Octane Number's Modeling With Oxygenate/Hydrocarbon Synergy Included

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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 β 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 β 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)

$$ON = \frac{\sum_{PONA} v_i \beta_i ON_i + I_p \sum_{P} v_i \beta_i ON_i}{\sum_{PONA} v_i \beta_i + I_p \left(\sum_{P} v_i \beta_i - \sum_{P} v_i \right)} \qquad (1)$$

where $\sum_{pona}$ means sum across all groups, and $\sum_{p}$ means sum across paraffinic groups only.

$$I_P = \left[\left(\frac{k_{PN}^{(a)} v_N + k_{PO}^{(a)} v_O}{1 + k_{PN}^{(b)} v_N + k_{PO}^{(b)} v_O} \right) \right] \qquad (2)$$

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

$$\sum_{p} (\beta_i - 1) v_i = \sum_{pona} (\beta_i - 1) v_i p_i \qquad (3)$$

then eq. (1) may be rewritten as

$$ON = \frac{\sum_{pona} \beta_i v_i ON_i + I_p \sum_{pona} \beta_i v_i p_i A_i}{\sum_{pona} \beta_i v_i + I_p \sum_{pona} (\beta_i - 1) v_i p_i} \qquad (4)$$

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_i 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

$$I_p = \frac{k_n v_{et}}{1 + k_d v_{et}} \qquad (5)$$

where v_{et} is the ethanol volumetric fraction and k_n, k_d are parameters determined by regression.

To complete the model the coefficients A_i, β_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 β_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, and β 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	Unit 2	Unit 3	Unit 4	Unit 5	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	0	3,1	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	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	0	52	0,000	51,9	0,1
8	78,3	19	0	81	0	0	0	70,8	0,092	71,5	-0,7
9	73,5	24	0	76	0	0	0	75,7	0,116	75,1	0,6
10	87,2	0	100	0	0	0	0	56	0,000	56,0	0,0
11	70,6	19	81	0	0	0	0	74,2	0,092	74,6	-0,4
12	66,3	24	76	0	0	0	0	78,2	0,116	77,8	0,4
13	77,1	0	0	0	100	0	0	60	0,000	60,0	0,0
14	62,5	19	0	0	81	0	0	75,4	0,092	75,8	-0,4
15	58,6	24	0	0	76	0	0	78,7	0,116	78,6	0,1
16	35,8	0	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	0	100	0	82,5	0,000	82,7	-0,2
20	35,4	19	0	0	0	81	0	85	0,092	84,9	0,1
21	33,2	24	0	0	0	76	0	85,5	0,116	85,4	0,1
22	0,0	100	0	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.

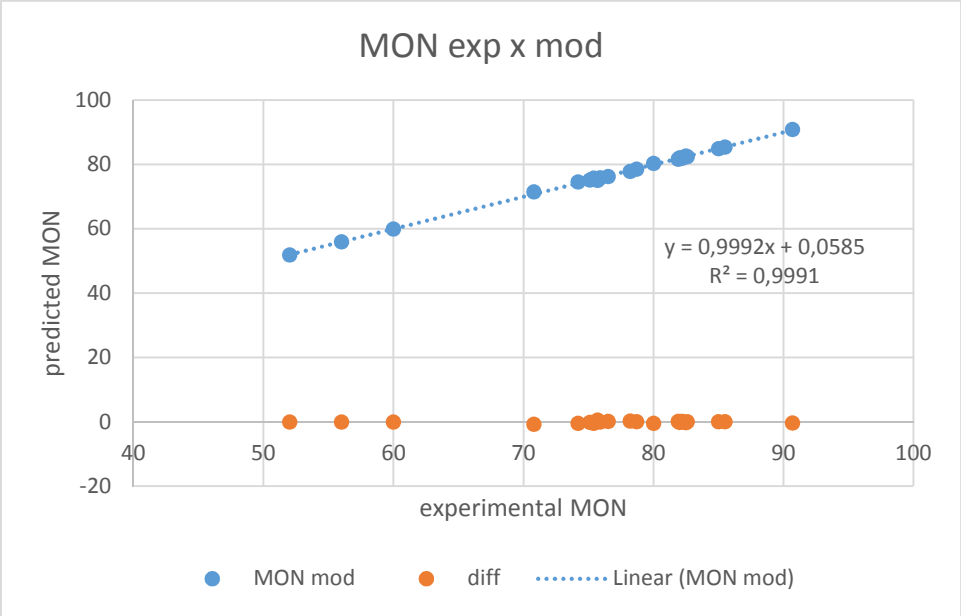

Figure 1: Experimental vs predicted values of MON.

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	0,0	26,4	15,4	31,9	94,5	0,000	93,6	0,9
5	53,0	0	0	6,6	33,5	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	0	100	0	0	0	56	0,000	55,9	0,1
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	0	100	0	0	64	0,000	63,7	0,3
14	62,5	19	0	0	81	0	0	79,8	0,000	80,8	-1,0
15	58,6	24	0	0	76	0	0	84	0,000	84,0	0,0
16	35,8	0	0	0	0	0	100	92,4	0,000	92,6	-0,2
17	29,0	19	0	0	0	0	81	97	0,000	97,1	-0,1
18	27,2	24	0	0	0	0	76	97,6	0,000	98,1	-0,5
19	43,7	0	0	0	0	100	0	92,8	0,000	92,9	-0,1
20	35,4	19	0	0	0	81	0	98,1	0,000	98,1	0,0
21	33,2	24	0	0	0	76	0	99	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.

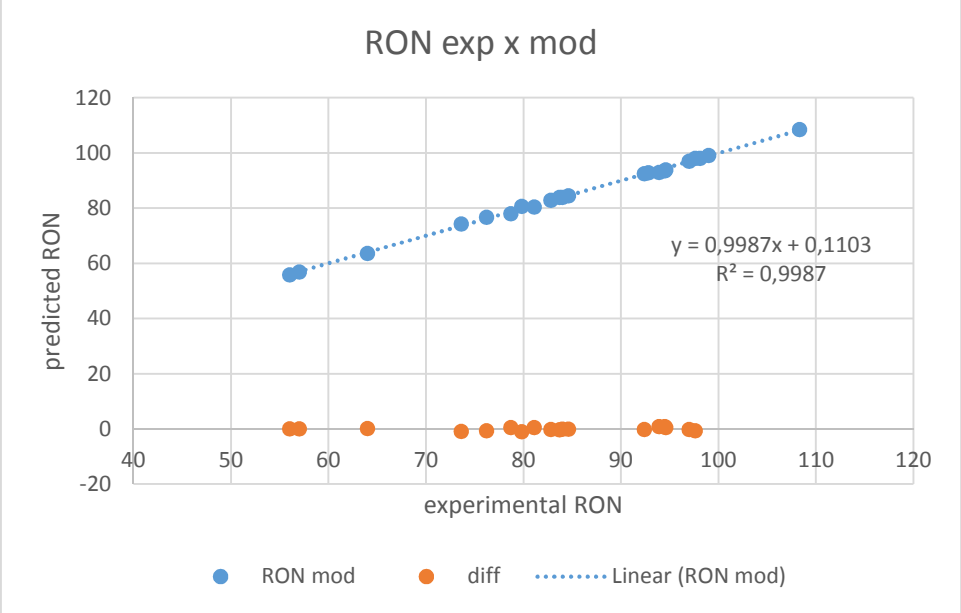

Figure 2: Experimental vs predicted values of RON.

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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