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Linear vs. nonlinear: Calculate gasoline component properties

The US is the largest "gasoline guzzler" in the world, producing and consuming about 9 MMbpd of gasoline—global production is approximately 45 MMbpd. Considering current gasoline prices (Regular 87 octane discounted at $2.22/gal), and a $2.5-B/yr gasoline production cashflow for an average-size US refinery, the capital involved is a staggering $250 B/yr. This means that even small production improvements have an enormous impact on the economics of the US refining industry.

However, sloppy gasoline production costs the blender money. A simple example illustrates the "sloppiness" value in terms of easily understood property giveaway; that is, the gap between a spec (e.g., 87 octane) and the actual produced gasoline property (for example, measured at 87.9 octane).

A 2013 study undertaken by Valero[1] indicates a US refining industry conservative octane giveaway of approximately 0.5 octane number (ON) and a Reid vapor pressure (RVP) giveaway of approximately 0.3 psi. This is valued at approximately $3 B/yr. Since there are 121 US refineries, $3B/121 = $25 MM per US refinery in property giveaway alone.

Several alternatives can reduce the giveaway:

- Properly optimizing a recipe using adequate tools
- Using better measurement systems—e.g., more precise analyzers
- Accounting for the nonlinearity of gasoline component properties.

This article is focused on the nonlinearity of gasoline component properties. This might appear an easy task, but more than 60% of US refineries calculate the gasoline component properties linearly. This is a mistake that can waste significant capital because it is overestimating or underestimating valuable properties (i.e., ON or RVP).

Linear vs. nonlinear. The perennial question is: what is the difference between linear and nonlinear worth? It is actually a simple blend of subjects that include physics, chemistry, engineering and math.

Since gasoline and hydrocarbon-based components don't really "like" each other when combined, chemical interactions modify the behavior of the solution or blend.

This means that 1 + 1 does not equal 2 but might be equal to 3 or 1.5. The following example illustrates the concept behind this complicated behavior.

FIG. 1 shows the blending of two components (same quantity, 1 bbl each): reformate with a research octane number (RON) of 100 and a light straight-run with a RON of 74. If the linear calculation is done [i.e., (100 + 74) ÷ 2], the result is 87, but if a blend sample is analyzed by a lab, the result is 88.

The reason for this difference is the strong interactions between molecules in the blend that make the phenomena highly nonlinear (i.e., 1 + 1 does not equal 2).

For example, molecules differ in structure, size or thermal stability (differing blend behavior). The nonlinear molecular interactions show a difference in class:

- Nonlinear blends at PONA (parafines, olefins, naphthenes, aromatics)
- Paraffins and naphthenes
- Paraffins and olefins.

Despite this behavior, the linear blends show same molecular class—e.g., paraffins and paraffins, or olefins and olefins, and so on.

Gasoline has more than 30 specifications[2] to be met simultaneously, and most of them are nonlinear. Focusing on the most important one from a revenue perspective, **TABLE 1** shows which gasoline properties are linear and which are nonlinear.

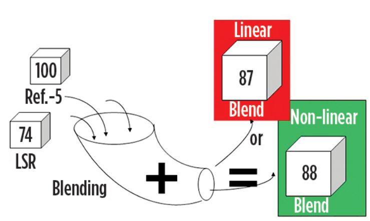

FIG. 1. Linear vs. nonlinear RON analysis.

TABLE 1. Main gasoline properties behavior

Property	Type	Linear/ nonlinear
Research octane	Performance	Nonlinear
Motor octance	Performance	Nonlinear
RVP	Valatility	Nonlinear
TVL = 20 of VLI or DI	Volatility	Nonlinear
Dist 10%	Volatility	Nonlinear
Dist 50%	Valatility	Nonlinear
Dist 90%	Volatility	Nonlinear
Endpoint	Volatility	Nonlinear
Density	Performance	Linear
Sulfur	Health and climate	Linear
Oxygen	Health and climate	Linear
Aromatic	Health and climate	Linear
Olefins	Health and climate	Linear
Benzene	Health and climate	Linear

Optimize L | Optimize NL | BATCH SIZE [BBL] 100,000 | Feasible (Specs) YES

COMPONENT	RECIPE VOL%	RECIPE BBL	INVENTORY [BBL] INITIAL	INVENTORY [BBL] FINAL	INVENTORY [BBL] REMAINING	PRICE $/bbl
N-C4	4.25	4249.52	0.00	40,000.00	35,750.48	40.00
Lt. Naphtha	18.65	18654.44	0.00	40,000.00	21,345.56	64.50
Hvy Naphtha	0.00	0.00	0.00	40,000.00	40,000.00	71.60
Alkylate	18.32	18319.54	0.00	40,000.00	21,680.46	75.30
FCC HCN	13.10	13100.58	0.00	40,000.00	26,899.42	77.90
FCC LCN	40.00	40000.00	0.00	40,000.00	0.00	72.20
Toluene	0.00	0.00	0.00	40,000.00	40,000.00	76.30
Refromate	5.68	5675.92	0.00	40,000.00	34,324.08	73.90
TOTAL %	100.00	100,000.00	MIN 10.00	MAX 100,000.00	220,000.00	

SPEC (M2-Neat)	Minimum	Maximum
☐ RON		
☑ MON	82.00	
☑ AKI	87.00	
☑ RVP	9.00	10.00
☑ T-10		158.00
☑ T-50	170.00	250.00
☑ T-90		374.00
☑ FBP		430.00
☐ E-200		
☐ E-300		
☑ DI INDEX		1250.00
☑ TV/L	133.00	
☑ API GRAVITY	50.0	80.0
☐ SP Gravity		
☑ SULFUR	0.0	80.0
☐ OXYGENATE		
☐ OXYGEN		
☑ BENZENE	0.0	3.8
☑ AROM	0.0	50.0
☑ OLEFINS	0.0	25.0
☐ VOC		

FIG. 2. Gasoline recipe for making M2 grade (87 AKI and 10-psi RVP).

TABLE 2. Gasoline final blend properties using linear and nonlinear equations

	Linear	Nonlinear
x AKI	87	87.25
x RVP	8.8	10

TABLE 3. Economics comparing M2-grade finished price (using nonlinear equations) vs. M2 grade finished price (using linear equations) and relative giveaway per batch, 100,000 bbl

Economics		
M2 grade, nonlinear	$/bbl	$70.87
M2 grade, Linear	$/bbl	$70.78
Giveaway, linear vs. nonlinear	$/bbl	$0.09
$ per batch	$	$9,000
$ per batch, 1 yr	$	$450,000

TABLE 4. Comparing linear, nonlinear and lab results

	Linear	Nonlinear	Lab
x AKI	87	87.25	87.2
x RVP	8.8	10	10.2

Comparing gasoline properties. The most important gasoline properties are ON and vapor pressure RVP. In this example, the focus is on these two properties.

For example, if the goal is to produce an M2 grade [an anti-knock index (AKI) of 87 and an RVP of 10 psi], **FIG. 2** shows the recipes and blend results. There are eight blend components with the recipes in bbl (barrels) and the volume fraction, inventory, prices and specs (M2). The goal is to make a finished M2 grade with an AKI of > 87 and a maximum RVP of 10 psi. If the blend results are compared using linear equations vs. nonlinear equations, the difference is shown in **TABLE 2.**

TABLE 2 indicates a discrepancy calculating the AKI and RVP (besides other nonlinear properties, the focus here is only on the main mentioned two properties) linearly or nonlinearly.

If the AKI and RVP are calculated nonlinearly, then the final values are 87.25 ON and the RVP is 10 psi; this means that while the 10 psi RVP is reached, a giveaway on the AKI exists. Conversely, if the AKI and RVP are calculated linearly, the final values are 87 ON and the RVP is 8.80 psi. This means the 87 ON for the AKI has been met, but there is a giveaway on the 8.8-psi RVP. This means that money is being left on the table for each batch.

TABLE 3 indicates some important observations. If the linearly calculated final gasoline blend AKI and RVP are considered, the result is sellable gasoline that is on-spec for the AKI (87) but shows a giveaway of 1.2 psi in RVP—the giveaway is the difference between the spec (i.e., 10 psi) and the calculated values (i.e., 8.80 psi). The selling price for this gasoline batch is $70.78/bbl. This appears to be ideal, as the gasoline producer, refinery or terminal has made a sellable gasoline with an ON of 87 but with a giveaway on vapor pressure.

However, if nonlinear equations are used to calculate AKI and RVP, the results are surprising:

- With nonlinear correlations, the final AKI is 87.25 and the final RVP is 10 psi
- The linear AKI is 87 ON and the RVP is 8.8 psi.

Comparing linear and nonlinear equations, the Delta AKI (linear AKI–nonlinear AKI) is a clear 0.25 ON giveaway, and the Delta RVP (linear RVP–nonlinear RVP) is 1.2 psi.

If gasoline is produced using the linear correlation, then the selling price is $70.78/bbl. If the nonlinear correlation is used, the selling price is $70.87/bbl. The price difference is $0.09/bbl. If the refinery produces 100,000 bpd, assuming the refinery operates for 50 weeks per year, this equals roughly $500,000/yr. The example refinery or oil storage blending terminal is losing $500,000/yr due to the linear/nonlinear issue. The focus in this case has been on one batch per day. Large refineries make more than one batch per day, and certainly more than 100,000 bpd.

This example shows the financial importance of the nonlinearity of gasoline blends in blending calculations.[3]

Properties calculation methods. The concept of linear and nonlinear blending are summarized here, underlining the main differences between the two.

The primary and easiest approach taken is the linear approximation, which clusters classes of molecules into "lumps" and can use the following volumetric equation (Eq. 1) to describe this behavior:

$$Q_b = Q1_1V_1 + Q_2V_2 + \ldots Q_iV_i \qquad (1)$$

where:

Q_b = Property of blend
Q_i = Property of component *i*
V_i = Volume fraction of component *i* in blend

The molecular interaction that the linear approach ignores must be considered. The nonlinear blending properties can be calculated using many methods, including:

- Linear approximation with bonuses (good results if bonuses are updated constantly)
- Blending values method
- Developing regressed equations using lab blend data
- Generic property models: Ethyl RT-70 or DuPont interactions to generate blending values.

Octane. Generally, the ON is one of the most important and valuable gasoline properties and is calculated using the Ethyl RT-70 equations. Those equations were developed in 1950, approximating lab results over wide blending recipes, using tens of thousands of US gasoline blends from many refineries.

Today, it is one of the most common methods to predict RON and MON. It is easy to use even in its "shrink-wrapped" form and does not require significant lab data, like the DuPont interaction or the regressed equation method.

The results in **TABLE 2** were analyzed with the RT-70 equation.

Vapor pressure. The other important gasoline blend property is RVP, because it is essential for using cheap butane in blends, and for complying with the EPA complex model.[4] For RVP, the equation that has been used for several years showing adequate accuracy is the Chevron Research index method equation.

The results in **TABLE 2** were analyzed with the Chevron equation.

Disputes. In case of dispute, proof can be determined in the lab. A certificate of analysis can resolve any doubts regarding the accuracy of a method. The good quality of the nonlinear correlation may be surprising. The results in **TABLE 4** show how the lab data are very close to the nonlinear correlation (within the reproducibility of the test method), answering whether the nonlinear equations must be used.

Takeaway. This paper has focused on the two major gasoline non-linear properties (RVP and ON). However, gasoline has more than 30 specs in addition to these two non-linear properties. For example, other non-linear properties to be taken into account are drivability index, TVL/20, and distillation temperatures (initial boiling point, T10-T50-T90 and final boiling point). Refineries and oil terminals must take the non-linearity into account by using blend optimizer software and not simple linear blend calculators to save money on software. With more than 9 MMbpd of US gasoline production, it is economically vital to consider the difference between linear and nonlinear property calculation results and understand the potential impact on profit or loss. Refineries and oil terminals must consider, at the minimum, using nonlinear calculations for octane and vapor pressure to minimize giveaway or being off-specification. HP

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