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Formulation optimization and physicochemical properties prediction of E10 fuel

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ABSTRACT/RESUME

Abstract: *Nowadays, large range of fuels supplied has diverse composition. To optimize the combustion process, engine performance and to meet EPA emissions standards, the knowledge of gasoline properties should be obtained in real time. Evaluation and prediction of physicochemical parameters such as octane numbers and densities still play an essential role in the quality control of gasoline and similar fuels. Their measurements, according to standard ASTM procedures are time and work consuming and demand specific equipment's. This study presents an alternative approach based on the use of Design of Experiments (DOE) method and its application for E10 fuel formulation optimization and then the prediction of the principal gasoline properties such as octane number and density using mathematical models. The optimization of gasoline composition is performed by the implementation of a mixing plan with different gasoline refinery blending stocks (toluene, reformate, naphtha, heavy reformate, pentane) and ethanol, with 10% in volume. The variation influence of each component proportion in the mixture, on the two essential properties of gasoline as indicated above, has been studied with comparison to the commercial gasoline, considered as a base line. We reveal a strong correlation between these properties and the gasoline blend composition. Blend stocks and formulated E10 fuel samples, previously tested according to standard methods, were used to build mathematical models, which were evaluated by experimental validation. The obtained root mean square prediction differences (RMSPD) are respectively 0.64% and 0.33% for RON and density. These results suggest that our models can be used to predict different physicochemical properties, furthermore, the obtained E10 fuels found to have the same properties as commercials gasoline.*

I. Introduction

Gasoline is the most widely used fuel for on-road vehicles worldwide and therefore the main power source for this energy user. Demand for gasoline is continually expanding with the increasing number of on-road vehicles supported by the development

of fuel efficient direct gasoline injection and hybrid engines [1]. Gasoline engine formulation is mainly indexed with respect to Octane number. Octane ratings is considered among the most important parameters in determining the fuel quality and influencing engine performance and emissions of the vehicle [2], this parameter is affected by branched-chain alkanes (isoparaffins), aromatic hydrocarbons, sulfur, olefin, and additives [3-5].
Commercial gasoline is built by mixing various fuel streams from the refinery process and proportions must not ably be chosen to reach target values for Octane Numbers. Similarly, the design of gasoline surrogates requires to match the Research Octane Number (RON) and/or the MON Motor Octane Number value of the commercial gasoline [6, 7], so that the effect of mixing pure compounds must be known. The composition of gasoline depends on the nature of the crude oils from which it originates, variations in the conditions in which the gasoline is removed from the distillation tower, transportation, storage time, which can lead to volatilization losses, the end use for which it is intended and the legislation of the country where the production and distribution are located [8]. Density and octane rating are properties closely related to the fuel composition and the characteristics of its components [9-11].

The most used solvents to produce gasoline are the ethanol. The addition of ethanol to gasoline fuel enhances the octane number of the blended fuels. Ethanol is reported to be an important contributor to decreased engine-out regulated emissions and decreased brake specific energy consumption [12-15]. The use of E10 blended fuel can generally reduce pollutant emission components [16]. The effect of ethanol fuel on the pollutant emissions and performance of an engine holds many researchers' [17-22] interests.

The estimation of physicochemical parameters such as RON and density still plays an important role in the quality control of gasoline and similar fuels. Their measurements according to standard ASTM procedures demand specific equipments and are time and work consuming. The use of experimental design techniques can provide a systematic way to carry out the experiments needed for the model development, with the same degree of success that has been already accomplished in several research fields [23]. The challenge involved in the analysis of experimental design results when more than one response variable is present. The application of a design of experiment with D-optimal method, combined with a simultaneous optimization method based on mixture plan, provide a systematic and efficient way to perform gasoline formulation and its optimization. In this way, key properties such as density and octane number (RON) were modeled. In this paper, the use of experimental design modelling to correlate the physicochemical properties measured according to ASTM standard procedures is described. The influence of the input variables was evaluated through significance analysis of residuals charts. Such analysis was also supported by the use of the ANOVA table evaluation. The evaluation of the effect coefficients and respective standard errors from multiple linear regressions provided more detailed and precise information on the significance of main and interaction effects in each response variable [24].

II. Materials and methods

A mixture plan is used for the experimental design, and the following steps are used as follows:

1. Characterization of blending stocks used in gasoline reformulation, making the evidence of principal properties such as: RON and density.
2. Experimental design setup after defining the maximal and minimal contributing values of each blending stocks in mixtures.
3. Formulation and characterization of obtained gasoline.
4. Elaboration and validation of mathematical models for each property (RON and density).
5. Optimization of the formulation that allows the determination of optimal volumetric contribution of each blending stocks in the mix, in order to obtain gasoline that meets specifications in terms of RON and density.

The formulation of gasoline is the sum of operations that consists on the mix of different blending stocks issued from refining to obtain sufficient quantity of final product conforms to required specifications. The most constraint concern essentially octane numbers (RON).
All calculations and graph generation were performed on a Design Expert 9 platform.

II.1. Samples

A total of 5 blendstocks were supplied by the Algerian refinery SKIKDA and kept at 4°C until use: Toluene Cut (x_1), Reformate (x_2), Naphtha (x_3), heavy reformate (x_4) and Pentane cut (x_5), in which, the ethanol (x_6) is added to them at 10%, fixed volumetric contribution. This combination or formulation permits to obtain E10 fuel.

The procedure of physicochemical tests is based on American Society for Testing and Materials (ASTM) methods. Measurements of octane number (RON) and density have been performed using respectively the following standards: ASTM D4052[25] and ASTM D2699 [26].It is important to point out that an Algerian commercial unleaded gasoline without any oxygenated additives is used as a reference to compare its properties with those gasoline reformulated with ethanol. The experimental results are shown in table1, here under.

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Table 1. *Blendstocks and reference gasoline characteristics*

Blendstock Characteristics	x_1	x_2	x_3	x_4	x_5	x_6	Reference Commercial gasoline
Density	*0.8308*	*0.8048*	*0.6649*	*0.8715*	*0.6620*	*0.7935*	*0.7780*
RON	*107.8*	*98*	*71.1*	*108*	*78.8*	*125*	*95.1*

The results indicate that (x_3) and (x_5) blendstocks are presented a low RON values. However, (x_1), (x_2) and (x_4), and due to their aromatic nature tendency, the RON values are high. Ethanol presents the highest RON comparing to all components. Each base in the mixture, from its properties, contributes to increase or decrease a given characteristic. To meet the standards the RON should be greater or equal 95 and the density includes between 0.72 and 0.78.

II.2. Experimental aspect

The experimental data are included in the following table

Table 2. *Blend stocks, min and max contribution*

Blendstock	Notation	Composition (%vol)	
		Min	Max
Toluene cut	x_1	*0*	*8*
Reformate	x_2	*40*	*45*
Naphtha	x_3	*17*	*25*
Heavy Reformate	x_4	*10*	*15*
Pentane cut	x_5	*3*	*5*
Ethanol	x_6	*10*	*10*

Due to the variability of the gasoline chemical composition of, its quality is always specified through minimum and, maximum values, with the exception of ethanol content which is fixed.

The data in table 2 enable us to build an experimental design in order to optimize the number of tests in the laboratory.

III. Results and discussion

Twenty five (25) formulations have been conducted, in which the first twenty ones are used to establish the model. The last five tests, from 21 to 25, are used to validate the model. Reformulated gasoline have been prepared with the incorporation of different proportions of components from (x_1) to (x_5), and the 10% of ethanol volume (x_6) as indicated in Table 2. For each formulation, the RON and density have been measured; the obtained results are shown in Table 3.

It was noted, that during the experiments, small additions of the compound greatly affect the properties have been studied. It is shown that each blend stock has an effect on the physicochemical properties of gasoline, depending on the concentration and chemical nature of the blendstock (oxygenated, aliphatic, aromatic) as found in reference [27].

Also, the ethanol concentration does not significantly modify the global composition of the mix but, it has an important influence on the measured properties. We have considered this variable as an external quantitative factor that may vary independently from proportions of other gasoline components. In addition, the density values vary simultaneously with gasoline composition and are within tolerance intervals as fixed by industrial. For this raison, we did not optimize this response.

III.1. Developed models

The purpose of the developed mathematical models is to combine different kinds of blend stocks coming from Algerian refineries blended with ethanol to produce the E10 fuel that meets the standards of national and international market**.**

III.1.1. Octane Number (RON)

The fuel octane rating is a measure of the fuel's ability to resist auto-ignition and knock in a spark-ignited engine. Higher octane-rated fuel is desirable as it enables improved engine efficiency [28].

Equation (4) gives different effects and interactions of the blend stocks in the mixture.

$$\boldsymbol{RON} = y = 343.25x_1 + 27.64x_2 + 452.11x_3 + 499.70x_4 - 19213.83x_5 - 411.63x_1x_2 - 237.67x_1x_3 - 1624.64x_1x_4 + 24134.39x_1x_5 - 669.42x_2x_3 + 446.90x_2x_4 + 23147.59x_2x_5 - 2404.42x_3x_4 + 25402.06x_3x_5 + 20315.78x_4x_5 \quad \textbf{(4)}$$

Table 3. *Applied Design of experiments and measured responses*

	Mixing plan for gasoline formulations (Vol)						Measured responses	
Trials	x_1	x_2	x_3	x_4	x_5	x_6	**Density**	**NOR**
1	*0.070*	*0.450*	*0.210*	*0.140*	*0.030*	*0.100*	*0.7814*	*94.6*
2	*0.080*	*0.450*	*0.195*	*0.125*	*0.050*	*0.100*	*0.7819*	*94.6*
3	*0.055*	*0.450*	*0.195*	*0.150*	*0.050*	*0.100*	*0.7745*	*95.8*
4	*0.055*	*0.425*	*0.220*	*0.150*	*0.050*	*0.100*	*0.7772*	*95.2*
5	*0.070*	*0.450*	*0.250*	*0.100*	*0.030*	*0.100*	*0.7749*	*93.9*
6	*0.040*	*0.450*	*0.210*	*0.150*	*0.050*	*0.100*	*0.7780*	*95.0*
7	*0.000*	*0.450*	*0.250*	*0.150*	*0.050*	*0.100*	*0.7673*	*94.5*
8	*0.080*	*0.400*	*0.220*	*0.150*	*0.050*	*0.100*	*0.7759*	*95.1*
9	*0.020*	*0.450*	*0.250*	*0.150*	*0.030*	*0.100*	*0.7721*	*95.0*
10	*0.080*	*0.450*	*0.220*	*0.100*	*0.050*	*0.100*	*0.7693*	*96.0*
11	*0.080*	*0.425*	*0.195*	*0.150*	*0.050*	*0.100*	*0.7806*	*95.4*
12	*0.080*	*0.450*	*0.195*	*0.125*	*0.050*	*0.100*	*0.7798*	*95.1*
13	*0.020*	*0.450*	*0.250*	*0.150*	*0.030*	*0.100*	*0.7755*	*94.3*
14	*0.025*	*0.425*	*0.250*	*0.150*	*0.050*	*0.100*	*0.7650*	*94.2*
15	*0.075*	*0.400*	*0.245*	*0.150*	*0.030*	*0.100*	*0.7771*	*94.0*
16	*0.000*	*0.450*	*0.250*	*0.150*	*0.050*	*0.100*	*0.7711*	*96.0*
17	*0.070*	*0.450*	*0.210*	*0.140*	*0.030*	*0.100*	*0.7815*	*96.7*
18	*0.080*	*0.450*	*0.190*	*0.150*	*0.030*	*0.100*	*0.7853*	*97.0*
19	*0.057*	*0.425*	*0.227*	*0.150*	*0.040*	*0.100*	*0.7781*	*98.0*
20	*0.058*	*0.450*	*0.227*	*0.125*	*0.040*	*0.100*	*0.7757*	*95.2*
21	*0.040*	*0.450*	*0.210*	*0.150*	*0.050*	*0.100*	*0.7791*	*96.0*
22	*0.080*	*0.420*	*0.250*	*0.120*	*0.030*	*0.100*	*0.7758*	*94.8*
23	*0.080*	*0.450*	*0.170*	*0.150*	*0.050*	*0.100*	*0.7862*	*97.0*
24	*0.050*	*0.400*	*0.250*	*0.150*	*0.050*	*0.100*	*0.7722*	*95.3*
25	*0.025*	*0.450*	*0.250*	*0.125*	*0.050*	*0.100*	*0.7705*	*95.0*

The figure 1 hereunder shows RON model coefficients and highlights theirs effects and interactions.

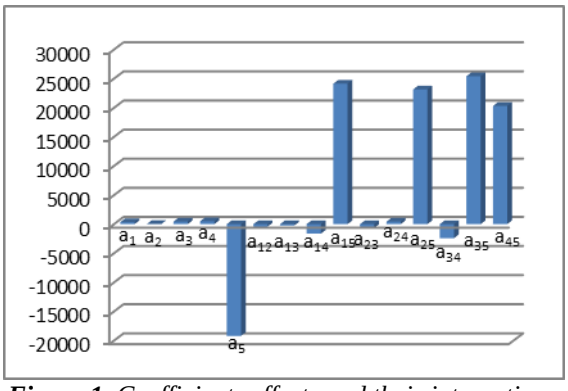


Figure 1. *Coefficients effects and their interactions on RON model.*

From the figure above, we conclude that the interactions created by pentane and other blending stocks such as: pentane – toluene, pentane – reformate, pentane – naphtha, and pentane-heavy reformate have notable influence on the RON. Contrary to that, interactions generated by other blending stocks have negligible effects on this property. Residuals analyses according to predicted RON values are presented in figure 2.

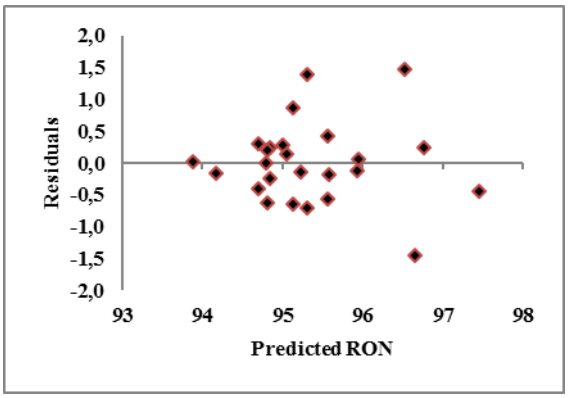


Figure 1. *RON Residual analysis*

The residuals seem to be distributed randomly. The mathematical model represents correctly the observed values with a coefficient of determination (R^2) equal to 94.57%.The RMSEP and the RMSPD values were (0.62 and 0.64)% respectively knowing that the standard method ASTM D2690 [26] reproducibility limits for RON is 0.7. Therefore, the

prediction results obtained in the proposed model are in accordance with the reproducibility value established in the norm.

III.1.2. Density

An important test used by refiners to analyze gasoline is the density one. The procedure to perform this test is the ASTM D4052 [25], and it depends on the entire composition of the sample. Although, the test to determine the gasoline density of carried out has a simple procedure and it is a faster test in comparison to octane number analysis, the model for density of gasoline is fashioned using the same mixing plan.

$$\boldsymbol{Density} = 0.92957x_1 + 0.90584x_2 + 0.74657x_3 + 0.92673x_4 + 0.74932x_5 \quad \textbf{(5)}$$

Relation (5) is a linear model without interactions. The effects of the five significant coefficients are represented in Figure 3.

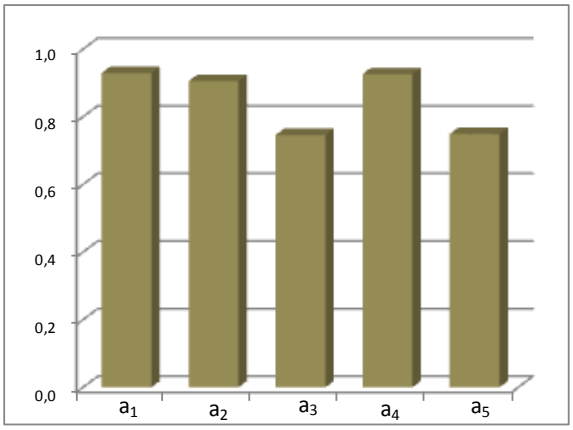


***Figure 3**. Coefficients effects and their interactions on density model.*

It is observed that practically all the blending stocks' contribution has the same influence with a value of 22% on density, and around 17% for naphtha and pentane (Figure 3).

Residuals analysis according to density predicted values are presented in figure 4.

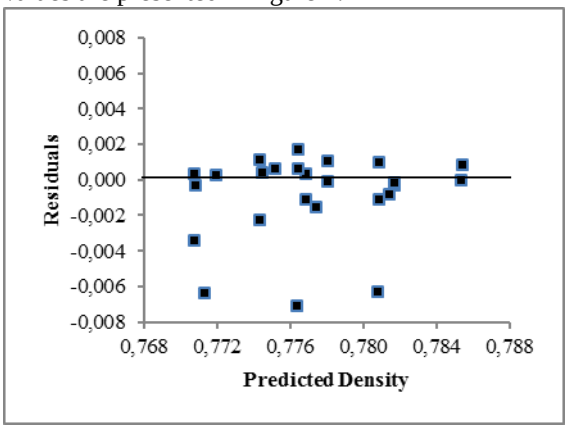


***Figure 4.** Density residual analysis.*

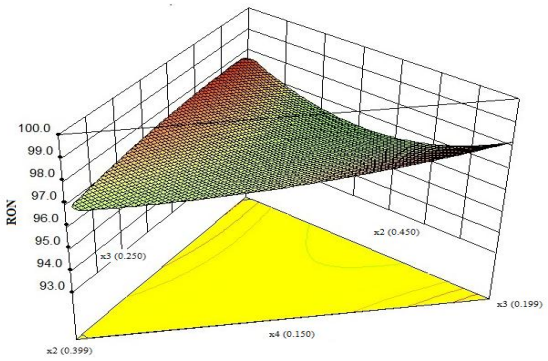
The residual dispersion does not present a particular tendency, the points are distributed randomly, and therefore the density selected model of is appropriate as the correlation coefficient (R^2) is 95.52%. The RMSEP and the RMSPD obtained are 1.7 kg/m^3 and 0.2% respectively. The reproducibility limit established in the ASTM D4052 norm is 2.0 kg/m^3. Therefore, the RMSEP value obtained in the proposed method is in accordance with the reproducibility limit of the ASTM norm.

III.2. Octane Number and Density graphical representation predicted in experimental domain

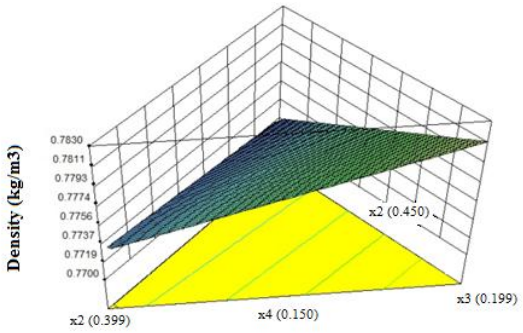
The following graphs generated from the two RON (equation 4) and density (equation 5) models are:

- Response surfaces, figure 5.
- Contour curves, figure 6

All points in the domain correspond to population responses located on the surface as shown in Figures 5.a and 5.b for RON and density respectively.



(a) RON

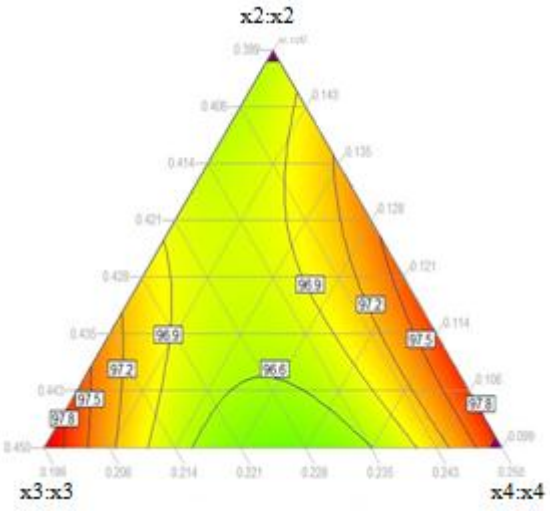


(b) Density

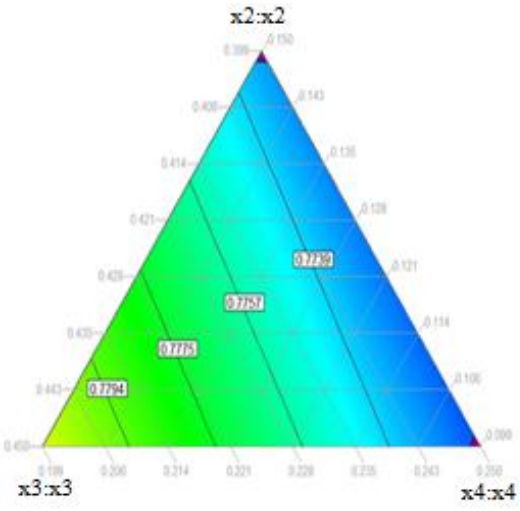
***Figure 5.** Response surfaces.*

The results show that the density increases with the concentration of reformate and heavy reformate. The Iso-responses curves analysis (Figures 5.a and 5.b) reveal the existence of relatively large domain of compositions, where the proprieties of RON and density are in the interval of gasoline specifications. Generally, the RON varies with the chemical nature of blendstocks, paraffinic (Naphtha) or/and aromatic (reformate and heavy reformate). Figure 5.a shows that the variation of blending stocks in the mix let to obtain 95 and more for RON.

The 3D representation gives good insight on the localization of the best responses inside the experimental domain. With the association of corresponding contour curves, it becomes easiest to generate these values (Figures 6.a, 6.b).



(a) RON



(b) Density

Figure 6. *Contour curves (iso-responses).*

The objective of this present work is achieved, so, it is possible to calculate RON and density for all compositions of the study domain. The contour curves indicated in Figure 6 show the contribution influence of blending stocks respectively: reformate, naphtha, and heavy reformate on the different responses; RON and density. It is important to notice that these components have been selected for drawing diagrams due to their predominant presence in gasoline blends. The obtained results show that the density increases as the concentration of reformate and heavy reformate increases**.**

III.3. Optimization study

The optimization was performed using mathematical models which represent the typical composition of E10 fuel obtained by maximizing the RON. The characteristics of this formulation are reported in table 4.

Table 4. *E10 fuel Characteristics after optimization.*

Characteristics	Reformulated E10 Fuel	Reference Commercial gasoline
Density (kg/cm^3)	0.7748	0.7780
RVP(kPa)	51.4	51.7
NOR	96.1	95.1

The optimization results show that the formulated E10 fuel in this study from blending naphtha, toluene cut, n-pentane cut, reformate, heavy reformate and ethanol using Design Of Experiments method present almost save characteristics to commercial gasoline, taken as reference (Table 4).

IV. Conclusion

Our present study allows us to determine experimentally blendstocks amounts of Algerian refineries that permit in one hand to get the two principal properties (RON and density) within international gasoline specifications, and to establish mathematical predicting models which will help to make future simulations of different blendstocks. Also, they let us to reproduce experimental results with an accepted agreement: R squared values are 94.57% for RON and 95.52% for density. The root mean square prediction differences (RMSPD) obtained are 0.33% for density and 0.64% for RON.

The obtained data analysis revealed that there is a good correlation between numerical and experimental. Therefore, the experimental design proved to be a useful tool for optimization, formulation of gasoline and prediction of its properties. It is important to highlight that physicochemical properties of E10 fuel predicted

by proposed models are similar to those of commercial gasoline.

This work were performed with samples of one Algerian refinery, it can be extended to others since the study is done using samples collected in the region of interest.

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