## Question 46: Ethanol blending, and benzene management has shifted refinery octane and hydrogen balances. How are you managing hydrogen demand without giving away octane? Conversely, how are you, with excess hydrogen, maximizing availability for volume swell?

**Praveen Gunaseelan** (Vantage Point Consulting)

Mandated ethanol blending and limits on benzene in gasoline tend to lower the ceiling on the operating severity of catalytic reformers. While lower severity operation is theoretically desirable, in practice it can constrain H2 production, and impact regenerator operation due to lower coke make, which may require operational workarounds.

In instances where reformer derived H2 is a critical feed to other refinery units, the reduced reformer H2 make could be compensated from other sources, such as the refinery H2 plant (if present), pipeline H2 (if available), or installing an adsorption unit to recover H2 from refinery off gases. If these options are not feasible, and the reformer needs to be operated at high severity to meet refinery H2 needs, some octane giveaway may be an economical most favorable alternative.

**Brad Palmer** (ConocoPhillips)

In general, the lower demand for octane has cut Reformer severity which has increased C5+ yields, reduced coke make (increased catalyst stability and run life) and reduced hydrogen yields. For refineries with the flexibility of alternate hydrogen sources (pipelines or SMRs), the lower Reformer hydrogen yields has not been as difficult to manage; the hydrogen load on these alternative sources has been increased. For refineries with tight hydrogen supplies, this regulation, combined with the new reduced benzene requirements, has required the addition of hydrogen recovery projects and/or SMR revamps to meet hydrogen demand. Octane giveaway has been one of the knobs to optimize refinery economics.

Each refinery operates an LP model to determine the economic optimum given current constraints. In some cases, giving away octane has been an economic decision. Refineries have continued to make changes to reduce octane giveaway if economic to do so; changes have included blending more sweet naphtha and selling blend components on the market.

Most refineries are using hydrogen to meet the desulfurization and benzene saturation demands, but some refineries are operating FCC feed hydrotreaters more severely than required to maximize swell of cat feed. Again, the LP model is used to determine the most economic strategies for each refinery.

**Roberto Amadei** (Chemical & Energy Development srl)

1. Question 46 first point: How are you managing hydrogen demand without giving away octane? By carrying out a technology of ours it is possible, besides very hugely profitable, increasing by an important quantity the catalytic reforming hydrogen production.

As for the quantity: the gained catalytic reforming hydrogen production - net of isomerization use increase - is estimated to be comprised between around 28 and over 48 percent on catalytic reforming current hydrogen production, without any octane give-away.

In fact: when removing all or nearly all of the C6 molecules (shifting them to the isomerization process) from the catalytic reforming feed - as our technology does - it is experimentally proven, in 2 the refinery, that the catalytic reforming hydrogen production yield increases much, as indicated above, and this is in agreement with the theory in that the reforming feed quality, after the C6 removal, becomes much more favorable to the reforming dehydrogenation reactions, hydrogen producing, and much less favorable to the reforming hydrocracking reactions, hydrogen consuming.

The theory, somewhat deepened, can also give an idea of the hydrogen gain size. We show it in the following paragraphs a. and b.

a. Catalytic reforming reformate octane

Let’s start considering the aromatization catalytic reforming reactions:

1 naphthene = 1 aromatic + 3 $H_2$ – 48-55 Mcal / kmol (1)

1 paraffin = 1 aromatic + 4 $H_2$ – 60-65 Mcal / kmol (2)

As it is of common knowledge, the ? octane [C8+ aromatics – C8+ (naphthenes + paraffins)] is much higher (around 4 times) in comparison with the [C6 aromatics – C6 naphthenes] one1. The heat absorbed in the catalytic reforming by a one molecule aromatization reaction, generating one aromatic molecule, is, as the above well-known reactions show, roughly speaking about same independently from the carbon atoms number contained in that molecule. Hence: with about the same heat absorption, the C8+ gets a ? octane, from the aromatization of one molecule, about 4 times higher than the C6.

That is, with reference, as said, to one molecule: with about the same heat absorption, the C8+ gets a ? octane 4 times higher than the C6 for a gasoline quantity as an average about 40% higher (because the relevant gasoline quantity, exactly the weight quantity, approximately the volume one, is proportional to the molecular weight). 1 As it is well known the C6 paraffins, passing through the catalytic reforming, do not practically increase their octane number. In fact, the C6 paraffins either crack or pass unconverted (exception made for a quota of the normal hexane, having a RON of about 25, pacifically established in a 10% maximum). The hydrocarbons C6, C7, C8, C9, etc. compete with one another in order to make use of the available heat. When the C6 is present it provides a modest octane increase by making use of a heat portion subtracted from the C7+ availability. When the C6 is present in order to increase the available heat, the only option is to increase the temperature.

When, on the contrary, the C6 is removed automatically the reformate octane increases due to the strong octane upgrading become available for the C7+, particularly strong for the C8+, thanks just to the C6 absence: the C6 presence appears to be very harmful for the catalytic reforming performance.

The highest boiling hydrocarbon among all the C6 is cyclohexane, which has in the reforming a fair conversion rate (although lower than the C7+ naphthenes), but unfortunately with a relatively very modest octane increase potential. As a consequence it appears mandatory taking off the reforming feed as much C6 as it is possible. The more C6 is removed the better the reforming performance and the refinery economy.

The above theory that applies to any crude oil and to any refinery configuration is in agreement with the surprising refinery experimental results.

The conclusion is that the process variables being equal and being also equal the catalytic bed temperature and consequently the catalyst life, the reformate octane number increases much: in order to keep it constant it is mandatory decreasing much the catalytic bed temperature.

b. Catalytic reforming hydrogen production

The hydrocracking reactions are rather slow, and are very sensitive to temperature, hydrocracking rates decreasing rapidly with decreasing temperature. Hence, as a consequence of the C6 removal, the reformate octane being equal, the hydrocracking reactions, consuming hydrogen, decrease much - due to the much lower temperature - and much increases the hydrogen production.

But there are other important causes of the net catalytic reforming hydrogen production increase, among which the higher favorableness - that we will not discuss here - for the paraffin aromatization vs. the napthene one. The one paraffin molecule aromatization, as we can see from the (1) and (2) reactions above, produces 4/3 times more hydrogen, or 33% more, than the one naphthene molecule aromatization.

We are fully available for providing details and projects.

2. Question 46 second point: How are you, with excess hydrogen, maximizing availability for volume swell?

The maximum gasoline volume is obtained, in any situation, including the excess hydrogen case, by carrying out the above technology. The relevant gasoline volume gain is higher than 4 %vol on the reformate + isomerate part of the gasoline.

The reasons backing these experimental results, besides paragraph a. above, are the good C6 isomerate octane plus the C6 isomerate yield much higher and the C6 isomerate density much lower than the reformate ones.

As a general information about the technology, worth a few dozen million $ profit per refinery / year, we can yet say that its effects are all positive and, on top of the above, we mention:

- the strong gasoline octane number gain (changeable at will into an additional strong gasoline yield gain),

- the prevention of benzene formation in the refinery,

- the accomplishment with margin of the 0.62 %vol average benzene content USEPA requirement for the whole gasoline pool, resulting in saleable benzene requirement credits,

- the huge energy savings, besides the hydrogen availability gain one,

- the reduction of all the pollutants and greenhouse gas types of emissions, on top of the above, both in the gasoline production and consumption segments,

- the higher-octane gasoline production capacity increase,

- the improvement of the engine operation and maintenance.

As for the above point, we are fully available for providing details and projects.

**Erik Myers** (Valero)

Valero Reforming units are operating at minimum pressure and minimum chloride levels to maximize liquid volume yield for our low severity gasoline operations. Additionally, it is important to maintain continuous regenerator operation to achieve optimum yields. Modifying the regenerators for maximum coke turndown is important. On/Off catalyst circulation is preferred to circulating coked up catalyst when the regenerator is down. We also believe the key to optimum yields is replacing catalyst when economic, not based strictly on surface area.

Refineries with excess octane simply blend low octane naphtha to reduce gasoline octane give away.

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