Mathematical Model for Studying the Variation of Gasoline-Bioethanol Blend Properties

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Because of bioethanol properties and of the way it interacts with commercial reformulated gasoline, studying the variation of the blending properties with the bioethanol quantity is important. This paper aims to present, based on original experimental data and on a blending mathematical model, the variation of the main gasoline properties with the bioethanol content from the blending. The experimental data was obtained using 10 base blendings, each containing fluid catalytic cracking gasoline (FCC), catalytic reforming gasoline (CR) and iC_5 fraction, to which bioethanol was added, in different proportions, thus obtaining 60 gasoline blendings.

Keywords: commercial gasoline, bioethanol, commercial gasoline properties, mathematical model, property variation

Nowadays, ecological commercial gasoline must fulfill some quality standards, imposed by today legislation. To fulfill these standards, the commercial ecological gasoline is obtained by blending its components, process which is called *formulation*. Blending the gasoline components is done according to a *blending recipe*. The formulated gasoline has three types of components: *base components* (in proportion of about 60%), *correction components* (about 40%) and *additives* (less than 1%) [1, 2].

In a refinery, the process of obtaining commercial ecological gasoline is very important. Starting about 60 years ago, research was directed both to determine new blending mathematical models and to perfect the existing ones.

One of the first blending mathematical models presented in the literature belongs to Bărbatu and his collaborators [3], and is bases on the experimental data taken at that time.

Another mathematical model, based on linear programming optimization, is proposed by Julija Ristic and her collaborators [4]. The model takes into consideration the properties of the components utilized to obtain various petroleum products and the economical necessities of the refinery and it offered very good results in practice.

In his work, W. E. Morris uses the concept of *interaction coefficients* to correlate blending octane numbers of the blendings that contain oxygenates into a 1st degree equation, easier to use [5]. The necessity of recomputing these interaction coefficients for the petroleum components – oxygenates blendings if the blending components properties' change is emphasized.

Another blending mathematical model was published by Maria Kirgina and her collaborators, model which was based on both the intermolecular interactions' intensities between the blending components and the interaction mechanism and between the anti-knocking components and the hydrocarbons from the gasoline [6]. Based on this model, a sofware program was developed to determine the optimum blending recipe.

Okoto Anson Francis ellaborated a blending mathematical model, which uses the process mass balance to generate three first order differential equation systems, to solve the model the numerical method Runge-Kutta of the 4th order was being used [7]. The mathematical model was conceived to estimate the blending octane numbers of blendings made of two components, but it can be extended according to necessities.

In the last three decades, artificial neural networks (ANNs) began to be used in a wide area, one of these areas being gasoline blending modelling. One of these models can be found in [8, 9]. In this model, the gasoline properties which are taken into account are divided into *static properties* and *dynamic properties*. These two types of properties are modelled using two types of ANNs: to model the static properties a *feedforward* ANN was used and to model a dynamic property, a *recurrent ANN* was used. The obtained results prove the fact that the delevoped mathematical model is adequate for gasoline blendings estimation.

This paper aims to determine, based on original experimental data, the variation of the main gasoline properties with the bioethanol quantity that is used and the determination of the adequacy of a blending model which can be found in the literature.

Experimental part

Gasoline Blending Mathematical Model

The fulfill the goals aimed in this work, a gasoline mathematical blending model was adopted, model which is based on eight properties: blending density, Research and Motor octane number, aromatic hydrocarbons content, olefinic hydrocarbons content, oxygenates content, benzene content and the vapour pressure. The blending model's starting point was the model proposed by Bărbatu and his collaborators in [3]. The equations that made the blending mathematical model are the following:

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Blending density:

$$\bar{d} = \frac{\sum_{i=1}^{nc} x_i}{\sum_{i=1}^{nc} \frac{x_i}{d_i}} \left(g/cm^3\right) \quad (1)$$

The significance of the terms specific for equation (1) are the following:

- $\bar{d}$ is the blending density (g / cm^3);
- d_i is the density of the *i*-th component (g / cm^3);

Blending Research octane number:

$$\overline{COR} = \sum_{i=1}^{nc} COR_i * x_i \quad (2)$$

The specific terms for equation (2) have the following significance:

- $\overline{COR}$ is the blending Research octane number;
- COR_i is the Research octane number of the *i*-th component;

Blending Motor octane number:

$$\overline{COM} = \sum_{i=1}^{nc} COM_i * x_i \quad (3)$$

The specific terms for equation (3) have the following significance:

- $\overline{COM}$ is the blending Motor octane number;
- COM_i is the Motor octane number of the *i*-th component;

Blending aromatic hydrocarbons' content:

$$\overline{Ar} = \sum_{i=1}^{nc} (Ar_i * x_i) \quad (\%vol.) \quad (4)$$

The significance of the terms of the equation stated above is:

- $\overline{Ar}$ is the blending aromatic hydrocarbons' content %vol;
- AR_i is the aromatic hydrocarbons' content of the *i*-th component % vol;

Blending olefin hydrocarbons' content:

$$\overline{Ol} = \sum_{i=1}^{nc} (Ol_i * x_i) \quad (\%vol.) \quad (5)$$

The specific terms of equation (5) have the following significance:

- $\overline{Ol}$ is the blending olefin hydrocarbons' content % vol;
- Ol_i is the olefin hydrocarbons' content of the *i*-th component % vol;

Blending oxygenates content:

$$\overline{Ox} = \sum_{i=1}^{nc} (Ox_i * x_i) \quad (\% vol.) \quad (6)$$

The significance of the terms specific to the equation above is:

- $\overline{Ox}$ is the blending oxygenates content % vol;
- Ox_i is the oxygenates content of the *i*-th component % vol;

Blending vapor pressure:

$$\overline{Pv} = \sum_{i=1}^{nc} (Pv_i * x_i) \quad (kPa) \quad (7)$$

In the above equation, the significance of the specific terms are:

- $\overline{Pv}$ is the blending vapor pressure (kPa);
- Pv_i is the vapour pressure of the *i*-th component kPa;

Blending benzene content:

$$\overline{Bz} = \sum_{i=1}^{nc} (Bz_i * x_i) \quad (\%vol.) \quad (8)$$

The significance of the specific terms from the above equation is:

- $\overline{Bz}$ is the blending benzene content % vol;
- Bz_i is the benzene content of the *i*-th component % vol ;

Equations (1)-(8) have two common terms. Their significance is:

- nc is the number of the components of the blending;
- x_i is the proportion in which the *i*-th component is used % vol;

Gasoline Blending

To test the blending mathematical model, four components utilized in the industrial process of gasoline reforming were selected: fluid catalytic cracking gasoline (FCC), catalytic reforming gasoline (CR), *i*-C_5 fraction and bioethanol. For each of the eight components, the eight properties presented above were determined: density, Research and Motor octane number, aromatic hydrocarbons content, olefinic hydrocarbons content, oxygenates content, benzene content and the vapour pressure. The properties taken into account by the adopted mathematical model were analyzed both for the four components and for 60 gasoline blendings obtained from blending the studied components.

Equipment

To determine the properties of the selected components and of the blendings that will be utilized in the experimental program, the IROX 2000 equipment was chosen [10]. This equipment determines the concentrations of some chemical components from the ethers, alcohols and aromatics classes. IROX 2000 also determines the oxygen content, the total content of aromatic, olefin and saturated hydrocarbons, Research and Motor octane numbers, vapor pressure and distillation properties. To determine the properties of the components and of the blendings utilized in the experimental program, IROX 2000 was operated according to the specific indications from the manual. The device measurement precision varies with the component that need to be determined. Thus, for ethers and alcohols, the measurement precision is ±0.5 % mass and for the aromatic hydrocarbons, the measurement precision is ±0.8 % mass [11].

The blendings were obtained in the laboratory, in working conditions, and its components were stored safely, to prevent the alteration of their properties.

Properties of the Components Used for Gasoline Blendings

During this experimental program, the IROX 2000 device was used to analyze the properties taken into account by the adopted mathematical model. In table 1, the experimentally obtained values for these 8 properties, for FCC, CC and the *i*C_5 fraction are presented.

The bioethanol is a pure substance, having the same properties like the ethanol obtained through other means or from other raw materials has. Because of this reason, in table 1, the tabled properties for bioethanol were presented [12, 13].

Properties of the Gasoline Blendings

Property	UM	Component			
		FCC gasoline	CR gasoline	iC_5 fraction	Bioethanol
Density	g/cm^3	0.776	0.809	0.616	0.789
RON	-	94.0	96.0	94.3	108.6
MON	-	83.7	83.0	87.6	89.7
Benzene content	% vol	1.02	0.51	0	0
Vapor pressure	kPa	53.60	70.70	71.50	5.95
Olefins	% vol	14.90	0	0	0
Aromatics	% vol	33.61	53.60	0	0
Oxygen content	% mass	0	0	0	34.7

Table 1
PROPERTIES OF THE COMPONENTS USED FOR GASOLINE BLENDINGS

For the experimental study of the gasoline blendings, the following procedure had been elaborated:

- 10 base blendings were defined, each blending having three components: FCC gasoline, CR gasoline and the iC_5 fraction. The base blendings are defined in table 2;
- To each base blending, various quantities of bioethanol were added, thus being obtained 6 blendings for each base blending. The components concentration in the final blending was calculated using the equation:

$$y_i = \frac{x_i}{\sum_{j=1}^{3} x_j + x_4}, \qquad i = 1 \ldots 4 \qquad (9)$$

In equation (9), x_i, i = 1...3 represents the concentration of the components from the base blending, x_4 is the bioethanol concentration related to the base blending. The bioethanol concentration varied in the interval $x_4 \in [0; 2; 4; 6; 8; 10]$ % vol.

In table 2 it can be noticed that some formulated blendings have a large quantity of iC_5 fraction. This formulation is justified by the necessity of gasoline behaviour improvement during winter time, by increasing the vapour pressure and because the same set of blendings was used as a training database to train an artificial neural network, obtaining and analyzing this type of blendings being mandatory to an efficient training [14]. Fulfilling the gasoline quality standards was not, at this stage, a criterion for choosing the compositions of these blendings. The same properties determined for each of the components were also determined for each blending obtained from a base blending and a quantity of bioethanol.

As an example, in table 3 the experimental results associated with the base blending 5 are presented.

Table 2
BASE BLENDINGS COMPOSTIONS USED IN THE EXPERIMENTAL STUDY (% VOL)

	FCC gasoline	CR gasoline	iC_5 fraction
Base blending 1	40	40	20
Base blending 2	45	30	25
Base blending 3	35	45	20
Base blending 4	40	45	15
Base blending 5	50	25	25
Base blending 6	30	45	25
Base blending 7	25	60	15
Base blending 8	60	25	15
Base blending 9	30	50	20
Base blending 10	35	30	35

Results and discussions

The way in which each property is influenced by the bioethanol content was studied. In figures 1-8, the variation of the studied properties with the bioethanol quantity from the blending are presented.

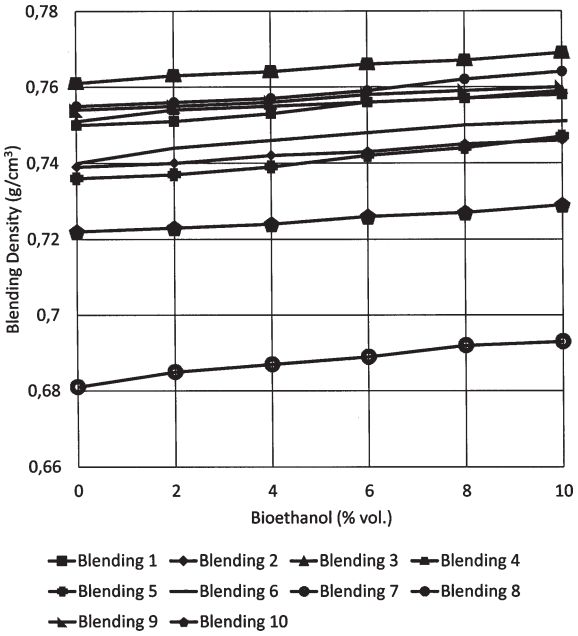

Fig. 1. Blending Density Variation with the Bioethanol Quantity

Property	0%	2%	4%	6%	8%	10%
RON	95.1	95.6	96.5	97	97.2	97.4
MON	85.2	85.5	85.6	86.1	86.4	86.8
Benzene content (% vol.)	0.64	0.62	0.61	0.6	0.59	0.57
Vapor pressure (kPa)	63.8	62.2	60.7	60.4	59.1	58
Olefins content (% vol.)	7.45	7.3	7.16	7	6.85	6.71
Aromatics content (% vol.)	30.2	29.6	28.99	28.39	27.78	27.18
Saturated content (% vol.)	62.35	61.6	59.85	58.61	57.37	56.11
Oxygen content (% mass)	0	0.6	1.2	2.3	2.5	3.2
Density (g/cm^3)	0.736	0.737	0.739	0.742	0.744	0.747

Table 3
EXPERIMENTAL RESULTS ASSOCIATED WITH THE BASE BLENDING 5

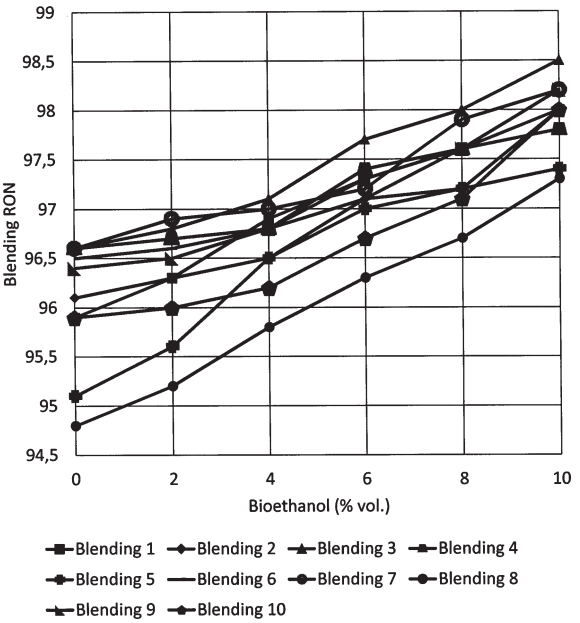

Fig. 2. Blending RON Variation with the Bioethanol Quantity

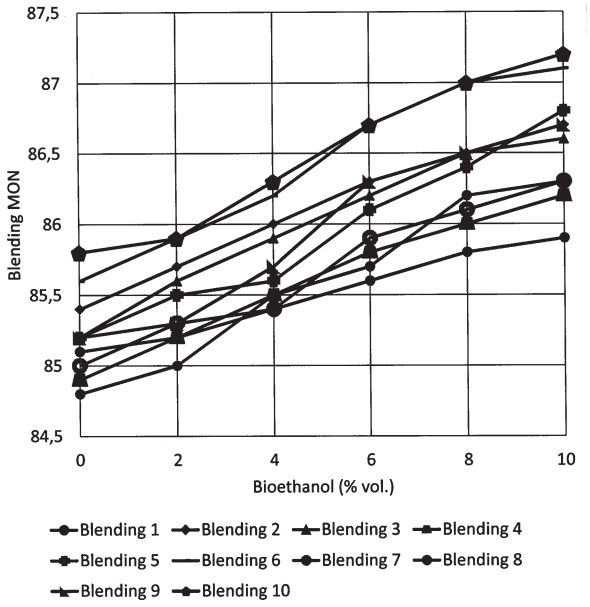

Fig. 3. Blending MON Variation with the Bioethanol Quantity

In figure 1 the variation of the blendings density with the bioethanol quantity is presented. According to this figure, an increase of the bioethanol quantity leads to an increase of the density of the analyzed blendings with a maximum of 0.02 g/cm^3. This increase happens because the bioethanol density (0.789 g/cm^3) is higher than the densities of the three initial components, presented in table 1 (between 0.68 and 0.76 g/cm^3).

Regarding RON, its variation with the bioethanol quantity from each blending can be seen in figure 2. The graph shows the proportionality relationship between the bioethanol quantity from the blending and the blending RON. This relation is explained because the bioethanol's RON (108.6) is higher than the values of the RON of the other utilized components (94, 96 and 94.3). The RON increases with maximum 3.5-4 octanes and is not linear, due to the presence of the oxygenate into the blending.

The blending MON variation with the bioethanol quantity can be observed in figure 3. Like in the RON case (fig. 2), an increase in MON takes place due to the higher MON value for bioethanol (89.7) compared to the values for the other components (83.7, 83 and 87.6). The increase is of maximum 2 octanic units than the similar increase for the

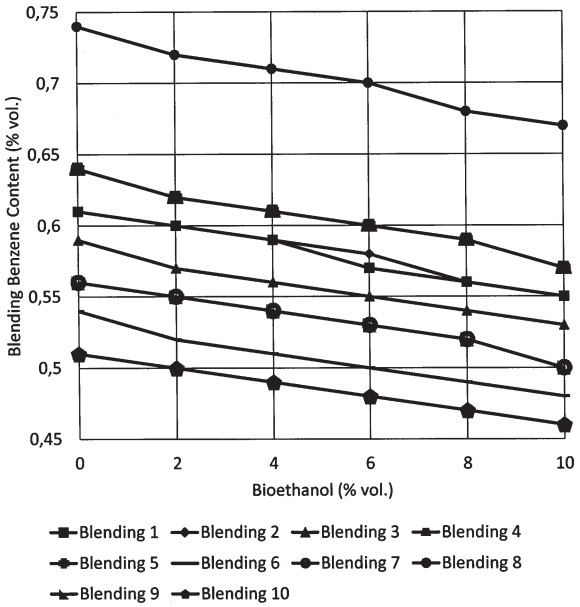

Fig. 4. Blending Benzene Content Variation with the Bioethanol Quantity

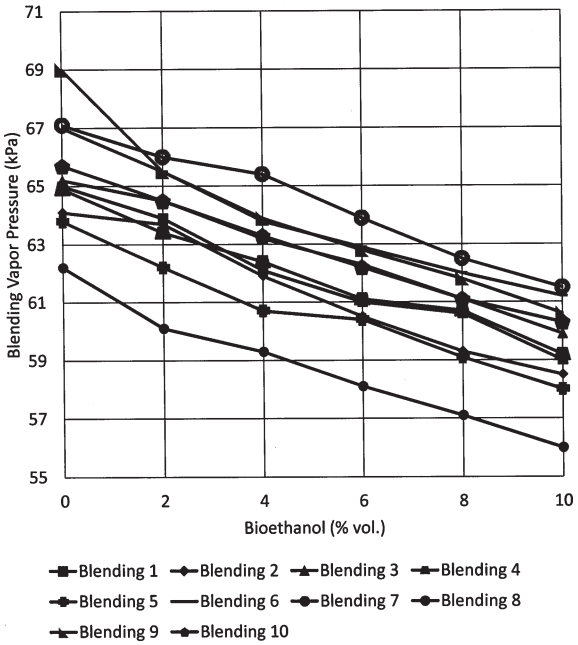

Fig. 5. Blending Vapour Pressure Variation with the Bioethanol Quantity

RON of the same blendings. The MON increase is non-linear, due to the presence of the oxygenated compound into the blending.

In figure 4, the variation of the benzene content with the blending bioethanol ratio is represented. According to this figure, the increase of the bioethanol ratio leads to a decrease of maximum 0.05-0.07 % vol. of the benzene content of the blending. This thing happens because the benzene is not present into the bioethanol, a benzene contentration dillution taking place, benefic for the case of using high proportions of CR gasoline (blendings 7 and 9).

The variation of the blending vapour pressure with the bioethanol ratio is presented in figure 5.

It can be noticed the decrease of the vapour pressure at the same time with the increasing of the bioethanol quantity because of the low alcohol pressure (5.95 kPa), 10 times lower than the CC gasoline. The low value of the bioethanol pressure is also reflected in the maximum value of the decreasing of the vapour pressure of the whole blending.

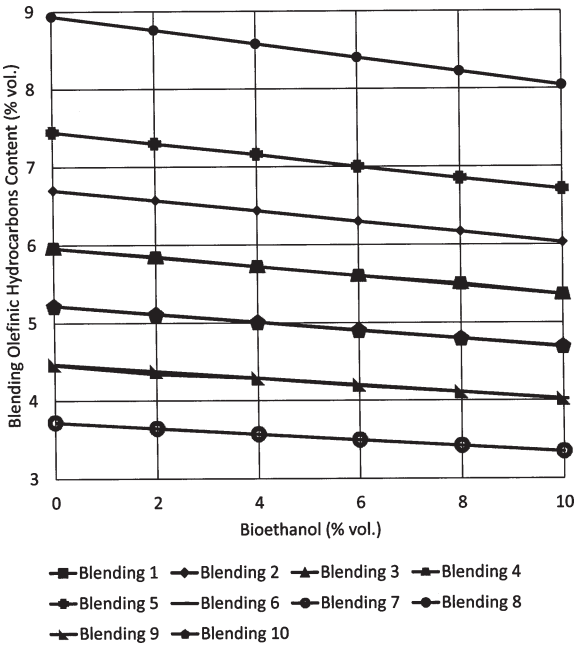

Fig. 6. Blending Olefins Content Variation with the Bioethanol Quantity

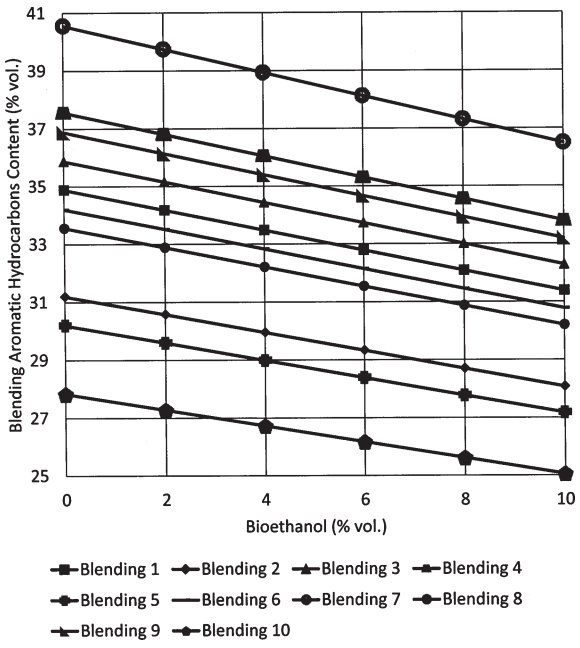

Fig. 7. Blending Aromatics Variation with the Bioethanol Quantity

The variation of olefinic hydrocarbons content with bioethanol ratio is presented in figure 6. According to this figure, there is a drop of the olefinic hydrocarbons content with maximum 1% vol., because bioethanol doesn't have olefinic hydrocarbons. The decrease of the olefines content is benefic especially in the blends with a high concentration of FCC gasoline (blends 5 and 8), which have a high olefines content.

In figure 7 the variation of the aromatic hydrocarbons content with the bioethanol ratio from every blending is represented. From figure 7 it can be seen that an increase in bioethanol proportion leads to a decrease in the aromatic hydrocarbons content, the maximum decrease being of 4% vol. This is due to the fact that bioethanol does not have aromatic hydrocarbons.

Figure 8 represents the variation of the oxygen content with the bioethanol ratio existent in each blending. According to this figure, adding bioethanol to the blending

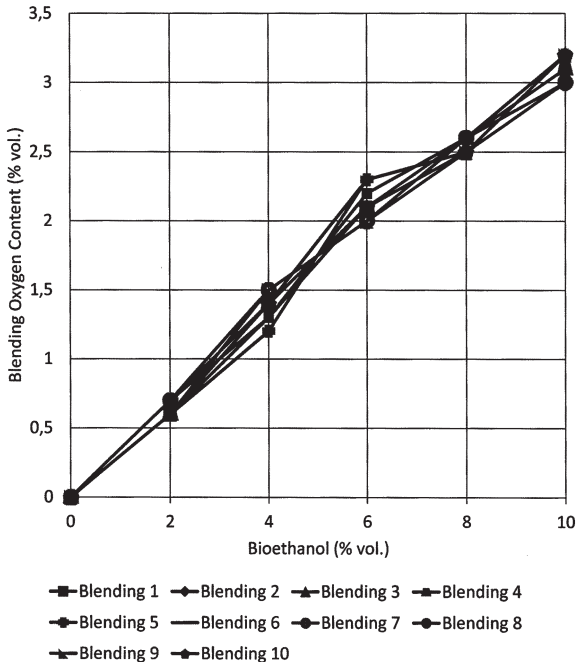

Fig. 8. Blending Oxygen Content Variation with the Bioethanol Quantity

will lead to an increase in the oxygen content to a maximum of 3% mass because bioethanol is the only component, from this experimental plan, that has oxygen in its structure (34.7% mass).

The adequacy of the mathematical model presented in this paper was tested using the experimental data obtained during the experimental program. Thus, it was proved that the mathematical model is accurate.

Conclusions

In this paper, the variation of the main gasoline properties with the bioethanol quantity was studied and a mathematical model, presented in the literature, was validated using the obtained experimental data. To accomplish the goals of this paper, obtaining and analyzing 60 blendings containing FCC gasoline, CR gasoline, iC_5 fraction and bioethanol was necessary.

The obtained results during the experiments were according to the theoretical specifications, both regarding the variation of the studied properties with the bioethanol content from the blending and regarding mathematical model validation. The causes for which the studied properties in the experimental program have the respective variations were presented and discussed.

Original experimental data regarding the utilized blendings and their properties were supplied.

References

1.DOICIN, B., ONUU, I. Tendine în Reformularea Benzinelor Auto Ecologice Românesti, conferinta "Chimies si dezvoltare", Pitesti. 2010.
2.SUCIU, G. C., Ingineria Prelucrării Hidrocarburilor. Vol. 4. 1993: Editura Tehnică. p. 431
3.BĂRBATU, G., MĂNESCU, M., DUMITRU, V., IONESCU, V., Programarea matematică în industria petrolieră. 1970: Editura Academiei
4.RISTIC, J., TRIPCEVA-TRAJKOVSKA, L., RIKALOSKIT, I., MARKOVSKA, L., Optimization Of Refinery Products Blending. Bulletin of The Chemists and Thechnologists of Macedonia, 1999. Volumul **18**: p. 171-178.
5.MORRIS, W. E., Optimum Blending Gives Best Pool Octane. Oil & Gas Journal, 1986: p. 63-65.

6.KIRGINA, M., GYNGAZOVA, M., IVANCHINA, E. Mathematical Modeling of High-Octane Gasoline Blending, conferina Strategic Technology (IFOST), 2012 7th International Forum. 2012.Tomsk.
7.FRANCIS, O. A., A Model for Blending Motor Gasoline. Case Study: Tema Oil Refinery Ltd. 2013, Kwame Nkrumah University of Science and Technology. Pag. 28
8.YU, W., MORALES, A., Gasoline Blending System Modeling via Static and Dynamic Neural Networks. International Journal of Modelling and Simulation, 2004. Volumul **24**: p. 151-160.
9.*** Artificial Neural Network. [citat la 4 Aprilie 2014]; Disponibil la: http://en.wikipedia.org/wiki/Artificial_neural_network.
10.*** IROX 2000 Gasoline Analyzer. [citat la 21 Octombrie 2013]; Disponibil la: http://www.grabner-instruments.com/products/fuelanalysis/irox2000.aspx.
11.*** Manual de utilizare IROX 2000. 2000: Grabner Instruments
12.CRC Press LLC, CRC Handbook of Chemistry and Physics. 2010.
13.*** Ethanol.[citat la 15 Nov. 2013]; Disponibil la: http://en.wikipedia.org/wiki/Ethanol.
14.DOICIN, B., Raportul de cercetare: Studiul si optimizarea reetelor de amestec pentru reformularea combustibililor ecologici de tip benzine. 2013, Ploiesti: Editura Universităii de Petrol si Gaze

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