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Approach to Accurate Octane Number Calculation for Gasoline Blending

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Abstract

The octane number of gasoline is one of the most important measures of gasoline quality to predict accurately the octane ratings of blending gasolines. This measured on a scale that ranges from that equivalent to isooctane (octane number of 100) to that of n-heptane (octane number of zero) octane no is effected by the saturates, aromatics, and olefins contents of gasoline. We take it as a standard and measure octane number by comparison with this standard. The accurate octane blending method will optimize the blending of gasoline components, when gasoline components are blended together, we will calculate the octane number of the blend with different octane number of the component or if the four components are of equal octane number. The blend octane number may be greater than, equal to or less than that calculated from the volumetric average of the octane numbers of the blend components, which indicates nonlinear blending. Blending would be linear if octane number of a blend was equal to that predicted by summing the octane numbers of the components in proportion to their concentrations. In practices, the discrepancies between the octane numbers of blends and the linearly predicted values have been correlated by specific empirical equations and these have been used to correct the linear predictions.

1. Introduction

In (1955) Schoen and Mrstik developed a graphical correlation for predicting octane numbers of blends as a series of binary systems based on the octane rating and volumetric olefin contents of the two components being blended. Stewart (1959) refined this method to be applicable to multicomponent blends yielding more self-consistent results. Stewart's correlation also required the octane rating and volume percent olefins of the components being blended.

Auckland and Charnock (1969) developed a blending index to blend octane number linearly. The blending is obtaining blend values by blending indices linearly which obtain the molar property of a real solution by a linear combination of the partial molar properties of its components. This method can only be used to find the blending value of a component at a particular composition and cannot be used to predict its blending values in other mixtures.

In (1981) Rusin *et al.* presented a method consists of three steps: (a) transformation of component properties (b) linear blending of these transformed properties, and (c) inverse transformation of the results. This method is similar to the blending index method. Due to the back and forth transformation, this method may also cause inconsistency in data transformation between these three steps.

In (1959) Healy *et al.* correlated gasoline component blending with differences in octane level and hydrocarbon type among components. Sometimes this method gives unreasonable blending values especially if the hydrocarbon

type or octane number of the new component is outside the range of the component previously tested (Morris, 1975).

An interesting equation was proposed by Morris *et al.* (1975) for describing nonlinear gasoline blending behavior as follows:

$$octane\ number = x_1 a_1 + x_2 a_2 + b_{12}\, x_1\, x_2 \quad (1)$$

Where a_i and x_i are the octane number and the volume fraction of component i, respectively and b_{12} is the interaction coefficient for components 1 and 2.

This Equation (1), is effective in correlating the octane numbers of gasoline blends.

Therefore, an additional blending study with the new component and other components must be carried out to determine the additional interaction terms. With n components, n(n-1)/2 interaction parameters are required. If two components are blended so K = 2(2-1)/2 = 1

∴The equation will be octane no. $ON)_2 = a_1x_1+a_2x_2+b_{12}x_1x_2$ ((b_{12}) one binary interaction parameter). If three components are blended together so K = 3(3-1)/2 = 3

∴ The equation $ON)_3 = a_1x_1 + a_2x_2 + a_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3$ ((b_{12}), (b_{13}), (b_{23}) are the binary interaction parameters) if four new components are added to an eight-component gasoline pool, K = 4(4-1)/2 = 6

∴ The equation $ON)_4 = a_1x_1 + a_2x_2 + a_3x_3 + a_4x_4 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{14}x_1x_4 + b_{23}x_2x_3 + b_{24}x_2x_4 + b_{34}x_3x_4$ ((b_{12}), (b_{13}), (b_{14}), (b_{23}), (b_{24}), (b_{34}) are the binary interaction parameters) the number of interaction parameters increases drastically from 28 to 66. This means that the thirty-eight blending studies with the new components and the other components must be carried out to determine these additional 38 interaction parameters.

In (1993) Zahed *et al.* proposed a model with five independent variables for predicting the octane number of gasoline blends. The octane numbers predicted from this equation are no longer even close to the original octane numbers of the gasoline components. The octane number of n-heptane predicted from this model is 108.77 versus the defined value of zero. Similarly, the octane number of iso-octane predicted from this model is -108.95 versus the defined value of 100. The usefulness of this kind of approach is very limited. Using this model to predict the octane number of blend at other conditions will be very unreliable.

2. Materials:

Table 1 represents a typical industrial blending process employed to produce a quality gasoline from various product streams. Four blending data (Table 1) for gasoline produced from four different blend cuts: Straight Run Gasoline (SRG), Straight Run Naphtha (SRN), Reformate (REF) and Fluidized Catalytically Cracked Gasoline (FCCG). The raw gasoline cut qualities (RON, RVP and SG) were determined by the Quality Control department prior to blending using standard ASTM analytical methods.

We used four kinds of additives from methanol and originate, such as XXX, XXY and XXYY. We noticed the effect of each one of them on at least four blends to determine the results for each of them to reach Maximum Octane Number. And we determined the objective function

Table 1. shows gasoline (RON 95) specification: EUROGRADE GASOLINE (RON 95)
PRODUCT SPECIFICATIONS

Test	Unit	Method	Limits	
			Min	Max
Density 15^{o}C	kg/m3	ASTM D 4052		775
Appearance		Visual	Clear&Bright	
Colour			Undyed	

Continued on next page

Table 1 continued

Research Octane Number, RON		ASTM D2699	95	
Motor Octane Number, MON		ASTM D2700	85	
Distillation		ASTM D86		
Initial boiling point	^{o}C		To be reported	
10%	^{o}C			70
50%	^{o}C			120
90%	^{o}C			180
Final boiling point	^{o}C			210°C
Evaporated at 150 oC	%vol		75	
Vapor Pressure				
Summer (1st May till 30th September)	bar	ASTM D5191	0.4	0.6
Winter (1st October till 30th April)	bar	ASTM D5191	0.4	0.7
Copper Corrosion (3hrs at 50 oC)		ASTM D130		1a
Induction Period	min.	ASTM D525	360	
Existent Gum	mg/100ml	ASTM D381		5
Total Sulphur	mg/kg	ASTM D 5453		10
Benzene Content	%vol	UOP 744		1
Olefins	%vol	ASTM D 1319/ ASTM D 5134		18
Aromatics	%vol	UOP 744		42
Oxygenates	%wt	ASTM D4815		NIL
Doctor Test		ASTM D4952		Negative
Lead	mg pb/ L	I P 224		5

Table 2. Blend data

Sample			Reformate	Isomerate	MTBE	Blend A	Blend B	Blend C	Blend D
Test	Method	Units							
RON	ASTM D2699		101.2	87.3	115	95.1	95.2	95.2	95.2
MON	ASTM D2700		90	77	99	84.2	84.2	84	84
Aromatic	UOP 870	%VOL	75.6	0	0	41.7	38.9	34.4	31.5
Density 15ºC	ASTM D4052	kg/m3	826.1	663.2	740.5	754.3	744.9	742.0	734.9
Vapor pressure	ASTM D5191	Bar	0.2	0.89	0.25	0.50	0.522	0.57	0.559
Exhaust Emission	UOP 539								
CO		%mol				2.6	2.65	2.7	2.7
CO2		%mol				12.3	12.36	11.9	11.8
H2		%mol				1.2	1.22	1.2	1.2
N2		%mol				83.9	83.8	84.3	84.2

3. Results and Discussion

3.1. Statistical model for prediction of octane number (ON)

In a previous work by the author, a third order statistical model was elaborated to predict the value of ON upon adding naphta to gasoline (manal, 2012). It was found that a third degree model was adequate for describing the required correlation. In the present work, a more ambitious aim was set to predict the effect of four additions in different percentages on the ON of gasoline. The masses of different additives are represented by the following symbols:

X_1 = Mass of ... (g)

X_2 = Mass of ... (g)

X_3 = Mass of ... (g)

X_4 = Mass of ... (g)

As a first trial, a factorial 2^4 first order model was suggested.

3.2. First order (linear) model

The center of design and the normaliXed values of the four variables as well as the minimum and maximum value of each are shown in Table 3. 1.

Table 3. Levels of design in 2^4 factorial experiment

Variable	Coded value X = – 1	Center X = 0	Coded value X = + 1	ΔX
X1	71	76.5	82	5.5
X2	7	9.5	12	2.5
X3	1	2.5	4	1.5
X4	5	10	15	5

20 mixes were prepared including 16 with different combinations of X values and 4 at the center of design. Percentages in Table 1 were normaliXed to add up to 100% each time.

The coded first order design equation for 4 variables takes the form:

$$\begin{aligned} ON = {} & a0 + a_1X_1 + a_2X_2 + a_3X3 + a_4X_4 + a_{12}X_1X_2 \\ & + a_{13}X_1X_3 + a_{14}X_1X_4 + a_{23}X_2X_3 + a_{24}X_2X_4 \\ & + a_{34}X_3X_4 + a_{123}X_1X_2X_3 + a_{124}X_1X_2X_4 + a_{134}X_1X_3X_4 \\ & + a_{234}X_2X_3X_4 + a_{1234}X_1X_2X_3X_4 \end{aligned} \tag{4.1}$$

Where X_i is the coded value of X_i defined as:

$$Xi = \frac{X_i - X_o}{\triangle X} \tag{4.2}$$

Where: X_0 is the central value of X_i.

A first regression using Design Expert® software was obtained neglecting three order and four order interaction terms because of the negligible interaction between light and heavy naphta and methanol. The following coded equation was obtained:

$$\begin{aligned} ON = {} & 97.70 - 0.62\,X1 + 0.39\,X2 + 2.75\,X3 + 1.37\,X4 \\ & + 0.068\,X1X2 - 0.075\,X1X3 - 0.069\,X1X4 - 0.12\,X2X3 \\ & + 0.4\,X2X4 - 1.4\,X3X4 \end{aligned} \tag{4.3}$$

This equation can be transformed in terms of actual variables using equation (4.2) to get

$$\begin{aligned} ON &= 77.857 + 0.1129\,X1 - 0.4586\,X2 + 4.713\,X3 \\ &+ 2.351\,X4 + 0.0049\,X1X2 - 0.0091\,X1X3 - 0.025\,X1X4 \\ &- 0.033\,X2X3 + 0.032\,X2X4 - 0.1866\,X3X4 \end{aligned} \tag{4.4}$$

This equation yielded a determination coefficient $R^2 = 0.951$.

On performing the ANOVA and calculating the F – values the software was able to eliminate all interaction terms to obtain a simpler equation in the form:

$$ON = 99.4 - 0.156\,X1 + 0.315\,X2 + 1.834\,X3 + 0.2656\,X4 \tag{4.5}$$

However, the value of R^2 in that case decreased to 0.847 which suggests that the original equation (3.1) was more suitable in interpreting experimental data.

To further emphasiXe that result, a plot of predicted values against actual values of ON is shown in Figure (3.2) showing a reasonable match between the two values. Also Figure (3.3) illustrates a three dimensional plot of *ON* against X_3 and X_4 indicating an increase in *ON* with increasing values of the two variables, which is in accordance with their positive coefficients in equation (3.4). Also, Fig (3.6) shows contour lines corresponding to that figure. The point (5) shown in figure corresponds to the calculated value of *ON* corresponding to values of X_3 and X_4 = 2.5 and 9.8 respectively.

3.2.1. **Second order (quadratic) model**

Whereas first order models require performing experiments at the upper and lower ends of the design ($X = \pm 1$) with replicate runs at the center of design ($X = 0$), quadratic models also require performing more experiments at selected coded levels ($X = \pm\ \alpha$). The value of α depends on the number of independent variables.in case of 4 variables, $\alpha = 1.68$. Consequently, besides the 16 runs, 8 more runs were performed at levels ± 1.68 besides 2 replicates at center of design, a total of 26 runs.

Generally, a coded second order model shows as:

$$\begin{aligned} ON &= a0 + a1X1 + a2X2 + a3X3 + a4X4 \\ &+ a12X1X2 + a13X1X3 + a14X1X4 + a23X2X3 \\ &+ a24X2X4 + a34X3X4 + a11_1^2 + a22_2^2 \\ &+ a33Z_3^2 + a44Z_4^2 \end{aligned} \tag{4.6}$$

The following coded regression equation was obtained using Design Expert® software:

$$\begin{aligned} ON = 98.55 &- 0.62\,Z1 + 0.39\,Z2 + 2.75\,Z3 \\ &+ 1.37\,Z4 + 0.068\,Z1Z2 - 0.075\,Z1Z3 \\ &- 0.69\,Z1Z4 - 0.12\,Z2Z3 + 0.4\,Z2Z4 - 1.4\,Z3Z4 \\ &- 0.15\,{}_1^2 - 0.29\,{}_2^2 - 0.68_3^2 - 0.2_4^2 \end{aligned} \tag{4.7}$$

This equation transforms to the following form on using actual variables through equation (4.3):

$$\begin{aligned} ON = 42.935 &+ 0.868\,X_1 + 0.4218\,X_2 + 6.223\,X_3 + 2.5128\,X_4 \\ &+ 0.0049\,X_1X_2 - 0.0091\,X_1X_3 - 0.025X_1X_4 - 0.033\,X_2X_3 \\ &+ 0.032\,X_2X_4 - 0.1866\,X_3X_4 - 0.0.00493\,{}_1^2 - 0.0465\,{}_2^2 \\ &- 0.302\,{}_3^2 - 0.0081\,{}_4^2 \end{aligned} \tag{4.8}$$

All coefficients were significant on applying the F – test except the coefficients of $\boldsymbol{X}_1\boldsymbol{X}_2$, $\boldsymbol{X}_1\boldsymbol{X}_3$ **and** $\boldsymbol{X}_2\,\boldsymbol{X}_3$.

The value of R^2 was exceptionally high = 0.9987 proving that the regression equation models perfectly the experimental data.

To confirm these findings, Figure (3.1) was drawn to compare experimental and calculated *ON* values showing a perfect alignment of points along the 45^o line. Also, Figure (3.2) shows a three-dimensional plot of *ON* against X_3 and X_4 indicating an increase in *ON* with increasing values of the two variables, which is in accordance with their positive coefficients in equation (3.3). Contour lines were drawn in Fig (3.4) displaying calculated values of *ON* as function of X_3 and X_4 revealing an increase in *ON* as both variables increase. Point (5) indicates a predicted value of ***ON* = 98.4 for X_3 = 2.5 and X_4 = 9.8.**

To conclude, the quadratic model obtained for factorial 2^4experiments has been successfully used to predict exactly the Octane Number values as function of the 4 addition levels.

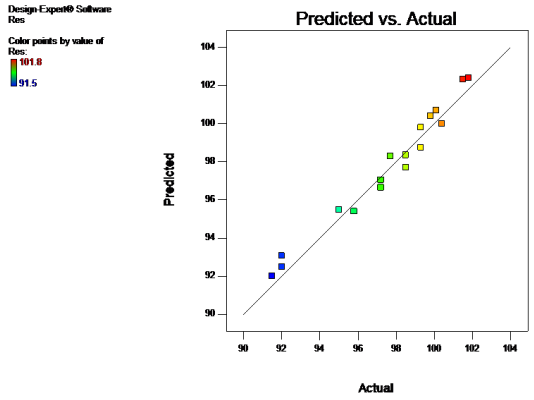

Figure 1. Comparisonbetween actual and calculated values of ON from linear model

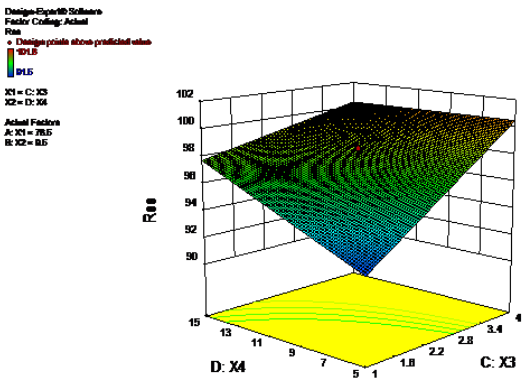

Figure 2. ONvariation as function of variables X3 and X4 for linear model

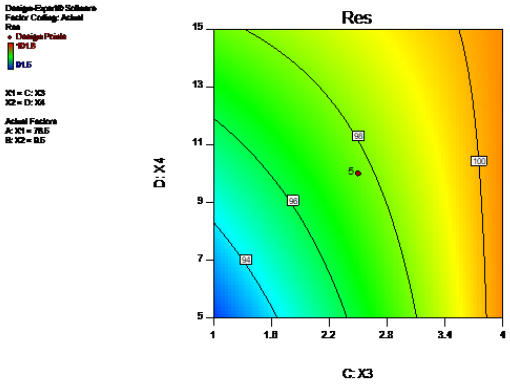

Figure 3. Contourlines for dependence of ON on variables X3 and X4 for linear model

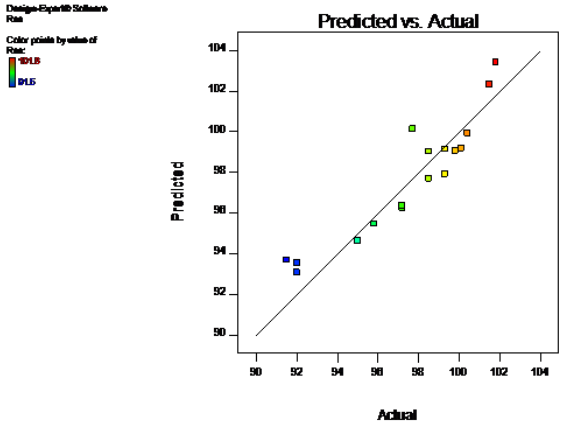

Figure 4. Comparison between actual andcalculated values of ON from quadratic model

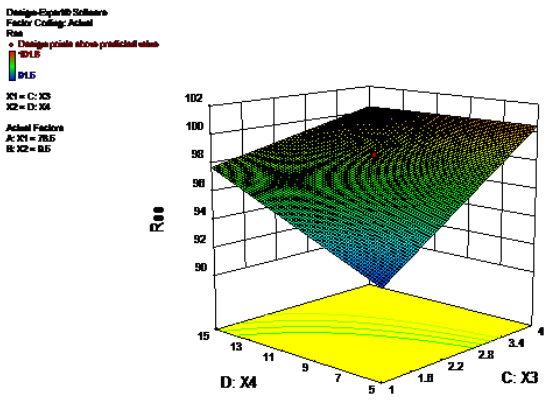

Figure 5. ONvariation as function of variables X3 and X4 for quadratic model

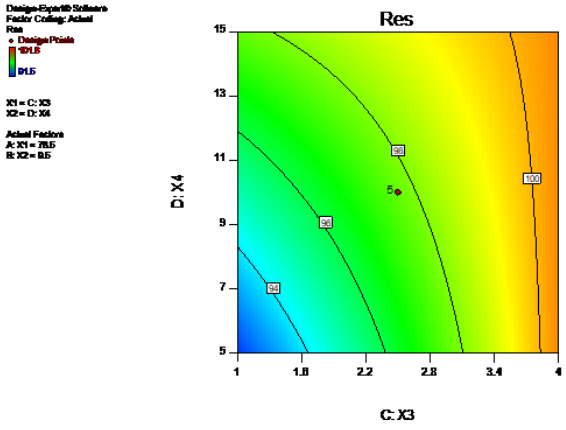

Figure 6. Contourlines for dependence of ON on variables X3 and X4 for quadratic model

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