

# Improved hydrogen yield in catalytic reforming

A process step that sends higher-boiling C<sub>6</sub> hydrocarbons to light tops isomerisation delivers an increase in hydrogen production from naphtha catalytic reforming

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The “advanced fuel” technology is a patented invention (US Patent 6207040, European Patent 0914405) and states that the higher-boiling C<sub>6</sub> hydrocarbons, including naphthenes, benzene and hexane, are more profitably sent to the light tops isomerisation process rather than to catalytic reforming. The critical full-range naphtha-splitting mode to be constructed in the refinery (see Figure 1) requires negligible investment.

The economic gains of advanced fuel technology<sup>1</sup> include:

- A gain of more than 4% on the recombined isomerate-reformate blend volume yield per 100 tonnes of isomerisation-reforming feed.<sup>2</sup> (This is mainly explained by the good C<sub>6</sub> isomerate octane and, in particular, by the even better C<sub>6</sub> blending isomerate octane, plus the C<sub>6</sub> isomerate weight yield being much higher and the C<sub>6</sub> isomerate density being much lower than the reformate weight yield and density.)

- A gain of around three octane number points on the recombined isomerate-reformate blend (resulting from 5-6 more points of the reformate RON<sup>1,3</sup> acquired thanks to the better reformability quality of the reforming feed), exchangeable for an additional gasoline yield.

These results are obtained by managing the full-range naphtha splitting unit in such a way as to determine the two ranges of concentrations (0-4 vol% C<sub>7</sub> hydrocarbons in the tops, 0-0.5 vol% C<sub>6</sub> hydrocarbons in the bottom, see Figure 1), which define the splitting mode and are the necessary and sufficient condition for performing

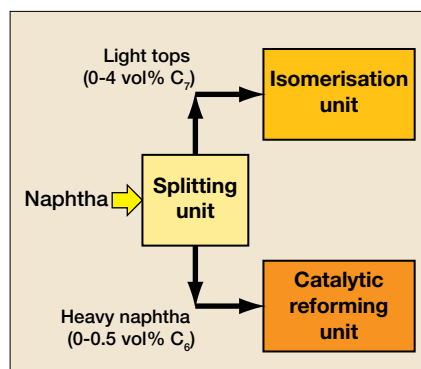


Figure 1 The “advanced fuel” flow diagram

the advanced fuel technology’s functions.

Efficient separation by distillation in the full-range naphtha splitting unit can be achieved according to different strategies, depending on choices the refiner has to make between highly efficient equipment, which is more capital intensive, and highly efficient operation, which consumes more energy. The development in no way limits freedom of choice in a compromise between these options.

In practice, separation efficiency can be improved by modifying the equipment (for instance, number and type of distillation stages, internals type) and/or the reflux ratio. There is also the option to determine an optimum compromise between improvements in equipment and reflux ratio.

## Hydrogen

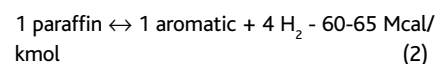
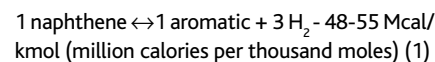
A further important feature of advanced fuel technology is the gain it offers in catalytic reforming hydrogen production/availability. The gain in production of catalytic reforming hydrogen (net of increased use in isomerisation) is

estimated in the range of 28% to over 48% based on conventional hydrogen production in catalytic reforming. When removing all or nearly all of the C<sub>6</sub> molecules (shifting them to the isomerisation process) from the catalytic reforming feed, it has been demonstrated in the refinery that the yield of catalytic reforming hydrogen increases significantly. This is in agreement with the theory that the reforming feed quality, after C<sub>6</sub> removal, becomes much more favourable to reforming’s dehydrogenation reactions with hydrogen production and much less favourable to reforming’s hydrocracking reactions with hydrogen consumption.

We will first analyse the basis of the technology before examining the results of the refinery runs.

## Reformate octane number

First, we can consider the aromatisation catalytic reforming reactions:



It is well known that the delta octane number [C<sub>8</sub>+ aromatics - C<sub>8</sub>+ (naphthenes + paraffins)] is much higher (around four times) than for [C<sub>6</sub> aromatics - C<sub>6</sub> naphthenes]. C<sub>6</sub> paraffins cannot be considered because the C<sub>6</sub> paraffins that pass through catalytic reforming do not, for practical purposes, increase their octane number. In fact, C<sub>6</sub> paraffins either crack or pass through unconverted (although an exception is

made for a 10% maximum quota of normal hexane with a RON value of about 26).

The heat absorbed in catalytic reforming by a one-molecule aromatisation reaction, generating one aromatic molecule, is roughly speaking about the same, irrespective of the number of carbon atoms. This means that, with about the same heat absorption,  $C_{8+}$  has a delta octane from the aromatisation of one molecule about four times higher than for a  $C_6$  molecule.

Regarding one molecule, with approximately the same heat absorption,  $C_{8+}$  has a delta octane four times higher than  $C_6$ 's delta octane for a gasoline quantity on average about 40% higher (because the relevant gasoline weight is exactly proportional to the molecular weight, while the relevant gasoline volume is approximately proportional).

The hydrocarbons  $C_6$ ,  $C_7$ ,  $C_8$ ,  $C_9$  and so on compete with one another in order to make use of the available heat. When  $C_6$  is present, it provides a modest octane increase by making use of a portion of the heat subtracted from the availability of  $C_7+$ . When  $C_6$  is present, in order to increase the available heat, the only option is to increase the catalytic bed temperature.

When  $C_6$  is removed, the reformate octane increases automatically due to the strong octane upgrading available for  $C_7+$ , which is simply a result of the absence of  $C_6$ . The presence of  $C_6$  appears to be very harmful to catalytic reforming performance.

The highest boiling hydrocarbon among all of the  $C_6$ s is cyclohexane, which in reforming has a fair conversion rate (although lower than the  $C_7+$  naphthenes), but a relatively modest potential for octane increase. As a consequence, it is important to transfer as much  $C_6$  as possible from the reforming feed to the isomerisation feed. The more  $C_6$  transferred, the better the reforming performance and the refinery economics.

The theory applies to any crude oil and to any refinery configuration. This theory is in full agreement with refinery experimental results.<sup>1</sup>

The first conclusion is that the removal of  $C_6$  hydrocarbons increases significantly the reformate octane number — process variables being equal and the catalytic bed temperature, and consequently the catalyst life, being equal. In order to keep the reformate octane number constant, it is necessary to decrease significantly the catalytic bed temperature.

### **Catalytic reforming hydrogen production**

#### **Catalytic bed temperature decrease**

When  $C_6$  is removed from the catalytic reforming process, the reformate octane number increases significantly, which means that a large decrease in the catalytic bed temperature is necessary to obtain a determined reformate octane number.

We will now discuss hydrocracking reactions on the premise that the categories of hydrocracking reactions include the dealkylation reactions. Hydrocracking reactions are rather slow and very sensitive to temperature, hydrocracking rates decreasing rapidly as temperature decreases. Thus, as soon as the  $C_6$ s are removed from the catalytic reforming process, hydrocracking decreases sharply. As a result, the following main consequences arise, all favouring a net increase in hydrogen production during catalytic reforming:

- A quantity of hydrogen molecules is not consumed and is therefore saved, the proportion of saved hydrogen molecules being one molecule for each hydrocarbon molecule not cracked. In other words, catalytic reforming hydrogen production increases by one molecule for each molecule not cracked
- The decrease in the contribution of paraffins hydrocracking to reformate octane causes a compensating increase in aromatisation, implying a further increase in hydrogen production
- The decrease in paraffins and naphthenes hydrocracking favours dehydrogenation reactions and produces hydrogen
- By means of dealkylation, the heavier aromatics are converted into light aromatics such as toluene

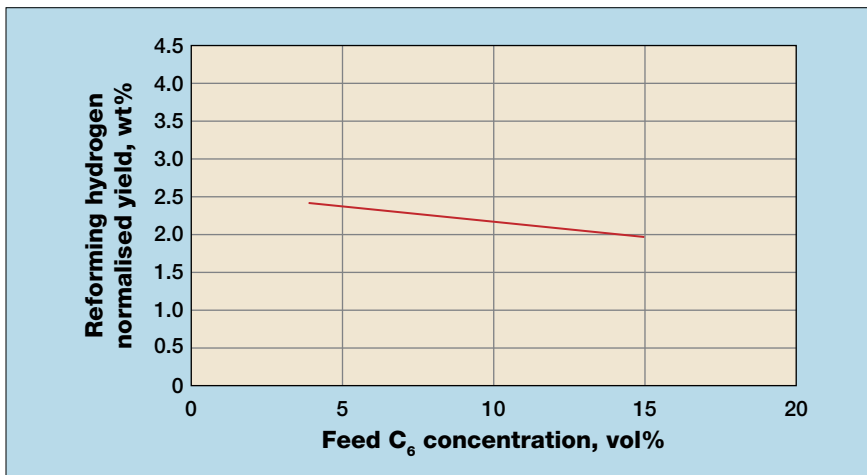


Figure 2 Reforming hydrogen normalised production vs C<sub>6</sub>- vol% in feed

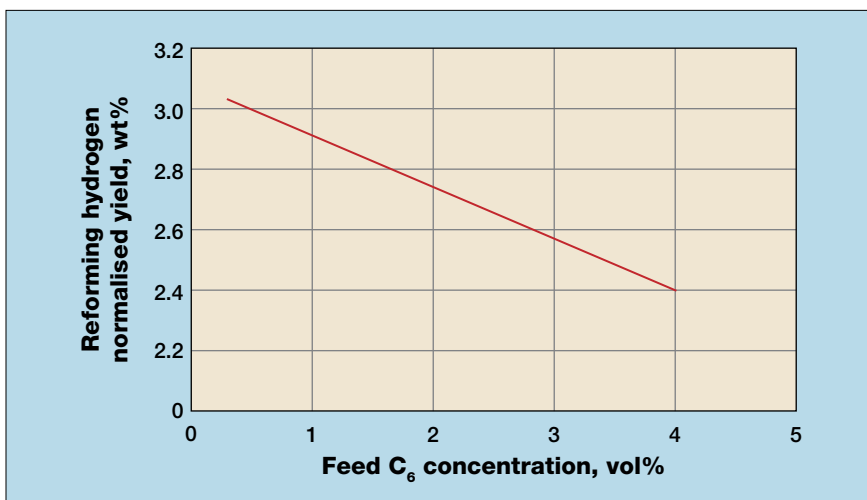


Figure 3 Reforming hydrogen normalised production vs C<sub>6</sub>- vol% in feed

and xylenes. As C<sub>7</sub> and C<sub>8</sub> paraffins are unfavourable for conversion to aromatics, dealkylation has an unfavourable effect on aromatisation of these light paraffins; hence, the implied decrease in dealkylation favours aromatising dehydrocyclisation reactions of light paraffins, producing significant quantities of hydrogen.

#### Replacement of C<sub>6</sub> naphthenes aromatisation by C<sub>7+</sub> paraffins aromatisation

Aromatisation of C<sub>6</sub> naphthenes is for the most part replaced by C<sub>7+</sub> paraffins aromatisation rather than by C<sub>7+</sub> naphthenes aromatisation. The reason for this is that, at the stage when C<sub>6</sub> is present, the concentration of C<sub>7+</sub> naphthenes in the reformate is low, while the C<sub>7+</sub> paraffins concentration is high. As the reaction rate depends on the concentration of the reactants, when the equilibrium of catalytic reform-

ing reactions is broken by the removal of C<sub>6</sub>, the C<sub>7+</sub> paraffins are more likely to aromatised than are the C<sub>7+</sub> naphthenes. As we see from reactions 1 and 2, the paraffin aromatisation reaction yields 33% more hydrogen than does the naphthene aromatisation reaction.

The second conclusion is that, process variables being equal, including the catalytic bed temperature and consequently the catalyst life, the removal of C<sub>6</sub> hydrocarbons increases significantly the hydrogen production yield from catalytic reforming.

#### Confirmation of increased hydrogen production

"Any [full-range naphtha splitting] unit built after 1950...is either a simple depentaniser or a rather intense deisohexaniser." *Oil & Gas Journal*, 21 March 1994, p52.

"Typical splitter designs...only deisohexanise the reforming unit

feed." *Oil & Gas Journal*, 11 September 2006, p40.

We decided to conservatively consider the typical naphtha splitter as a deisohexaniser. A naphtha deisohexanising splitter generates a bottom cut (the "heavy naphtha"), feeding catalytic reforming, containing around 15 vol% of the total C<sub>6</sub> hydrocarbons. This is the base case of our study.

That said, experimental confirmation of the gain in catalytic reforming hydrogen production versus C<sub>6</sub> hydrocarbons removal was examined. To this end, we constructed a normalisation algorithm in order to bring proper refinery run data to constant process variables.

We then considered normalised catalytic reforming hydrogen production versus the relevant vol% content of feed C<sub>6</sub>. Our goal was to describe the catalytic reforming hydrogen production yield in two situations:

- A scarce concentration of C<sub>6</sub> naphthenes, in particular of cyclohexane originating aromatisation reactions, in the reforming feed
- A fair concentration of C<sub>6</sub> naphthenes, in particular of cyclohexane, in the reforming feed.

To this end, we constructed two regression lines, corresponding to these situations:

- Catalytic reforming normalised hydrogen production wt% on the reforming feed versus feed total C<sub>6</sub> hydrocarbons content vol%, for a feed total C<sub>6</sub> hydrocarbons content from 15 vol% to 4 vol% (see Figure 2)
- Catalytic reforming normalised hydrogen production wt% on the reforming feed versus feed total C<sub>6</sub> hydrocarbons content vol%, for a feed total C<sub>6</sub> hydrocarbons content from 4 vol% to 0.3 vol% (see Figure 3).

The plots gave us a percentage increase of catalytic reforming hydrogen production, when the total C<sub>6</sub> hydrocarbons content of the reforming feed decreases from 15 vol% to 0.3 vol%. The resulting increase is 54.59 vol%, the reformate octane number and all the process variables being equal (see Figures 2 and 3).

We applied a safety margin of 15%, thus reducing the gain in catalytic reforming hydrogen production from 54.59 wt% to 46 wt% compared with hydrogen production in the reforming base case. The reforming feed of the base case contains 15 vol% of the total C<sub>6</sub> hydrocarbons.

Should the removed C<sub>6</sub> not be replaced at all — that is, should catalytic reforming not be replenished at all with good-quality feed, almost free of C<sub>6</sub> — we would have a decrease in the reforming feed rate. This decrease would entail a reduction in the gain of hydrogen production from 46 wt% to 25 wt% based on hydrogen production in the reforming base case.

### Trend in hydrogen production increase

Generally speaking, C<sub>6</sub> paraffins originate nearly zero hydrogen. Line 2 in Figure 3 is steeper than line 1 in Figure 2; this was expected because, from 4 vol% to 0.3 vol% C<sub>6</sub> (see Figure 3), the cyclohexane concentration in the C<sub>6</sub> of the reforming feed grows much more rapidly versus the total content of C<sub>6</sub> hydrocarbons in the feed. In such a situation, the beneficial effects of C<sub>6</sub> transfer from reforming to isomerisation, also enhancing the hydrogen generation, grows much more rapidly. That is to say, in this range of feed total C<sub>6</sub> hydrocarbons content, the hydrogen production yield grows more rapidly compared with the decrease in feed total C<sub>6</sub> hydrocarbons content. This also means that, in this range of feed total C<sub>6</sub> hydrocarbons content, the improvement in refinery economics, environmental performance and energy savings delivered by the technology increases more rapidly with the decrease in feed total C<sub>6</sub> hydrocarbons content.

As for line 1 in Figure 2, we can also say that the increase in hydrogen production yield with the decrease in feed total C<sub>6</sub> hydrocarbons content is largely due to a reduction in dilution of the reforming feed with a component (the C<sub>6</sub> paraffins) that effectively does not produce hydrogen.

### Hydrogen production increase through partial exploitation of reformate octane gain

We have seen that, through C<sub>6</sub> removal, there is an important gain in reformate octane points, the catalytic bed temperature being constant. In order to keep constant the octane number of the isomerase-reformate blend — which would otherwise decrease as a consequence of the shift of about 11 wt% on full-range naphtha from reforming to isomerisation<sup>1</sup> — we must retain a minor fraction of this gain; that is, the reformate octane number is increased above the base case value. The increase in reformate octane entails an increase in reforming hydrogen production. Hydrogen production will increase from 1.25 to around 1.32 times the base case value.

If we keep the other gained octane points in reformate, the gain in hydrogen production yield in catalytic reforming will further increase. But we can change at will these supplemental gained reformate octane points into an additional strong gain in volume yield, on top of the gain resulting directly from the C<sub>6</sub> shift from reforming to isomerisation. The reforming catalytic bed temperature will thus decrease, so further increasing the reforming catalyst's life, which has already increased due to the lower feed rate (in the case of non-replacement of C<sub>6</sub>).

Returning to reforming hydrogen production: as the base case hydrogen production is approximately 2 tonnes per 100 tonnes of reforming feed, reforming hydrogen production after C<sub>6</sub> removal is 2\*1.32 tonnes% (2.64 tonnes%) on the base case reforming feed rate.

### Hydrogen production gain net of increased use for isomerisation

Isomerisation hydrogen use of the shifted C<sub>6</sub> (11 tonnes per 78 tonnes of reforming throughput<sup>1</sup>), evaluated at 0.6 wt% of the isomerisation throughput, is worth  $11*0.6/100*100/78 = 0.08$  wt% on the base case reforming feed rate.

By subtracting isomerisation use from the hydrogen production

figures, we arrive at  $2.64 - 0.08 = 2.56\%$  on the base case reforming feed rate, equivalent to  $2.56/2 = 1.28$  times the base case hydrogen production, or a 28% net gain in hydrogen production on the reforming base case.

If the reforming feed rate is fully replenished with good-quality feed, we will have the full 46 wt% yield increase and will retain a smaller fraction of the gain in reformate octane points obtained.

The result of the relevant calculation gives a net gain in reforming hydrogen production of around 48% on base case hydrogen production.

### Economic and environmental improvements

It is possible to exceed a 48% gain in reforming hydrogen production through the installation of additional catalytic reforming and isomerisation capacities. This option could be evaluated if we consider that the current trend in crude oil towards heavier and sourer quality, as much as the trend towards better-quality products, requires a bigger and growing addition of hydrogen (also keeping in mind that on-purpose hydrogen production processes consume enormous energy quantities).

In addition to the gain in hydrogen, the advanced fuel technology delivers:

- A strong gain in gasoline yield
- A strong gain in gasoline octane number (exchangeable at will for an additional strong gain in gasoline yield)
- Prevention of benzene formation
- Accomplishment, with a margin, of the most stringent specifications for gasoline benzene content (in particular, for the US, accomplishment of the US Environmental Protection Agency's requirement of 0.62 vol% average benzene content for the whole gasoline pool, resulting in saleable benzene requirement credits)
- Major energy savings
- Reduction in pollutants, both in gasoline production and consumption
- Higher capacity increase in gasoline octane production

- Improved engine operation and maintenance.<sup>1,4</sup>

### Economic value

Calculations are provided with the purpose of demonstrating the order of magnitude of the economics involved. We will conservatively consider two of the approximately three points of octane number gained by the technology. These two points of octane gain are commercially worth, on the basis of the revenue difference between premium and regular grades, about  $\text{€}0.02 \times 2 = \text{€}0.04/\text{litre}$  of isomerate-reformate blend, or about  $\text{€}0.05/\text{kg}$  of full-range naphtha ( $\text{\$}0.07/\text{kg}$  or  $\text{\$}70/\text{tonne}$  of full-range naphtha).

We assume a gasoline revenue of  $\text{\$}3/\text{gal}$ , equivalent to  $\text{\$}0.7926/\text{litre}$ . On the basis of a conservative 3 vol% gain and proportioning from earlier calculations,<sup>1</sup> where the assumed price of gasoline was  $\text{\$}0.20/\text{litre}$ , we obtain a value of the higher gasoline yield of  $\text{\$}20.80/\text{tonne}$  of full-range naphtha and a lower byproducts value, to be subtracted from the above figure, of  $\text{\$}8.14/\text{tonne}$  of full-range naphtha. Hence, the better gasoline yield gives us a total net economic gain of  $\text{\$}(20.80 - 8.14) = \text{\$}12.66/\text{tonne}$  of full-range naphtha.

We assume a hydrogen cost of  $\text{\$}2150/\text{tonne}$ .<sup>5</sup> On this basis, as the reforming feed heavy naphtha of the base case represents about 78% of the full-range naphtha,<sup>1</sup> and base case hydrogen production is 2 tonnes per 100 tonnes of reforming feed rate, the hydrogen gain is basically worth between  $0.02 \times 0.28 \times 0.78 \times 2150 = \text{\$}16.10/\text{tonne}$  of full-range naphtha and over  $0.02 \times 0.48 \times 0.78 \times 2150 = \text{\$}16.10/\text{tonne}$  of full-range naphtha.

Based on the figures above, we obtain a profit of  $\text{\$}92.05\text{--}98.76/\text{tonne}$  of full-range naphtha. In an average refinery, with a full-range naphtha splitting feed rate of 4000 tonnes/day, total annual gain offered by the invention considered results is  $\text{\$}134\text{--}144$  million.

### Conclusion

The technology described offers gasoline yield gain, gasoline octane

gain, net gain in catalytic reforming hydrogen production and abatement of refinery benzene production.

The transfer from catalytic reforming to isomerisation of any  $\text{C}_6$  hydrocarbon species appears to be beneficial. Among these species, the most beneficial transfer concerns the higher boiling ones, cyclohexane transfer bringing the biggest benefit.

The overall result of the technology encompasses important improvements in refinery economics and environmental performance, climate change mitigation, energy savings and improvement in gasoline technical quality.

### Acknowledgment

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### References

- 1 Amadei R, A proposal for an economic and environmental gasoline, *PTQ*, Summer 1999.
- 2 Amadei R, Opposition Appeal Patent proprietor reply, European Patent Office, European Patent Register, Munich, 16 June 2005, <https://register.epo.org/espacenet/application?documentId=E157C1OY1001J11&number=EP97937512&lng=en&npl=false> (accessed 29 Sep 2012).
- 3 Westphalen D, Shethna H, Refinery wide simulation, *Hydrocarbon Engineering*, March 2004.
- 4 Amadei R, in the Attachment to Industry comment for the GHG Scoping Plan - 1st Workshop: An economic and environmental gasoline, California Environmental Protection Agency, Air Resources Board, 30 July 2008, [www.arb.ca.gov/lispub/comm2/bccommlog.php?listname=sp-industry-ws\(#7\)](http://www.arb.ca.gov/lispub/comm2/bccommlog.php?listname=sp-industry-ws(#7)) (accessed 29 Sep 2012).
- 5 Parihar P, *et al*, Optimise hydrogen management for distillate production, *Hydrocarbon Processing*, March 2012.

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