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Short communication

Using the Doehlert matrix as a tool for studying the influence of gasoline components on octane numbers

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ABSTRACT

After production and formulation, but before being brought to market, gasoline must conform to the specifications set by regulatory agencies. Octane numbers are among the most important physico-chemical parameters to be evaluated because they are directly related to the performance and power of the engine. This study will evaluate the influence of the gasoline's components on its octane numbers. To identify and quantify the major organic compounds in the gasoline sold within the metropolitan area of Salvador, Bahia, Brazil, gas chromatography was used. Toluene, m-xylene, n-hexane, n-heptane and 2-methyl-2-butene were selected for this study. Several gasoline samples with different ratios of the selected compounds were formulated, and their octane numbers were measured in a CFR engine. Based on the results, the system was optimized using the Doehlert matrix as a mathematical tool, which allowed the effects of the different hydrocarbons on the octane numbers to be visualized. From the experimental results, important information has been gathered for use by the producers and formulators of gasoline to facilitate the production of a higher quality fuel with a lower environmental impact.

1. Introduction

Gasoline is a complex mixture of hydrocarbons that mostly range from 4 to 12 carbon atoms and are linked by single or double bonds. This mixture also contains oxygenates, sulfur compounds, nitrogen compounds and metal compounds in lower concentrations. The hydrocarbons comprising gasoline are divided into five major groups: n-paraffins, iso-paraffins, olefins, aromatics and naphthenics [1,2]. Their relative proportions depend on the type of oil used as a precursor, as well as the production process. Currently, the gasoline produced in refineries and petrochemical plants consists of mixtures that are carefully balanced to meet the performance requirements of engines while adhering to the specifications required by law [3,4]. Octane numbers or ratings are used to assess the quality of the gasoline; these values are related to the efficiency and power of an engine running on gasoline and are used to classify the gasoline by type (regular or premium) and price [5].

The octane number is a measurement of a gasoline's antiknock quality, or its capacity to withstand detonation when submitted to the temperatures and pressures generated in the combustion chamber of an engine. Various types of engines and test conditions have appeared over time, but the most common tests today are the Research Octane Number (RON) and Motor Octane Number (MON) assays. The MON is determined by running the fuel in a test engine under severe conditions, such as high speed and high load (equivalent to a car overtaking at high speed). The RON is determined by running the test engine with variable compression under controlled conditions, which is equivalent to a smooth ride, without using a heavy load on the engine. The "anti-knock index" (AKI) is the average of the RON and MON values [6,7].

Fuel, when classified according to its type and application, must adhere to minimum quality standards so that its energy can be used in the most efficient manner possible and, in Brazil, these minimum quality standards are established through technical specifications that are enforced by law [8]. The Brazilian regulatory agency (ANP – Agência Nacional do Petróleo, Gás Natural e Biocombustíveis) established the engine test developed by Cooperative Fuel Research (CFR engine) as the only acceptable method for the determination of octane numbers. Brazilian regulation also

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requires that gasoline sold within the national territory must have a minimum MON of 82 and an AKI value of at least 87. Gasoline sold as *premium*, which is suitable for motors with high compression ratios, is required by the same regulations to have an AKI of 91 or higher [9].

The chemical structures of the hydrocarbons present in gasoline greatly influence the fuel's physico-chemical properties, and their modulation may result in superior formulations from both the environmental and engine performance points of view. The resistence to auto-ignition is one of the properties affected by the gasoline's composition, hence the need for its evaluation [10,11]. Generally, it is known that long-chain hydrocarbons produce large amounts of linear species that are highly susceptible to self-ignition, while branched or aromatic hydrocarbons are more resistant.

The gasoline blending process mixes various component (or feedstock) streams to produce an automotive gasoline product stream, and a number of properties can be used to characterize the final product, such as octane number [12]. Experimental investigations and algorithmic methods have been proposed to control the blending systems and therefore produce fuel mixtures with some desirable properties [12–14]. However, the use of the Doehlert matrix to study of the influence of the gasoline components on octane numbers, to the best of our knowledge, has not yet been described.

This study aims to analyze the influence of some of the gasoline components on the octane number and therefore propose a new method to assist in the formulation of gasoline, which facilitates the production of a better quality fuel with a lower environmental impact. This work was based on the identification of the compounds found in the largest quantities and the most frequently in the samples of gasoline sold in the metropolitan area of Salvador, Bahia, Brazil. The octane number for each sample was measured in a CFR engine, and an experimental design and a Doehlert matrix were used to evaluate the extent of the different hydrocarbons' influence on the octane number.

2. Experimental

2.1. Experimental apparatus

Chromatographic analyses were performed with a Varian gas chromatograph (model CP-3800) equipped with an auto sampler (CP 8400), injector (CP 8410), a fused silica column (PONA CP 7530, 100 m long and diameter of 0.25 mm) and a flame ionization detector (FID). The analysis of the MON and RON were performed with a test engine developed by Fuel Cooperative Research (CFR) and manufactured by Valkation, Model F-1.

2.2. Materials

All reagents were of analytical grade. The toluene and m-xylene were purchased from Vetec and Reagan, respectively, while the n-hexane and n-heptane were purchased from Quimex. The oxygenates, methyl tert-butyl ether and t-butanol were purchased from Sigma–Aldrich. All of the above reagents had a purity above 99%; the 2-methyl-2-butene purchased from Merck had a purity of 95%.

2.3. Gasoline samples

Fifty samples were randomly collected directly from gasoline pumps at gas stations within the metropolitan area of Salvador and kept under refrigeration in 1 L amber polyethylene terephthalate (PET) bottles. Two samples of gasoline that complied with the Brazilian government's specifications were collected from different gas stations: (a) 20 L, which was designated "original sample 1," was used to prepare the 16 samples used in the factorial design to investigate which compounds influence the octane numbers the most significantly and (b) 25 L of gasoline, which were designated "original sample 2," were used to prepare the 23 samples used for the optimization procedure; this experiment examined how small changes in the concentrations of some gasoline components affected the octane numbers.

2.4. Chromatographic analysis

Gasoline samples were analyzed by gas chromatography. 1 μL of each sample was injected into the column with a 200:1 split ratio at 25 °C, which was kept constant for 15 min. Subsequently, the furnace was heated to 60 °C (with a heating ramp of 1 °C min^{-1}) and maintained at this temperature for 20 min. Finally, the oven was heated to 200 °C, via a heating ramp of 2 °C min^{-1}. The carrier gas was helium, which was operated at a linear velocity of 30 cm s^{-1}. The sample components were detected with a flame ionization detector (FID). The chromatograms revealed the separation of over 350 components and identified more than 95% of them over an analysis time of 150 min. Peaks and related hydrocarbons were identified with the DHA Star software version 5.0 and the aid of the chromatographic patterns for naphtha obtained from Supelco Sigma–Aldrich. Subsequently, the hydrocarbons were selected and cataloged according to their volumetric percentage and presence in most of the analyzed samples. After being grouped by their main organic function, such as aromatic hydrocarbons, oxygenates, olefinics, paraffinics and isoparaffinics, the hydrocarbons were subjected to a descriptive statistical treatment to obtain the arithmetic mean of their volume percentages, as well as their minimum and maximum concentration limits within the fifty-sample set.

2.5. Octane number measurement

Octane numbers were evaluated on a CFR engine following ASTM D2699 [15] and D2700 [16], which set standards for RON, MON and AKI (average of MON and RON). Patterns were formulated by using pre-determined mixtures of 2,2,4-trimethylpentane (isooctane) and n-heptane.

2.6. Sample preparation

The analysis of the chromatograms of the 50 samples indicated that toluene, m-xylene, n-hexane, n-heptane and 2-methyl-2-butene were present in most samples; these components were also present in higher concentrations than any of the other compounds. Therefore, these effects of these compounds on the octane rating were examined. To study the influence of oxygenates other than ethanol, which was maintained at 25% (v/v) as determined by Brazilian law, t-butanol and methyl tert butyl ether (MTBE) were also examined as gasoline components.

To investigate the influence of the gasoline compounds on the octane numbers (MON, RON and AKI) measured on a CFR engine, 16 experimental samples were prepared from "original sample 1". The compositions of these experimental samples were based on a two-level, saturated factorial design ($2^{(7-3)}$); each factor (hydrocarbon) was varied at two levels of volume concentration (maximum and minimum). The experimental design and its results are presented in Table 1. The concentration levels of each compound fell within the minimum (−) and maximum (+) concentrations found for each factor within the 50 samples that were collected and chromatographed.

Based on the results obtained from the analysis of the 16 experiments, another experiment was designed to elucidate the influence of each organic compound that affected the octane numbers the most dramatically through the Doehlert matrix method. The

Table 1
Experimental matrix and responses obtained from the two level fractional factorial design $2^{(7-3)}$.

Sample	Toluene	m-Xylene	t-Butanol	MTBE	n-Hexane	n-Heptane	2-Methyl-2 butene	MON	RON	IAD
Original sample 1[a]	1.2 ± 0.1	2.4 ± 0.2	nd	nd	3.4 ± 0.2	1.0 ± 0.1	1.8 ± 0.1	82.8	97.2	90.0
01	2.4 (−)	3.5 (−)	1.0 (−)	1.0 (−)	9.8 (+)	7.0 (+)	3.9 (+)	82.7	95.6	89.2
02	11.2 (+)	3.5 (−)	1.0 (−)	1.0 (−)	5.0 (−)	2.0 (−)	2.5 (−)	84.0	98.3	91.2
03	2.4 (−)	5.9 (+)	1.0 (−)	1.0 (−)	5.0 (−)	7.0 (+)	3.9 (+)	83.3	96.9	90.0
04	11.2 (+)	5.9 (+)	1.0 (−)	1.0 (−)	9.8 (+)	2.0 (−)	2.5 (−)	83.9	98.0	91.0
05	2.4 (−)	3.5 (−)	1.5 (+)	1.0 (−)	9.8 (+)	2.0 (−)	3.9 (+)	83.1	96.6	89.9
06	11.2 (+)	3.5 (−)	1.5 (+)	1.0 (−)	5.0 (−)	7.0 (+)	2.5 (−)	83.5	97.5	90.5
07	2.4 (−)	5.9 (+)	1.5 (+)	1.0 (−)	5.0 (−)	2.0 (−)	3.9 (+)	83.0	97.8	90.4
08	11.2 (+)	5.9 (+)	1.5 (+)	1.0 (−)	9.8 (+)	7.0 (+)	2.5 (−)	83.6	96.8	90.0
09	2.4 (−)	3.5 (−)	1.0 (−)	1.5 (+)	9.8 (+)	7.0 (+)	2.5 (−)	83.1	95.5	89.0
10	11.2 (+)	3.5 (−)	1.0 (−)	1.5 (+)	5.0 (−)	2.0 (−)	3.9 (+)	84.0	98.4	91.0
11	2.4 (−)	5.9 (+)	1.0 (−)	1.5 (+)	5.0 (−)	7.0 (+)	2.5 (−)	83.5	96.8	90.2
12	11.2 (+)	5.9 (+)	1.0 (−)	1.5 (+)	9.8 (+)	2.0 (−)	3.9 (+)	83.9	98.2	91.1
13	2.4 (−)	3.5 (−)	1.5 (+)	1.5 (+)	9.8 (+)	2.0 (−)	2.5 (−)	83.6	96.7	90.2
14	11.2 (+)	3.5 (−)	1.5 (+)	1.5 (+)	5.0 (−)	7.0 (+)	3.9 (+)	83.5	97.4	90.5
15	2.4 (−)	5.9 (+)	1.5 (+)	1.5 (+)	5.0 (−)	2.0 (−)	2.5 (−)	83.9	97.6	90.8
16	11.2 (+)	5.9 (+)	1.5 (+)	1.5 (+)	9.8 (+)	7.0 (+)	3.9 (+)	83.5	97.0	90.3

MON, motor octane number; RON, research octane number; AKI, anti-knock index; and nd, not detected.
[a] Concentrations found in the original sample 1: mean of two replicates and standard deviations (%, v/v).

required number of experiments was calculated as $N = K^2 + K + C$, where K is the number of investigated factors and C is the number of central point repetitions. Toluene, m-xylene, n-hexane and n-heptane percentages were the variables (or factors) studied using this experimental design. Therefore, 20 new samples plus three replications of sample 01 (central point) were prepared from "original sample 2" (for a total of 23 experiments), by varying the final concentrations of the studied hydrocarbons, as illustrated in Table 2. Experiment 01 was carried out in triplicate (central point) to evaluate the sources of experimental error: measurement, volatilization of the compounds and calibration of the engine. After the samples were prepared according to Table 2, the experimental tests were performed with the CFR engine.

3. Results and discussion

From the chromatograms obtained for the 50 samples, the aromatics (toluene and m-xylene), the paraffins (n-pentane, n-hexane, n-heptane and isopentane), and the olefins (2-methyl-1-butene, 2-methyl-2-butene, trans-2-pentene, trans-2-hexene and 1-metilciclopentene) were identified as the compounds present in the most samples and in the highest volumetric proportions. Table 3 summarizes the volumetric proportions of each compound. Among these compounds, toluene, m-xylene, n-hexane, n-heptane, 2-methyl-2-butene were selected to study their effect on the octane rating alongside the oxygenates, which were t-butanol and MTBE. The latter were added because they are used internationally to improve gasoline octane ratings.

The experiments described in Table 1 were carried out with the CFR engine and the resultant octane numbers are also listed in this table, where the symbols (−) and (+) indicate whether the hydrocarbon is present at a minimum or maximum concentration level, respectively. "original sample 1" presents values of MON, RON and AKI of 82.8, 97.2 and 90.0, respectively, while samples 02, 04, 10 and 12 exhibit the highest octane and AKI numbers, making them equivalent to a Premium gasoline. The higher octane values can be explained as follows:

1. Higher concentrations of aromatics (toluene and m-xylene) contribute directly to the higher octane values. This effect was observed via the comparison of the sample compositions and results of "original sample 1" with the analogous data for sample 04. In the latter, the concentrations of aromatics were maximized, while the other hydrocarbons (except n-hexane) were kept at a minimum. Because the levels of aromatic compounds in "original sample 1" were at their minimum, one can conclude that the increase in the AKI from 90.0 in "original sample 1" to 91.0 in sample 04 was caused by the increased aromatic content. If the concentration of only toluene is increased while keeping the concentrations of m-xylene and n-heptane constant, the octane numbers increase as well. This effect can be observed by comparing the composition of "original sample 1" with that of sample 02, which had an AKI of 91.2.
2. By maximizing the concentration of toluene and m-xylene and reducing the concentration of n-heptane, there was an increase in the octane rating. This was ascertained by comparing samples 04 and 08, which contained the maximum concentrations of aromatics and n-hexane. However, while the concentration level of n-heptane was at the minimum value in sample 04 (AKI of 91.0), it was at the maximum in sample 08 (AKI of 90.0).

The initial results reveal that a higher concentration of aromatic molecules leads to an increase in the octane number, while a higher concentration of paraffins reduces the octane number; these results were consistent with the work of Leeuwen et al. [6], as well as Myers et al. [7].

The quantitative effects of each factor on octane numbers and its standard errors at a 95% confidence level have also been determined, and their relative values with respect to those of "original sample 1" are shown in Table 4. Positive (+) or negative (−) signs indicate that the factor provoked an increase or decrease on the octane numbers.

To compare the relative effects of each factor on the octane numbers, the absolute values of the data listed in Table 4 must be analyzed. The results indicate that toluene increases octane numbers more than the other hydrocarbons, while n-heptane reduces octane numbers more than the other organic compounds. Generally, the aromatics and n-paraffins influence gasoline octane numbers more strongly (MON, RON and AKI) than t-butanol, MTBE and 2-methyl-2-butene. This result does not mean that the latter do not affect octane numbers, but rather the concentration of these oxygenates in the studied samples was much smaller than the concentrations of the aromatic and n-paraffinic compounds, which are at concentrations usually found in the gasoline sold in Salvador, Bahia, Brazil. Furthermore, the amount of ethanol present in the samples, which was approximately 25% (v/v), may have hidden the effects of the MTBE and t-butanol, which were added in proportions between 1.0% and 1.5% (v/v).

Table 2
Doehlert matrix applied in the investigation of toluene, m-xylene, n-heptane and n-hexane concentration levels (% v/v) and obtained responses in terms of octane numbers determined in a CFR engine.

Experiment	Levels of variables				Octane numbers determined in the CFR engine		
	Toluene	m-Xylene	n-Heptane	n-Hexane	MON	RON	AKI
Original sample 2[a]	1.5 ± 0.1	2.8 ± 0.2	3.1 ± 0.1	1.1 ± 0.1	83.8	97.4	90.6
01a (C)	5.0	5.0	3.5	5.5	83.3	97.0	90.1
01b (C)	5.0	5.0	3.5	5.5	83.3	97.0	90.1
01c (C)	5.0	5.0	3.5	5.5	83.3	97.0	90.1
02	5.0	5.0	5.5	5.5	83.6	96.6	90.1
03	8.0	5.0	4.5	5.5	83.5	97.1	90.3
04	6.0	7.0	4.5	5.5	83.4	97.3	90.4
05	6.0	5.5	4.5	7.5	83.6	96.6	90.1
06	5.0	5.0	1.5	5.5	83.9	97.6	90.8
07	2.0	5.0	2.5	5.5	83.5	96.8	90.2
08	4.0	3.0	2.5	5.5	83.5	97.0	90.3
09	4.0	4.5	2.5	3.5	83.9	97.5	90.7
10	2.0	5.0	4.5	5.5	83.4	97.1	90.3
11	4.0	3.0	4.5	5.5	83.3	97.1	90.2
12	4.0	4.5	4.5	3.5	83.5	97.3	90.4
13	7.0	3.0	3.5	5.5	83.4	97.3	90.4
14	7.0	4.5	3.5	3.5	83.9	97.7	90.8
15	5.0	6.5	3.5	3.5	83.7	97.6	90.7
16	5.0	3.5	3.5	7.5	83.6	97.1	90.4
17	3.0	5.5	3.5	7.5	83.5	97.0	90.3
18	6.0	5.5	2.5	7.5	83.5	97.1	90.3
19	3.0	7.0	3.5	5.5	83.3	97.2	90.3
20	6.0	7.0	2.5	5.5	83.6	97.4	90.5
21	2.0	5.0	2.5	5.5	83.4	97.1	90.3

MON, motor octane number; RON, research octane number; AKI, anti-knock index; and C, central point.
[a] Concentrations found in the original sample 1: mean of two replicates and standard deviations (%, v/v).

Table 3
Major hydrocarbons found in gasoline sold in the Metropolitan Region of Salvador with its maximum, minimum and average concentrations (%, v/v) and frequency of the 50 analyzed samples.

Organic function	Hydrocarbon	Maximum concentration	Minimum concentration	Medium concentration	Frequency
Aromatics	Toluene[a]	11.2	0.81	4.3	42
	m-Xylene[a]	5.9	0.60	4.0	47
Paraffins	n-Pentane	7.8	0.080	2.0	50
	n-Hexane[a]	9.8	0.13	2.9	42
	n-Heptane[a]	7.0	0.77	2.2	49
Olefins	2-Methyl-1-butene	2.2	0.03	1.3	49
	2-Methyl-2-butene[a]	3.9	0.02	2.2	50
	Trans-2-Pentene	2.6	0.05	1.6	49
	1-Methylciclopentene	1.3	0.05	0.81	46

[a] Hydrocarbons selected for the assessment of their influence on octane numbers.

Table 4
Variables effects and standards errors calculated from results of two level factorial fractional design ($2^{(7-3)}$) at confidence level of 95%.

Variables	Effect (Absolute values)					
	MON	Standard error	RON	Standard error	AKI	Standard error
Toluene	**+3.0**	**0.6036**	**+7.5**	**1.8746**	**+5.5**	**1.4227**
m-Xylene	**+0.4**	**0.1609**	+2.6	1.8140	+1.7	1.9865
n-Hexane	−0.7	0.6895	**−5.7**	**2.3589**	**−3.3**	**1.7146**
n-Heptane	**−2.1**	**0.5318**	**−7.5**	**4.3426**	**−5.1**	**2.2351**
t-Butanol	−0.2	0.2258	−0.4	1.7524	−0.2	0.8932
MTBE	+1.2	1.3941	+0.4	0.7805	+0.5	2.1011
2-Methyl-2-butene	+1.2	1.7278	−0.1	0.1301	+0.2	0.2747

MON, motor octane number; RON, research octane number; and AKI, anti-knock index. Significant effects are highlighted in bolded.

The tests performed during the first set of experiments (two level fractional factorial design) were unable to demonstrate the variations in the octane numbers in response to the small changes in the concentrations of toluene, m-xylene, n-heptane and n-hexane because the contributions of these compounds to the octane rating were estimated only when they were at their maximum and minimum concentration levels. To examine the behavior of the octane numbers when these compounds were present at intermediate concentrations, a Doehlert matrix-based second approach was applied. Therefore, a batch of 23 samples was prepared from "original sample 2" and analyzed with the CFR engine.

The results for the octane numbers (MON, RON and AKI) obtained with the second batch of samples are summarized in Table 2. The reproducibility of the octane values obtained for samples 1a,

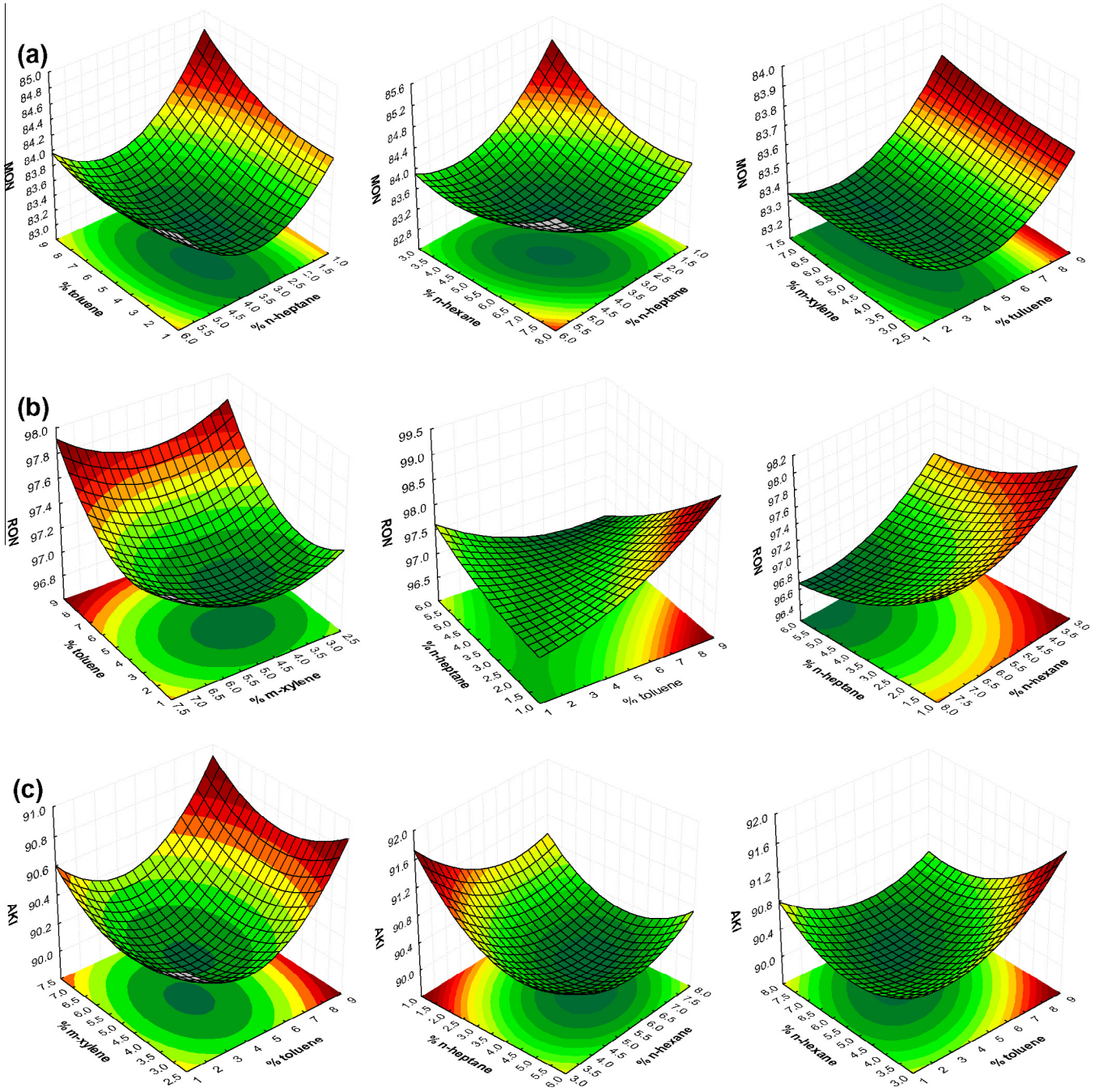

Fig. 1. Response surfaces obtained by fitting a quadratic model in the data set generated by Doehlert design application: (a) MON as response, (b) RON as response and (c) AKI as response. Surfaces are characterized as having a minimum as critical point.

1b and 1c validates the reliability of the results obtained during the CFR engine tests. For "original sample 2", the octane numbers (MON, RON and AKI) were 83.8, 97.4 and 90.6, respectively. The results were treated with the *Statistica* computer program (version 5.5) to evaluate the synergic effects of the hydrocarbons on octane numbers when only slight variations in the volumetric percentage of the selected compounds were observed. A quadratic function was fitted to data set that was obtained from this experimental application, which aimed to predict the system's behavior. By using a 95% confidence level and applying an analysis of the variance (ANOVA), it was observed that the lack of fit was not significant for MON ($p = 0.4466 > 0.05$), RON ($p = 0.2103 > 0.05$) or AKI ($p = 0.06752 > 0.05$). Subsequently, the generated surfaces can be used to make predictions about the sample behavior.

The use of *Statistica* allowed the application of the Doehlert matrix to the data optimization of the evaluated system; it was possible to plot the response surfaces, as illustrated in Fig. 1, that depict the interactions between two separate factors on the octane numbers, while keeping all others constant. The analysis of Fig. 1 reveals that all of the response surfaces include a region of minimized octane numbers, depending on the concentrations of the hydrocarbons being evaluated. In this study, these concentrations were deemed "critical values". Table 5 presents these "critical values" for toluene, m-xylene, n-hexane and n-heptane. Because Brazilian regulation [8] establishes the minimum values of MON (82.0) and AKI (87.0) for regular gasoline, the minimum values of the octane numbers obtained in this study with regard to the concentration levels and the "critical values" of the major gasoline

Table 5
Coordinates of the critical points (characterized as minimal point) and the maxima estimated from response surfaces of the surfaces obtained by fitting a quadratic function to experimental data from Doehlert design.

Variables	MON		RON		AKI	
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
Toluene (%, v/v)	3.81	8.0	1.24	8.0	5.14	8.0
m-Xylene (%, v/v)	4.97	6.5	4.51	6.5	3.01	6.5
n-Hexane (%, v/v)	6.43	3.5	2.74	3.5	5.50	3.5
n-Heptane (%, v/v)	3.28	1.5	3.88	1.5	3.92	1.5
Predicted response	83.99	85.29	97.13	99.30	90.30	92.55

MON, motor octane number; RON, research octane number; and AKI, anti-knock index.

components must be discussed. In this analysis, when the concentrations of a pair of compounds (factor) were varied, all other compounds were maintained at their "critical values" of concentration. This limitation was caused by the extreme complications caused by analyzing four factors simultaneously.

Fig. 1 allows the researcher to estimate the maximum and minimum octane numbers (MON, RON and AKI) generated by the slight variations in the component concentrations. Table 5 also presents the estimated maximum values of these octane numbers. By analyzing each surface, one may conclude that the manipulation of only a single hydrocarbon in the system is insufficient to cause significant changes in the octane number. Therefore, if the goal of the producer/formulator is to mix certain hydrocarbons into the gasoline to raise the octane numbers (MON, RON or AKI), increasing only the olefins or aromatics is not a good strategy. First, the amount of n-paraffins (n-hexane and n-heptane) present in the system should be evaluated.

By the analyzing the surfaces one can see that the n-heptane has a strong negative effect on octane numbers: the highest octane ratings were obtained when n-heptane was present in concentrations less than 1.5% (v/v), while the aromatics were present at concentrations four times higher (6.0%, v/v). Although the data in Table 1 indicated the reductive capabilities of this compound, only the use of Doehlerťs surfaces allowed the evaluation of the effect of the n-heptane on the octane numbers. Therefore, this work provides a systematic approach to allow gasoline formulators to have full control over the octane number of a produced fuel, while optimizing the use of materials by carrying out only a limited number of experiments.

4. Conclusions

This study gathers important information and establishes a procedure that may encourage gasoline producers and formulators to develop a fuel with superior antiknocking properties. The described procedure allows one to choose which compound in which amount is the best additive for a given sample of gasoline, while simultaneously evaluating the improvements in automotive performance, cost of hydrocarbons, environmental pollution and harm to human health.

The proposed factorial design methodology allows one to estimate the effects of the major gasoline components on a fuel's octane rating; the methodology can be extended to other compounds, which appear in lower concentrations. Furthermore, the Doehlert matrix, which is a mathematical tool based on statistical principles, was applied for the first time to systems involving gasoline samples and has proven to be a good choice because it allowed the visualization and estimation of the effects caused by the different hydrocarbons on octane numbers; this successful application facilitates the formulation of better fuels.

Finally, the proposed methodology is a powerful tool that can extrapolated for use in studies involving other fuel properties, such as the distillation curve; therefore, this method contributes to the formulation of more efficient and, simultaneously, less environmentally harmful fuels by evaluating the relative concentrations of certain compounds.

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