; α and β – the kinetic parameters determined the intensity of intermolecular interactions, depending on the dipole moment D; D_{max} – the maximum dipole moment of the hydrocarbon molecules.

The further studies showed that not only the gasoline hydrocarbons, but also additives involved in compounding process displayed nonadditivity on blending due to their polarity.

Mathematical model of compounding process, which takes into account the influence of anti-knock additive to increase general gasoline octane number based on the mechanism of anti-knock additives action, which is in destruction of peroxides, was created:

$$RON_i(MON_i) = RON_0(MON_0) + Inj \cdot \Delta RON_{\max}(MON_{\max}) \cdot (1 - e^{-K_{eff} \cdot C_{red}}) \quad (9)$$

$$C_{red} = C_i / C_{\max} \quad (10)$$

where Inj – quantity that characterizes different types of fuel anti-knock additives injectivity; K_{eff} – the coefficient of anti-knock additives efficiency; C_{red} – reduced concentration of anti-knock additive, equal to the ratio of the additive concentration C_i to the maximum permissible concentration of the additive in gasoline C_{max}.

The computer modeling system «Compounding» for calculation of gasoline octane numbers was designed on the basis of the developed models.

4. Calculation of hydrocarbon streams octane numbers

Composition and properties of isomerizates, alkylates and reformates were investigated. With the help of program «Compounding», research octane numbers (RON) methods were calculated, and also composition of streams was investigated. Calculated numbers of model were compared to octane numbers, which were calculated on the additive formula (RONad).

Table 1. Characteristics of isomerizates

Characteristic	1	2	3	4	5	6
RON	**86.4**	**80.9**	**93.2**	**91.7**	**94**	**93.2**
RONad	**85.8**	**80.4**	**92.9**	**91.5**	**93.7**	**93**
SVP, kPa	94.92	101.03	141.55	140.5	201.99	120.79
Density, g/m^3	625.43	624.86	624.62	620.95	619.51	624.11
Composition of isomerizates, wt.%						
n-C_5	9.7	14.8	0	0	0	0
n-C_6	0.3	4.9	0	0	0	0
i-C_5	28.1	38.4	50.8	54.9	47	56.6
2,2-dimethylbutane	25.7	10.3	26.4	24.3	31	22.9
2,3-dimethylbutane	8	3.7	9.5	8.1	10	9.6

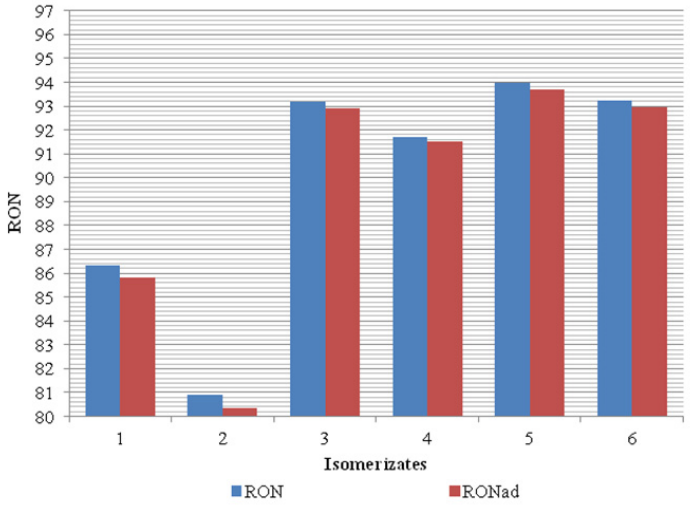

Fig. 1. Comparison of octane numbers of the isomerizates calculated by modeling, with the octane numbers calculated with the additive formula

Six izomerizates were investigated during the research work (tab. 1, fig. 1). As it is apparent from fig. 1, octane numbers calculated taking into account intermolecular interactions always exceed calculated with the additive formula. It is caused by a large number of hydrocarbons of a branched structure. These molecules form the steady connections less subject to detonations. It leads to increase in cumulative octane numbers of a stream. Thus, it is possible to make a conclusion that for octane numbers of isomerizates, the **synergetic effect** is observed. Thus, it is possible to see that the difference between the octane numbers calculated by modeling and octane numbers, calculated with an additive formula is small. It can be explained by the fact that a deviation of octane numbers of streams from rules of additivity is mainly contributed by the most polar hydrocarbons, in particular aromatic and olefinic hydrocarbons, and in isomerizates these substances are not contained or contained in slight quantities.

Raw materials for isomerization process are light paraffin – n-pentane and n-hexane from which at the output isomers and alicyclic rings with higher octane number are obtained. Calculations showed that the isomerizate No.5 has the highest octane number; it is caused by absence of an n-pentane, n-hexane in a stream and the highest content of high-octane products of this process. Thus, it is possible to make a conclusion that octane number of a stream will be higher if the isomerizate contains more hydrocarbons of a branched structure and less light paraffins. Two alkylates were investigated during the research (tab. 2, fig. 2). As it is apparent from fig. 2, the synergetic effect of cumulative octane numbers of streams is also observed for alkylates.

Table 2. Characteristics of alkylates

Characteristic	1	2
RON	**97.3**	**100.9**
RONad	**96.1**	**100**
SVP, kPa	35.67	37.01
Density, g/m^3	679.57	682.2
Composition of alkylates, wt.%		
2,2,3- trimethylpentane	44.8	30.1
2,3,4- trimethylpentane	14.3	12.7
2,2,3- trimethylhexane	0.1	5.7

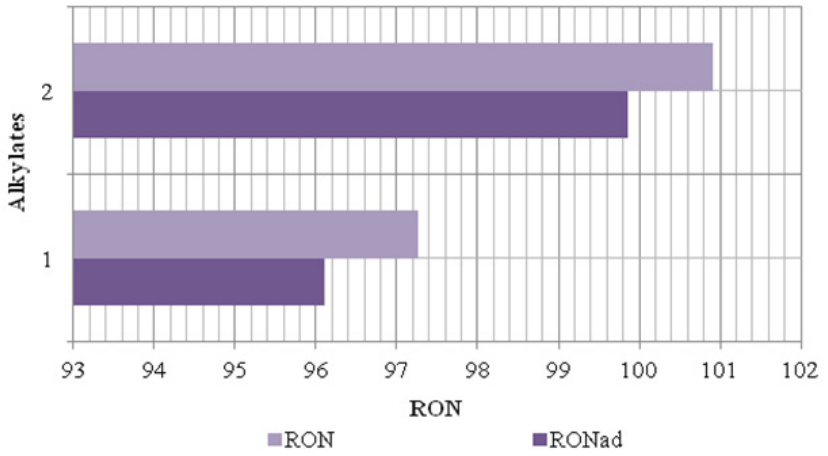

Fig. 2. Comparison of octane numbers of the alkylates calculated by modeling, with the octane numbers calculated with an additive formula

In the process of alkylation from n-butane and unsaturated hydrocarbons isoalkanes are obtained with the larger amount of carbon atoms in the chain with higher octane number. As it can be seen from tab. 2, alkylate No.1 has higher octane number that is caused by larger content of isoparaffins and less content of paraffins of normal structure in a stream. Thus, it is possible to make a conclusion that alkylate has higher octane number if it contains more components of isostructure and less light saturated hydrocarbons. Thirteen reformates were investigated during the research (tab. 3, fig. 3).

Table 3. Characteristics of reformates

Reformates	1	2	3	4	5	6	7	8	9	10	11	12	13
RON	**100**	**100.7**	**101.5**	**102.3**	**101.9**	**102.1**	**101.7**	**101.4**	**102.8**	**103.5**	**104.7**	**104.3**	**105.3**
RONad	**102.5**	**103.4**	**104.4**	**105.2**	**104.9**	**105**	**104.6**	**103.1**	**104.5**	**105.3**	**106.8**	**106.1**	**1069**
SVP, kPa	17.07	16.58	22.24	21.33	19.31	18.21	17.94	19.27	18.23	24.25	13.98	14.26	13.97
Density, g/m^3	803.56	807.64	807.06	810.93	810.74	812.36	810.18	807.53	811.14	813.28	818.63	819.56	820.9
Composition of reformates, wt.%													
Benzene	5.73	5.27	6.07	5.94	6.2	4.69	5.17	1.6	1.7	1	2.1	3.09	2
Aromatic hydrocarbons	72.21	74.08	76.45	78.16	77.82	78.34	77.25	74.98	76.98	79.58	79.85	80.54	81.25

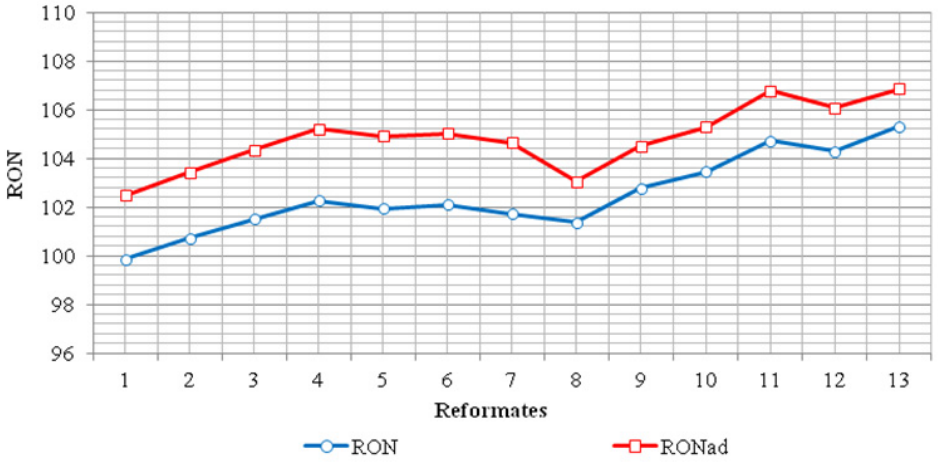

Fig. 3. Comparison of octane numbers of the reformates calculated by modeling, with the octane numbers calculated with an additive formula

As it is apparent from fig. 3, the octane number calculated with the additive formula always exceeds the one calculated taking into account intermolecular interactions. The maximum difference between octane numbers is 3 points. It can be explained by the fact that the reformates contain a large number of aromatic compounds molecules of which are polar and tend to intermolecular interactions. Because of intermolecular interactions, connections in molecules of hydrocarbons weaken and less steady compounds are formed; it leads to decrease in stability of hydrocarbons, detonation and, as a result, to decrease in cumulative octane numbers of a stream. Thus, it is possible to make a conclusion that for octane numbers of reformates, the **antagonistic effect** is observed.

As it can be seen from tab. 3, octane numbers of reformates differ substantially (from 100 to 105 points). Such difference between octane numbers is explained by differences in the composition of streams. Calculations show that the reformate №13 has the highest octane number; it is caused by the highest content of high-octane aromatic components. Thus, it is possible to make a conclusion that reformate has higher octane number if it contains more aromatic components.

5. Conclusions

During the research, it was found that octane numbers of commercial gasoline do not obey the laws of additivity. It is necessary to use a mathematical model taking into account the intensity of intermolecular interactions of mixture components and the mechanism of interaction of antiknock additives with hydrocarbons for accurate calculation of detonation characteristics.

It was determined that for octane numbers of alkylates and isomerizates, synergistic effect is observed, and for octane numbers of reformates, antagonistic effect is observed.

Based on these results, it can be concluded that it is impossible to develop a universal formulation of gasoline blending because hydrocarbon streams significantly differ from each other in composition. For optimal compounding process, it is necessary to take into account the composition of involved streams.

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