BENZENE REDUCTION USING OCTGAIN® - A NEW WAY TO MEET RFG SPECIFICATIONS

P. P. Durand, N. A. Collins, R. Hu, J. C. Trewella and T. L. Hilbert
Mobil Technology Company, PO Box 480, Paulsboro NJ 08066-0480

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Introduction

Phase II reformulated gasoline specifications in the U.S. requires refiners to reduce the sulfur, olefins and benzene content of gasoline. Conventional solutions for sulfur reduction such as FCC feed hydrotreating or gasoline hydrofinishing require a large capital investment or lead to a large loss in octane. Mobil's OCTGAIN® process lowers FCC gasoline sulfur and olefin content without a high capital investment and without a loss in octane[1]. This same process can also be used for benzene reduction. Cofeeding a benzene rich reformate fraction to the OCTGAIN process leads to benzene conversions of up to 47%. Depending on the feedstock, there may also be an octane boost of 1.5 numbers for processing heart-cut reformate.

Experimental - feeds

The feedstocks for the study were four different FCC naphthas with different boiling ranges and two heart-cut reformates. The properties are given in Table 1. The octane of the reformates are low despite their high benzene content (39 and 24 wt%) because they also contain significant amounts of low octane n-hexane (24.8 research octane number, 26 motor octane number) and isohexanes (73.4 RON, 73.5 MON). The properties of the different blends were also measured, and these are reported in Table 2.

Experimental - Pilot plant setup

The experiments were conducted in a continuous, fixed-bed pilot plant. Hydrogen flow was once through and liquid feeds were downflow. Pressure was maintained on the system by a high pressure separator with a back-pressure regulator on the gas side and a liquid level control valve. Gases were metered using a wet-test flowmeter, and then sampled by on-line GC. The liquid product was weighed, chilled and sent for octane and composition analysis. All octanes reported in this work are based on full engine tests. Octanes were corrected by subtracting on a volumetric basis the octane of C4- material in the liquid sample, and adding in the contributions of any C5+ material that was found in the offgas. Similarly the C5+ yields are corrected to include any C5+ material in the offgas. Mass closures were typically in the range 97-103 wt%.

Experiments were conducted at typical OCTGAIN process conditions with the OCT-100 catalyst system. The next generation of the catalyst system [2] is expected to show similar benzene reduction performance. Benzene content was measured by GC FTIR or PIONA.

Results - Benzene content

As shown in Figure 1, up to 47% benzene conversion was obtained depending on the feedstock and the temperature of the catalyst system. Benzene is removed by alkylation, but there is also benzene formation by dealkylation of alkylbenzenes. As the temperature of the catalyst system increases, both of these rates increase. When reformate is present benzene alkylation dominates. At sufficiently severe conditions there is also some dehydrogenation of naphthenes, providing an additional route for benzene formation. This is particularly true as pressure is reduced, shifting the equilibrium towards the aromatic species.

The compositional changes that are occurring are shown in Figure 2 as a function of benzene conversion for the two lightest FCC blends. The separation between the curves gives the relative amounts of the different components. As benzene conversion increases, there is initially a reduction in C_7-C_{10} aromatics due to hydrogenation. As severity is increased, aromatics in this boiling range increase due to the desired alkylation of benzene. The technology also gives a dramatic reduction in olefin content. Sulfur removal is not shown in this plot, but is also essentially complete (i.e. > 95 wt%), even at modest benzene conversion levels. At the highest benzene conversion levels there is a yield loss caused by formation of light hydrocarbons, labeled offgas HC in Figure 2. The composition by weight of the light hydrocarbons is typically 2-7% C_1 and C_2, 30-40% C_3, 5-15% mixed C_3 and C_4 olefins, 25-30% iC_4, 25-30% nC_4. Without the presence of reformate, dealkylation of heavy aromatics causes an increase in feed benzene content, the extent of the increase being feed dependent.

The feed benzene content is an important variable affecting overall benzene conversions. The higher the feed benzene content, the higher the conversion. Figure 3 shows the benzene conversion as a function of catalyst temperature for the 215°F+ FCC naphtha feed on its own and in the two blends with reformate. Clearly there is benzene formation for the 215°F+ FCC feed when processed on its own. Note that we have also observed benzene formation in hydroprocessing of FCC gasoline[3]. The feed with 4 wt% benzene shows little benzene conversion, while there is appreciable conversion for the feed with 6.9 wt% benzene. These results suggest that an equilibrium is established between benzene formation by dealkylation of heavy aromatics and benzene removal, which occurs primarily by alkylation of benzene. Higher feed alkylaromatics will thus be more detrimental to high benzene conversions. This is a function of FCC operation and naphtha end point.

Reducing pressure from 600 to 300 psig causes increased benzene formation by aromatization of cycloparaffins, and so benzene conversion is lower. Consider Table 3 below:

Table 3: Effect of pressure on benzene conversion in OCTGAIN™

Pressure	300 psig	600 psig
C5+ Road Octane	91.2	89.6
Cycloparaffins in product, wt% of total feed	8.9	11.2
Benzene Conversion, wt%	26.1 %	33.1 %

Feed: 215°F+ FCC naphtha, with 2.14:1 v/v FCC naphtha, reformate 2
The same temperature was used for each experiment

The shifts in benzene and other aromatics are driven by thermodynamic equilibrium. Reducing pressure and increasing temperature shifts the hydrogenation / dehydrogenation equilibrium towards aromatics formation. The higher aromatics level at lower pressure also contributes to the improved octane. Note that in each case the product octane is significantly greater than 85.6 which is the feed road octane.

Results - Yield and Octane

By cofeeding reformate, a substantial yield-octane improvement over conventional OCTGAIN was obtained. Figure 4 shows the C5+ yield plotted versus road octane (product - feed). The solid line is the yield versus octane curve for the blend of FCC naphtha and reformate. The yield at 86 octane is slightly above 100% due to a volume expansion over the OCTGAIN catalyst system. A similar yield-octane curve was measured for the FCC naphtha on its own. The dashed line represents what would be achieved if the refiner chose to blend reformate with the OCTGAIN product from processing FCC naphtha on its own. The curve is calculated from volumetrically blending reformate yield and octane (100%, 76.2 road) and FCC naphtha yield and octane (measured in a pilot plant run) in a 1:2 v/v proportion. The data in Figure 4 show a clear improvement when reformate is cofed to the OCTGAIN unit with the FCC naphtha. In particular, at 98 vol% C5+ yield, there is an octane benefit of 1.5 road numbers. We believe that the benefit is due to improved octane uplift for the heart-cut reformate cofeed.

Conclusions/Summary

Benzene conversions as high as 47% were obtained when coprocessing heart-cut reformate with FCC naphthas over the OCTGAIN catalyst system. A road octane benefit of about 1 number at 99 vol% C5+ yield was also observed from cofeeding reformate. This octane benefit may result in an even higher defacto benzene reduction via reoptimization of reformer severity. These results highlight the versatility of the OCTGAIN process in helping refiners meet their RFG needs.

The process with reformate cofeed retains all the other advantages of OCTGAIN. We continue to exploit the unique chemistry of the process, which allows us to have deep desulfurization of the gasoline and a high level of saturation of olefins while retaining a high product octane. This is in contrast to conventional hydrotreating or mild hydrofinishing of FCC gasoline at high LHSV. The economic evaluation of the OCTGAIN process [4] looks attractive, even when the benzene reduction capabilities of the process are not comprehended. With this additional benefit, the technology offers refiners a powerful new tool for manufacture of RFG.

References:

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Table 1 : Feed Properties

Feed	Heavy FCC Naphtha	215+ FCC Naphtha	230+ FCC Naphtha	Full-Range FCC naphtha	Reformate 1	Reformate 2
Research Octane	96.4	95.5	93.0	93.3	78.5	74.8
Motor Octane	84.0	83.8	81.5	81.1	73.8	71.8
API	22.8	34.6	41.1	46.3	61.0	67.9
Bromine Number	10.4	17.8	37.1	59.9	5.2	4.9
Sulfur, wt%	1.90	1.00	0.2	0.11		
Nitrogen, ppmw	180	76	98	52		
Distillation (D86), F						
IBP	194	215	232	107		
5 %	382		256	134	150	
10%	394	267	261	146	151	
20%	408		269	165		
40%	427		289	209		
50%	435	319	303	237	157	
60%	443		318	265		
80%	462		352	325		
90%	476	443	373	357	172	
95%	488		387	377	179	
EP	511	491	401	395		
Composition, wt%						
Isopentane					1	0.5
n-Pentane					1.6	1.7
Cyclopentane					1.8	2.4
Benzene	0.1	0.2	0.2	0.9	39.3	24.0
C6 Isoparaffins					28.6	39.9
n-Hexane					14.4	16.6
C6 Naphthenes					1.4	1.3
Toluene					2.3	0.7
C7 Isoparaffins					8.5	9.8
n-Heptane					0.9	1.1
C7 Naphthenes					0.3	0

Table 2: Properties of the blends (Measured, not calculated)

FCC Feed	Heavy Naphtha	230+ Naphtha	Full Range	215+ Naph	215+ Naph
Reformate Feed	Ref 1	Ref 1	Ref 1	Ref 2	Ref 2
FCC/Reformate ratio, vol/vol	2/1	3/1	5/1	2.14/1	4.28/1
Research Octane	91.2	90.9	91.9	90.8	93.4
Motor Octane	80.8	80.6	80.5	80.3	81.5
API	32.9	45.7	56.4	43.9	40.0
Bromine Number	12.7	36.3	56.1		
Sulfur, wt%	1.5	0.14	0.11	0.72	0.84
Nitrogen, ppmw	130	71	47	55	64
Distillation (D86), F					
IBP	141	156	106		
5 %	166	190	135		
10%	177	199	143		
20%	197	212	154		
40%	386	253	180		
50%	418	276	197		
60%	425	298	221		
80%	452	338	303		
90%	469	366	345		
95%	494	382	368		
EP	510	398	411		
Benzene, wt%	10.4	9.2	8.3	6.9	4.1

Figure 1

Heart Cut Reformate Cofeed in Octgain
Benzene Conversion Increases with Temperature

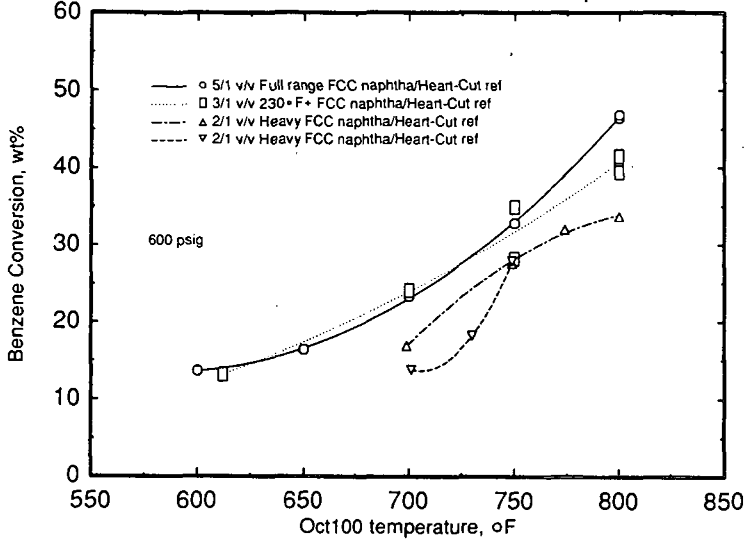

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Figure 2

Heart Cut Reformate Cofeed in Octgain®

GC Analyses of Raw Liquid Product

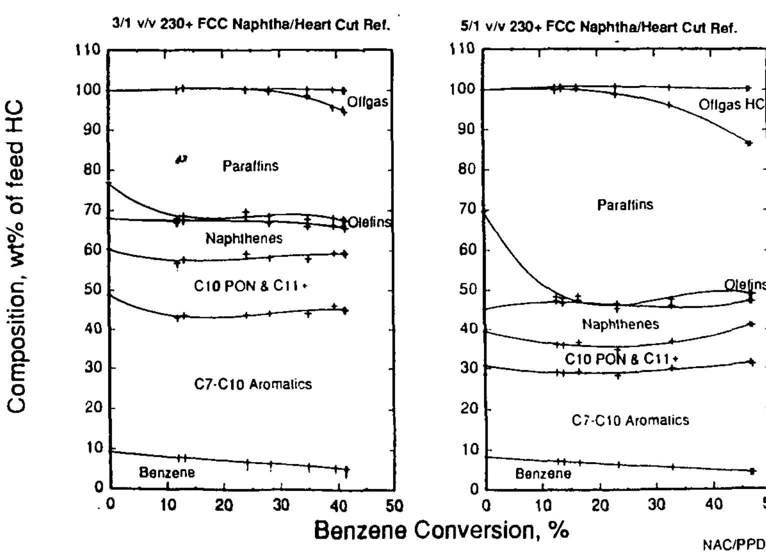

Figure 3

Effect of Feed Benzene Content

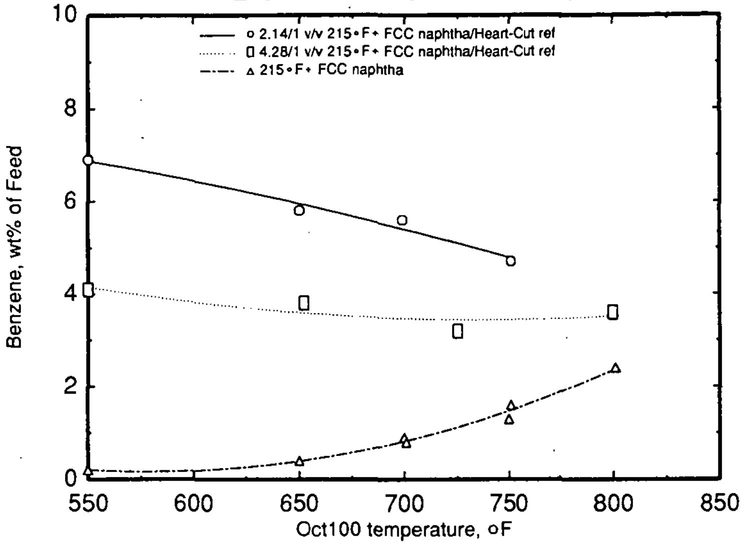

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Figure 4

Yield-Octane benefit
Heavy FCC naphtha with Reformate co-feed