FCC gasoline desulphurisation for Tier 3 sulphur compliance

George Hoekstra *Hoekstra Trading LLC*

FCC gasoline desulphurisation is used widely in refineries around the world. It is growing in importance because of new regulations that require sulphur in gasoline to be reduced to 10 ppm. FCC gasoline is desulphurised in fixed bed hydrotreaters. Side reactions occur that cause octane loss. The key to the process is to remove the sulphur with minimum octane loss.

When designing and optimising these units, it is critical to know how much octane will be lost and how octane loss is affected by changes in gasoline feed quality, catalysts, process design, and process severity.

Hoekstra Trading has done three years of research on this process culminating in development of a new process model that makes modern octane analysis available to refining engineers for the first time, using modern chemical engineering tools and the most detailed data ever used for this purpose.

The model is being used today by refiners, technology suppliers, and catalyst suppliers to optimise feed, sulphur specifications, unit operations, and catalysts for this process; and to evaluate revamps, new unit investments, and Tier 3 gasoline sulphur strategies.

This paper describes how two refiners have used our data, methods, and software to help make decisions relating to their Tier 3 gasoline strategy.

Case 1 - Tier 3 gasoline sulfur credit strategy

This US refinery has an FCC gasoline desulphuriser with extra desulphurisation capacity. They qualify as a small refiner, and so are not required to make 10 ppm sulphur gasoline until 2020. But they are considering making sub-10 ppm sulphur gasoline now and banking Tier 3 sulphur credits for future sale to other refiners.

This strategy would involve increasing reactor severity and taking a penalty in octane loss today in exchange for revenue from future sale of Tier 3 credits. To evaluate this option, they needed reliable estimates of how much octane loss would occur in more severe operation on different feeds.

We analysed samples of the current feed and product using a detailed chemical analysis that identifies every compound in the gasoline. This detailed analysis is a cornerstone of our model. The data was run through Hoekstra Trading's software which analyses the individual reactions occurring in the unit, the octane impact of those reactions, the effects of feed composition

	Product			wt%	Feed			wt%
Segment of input table								
1	propane minus	3	P3	0.006	propane minus	3	P3	0.000
2	i-butane	4	I4	0.018	i-butane	4	I4	0.021
3	methanol	15	oxy	0.000	methanol	15	oxy	0.000
4	isobutylene	4	O4	0.021	isobutylene	4	O4	0.033
5	butene-1	4	O4	0.048	butene-1	4	O4	0.040
6	1,3-butadiene	4	O4	0.000	1,3-butadiene	4	O4	0.005
7	n-butane	4	P4	0.125	n-butane	4	P4	0.130
8	Vinyl acetylene	16	die	0.000	Vinyl acetylene	16	die	0.000
9	t-butene-2	4	O4	0.362	t-butene-2	4	O4	0.323
10	2,2-dimethylpropane	5	I5	0.004	2,2-dimethylpropane	5	I5	0.006
11	c-butene-2	4	O4	0.219	c-butene-2	4	O4	0.004
12	1,2-Butadiene	16	die	0.000	1,2-Butadiene	16	die	0.470
13	Ethanol	15	oxy	0.000	Ethanol	15	oxy	0.000

Table 1

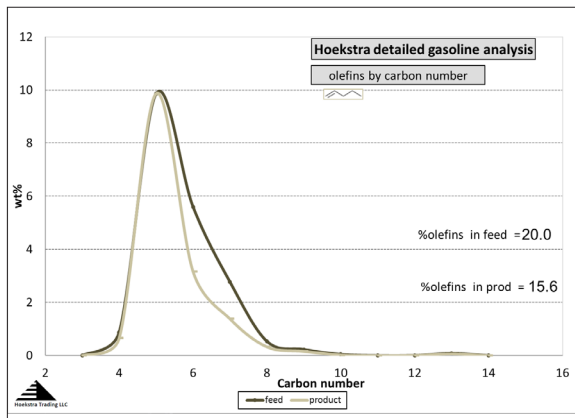**Figure 1** Olefin-by-carbon number distributions, Case 1

Figure 2 n-paraffin by carbon number distributions, Case 1

and process severity on process performance and octane loss.

Detailed feed composition – case 1

The feed to this gasoline desulphuriser contains 528 compounds, and the product contains 455 compounds. The data was fed into the input table of the Hoekstra Trading software. Table 1 shows a segment of the input table. This input table continues for 759 rows which is the total number of different compounds we have found in 70 gasolines we have analysed.

Reaction analysis – case 1

We are especially interested in olefins because olefin saturation is a major cause of octane loss.

On Figure 1, the black curve shows the olefin-by-carbon number distribution in the feed. The feed contains C_4-C_{10} olefins, mostly C_5s.
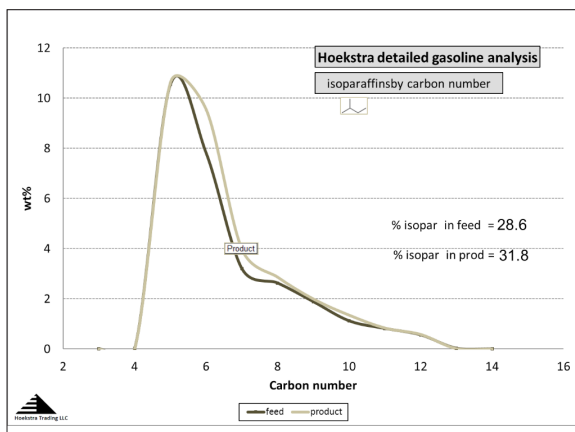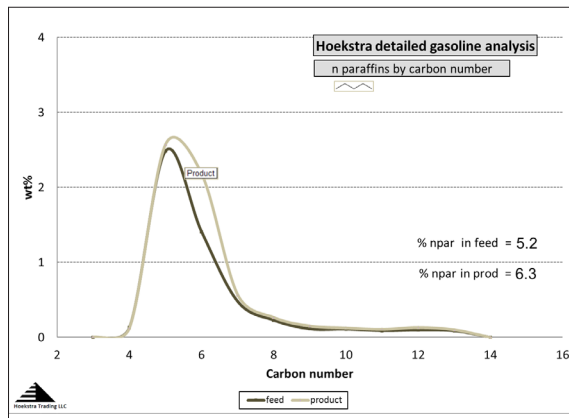

Figure 3 Isoparaffin-by-carbon number distributions Case 1

The tan curve is the olefin distribution in the product. Comparison of the two curves shows that no C_5- olefins have been converted in the unit. This is because C_5- olefins have been split out in an interstage splitter, bypassing the desulphurisation reactor. C_6, C_7, and C_8 olefins have been partly converted. The feed contains a total of 20 wt% olefins, and the product contains 15.6% olefins, so the total olefin saturation is 4.4 wt% on feed.

Octane impact – case 1

How much octane is lost by saturation of 4.4 wt% olefins? The answer depends strongly on which particular olefins are being saturated.

The saturation of linear olefins – produces normal paraffins, which are very low in octane. The extent of linear olefin conversion is seen by comparing the normal paraffin distribution curves of feed and product (Figure 2):

Comparison of the tan and black curves shows that normal paraffins are produced to the extent of 1.1 wt% on feed. It is mostly C_6 (n-hexane) that is being formed by saturation of linear C_6 olefins.

The saturation of iso-olefins – produces iso-paraffins, which are higher in octane than normal paraffins. The extent of these reactions is seen by comparing the feed and product iso-paraffin distributions (Figure 3):

We see iso-paraffins being produced across a wide range, C_6-C_{11}. The feed contains a total of 28.6% isoparaffins, and an additional 3.2 wt% has been produced, mostly by saturation of iso-olefins.

Similarly, we compared the distribution curves

for reaction of other compound groups which include cyclic olefins, naphthenes, aromatics, unknowns, oxygenates, and C_{14}+ hydrocarbons. All these charts are produced immediately in the Hoekstra software upon entering the feed analytical data.

Octane/sulphur performance curve – case 1

The software contains an octane model that calculates octane and octane loss from the detailed gasoline composition at the molecular level. Figure 4 summarises the factors that contributed to octane loss in this unit on the day the samples were taken:

Starting at the left, consumption of olefins caused 2.7 octane loss. Production of normal paraffins reduced octane another 0.6 RON. Those octane losses were partly offset by production of relatively high octane isoparaffins and naphthenes. Another 0.7 octane loss came from reactions involving higher molecular weight aromatics and unknowns (contrary to common perception, these reactions often contribute appreciably to octane changes in this process).

The total octane loss was 1.3 RON units, mostly due to saturation of linear C_6-olefins and dienes to form normal hexane.

The Hoekstra model then predicts the octane/sulphur performance curve for different scenarios based on feed composition, gasoline cut points, unit design, catalyst and process selectivity. The prediction is based on desulphurisation and olefin saturation rates and rates of other reactions that we have measured in pilot plant and commercial unit tests. Figure 5 shows the predicted octane/sulphur performance curve for Case 1, given the feed processed on the day of our test. The leftmost point on this curve shows that at 10 ppm sulphur, the predicted octane loss is 3 RON.

We compared this octane/sulphur performance curve to those for a wide range of cases from our pilot plant and commercial tests. By comparison with other units, this feed is easy to desulphurise. The olefin type distribution is favourable from the standpoint of minimising octane loss. The unit has excess kinetic capacity, and deep desulphurisation can be achieved at moderate temperature.
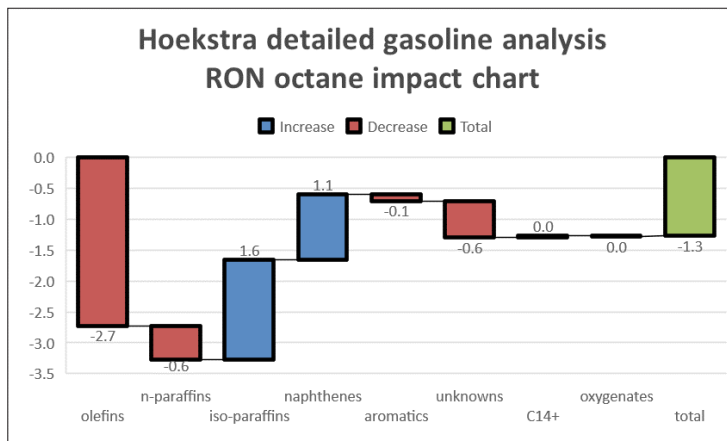

Figure 4 Octane impact chart, Case 1

We concluded the octane/sulphur performance capability of this unit is high compared to others in the United States, and that this refinery is well-positioned to make sub-10 ppm gasoline at relatively low incremental cost. This is a competitive advantage that can be exploited by generating and banking standard Tier 3 sulphur credits

Case 2 – Unit performance improvement options

This US refinery currently has higher octane loss on their gasoline desulphuriser than anticipated based on common industry expectations. We ran our detailed chemical analysis and performed the same analysis for this unit:

Reaction analysis – case 2

The olefins distribution chart (Figure 6) shows that this unit is saturating olefins across the full range from C_4 to C_9 olefins. The total feed olefins are 27.4 wt%, of which 8.1wt% are converted in the unit, leaving 19.3 wt% in the product.

Octane impact – case 2

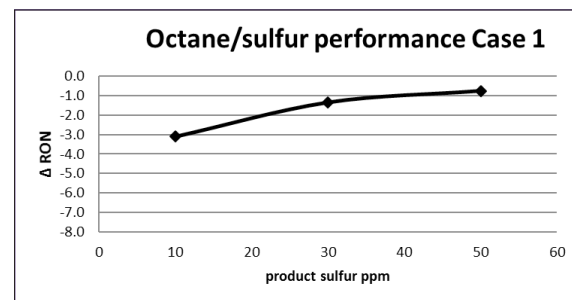Figure 7 shows the factors contributing to octane loss, which add to a total of 2.5 RON octane loss.

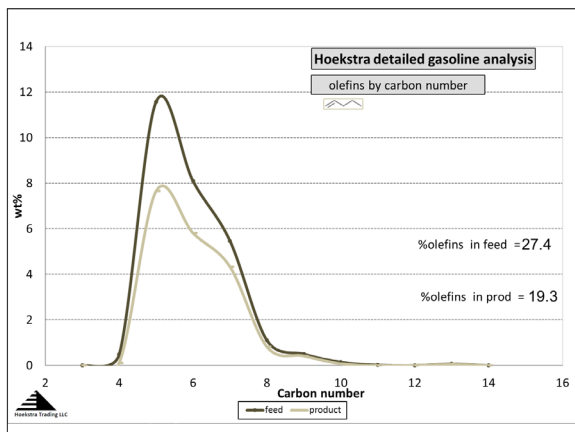**Figure 5** Octane/sulphur performance curve, Case 1

Figure 6 Olefins-by-carbon number distribution, Case 2

Octane/sulphur performance curve – case 2

Figure 8 shows the predicted the octane/sulphur performance curve for Case 2.

This refinery faces a larger octane penalty for making Tier 3 gasoline sulphur. The reasons are understood from our analysis. In a 3-week field test, the refinery confirmed octane loss above 6 RON when making 10 ppm sulphur gasoline.

Process improvement options – case 2

Our model is now being used to help analyse possible improvement options like end point cutting, addition of a splitter, improved catalysts, and a revamp that would deliver higher sulphur/octane selectivity for this refinery.

Figure 9 shows that octane loss for case 2, at 10 ppm sulphur, can be reduced from 6 to 5 RON by reducing the end point of the feed:

Figure 10 shows that this octane loss could be further reduced to 2 RON at 10 ppm sulphur by endpoint cutting combined with a split-
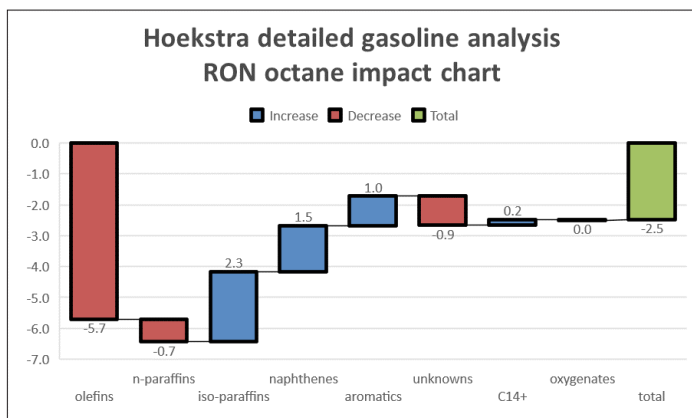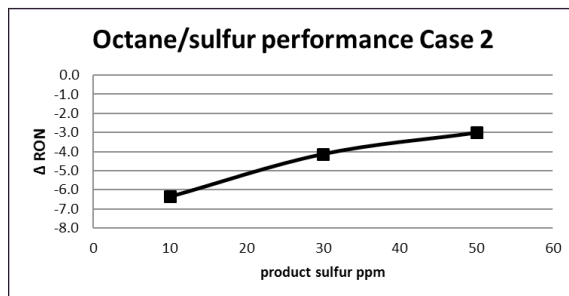

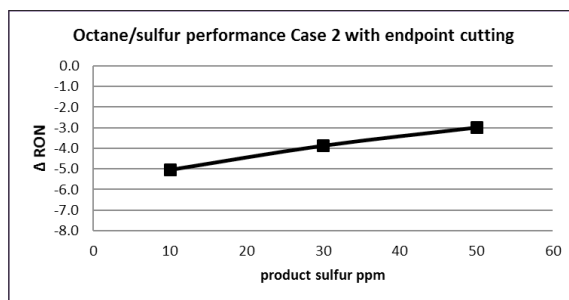**Figure 8** Octane/sulphur performance curve, Case 2

Figure 9 Octane/sulphur performance curve, Case 2 with endpoint cutting

ter, improved catalyst, and the high selectivity process.

Molecular-level accounting

The above presentation of our software's capability focused on hydrocarbon type distributions by carbon number. The calculations in the Hoekstra software actually work at the molecular level. The software tracks the extent of reactions affecting individual C_5-C_{12} olefins, paraffins, and naphthenes, and accounts for their impact on octane change.

For example, Table 2 summarises the accounting for reactions of individual C_6 linear olefins and dienes to form normal hexane.

The table shows that the feed contains eight different linear C_6 olefins in concentrations that sum to a total of 1.3 wt% on feed. Of this 1.3 wt%, we found 0.55 wt% remaining in the product, meaning that 0.75 wt% reacted to n-hexane. This balances with the increase in n-hexane concentration we found in the product.

Molecular level accounting means we calculate the effects of saturating different individual olefins which is critical for accurate octane calculation.

Figure 7 Octane impact chart, Case 2

All the above charts and tables, and many more, are produced immediately upon entering the analytical data into the Hoekstra software.

The Hoekstra software meets an industry-wide need

This is the first model of its kind available to the refining industry. Currently, refiners ask their process licensor to estimate octane loss for a proposed change, and accept the number they send. It often takes weeks to get one number.

Licensor publications contain generic octane vs. sulphur curves which have a lot of scatter, and are not site specific. That is the only technical basis for refiners to understand what is happening in their reactors. Refiners are left with no real awareness of the reactions happening or the true causes of octane loss in their gasoline desulphuriser.

The Hoekstra software provides the necessary data and tools

With detailed chemical analysis of feed and product, our software provides ability to see the specific reactions occurring in your unit and the causes of octane loss. You can easily adjust feed composition, end point, selectivity, process configuration, and splitter efficiency to see their effects on octane/sulphur performance.

Our software provides accurate estimates, much faster, and much easier than has been available before. It is a 21st century spreadsheet solution that allows decisions to be made based on a large database of pilot plant and commercial unit tests covering a wide range of industry operations. It is being used today by refiners, technology licensors, and catalyst suppliers to:

1. Analyse octane loss in commercial gasoline desulphurisers
2. Optimise gasoline desulphuriser performance
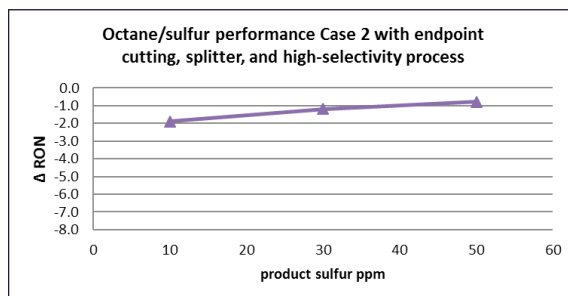3. Make process per-formance estimates for catalyst refills
4. Generate performance estimates for new units and revamps
5. Evaluate strategies for sulphur credit management
6. Develop LP model representations

It is available to anyone at a low, one-time cost through purchase of Hoekstra Trading's most recent report, Independent Catalyst Test Report 2016.

Figure 10 Octane/sulphur performance curve, Case 2 with endpoint cutting, splitter, and high selectivity process

LINKS

More articles from: Hoekstra Trading

More articles from the following categories:
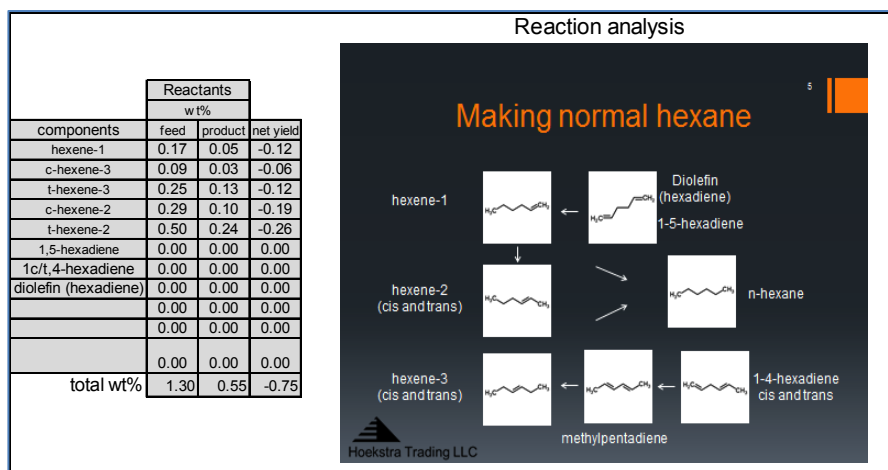Catalysts and Additives
Fluid Catalytic Cracking
Sulphur Removal and Recovery

Table 2 Molecular accounting for n-hexane precursors

	Reactants		
	wt%		
components	feed	product	net yield
hexene-1	0.17	0.05	-0.12
c-hexene-3	0.09	0.03	-0.06
t-hexene-3	0.25	0.13	-0.12
c-hexene-2	0.29	0.10	-0.19
t-hexene-2	0.50	0.24	-0.26
1,5-hexadiene	0.00	0.00	0.00
1c/t,4-hexadiene	0.00	0.00	0.00
diolefin (hexadiene)	0.00	0.00	0.00
	0.00	0.00	0.00
	0.00	0.00	0.00
	0.00	0.00	0.00
total wt%	1.30	0.55	-0.75