

GASOLINE PROCESSES Q&A

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GASOLINE PROCESSES Q&A SESSION

Isomerization

Question 36: What changes have you made to the C5/C6 isomerization unit to comply with the new benzene regulations? What changes have you made to the refinery operation? And, what have been your challenges and successes of implementing the new configuration?

ROBERTO AMADEI (Chemical & Energy Development srl)

We are very pleased to announce that our technology, “Process for Gasolines Production” – U.S. Patent #6207040 – “works very well,” as Mr. Le-Coz said. On the other hand, we never doubted it. Simply put, this technology provides many great advantages – economic, environmental, etc. – by shifting nearly all of the C6 hydrocarbons from catalytic reforming to isomerization. I want you to know that it is possible to obtain a license to use this technology. When you have the license, we will give you all of the information about our technology. However, right now we can tell everyone some good news: Our technology, far from being a good “Band-Aid” for treating the economic wound from the 0.62 vol% benzene standard, is an incomparable resource that produces several dozen million dollars per refinery each year and transforms gasoline into a bright future fuel (the “advanced fuel”).

I will also say that each year, our technology is worth, for instance, for a small refinery, \$50 million, plus a huge environmental improvement, plus a huge climate change mitigation contribution, plus the energy savings and improved engine management. The refiners who carry out our technology will not only gain all of the above, but they will also avoid the penalties incurred through the operation of special 0.62 benzene standard compliance methods (economic, environmental, and climate change-related penalties).

In order to clarify the point of the special methods that get a low gasoline benzene content, I can say that the so-called catalytic reforming post-fractionation obviously loses the great economic, environmental, climatic, and other gains provided by our technology. On top of these losses, such post-fractionation pollutes the air, water, and soil of the refinery area due to the formation of benzene, whose subsequent conversion does not mitigate either leakages from pumps and flanges or common operational procedures like draining, venting, or sampling.

Use of C5/C6 Isomerization/Catalytic Reforming for the “Advanced Fuel” Technology

- The technology, shifting nearly all the C6s from cat reforming to isom, while complying with the new benzene regulation, provides:
 - Several dozen million dollars per refinery each year,
 - huge improvements of environment, climate change mitigation and vehicles engine management, and
 - big energy savings.
- Moreover, the technology avoids the heavy economic, environmental, and climate change– related penalties entailed by the operation of special new benzene regulation compliance methods, like reformate post-fractionation or benzene extraction.

Furthermore, such post-fractionation also means choosing to process a naphtha fraction in the catalytic reforming instead of the isomerization. This means choosing to consume much more fuel, and then being compelled to re-process, with a second fuel consumption amount, the relevant product in order to convert it. Such post-fractionation causes the consumption of an extra-large amount of fuel, resulting in the loss of money and the generation of greenhouse gases and pollution. This is all due to the double process of making and unmaking the benzene. Moreover, this operation implies losing, on top of the lost octane gain our technology offers, other octane through the mandatory subsequent produced benzene saturation. I will not list here the economic and environmental penalties related to the isomerization or benzene saturation operations following such post-fractionation.

Another special method operated in order to get a low gasoline benzene content is the chemical grade benzene extraction. This method, carried out as a remedy adopted with the only purpose of complying with the benzene imposed specification, is comprised in the broad category of the post-fractionation. As a post-fractionation process, benzene extraction obviously loses all of the gains provided by our technology and incurs, in the post-fractionation, the aforementioned penalties. In addition, the investment capital expenditure of the chemical-grade benzene extraction is many times higher than the one entailed by our technology; while on its side, the actual cash-in per year of such investment, even when expecting to sell this benzene at a (not real) price double that of gasoline, is much lower than the actual cash-in of our technology. The actual economic gain of the refiners who choose our technology, as in our small refinery example, is much higher than \$50 million.

Reforming

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?

ROBERTO AMADEI (Chemical & Energy Development srl)

I want to mention an affirmation written in the *Answer Book* that the new reduced benzene specifications require additional hydrogen. According to our company, the reduced benzene specifications can, and do, require additional hydrogen only when carrying out methods different from our technology. In fact, according to our technology, as we said in the *Answer Book* response, if nearly zero C6 hydrocarbons are sent to catalytic reforming, the C6s being shifted, then the reforming hydrogen net production not only does not decrease, but it increases a lot. In this way, the refinery hydrogen net requirement decreases a lot while the refinery complies with the benzene specification.

Interaction of “Advanced Fuel” Technology with Hydrogen Production / Demand

- The technology, while complying with the new benzene regulation, significantly increases the cat reforming hydrogen net production and significantly decreases the refinery hydrogen net requirement.
- The more C6 removed from cat reforming feed, the better the reforming performance and refinery economics.

“Advanced Fuel” Technology Details, Intertwined with Hydrogen Production

- The technology not only provides refiners with paramount money gain, but it also results, by far, in the best quality fuel from the environmental, climate change, and technical points of view.
- Amid all of the plusses, the technology carries out a gasoline volume gain higher than 4 vol% on the reformate+isomerate part of the gasoline.

Question 46: Answer Book Responses

ROBERTO AMADEI (Chemical & Energy Development srl)

The first part of Question 46 asks how we manage hydrogen demand without giving away octane. By carrying out a technology of ours, it is possible, and also hugely profitable, to obtain an important increase of the catalytic reforming hydrogen production.

As for the quantity, the gained catalytic reforming hydrogen production (net of isomerization use increase) is estimated to be in the range of from around 28% to over 48% on catalytic reforming current hydrogen production, without any octane giveaway. 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 the refinery, that the catalytic reforming hydrogen production yield increases a lot, as indicated above. This is in agreement with the theory that the reforming feed quality, after the C6 removal, becomes much more favorable to the reforming dehydrogenation reactions/hydrogen production and much less favorable to the reforming hydrocracking reactions/hydrogen consumption.

By carefully examining what happens, we also have an idea of the size of the hydrogen gain. For clarity, we divide this analysis into two steps. The first step concerns the Catalytic Reforming Reformate Octane. Let's start considering the aromatization catalytic reforming reactions:

1) 1 naphthene = 1 aromatic + 3 H₂ – 48-55 Mcal/kmol (million calories per thousand moles)

2) 1 paraffin = 1 aromatic + 4 H₂ – 60-65 Mcal/kmol

It is common knowledge that the delta octane [C8+ aromatics – C8+ (naphthenes + paraffins)] is much higher (around four times) in comparison with the [C6 aromatics – C6 naphthenes] one. By the way, the C6 paraffins cannot be considered because, as is well known, the C6 paraffins that pass through the catalytic reforming do not practically increase their octane number. In fact, the C6 paraffins either crack or pass through unconverted (although an exception is made for a quota of the normal hexane, having a RON of about 25, established in a 10% maximum).

The heat absorbed in the catalytic reforming by the aromatization reaction of one molecule generating one aromatic molecule is, as shown above, roughly speaking about the same, irrespective of the molecule carbon atoms number. This means that with about the same heat absorption, the C8+ gets a delta octane, from the aromatization of one molecule, about four times higher than the C6.

Regarding one molecule, with approximately the same heat absorption, the C8+ gets a delta octane four times higher than the C6 for a gasoline quantity, an average of about 40% higher (because the relevant gasoline weight is exactly proportional to the molecular weight, while the relevant gasoline volume is approximately proportional to it).

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.

On the contrary, when the C6 is removed, the reformat octane automatically increases due to the strong octane upgrading that has become available for the C7+ (and which is particularly strong for the C8+) thanks simply to the absence of C6. The presence of C6 appears to be very harmful for the catalytic reforming performance.

The highest boiling hydrocarbon among all of the C6s is cyclohexane, which, in reforming, has a fair conversion rate (although lower than the C7+ naphthenes) but a relatively very modest potential for octane increase. As a consequence, it appears mandatory to take out as much C6 as possible from the reforming feed: the more C6 that is removed, the better the reforming performance and refinery economics. The above theory applies to any crude oil and any refinery configuration and confirms the surprising refinery experimental results.

The first step conclusion is that, process variables being equal, as well as the catalytic bed temperature and consequently the catalyst life being equal, the C6 hydrocarbons removal significantly increases the reformat octane number. In order to keep the reformat octane number constant, it is mandatory to significantly decrease the catalytic bed temperature.

The second step addresses the Catalytic Reforming Hydrogen Production. There are a few phenomenon that have to be examined. First, as we have seen above, when the C6 is removed from the catalytic reforming process, the reformat octane number increases a lot, which means that there is a large decrease in the catalytic bed temperature necessary to obtain a determined reformat octane number.

We will now speak about the hydrocracking reactions with the premise that the hydrocracking reactions categories include the dealkylation reactions. The hydrocracking reactions are rather slow and very sensitive to temperature; hydrocracking rates decreasing rapidly as temperature decreases. Thus, with the reformate octane being equal, as soon as the C₆s are removed from the catalytic reforming process, hydrocracking sharply decreases. As a result, the following main qualitative consequences arise, all favoring a catalytic reforming net hydrogen production increase:

1. A quantity of hydrogen molecules are saved and not consumed, the proportion of saved hydrogen molecules being one molecule per each hydrocarbon molecule not cracking anymore. This means that the catalytic reforming hydrogen production increases by one molecule per each molecule not cracking anymore.
2. The paraffins hydrocracking contribution to reformate octane decrease causes a compensating aromatization increase, implying a further hydrogen production increase.
3. The paraffins and naphthenes hydrocracking decrease favors the paraffins and naphthenes dehydrogenation reactions and produces hydrogen.
4. By dealkylation the heavier aromatics are converted into light aromatics such as toluene and xylenes. As C₇ and C₈ paraffins are unfavored for conversion to aromatics, dealkylation has an unfavorable effect on these light paraffins aromatization; hence, a dealkylation decrease favors the aromatizing dehydrocyclization reactions, producing much hydrogen.

Secondly, reformate octane being equal, the C₆ naphthenes aromatization is for the great majority replaced by the C₇₊ paraffins aromatization rather than by the C₇₊ naphthenes one. The reason for this is that at the stage where C₆ is present, the C₇₊ naphthenes concentration in the reformate is low while the C₇₊ paraffins one is high. As the reaction rate depends on the concentration of the reactants, when the catalytic reforming reactions equilibrium is broken by the C₆ removal, the C₇₊ paraffins are more likely to aromatize than the C₇₊ naphthenes. As we see from above reactions (1) and (2), the one molecule paraffin aromatization yields four-thirds more hydrogen, or 33% more, than the one molecule naphthene aromatization.

The catalytic reforming experimental hydrogen production results were found through proper refinery runs data normalized in order to bring them to constant process variables. Moreover, we took into account the necessity of compensating the lower isomerate octane by retaining a minor quota of the reformate octane gain obtained and the shifted C₆ isomerization hydrogen use (we deem the word “use” more proper than “consumption”).

We projected a hydrogen production gain, net of isomerization use increase, in the approximate range from 28% (no reforming feed rate replenishment with “good” quality – nearly exempt from C₆ – feed) to 48% (full reforming feed rate replenishment with “good” quality feed) on base reforming throughput, without any octane giveaway. It is possible to go over a 48% gain through the installation of additional catalytic reforming and isomerization capacities. This option is something that could be evaluated if we consider that the current crude oil quality trend towards a heavier and sourer quality, as much as the one towards better quality products, requires a bigger and increasing hydrogen addition (also keeping in mind that the on-purpose hydrogen production processes consume enormous energy quantities). The consideration is also suitable that the advanced fuel our technology produces not only provides refiners with paramount money gain, but it also results, by far, in the best quality fuel from the environmental,

climate change, and technical points of view. This is also in comparison with diesel fuel. We are fully available to provide further details and projects.

The second part of Question 46 asks how we maximize the availability for volume swell with excess hydrogen. 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 reformat+isomerase part of the gasoline. This is supported by the good C6 isomerase octane plus the C6 isomerase weight yield being very much higher, and the C6 isomerase density being very much lower than the reformat weight yield and density.

As general information about the technology, which is worth several dozen million profit dollars per refinery per year, we can still say that its effects are all positive. Some further specific results, in addition to the hydrogen and gasoline yield gains, are the:

- strong gasoline octane number gain (changeable at will into an additional strong gasoline yield gain),
- prevention of benzene formation in the refinery,
- accomplishment with a margin of the 0.62 vol% average benzene content USEPA (United States Environmental Protection Agency) requirement for the whole gasoline pool, resulting in saleable benzene requirement credits,
- huge energy savings, besides the hydrogen availability gain one,
- emissions reduction of all of the pollutants and greenhouse gases types, in addition to the above, both in the gasoline production and consumption segments,
- higher octane gasoline production capacity increase, and
- improvement of the engine operation and maintenance.

We are fully available to provide further details and projects with regard to this point.