ABSTRACT

Several physicochemical properties characterize a fuel that yields power, economy and low emissions: volatility, heating value, specific gravity, Sulphur content and antiknock performance. Octane Number (ON) measures the antiknock performance of a gasoline, in other words, its ability to resist knocking as it burns in the combustion chamber. An accurate ON predicting model is fundamental to enable formulation of gasoline at the maximum volumetric yield or at minimum cost [4]. Since the 1940’s technicians are trying to find better ON models [2, 3]. However, the existing models cannot yet accurately predict ON for gasoline formulations containing oxygenates, like ethanol or ether [1]. Even the trendiest models lead to gasohol formulas with either ON giveaway, or a higher than expected cost. Our work proposes an ON model including synergy parameters that capture nonlinear interactions between oxygenates and hydrocarbons. The analysis of an ON database including ethanol and hydrocarbon mixtures made it possible to find blend parameters that capture synergy, defined here as the property of a component possessing a blend ON higher than its own pure component ON. The model enables the formulation of specified gasolines with higher direct distillation naphtha and less ON booster content.

INTRODUCTION

Ghosh [2] proposed an ON model based on the contributions of 57 groups of gasoline components, which can be identified by chromatography in a fuel sample. Each group has a β coefficient, which may be viewed as the ratio of its
blending ON to its pure component ON. Interactions between paraffinic, naphthenic and olefinic hydrocarbons are also quantified by the introduction of an \( I_p \) parameter, which means interaction with paraffins. The ON and \( \beta \) coefficients for each group were determined by regression analysis of a large database of 1471 different fuels. The method was shown to give accurate results, however the \( \beta \) coefficients were not published due to proprietary reasons.

Foong [1] designed a large experiment to provide the experimental octane numbers of n-heptane, isooctane, toluene and ethanol mixtures, sweeping the ethanol content from 0% to 100%.

Commercial gasolines are composed of hundreds of different hydrocarbons, their fractions varying in wide ranges [2, 3]. Its composition depends primarily on the kinds of petroleum at the refinery input, and the process unit its blending streams come from.

Blending streams may come from direct distillation, fluid catalytic cracking, reforming, alkylation, and natural gasoline units. The main groups present in gasoline are paraffinic, olefinic, naphthenic, and aromatic hydrocarbons, called PONA for short. Oxygenates, as ethanol, ETBE, and MTBE are part of a different group.

Ghosh [2] defined each group as entirely paraffinic, olefinic, naphthenic or aromatic in his work, which may be good for a model based on chromatography, but is not so for a simpler model based on refinery streams, as each stream may have partial characteristics of each group. Defining the chemical characteristic of each stream as a 4-dimensional vector \( \{p, o, n, a\} \) where \( p, o, n, a \), are real numbers in the range from 0 to 1 enables the application of Ghosh’s model to refinery streams.

Ghosh’s model is defined by eq. (1)

\[
ON = \frac{\sum_{PONA} v_i \beta_i ON_i + I_p \sum_P v_i \beta_i ON_i}{\sum_{PONA} v_i \beta_i + I_p \left( \sum_P v_i \beta_i - \sum_P v_i \right)}
\]  

(1)

where \( \sum_{PONA} \) means sum across all groups, and \( \sum_P \) means sum across paraffinic groups only.

\[
I_p = \left[ \frac{k^{(a)}_{PN}v_N + k^{(a)}_{PO}v_O}{1 + k^{(a)}_{PN}v_N + k^{(a)}_{PO}v_O} \right] 
\]  

(2)

If the paraffinic content of each \( i \)th group is defined as a fraction \( p_i \) ranging from 0 to 1,

It can be shown that

\[
\sum_{P} (\beta_i - 1)v_i = \sum_{PONA} (\beta_i - 1)v_i p_i 
\]  

(3)
then eq. (1) may be rewritten as

\[
ON = \frac{\sum \beta_v i_i \Delta_i + I_p \sum \beta_v i_i p_i A_i}{\sum \beta_v i_i + I_p \sum (\beta_i - 1) v_i p_i}
\]

(4)

In addition, each refinery stream can be considered as a group, largely simplifying the model and avoiding the need for a detailed chromatographic analysis of each stream for octane number evaluation purposes. Note that \(ON\) was replaced by \(A_i\) in the right numerator term to explain interactions not proportional to octane numbers.

Interactions between ethanol and paraffinic hydrocarbons may be explained by redefining \(I_p\) as

\[
I_p = \frac{k_v \nu_{et}}{1 + k_d \nu_{et}}
\]

(5)

where \(\nu_{et}\) is the ethanol volumetric fraction and \(k_n, k_d\) are parameters determined by regression.

To complete the model the coefficients \(A_i, \beta_i, k_n, k_d\) still have to be determined by nonlinear regression on an experimental database while the coefficients \(p_i\) of each stream may be determined by chromatography, but there are now only \(n-1\) \(\beta_i\) coefficients to be determined instead of 56 as in the original model. The ON coefficients must be determined by testing each stream in the CFR engine. For a gasoline containing \(n\) streams, there are \(2n + 1\) parameters to be determined by regression, \(n\) by chromatography. At least \(2n + 1\) ON tests must be performed in the CFR engine to find the ON, \(k_n, k_d, \beta\) parameters by regression.

**EXPERIMENTAL**

The Table 1 shows experimental data for five refinery streams, plus ethanol. Several blends were prepared, each one tested in the CFR engine to determine its ON experimentally. The volumetric fraction of saturates for each stream was determined by chromatography.
Table 1: Experimental vs Predicted values of MON for a database of 22 fuels.

| gasoline | sat %v | eth %v | Unit 1 MON | Unit 2 MON | Unit 3 MON | Unit 4 MON | Unit 5 MON | MON exp | Ip | MON mod | dif  |
|----------|--------|--------|------------|------------|------------|------------|------------|---------|----|---------|------|
| 1        | 50,3   | 0      | 0          | 0          | 35,8       | 20,9       | 43,3       | 76,5    | 0,000 | 76,3    | 0,2  |
| 2        | 38,2   | 24     | 0          | 0          | 27,2       | 15,9       | 32,9       | 82,1    | 0,116 | 82,0    | 0,1  |
| 3        | 50,8   | 3,1    | 0          | 0          | 34,7       | 20,2       | 42         | 75,9    | 0,000 | 75,9    | 0,0  |
| 4        | 38,6   | 24     | 2,4        | 0,0        | 26,4       | 15,4       | 31,9       | 82,2    | 0,116 | 82,0    | 0,2  |
| 5        | 53,0   | 0      | 6,6        | 33,5       | 19,5       | 40,4       | 75,1       | 0,000   | 75,2   | -0,1   |
| 6        | 40,3   | 24     | 0          | 5,016      | 25,46      | 14,82      | 30,704     | 81,9    | 0,116 | 81,7    | 0,2  |
| 7        | 96,7   | 0      | 0          | 100        | 0          | 0          | 52         | 0,000   | 51,9   | 0,1    |
| 8        | 78,3   | 19     | 0          | 81         | 0          | 0          | 70,8       | 0,092   | 71,5   | -0,7   |
| 9        | 73,5   | 24     | 0          | 76         | 0          | 0          | 75,7       | 0,116   | 75,1   | 0,6    |
| 10       | 87,2   | 0      | 100        | 0          | 0          | 0          | 56         | 0,000   | 56,0   | 0,0    |
| 11       | 70,6   | 19     | 81         | 0          | 0          | 0          | 74,2       | 0,092   | 74,6   | -0,4   |
| 12       | 66,3   | 24     | 76         | 0          | 0          | 0          | 78,2       | 0,116   | 77,8   | 0,4    |
| 13       | 77,1   | 0      | 0          | 100        | 0          | 0          | 60         | 0,000   | 60,0   | 0,0    |
| 14       | 62,5   | 19     | 0          | 81         | 0          | 0          | 75,4       | 0,092   | 75,8   | -0,4   |
| 15       | 58,6   | 24     | 0          | 76         | 0          | 0          | 78,7       | 0,116   | 78,6   | 0,1    |
| 16       | 35,8   | 0      | 0          | 0          | 0          | 100        | 80         | 0,000   | 80,4   | -0,4   |
| 17       | 29,0   | 19     | 0          | 0          | 0          | 0          | 81         | 82      | 0,092 | 82,0    | 0,0  |
| 18       | 27,2   | 24     | 0          | 0          | 0          | 0          | 76         | 82,6    | 0,116 | 82,5    | 0,1  |
| 19       | 43,7   | 0      | 0          | 0          | 100        | 0          | 82,5       | 0,000   | 82,7   | -0,2   |
| 20       | 35,4   | 19     | 0          | 0          | 81         | 0          | 85         | 0,092   | 84,9   | 0,1    |
| 21       | 33,2   | 24     | 0          | 0          | 0          | 76         | 85,5       | 0,116   | 85,4   | 0,1    |
| 22       | 0,0    | 100    | 0          | 0          | 0          | 0          | 90,7       | 0,483   | 90,9   | -0,2   |

The A_i parameters were considered equal to 1 by hypothesis, to represent equal interaction strength between ethanol and any of the streams. The p_i parameters were considered equal to the volumetric fraction of saturates for each stream. All other parameters eqs. (4) and (5) shown in Table 2 were obtained by regression.

Table 2: Parameters of eqs. (4) and (5) obtained by regression of Table 1 data.

| ethanol | Unit 1 | Unit 2 | Unit 3 | Unit 4 | Unit 5 |
|---------|--------|--------|--------|--------|--------|
| MON     | 90,9   | 56,0   | 51,9   | 60,0   | 82,7   | 80,4   |
| β       | 1      | 0,348  | 0,372  | 0,363  | 0,507  | 0,804  |
| β-1     | 0      | -0,429 | -0,414 | -0,392 | 0,095  | 0,292  |
| p       | 0      | 0,872  | 0,967  | 0,771  | 0,437  | 0,358  |
| kn      | 0,00483|
| kd      | 0      |

The Figure 1 compares the experimental data with predicted values of MON.
The $R^2$ parameter is 0.9991 and the standard deviation of the residuals is 0.29, showing good agreement between predicted and experimental values of MON.

Table 3: Experimental vs Predicted values of RON for a database of 22 fuels.

| gasoline | sat %v | eth %v | Unit 1 | Unit 2 | Unit 3 | Unit 4 | Unit 5 | RON | Ip | RON mod | dif |
|----------|--------|--------|--------|--------|--------|--------|--------|-----|---|---------|-----|
| 1        | 50,3   | 0      | 0      | 0      | 35,8   | 20,9   | 43,3   | 84,6| 0,000| 84,6    | 0,0 |
| 2        | 38,2   | 24     | 0      | 0      | 27,2   | 15,9   | 32,9   | 94,6| 0,000| 94,0    | 0,6 |
| 3        | 50,8   | 0      | 3,1    | 0      | 34,7   | 20,2   | 42     | 83,7| 0,000| 83,9    | -0,2|
| 4        | 38,6   | 24     | 2,4    | 0      | 26,4   | 15,4   | 31,9   | 94,5| 0,000| 93,6    | 0,9 |
| 5        | 53,0   | 0      | 6,6    | 0      | 35,5   | 19,5   | 40,4   | 82,8| 0,000| 82,9    | -0,1|
| 6        | 40,3   | 24     | 0      | 5,016  | 25,46  | 14,82  | 30,704 | 93,9| 0,000| 93,0    | 0,9 |
| 7        | 96,7   | 0      | 100    | 0      | 0      | 0      | 56     | 0,000| 55,9 | 1,1     |
| 8        | 78,3   | 19     | 0      | 81     | 0      | 0      | 0      | 73,6| 0,000| 74,4    | -0,8|
| 9        | 73,5   | 24     | 0      | 76     | 0      | 0      | 0      | 78,7| 0,000| 78,1    | 0,6 |
| 10       | 87,2   | 0      | 100    | 0      | 0      | 0      | 0      | 57   | 0,000| 56,9    | 0,1 |
| 11       | 70,6   | 19     | 81     | 0      | 0      | 0      | 0      | 76,2| 0,000| 76,8    | -0,6|
| 12       | 66,3   | 24     | 76     | 0      | 0      | 0      | 0      | 81,1| 0,000| 80,5    | 0,6 |
| 13       | 77,1   | 0      | 0      | 100    | 0      | 0      | 0      | 64   | 0,000| 63,7    | 0,3 |
| 14       | 62,5   | 19     | 0      | 81     | 0      | 0      | 0      | 79,8| 0,000| 80,8    | -1,0|
| 15       | 58,6   | 24     | 0      | 76     | 0      | 0      | 0      | 84   | 0,000| 84,0    | 0,0 |
| 16       | 35,8   | 0      | 0      | 0      | 0      | 0      | 0      | 100  | 0,000| 92,6    | -0,2|
| 17       | 29,0   | 19     | 0      | 0      | 0      | 0      | 0      | 81   | 0,000| 97,1    | -1,1|
| 18       | 27,2   | 24     | 0      | 0      | 0      | 0      | 0      | 76   | 0,000| 98,1    | -0,5|
| 19       | 43,7   | 0      | 0      | 0      | 0      | 0      | 0      | 100  | 0,000| 92,9    | -0,1|
| 20       | 35,4   | 19     | 0      | 0      | 0      | 0      | 0      | 81   | 0,000| 98,1    | 0,0 |
| 21       | 33,2   | 24     | 0      | 0      | 0      | 0      | 0      | 76   | 0,000| 99,2    | -0,2|
| 22       | 0,0    | 100    | 0      | 0      | 0      | 0      | 0      | 108,3| 0,000| 108,6   | -0,3|

The $A_i$ parameters were considered equal to 1 by hypothesis, to represent equal interaction strength between ethanol and any of the streams. The $p_i$ parameters
were considered equal to the volumetric fraction of saturates for each stream. All other parameters eqs. (4) and (5) shown in Table 4 were obtained by regression.

Table 4: Parameters of eqs. (4) and (5) obtained by regression of Table 3 data.

|        | ethanol | Unit 1 | Unit 2 | Unit 3 | Unit 4 | Unit 5 |
|--------|---------|--------|--------|--------|--------|--------|
| RON    | 108.6   | 56.9   | 55.9   | 63.7   | 92.9   | 92.6   |
| beta   | 1       | 0.375  | 0.435  | 0.383  | 0.472  | 0.595  |
| beta-1 | 0       | -0.429 | -0.414 | -0.392 | 0.095  | 0.292  |
| p      | 0       | 0.872  | 0.967  | 0.771  | 0.437  | 0.358  |
| kn     | 0.000   |        |        |        |        |        |
| kd     | 0.000   |        |        |        |        |        |

The Figure 2 compares experimental data with predicted values of RON.

The $R^2$ parameter is 0.9987 and the standard deviation of the residuals is 0.50, showing good agreement between predicted and experimental values of RON.

CONCLUSIONS

The RON and MON of refinery stream blends can be represented by eqs. (4) and (5) after their parameters are fit to an existing ON database of these same streams. The standard deviation of the residuals is of the same order of
magnitude as the reproducibility of the ASTM D-2699 and D-2700 methods themselves.

This work shows that is possible the capture of hydrocarbon / ethanol synergy in the ON Model, with less ON booster content in the gasoline formulation, i.e., cheaper gasoline as a practical result.

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