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Property Estimation of Commercial Ecological Gasoline

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The paper presents the problem of the property estimation of commercial ecological gasoline. Biofuels are the components that are obtained from renewable sources and which are blended into the commercial gasoline in certain proportions. Among these, bioethanol has a number of advantages, compared to classic fuels, thing that recommends it among its most promising substitutes. The blending model needed the experimental determination to be validated. The laboratory experiments have determinate: a) physical properties for four components used to obtain commercial gasoline (FCC gasoline, reformer gasoline, izopentane and bioethanol); b) physical properties of 60 blends with known composition, using the four components studied earlier. The determined properties are: Research and Motor Octane Number, final boiling point, benzene content, vapor pressure, olefin hydrocarbons content, aromatic hydrocarbons content, density and oxygen content. All the aforementioned properties were determined using IROX 2000 device. The validation of the model was made by comparing the estimated properties with the experimental properties, using the 60 experimental data. The maximum estimation error was 1.62 %, error associated to the Motor Octane Number.

1. Introduction

Gasoline is a commercial product that must respect standards which guarantee that the emissions obtained by burning it don't increase the environment pollution. One way of obtaining commercial ecological gasoline is to use the adequate petroleum components and oxygenates, respectively alcohols. Commercial ecological gasoline is obtained by blending several components, process known as formulation. For gasoline in-flux blending, the knowledge of three elements is necessary: the components' physical and chemical properties, the mathematical model to estimate the blending properties and the numerical technique to determine the optimum blending recipe.

Regarding the mathematical model to estimate the blending properties, the investigation of different references showed the existence of two alternatives. The first alternative refers to mathematical models expressed through mathematical relations (Barbatu, 1970). This technique is general and can be applied when the experimental data regarding blending properties are missing. Lack of consistent references regarding gasoline blending properties' estimating relations focused the authors' research to verify the available mathematical relations with the experimental laboratory data specific to Romanian refinery characteristics.

The second alternative utilizes neural networks applied on a database containing experimental data regarding blending properties (Cuptasanti, 2013, Doicin and Onutu, 2014, Lauret, 2013). This technique was approached with the purpose of comparing the results with those obtained through using mathematical models.

2. Romanian ecological gasoline

The Romanian gasoline thus formulated is a blend of three types of components: base components (blended in proportion of about 60 %), correction components (in proportion of maximum 40 %) and additives (less than 1 %). The base components are petroleum fractions which must have properties close to those of the final gasoline, must be easy to obtain and they must have a low fabrication cost. Among these components they

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are catalytic reforming gasoline (CR) and fluid catalytic cracking gasoline (FCC). CR has a distillation curve similar to that of the commercial gasoline and a high RON. The drawbacks of the CR are the non-uniform distribution of the octane number along the distillation curve and its density, which is generally over the maximum permitted value for the commercial gasoline density. FCC is characterized by density and distillation curve similar to that of the commercial gasoline and a high octane number. The distribution of the octane number along the distillation curve is advantageous in the inferior part of the distillation curve, thing which compensates the similar disadvantage of the CR.
Additives are used to significantly improve some properties or to induce other new properties. In some cases, additive using is less costly and easier than gasoline reformulation. According to the EN 228 standard, the maximum allowed oxygen quantity in the finished gasoline is 2.7 % vol. Bioethanol is used as an additive to obtain commercial ecologic gasoline, alcohol which is obtained from bio waste and renewable raw material (Shayane, 2010). The main reason for the usage in spark ignition engines of bioethanol blended into the gasoline is the thermal efficiency improvement and pollution reduction by increasing stability at higher compression ratios. The EN 228 standard states that the gasoline must have ethanol (bioethanol) in proportion of maximum 5 % vol. Regarding the presented facts, obtaining the commercial gasoline involves component blending, the blending recipe having a very high importance. An example of a blending recipe used in a refinery is presented in Table 1 (Doicin and Onutu, 2014).

Table 1. Typical commercial gasoline composition

Component	Composition [% volume]
FCC Gasoline	44.63
CR Gasoline	38.32
Ethanol	6.74
MTBE	4.34
iC_4	5.97
Total	100.00

3. Laboratory experiments regarding commercial gasoline components

The experimental program's objective follows the physical properties of the blending components and the gasoline obtained by blending the components into different proportions determination. The analyzed components, specific to a refinery, are presented in Table 2.

Table 2. Components used to obtain ecological gasoline

Nr. Crt.	Component	Type
1	FCC Gasoline	Base component
2	CR Gasoline	
3	Izopentan	Correction component
4	Bioethanol	

To analyze the physical properties, the IROX 2000 equipment was used (IROX 2000 Gasoline Analyzer, 2010). The equipment's measuring principle is based on measuring the IR absorption according to the ASTM D5845 standard, in the range between 2.7 to 15.4 μ, using a Fourier-transform spectrometer. The analyzed petroleum product is equivalent with a blend of chemical components, components that exist in the device's database. The petroleum product's physical properties are computed according to the chemical components' share and its physical properties' values, existent in the analyzer database. The properties experimentally determined with the IROX 2000 analyzer are: Research octane number, Motor octane number, final boiling point, benzene content, vapor pressure, olefins content, aromatics content and density. In Table 3, the values of the properties of the four components (base and correction components) defined in Table 2 are presented.

Table 3. Physical property values of gasoline components

Property	Measurement unit	FCC Gasoline	CR Gasoline	*i*-C_5 Fraction	Bioethanol
Research octane number		94	96	94.3	108.6
Motor octane number		83.7	83	87.6	89.7
Benzene content	% volume	1.02	0.51	0	0
Final boiling point	°C	203.9	214.5	27.88	78.2
Vapor pressure	kPa	53.6	70.7	71.5	5.95
Olefins content	% volume	14.9	0	0	0
Aromatics content	% volume	33.61	53.6	0	0
Saturates content	% volume	51.49	46.4	100	0
Density	g/cm^3	0.776	0.809	0.616	0.789
Oxygen content	% mass	0	0	0	34.7

To estimate the ecological gasoline properties using a mathematical model, the following experimental determination procedure was elaborated:

a) 10 base blendings were defined, each blending having three components: FCC, RC and iC_5 fraction. The 10 blendings are defined in table 4;
b) To each base blending, quantities of bioethanol were added, obtaining 6 blendings for each base blending. The components concentration in the final blending was calculated using the equation

$$y_i = \frac{x_i}{\sum_{j=1}^{3} x_j + x_4}, \quad i = 1,\ldots 4 \tag{1}$$

In which: $x_i, i = 1,\ldots,3$ represent the concentration of the components in the base blending; x_4–the concentration of bioethanol related to the base blending. For each obtained blending, the same properties like the case of the four primary gasoline components were experimentally determined. To exemplify, the obtained results for the blending obtained from base blending 1 are presented in Table 5 (Doicin, 2014).

Table 4. Composition of the basic blendings

Basic blending	FCC Gasoline	CR Gasoline	i-C_5Fraction
1	40	40	20
2	45	30	25
3	35	45	20
4	40	45	15
5	50	25	25
6	30	45	25
7	25	60	15
8	60	25	15
9	30	50	20
10	35	30	35

The analysis of the 60 sets of experimental results allowed the highlight of the following conclusions:

1) The blendings density increases with the increase of the bioethanol proportion. The increase is caused by the fact that bioethanol density (0.789 g/cm^3) is higher than the densities of the three components utilized to obtain the ecological gasoline, densities which have the values between 0.68 and 0.76 g/cm^3.
2) The blending Research octane number (RON) increases with the increase of the bioethanol proportion in the blend, but the increase is not linear. This is explained by the fact that the bioethanol RON (108.6) is higher than the RON values of the other components utilized to obtain commercial gasoline. A similar situation is observed regarding Motor octane number (MON);
3) The benzene content of the blending decreases with the increase of the bioetanol proportion in the blending because of the benzene dilution from the base components, especially in the case of using higher CR proportions;

4) The increase of the bioethanol quantity in the blending leads to the decrease of the vapor pressure of the blending because of the low vapor pressure of the alcohol (5.95 kPa), 10 times lower than the FCC vapor pressure;
5) The olefins content of the blending decreases with the increase of the bioethanol proportion from the blending. A decrease of the olefins content with maximum 1% vol. takes place because bioethanol does not have any olefins. The decrease of the olefins content is beneficial especially for the blendings with high FCC gasoline concentrations, gasoline which has olefin hydrocarbons. A similar situation also characterizes the aromatic hydrocarbons content from the blending;
6) Bioethanol, the only component that contains oxygen, will increase the oxygen quantity from the blending up to 3 % mass.

Table 5 Experimental results using the basic blending 1

Property	UM	Bioethanol concentration [% volume]					
		0	2	4	6	8	10
Density	g/cm^3	0.750	0.751	0.753	0.756	0.757	0.758
RON	-	95.9	96.3	96.9	97.3	97.6	98.0
MON	-	85.1	85.2	85.4	85.6	85.8	85.9
Benzene content	% volume	0.61	0.60	0.59	0.57	0.56	0.55
Final boiling point	°C	190.9	190.5	190.3	186.3	182.8	171.2
Vapor pressure	kPa	70.1	71.4	72.5	73.8	76.1	78.0
Olefins	% volume	5.96	5.85	5.72	5.60	5.48	5.36
Aromatics	% volume	34.88	34.18	33.48	32.79	32.09	31.39
Saturates	% volume	59.16	57.97	56.80	55.61	54.43	53.25
Oxygen content	% mass	0	1.0	1.5	2.3	3.0	3.9

4. Validation of the commercial gasoline components' blending model

The authors have extracted from the literature a linear mathematic gasoline blending model which estimates blending properties (Bărbatu, 1970). For each physical property the model's error related to the experimental data was calculated using equation (2). In table 6 the elements of the mathematical model and the calculated error for each element of the mathematical model are presented. The minimum error was noticed for the density (0.18 %) and the maximum error was noticed for MON (1.62 %).Because these limit values are under the 2 % threshold, it can be stated that the mathematical model is adequate.

$$e_k = \frac{\left|\sum_{j=1}^{m}\left(y_j^{(exp)} - y_j^{(mod)}\right)\right|}{\sum_{j=1}^{m} y_j^{(exp)}} \times 100, \quad k = 1,\ldots,n \text{ .}[\%] \tag{2}$$

5. Gasoline Property Estimation Using Neural Networks

An artificial neural network (ANN) is a mathematical model, inspired from the animals' central nervous system, especially the brain (Artificial Neural Network, 2014). From a programmer's point of view, an ANN is an algorithm, with its own input and output data. Flexibility is one of the advantages of using an ANN.
To successfully use an ANN, it is mandatory for the network to be created and trained, using a training database. The necessary steps to create an ANN are: creating a blank ANN, determining the ANN architecture (especially the number of neurons from the hidden layer), training the ANN using the training database and saving the created and trained ANN. The necessary steps to train an ANN are: selecting the data that will be used by the training database, dividing the data from the database into training, validation and test data, and the actual ANN training.

Table 6 Adequacy of the gasoline blending model

Property	Measurement Unit	Error [%]	Model
Density	g/cm^3	0.18	$\overline{d} = \frac{\sum_{i=1}^{nc} x_i}{\sum_{i=1}^{nc} \frac{x_i}{d_i}}$
RON	-	1.46	$\overline{COR} = \frac{\sum_{i=1}^{nc} (COR_i \, x_i)}{\sum_{i=1}^{nc} x_i}$
MON	-	1.62	$\overline{COM} = \frac{\sum_{i=1}^{nc} (COM_i \, x_i)}{\sum_{i=1}^{nc} x_i}$
Benzene	% volume	0.44	$\overline{Bz} = \frac{\sum_{i=1}^{nc} (Bz_i \, x_i)}{\sum_{i=1}^{nc} x_i}$
Vapor pressure	kPa	1.14	$\overline{Pv} = \frac{\sum_{i=1}^{nc} (Pv_i \, x_i)}{\sum_{i=1}^{nc} x_i}$
Olefins	% volume	0.42	$\overline{Ol} = \frac{\sum_{i=1}^{nc} (Ol_i \, x_i)}{\sum_{i=1}^{nc} x_i}$
Aromatics	% volume	0.40	$\overline{Ar} = \frac{\sum_{i=1}^{nc} (Ar_i \, x_i)}{\sum_{i=1}^{nc} x_i}$
Oxygen content	% mass	1.38	$\overline{Ox} = \frac{\sum_{i=1}^{nc} (Ox_i \, x_i)}{\sum_{i=1}^{nc} x_i}$

The training database contains two matrices: the input data matrix and the target data matrix. These data were divided as follows: 70 % of the data are considered training data, 15% are considered validation data and 15 % are considered test data. The ANN architecture contains 10 neurons in the hidden layer (Doicin, 2014). To train the ANN, the Levenberg-Marquardt algorithm was used.

Verifying the training results is being done using the error histograms and the data regression analysis. The results analysis leads to the conclusion that the data from the training database have a high degree of correlation, fact that will lead to obtaining highly accurate results.

To evaluate the ANN model adequacy, the obtained experimental data were used. The ANN model adequacy is presented on Table 7 (Doicin and Onutu, 2014).

Table 7 ANN model adequacy

Property	UM	Error (%)
Density	g/cm^3	1.06
RON		0.03
MON		0.02
Benzene content	% vol.	3.28
Vapor pressure	kPa	0.46
Olefin hydrocarbons content	% vol.	1.02
Aromatic hydrocarbons content	% vol.	0.43
Oxygen content	% mass	-

From Table 7 it can be noticed that, for the octane numbers and the vapor pressure, the estimation error is higher in the case of classical blending mathematical model and for the other properties the estimation error of the ANN model is higher.

6. Conclusions

In this paper the problems of property estimation of the commercial gasoline have been investigated. These properties are estimated using a mathematical model, model which exists in the literature. Because references which validate the mathematical model weren't identified, the authors have elaborated a plan to experimentally determine the physical properties of the components that are used in the ecological gasoline and the physical properties of 60 blendings, in different proportions, of these components. Using the experimental data, the mathematical relations that make the model were verified. Because the errors are small, under the 2 % threshold, the authors consider that the mathematical model to estimate physical properties of the ecological gasoline is validated and can be used in the future to determine the optimum blending recipes.

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