

A proposal for an economic and environmental gasoline

The author describes how adopting identified C_6 - and C_7+ hydrocarbon concentrations in the reforming and isomerisation feeds can increase profits and transform gasoline into a new, more environmentally friendly grade

Roberto Amadei

Refining consultant

During the Eighties and Nineties, in Europe and worldwide, refiners had to face demands for a radical reduction of gasoline lead content. As a result, refiners had a problem: they had to send the light tops (LT) to the gasoline pool to compensate for the loss of revenues they would otherwise receive from the LT as eventual petrochemical feedstock. The consequence was that refiners were obliged to process LT through an isomerisation unit (until then the isomerisation was undoubtedly useful for profits, but not compulsory); in such a way, as long as the clear octane number of the straight-run LT was insufficient, they made up for the lost octane boosting previously accomplished by lead.

Against this background, it is intended to indicate the important increase of profit that can be obtained by choosing suitable, and critical, C_6 hydrocarbon concentration in reforming feed and C_7+ hydrocarbon concentration in isomerisation feed. The crucial refining (and environmental) problems that are solved by making this choice will also be indicated.

On the hypothesis of sending the whole available naphtha only to isomerisation or to reforming, reducing more and more the C_6 concentration in the reforming feed signifies shifting higher and higher quotas of C_6 (plus C_7+) from reforming feed to isofeed. Increasing more and more C_7+ concentration in isofeed signifies equally shifting higher and higher quotas of C_6 (plus C_7+) from reforming feed to isofeed.

A decisive yardstick in gasoline production is the octane capacity, which is increasingly important as lead-alkyls addition becomes progressively less. Another important yardstick for measuring the performance of gasoline production processes is the yield, which is also quite critical in connection with the reduction/

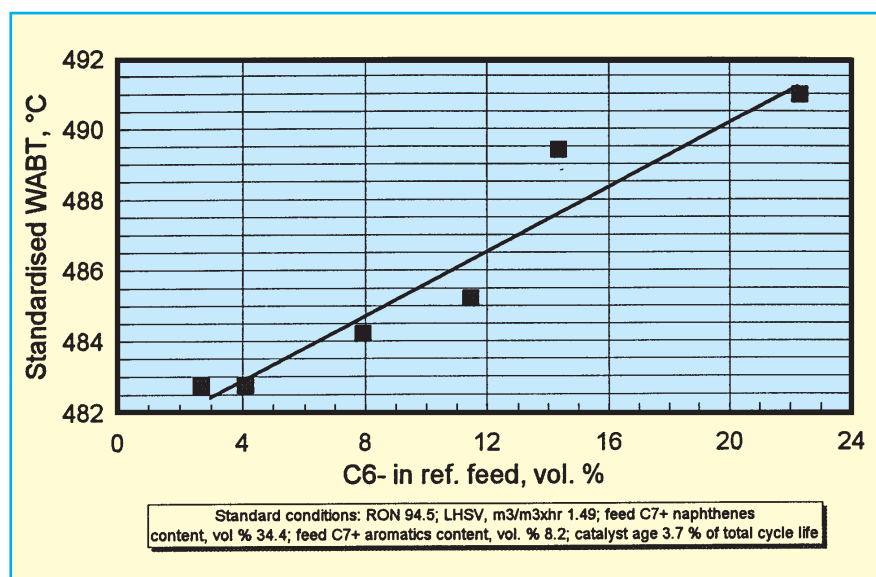


Figure 1 Catalytic reforming activity as a function of C_6 - concentration in reforming feed

elimination of lead combined with the demand increase. So we have to establish how the gasoline pool octane and yield depend on the above concentrations.

Reforming

We will start by showing what happens to the reforming performance when varying the C_6 (or C_6 -) hydrocarbon concentration in its feed. For this purpose we have rated the processing results of a semi-regenerative reforming cycle. This cycle turns out to be peculiarly suitable for clearly showing the influence of the above parameter on reforming performance. Such peculiar suitability is due to the widespread values, throughout this single cycle, of the recorded C_6 concentrations in feed. So we have retrieved the weighted average bed temperatures (WABT) and the reformat C_5+ yields recorded in processing runs characterised by largely varying C_6 concentrations in feed.

Activity

As far as WABT is concerned, we have adjusted all the recorded values by bring-

ing them to standard conditions, relevant to feed cyclic contents, reformat RON, volumetric space velocity and catalyst age in the cycle. In other words, we have standardised the recorded values. In the adjustment we have excluded the differences in feed quality due to the C_6 part of the feed, so as to succeed in leaving intact the thorough differential effect of the different C_6 content.

In this way, by the adjustments having cleared the performance of effects due to other causes, we have obtained the complete bare differential performances due to the differences of C_6 content. The results show the correspondence, exhibiting a strong correlation ($r=0.96$) between reforming activity (increasing with WABT decrease) and feed C_6 concentration (Figure 1).

From this figure a gain of activity, that is a decrease of WABT vs the decrease of C_6 - concentration from over 22 down to less than 3 vol%, can be observed (this gain of activity is worth about 9°C over the whole C_6 concentration span). A

gain of activity represents, when you keep feedrate and cycle length constant, a gain of octane number throughout the whole catalyst life.

To go down further (towards zero) with feed C_6 concentration, we have retrieved recorded WABT values, adjusted for the above parameters except catalyst age, relevant to a continuous regeneration reforming unit. This is shown in Table 1 and Figure 2.

From still lower values of C_6 concentration in feed, retrieved from runs of other reforming units and rated vs. the corresponding standardised WABT values, no correlation can be established.

We can say that the overall effect of octane boosting, at constant reforming feedrate and catalyst cycle length, is not lower than three points, for a C_6 concentration reduction from the traditional level to around 0.5 vol%.

This is the reforming gain due to the improvement of its feed quality, that is due to the better "reformability" of its feed. Of course, the gain of activity, as a possible alternative to a full transformation into octane boosting, could be realised in any combination of higher feedrate/cycle length/octane number parameters. By the way, from all the activity gain not realised into octane boosting, over and above the feedrate/cycle length increases, a yield increase is automatically obtained as well.

Moreover, when taking C_6 off reforming feed, the reforming throughput and the space velocity diminish, causing an important severity reduction. But it is also possible to keep reforming throughput constant, and thus severity, in order to take advantage of the new capacity created for the production of a super-reformate, with enhanced octane.

Yield

As far as reformate C_{5+} yield is concerned, as already mentioned, we have retrieved the recorded values relevant to the same, semi-regenerative unit cycle studied for the WABT results, so peculiarly suitable for our requirements. We then adjusted them for standard conditions, relevant to feed cyclics content, reformate RON and catalyst age in the cycle. As we did for the WABT, in the adjustment we excluded differences in feed quality due to the C_6 part of the feed, thus obtaining the above goal. The results show the correspondence between reforming C_{5+} yield and C_6 feed concentration (Figure 3).

In this figure, a gain of yield can be clearly observed vs the decrease of C_6 concentration. An increase of 2.4 points can be appreciated over the entire span. No correlation could be found between standardised yield and lower values of C_6 feed content.

Sets of continuous reforming observed data: C_6 - concentration in feed – catalyst age – standardised WABT

C_6 - concentration in reforming feed vol%	Total catalyst age bbls/lb	Standardised WABT °C
0.82	71.9	508.9
0.86	64.4	511.2
1.01	97.8	504.8
1.11	81.5	508.8
1.38	48.3	511.6
1.48	88.8	507.8
1.57	26.5	514.3
1.73	55.7	510.8
1.81	31.9	514.0
2.45	38.7	516.2

Standard conditions:
 Stabilised reformate RON 99.4.
 Feed liquid hourly space velocity, $m^3/m^3 \times hr$ 2.38.
 Feed C_{7+} naphthenes content, vol% 24.8.
 Feed C_{7+} aromatics content, vol% 8.0.

Table 1

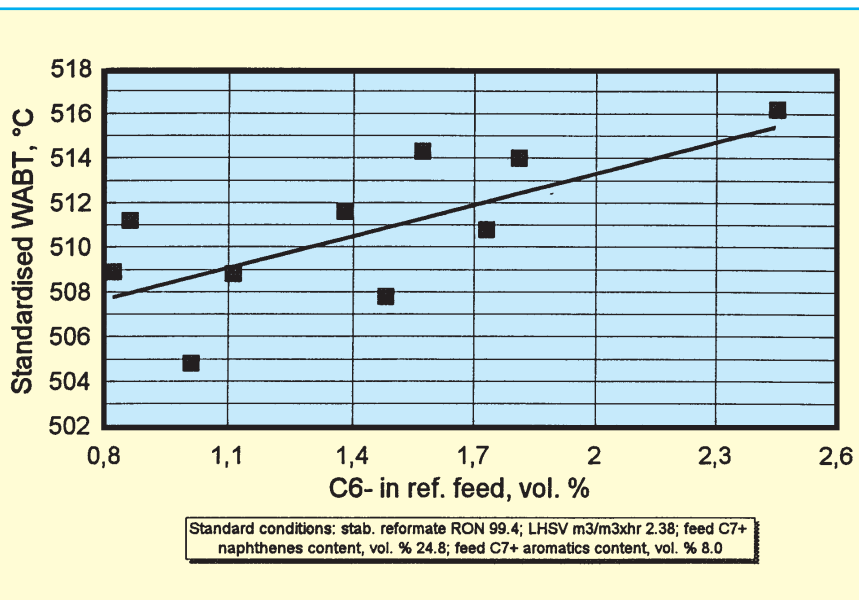


Figure 2 Catalytic reforming activity as a function of C_6 - concentration in reforming feed

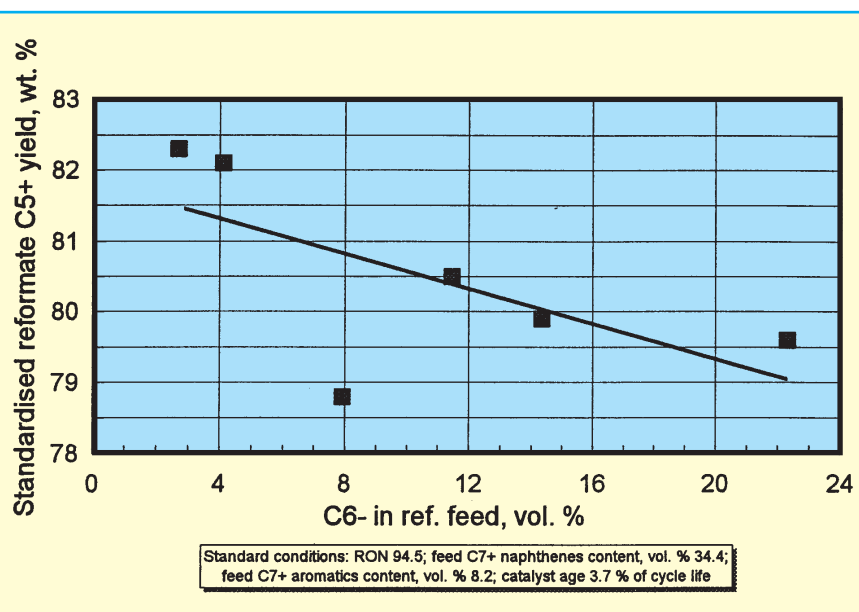


Figure 3 Reformate C_{5+} yield as a function of C_6 - concentration in reforming feed

Isomerisation results vs feed quality (Case: C₆₊ 38.68 wt%)

Fresh feed composition, wt %

C ₃ - paraffins	0.08
Butanes	2.28
Dimethylpropane	0.09
Isopentane	28.61
Normal pentane	28.17
Cyclopentane	2.09

C₅- total 61.32

2,2 Dimethylbut	0.73
2,3 Dimethylbut	2.37
2 Methylpentane	14.40
3 Methylpentane	6.66
Normal hexane	7.12
Methylcyclopent	3.30
Benzene	1.36
Cyclohexane	0.71

C₆ total 36.65

C ₇₊ paraffins	1.45
C ₇₊ naphthenes	0.56
Toluene	0.02

C₇₊ total 2.03

C₆₊ total 38.68

Total 100.00

Fresh feed density, kg/l 0.647

Fresh feed flow, t/h 52

Stabilised isomerate

RON 88.27

MON 85.83

Yield, wt % 95.18

Density, kg/l 0.640

Table 2

Isomerisation

We have seen what happens in the reforming stage when the C₆ hydrocarbon concentration in feed is progressively reduced. We will now see what happens in the isomerisation stage while, in parallel, increasing the isofeed C₇₊ hydrocarbon concentration, which implicitly means increasing the isofeed C₆₊ hydrocarbon concentration as well. That is to say, we will now see what happens in the isomerisation to both the feed added C₆ and C₇ hydrocarbons that we took off the reforming feed.

Referring to a molecular sieve recycle isomerisation unit, whose recent operation is suitably characterised by a wide range of C₇₊ concentration levels, outlined in Table 2 is an example of feed composition (relevant to a run of the first catalyst cycle), showing a C₆₊ wt. concentration of 38.68%, quite close to the traditional one, along with the feedrate and the obtained yield, octane numbers and density.

To make a sound comparison, Table 3 shows an example of feed composition relevant to a feedstock substantially richer in C₆₊ (48.30 vs 38.68 wt%, where the higher C₆₊ turns out, by calculation, to be quantitatively equivalent to an addi-

tion of 18.61 wt% to the feed illustrated in Table 2), along with processing feedrate and results.

Through linear interpolation we have figured out the marginal yield of the added quantity of C₆₊, turning out to be 92.06 wt%. The RON of the added C₆, likewise calculated, is 86.6, while the density is 0.6533kg/litre.

Hence the added heavier C₆₊, as far as weight yield and octane are concerned, performed almost as well as the traditional feed. Such performance level of the run with the higher C₆₊ was achieved in spite of the following: higher age of the catalyst, which moreover was just at the end of the cycle (2160th vs 1831st run day of the cycle), higher C₇₊ – that means a slight worsening of the performance, which turns out to start just above 2 per cent C₇₊ concentration in feed, higher feedrate of a unit already overloaded on design throughput by over 20 per cent. Coming to the density result, we must underline the huge reduction in respect of the added feed one, that by calculation turns out to be 0.702.

A further important factor to be considered is the blending isomerate RON, which is an average of two points higher than that of the component alone.

Another molecular sieve recycle isomerisation unit gave results apt to be compared for small increases of C₆₊ (and of C₇₊). These results align close to the situation of full removal of C₆ from the reforming: in Table 4 we can observe that, by increasing, from run A to run B, C₆₊ by 1.4 per cent and C₇₊ by 0.6 per cent on isomerisation feed, neither yield nor octane worsen (actually, they considerably improve). In general, up to a 2 per cent of C₇ hydrocarbons in isofeed, both yield and octane, turn out to average the same value as the traditional quality of the isofeed, and this irrelevant to the type of added C₆ hydrocarbons.

Above 2 vol% of C₇₊ in the isofeed, we observe, in particular in the first unit referred to, a slight decrease both of octane numbers and yields. Over a certain value of C₇₊ concentration, clearly shown by the results of first unit catalyst cycle, thanks to the wide range of its feed C₇₊ concentration, the slope of the decreasing yield of marginal added C₇ steepens quite suddenly. This is our optimum, and critical, value.

In the C₆ shift from the reforming to the isomerisation another gain is obtained: the C₆ obtains in the isomerisation a better yield, particularly the volumetric one, in respect to that obtained in the reforming.

The balance

The quantity of naphtha to be subtracted from the traditional reforming feed for reducing its C₆ concentration to not more than 0.5 vol% – to be added to the traditional isofeed, keeping the above limits on isofeed C₇₊ concentration – averages around 50 per cent of the traditional isofeed.

We will now examine how the octane number and the yield of the reformate plus isomerate blend change as a result. We will study the case of 100 tons of naphtha, 67 to be processed in the reforming and 22 in the isomerisation. For the remaining 11 tons located in the middle of the distillation we examine the two following alternative possibilities:

Case A (base case)

Process 11 tons of higher boiling C₆ naphtha in the reforming

Total reforming feed: 67 + 11 = 78 tons

Processing results:

Reformate blending RON (example assumption): 96; reformate blending MON: 85

Reformate yield: 81 wt%

Reformate density: 0.790

Reformate volume: 78 × 0.81/0.790 = 80.0m³

Case B

Process 11 tons of higher boiling C₆ naphtha in the isomerisation:

Differential isomerisation feed: 11 tons.

Isomerisation results vs feed quality (Case: C₆₊ 48.30 wt%)

Fresh feed composition, wt%

Butanes	3.38
Dimethylpropane	0.13
Isopentane	26.89
Normal pentane	19.55
Cyclopentane	1.75

C₅- total 51.70

2,2 Dimethylbut.	0.67
2,3 Dimethylbut.	2.47
2 Methylpentane	13.90
3 Methylpentane	7.52
Normal hexane	10.56
Methylcyclopent	6.63
Benzene	2.22
Cyclohexane	1.96

C₆ total 45.93

C₇₊ paraffins 1.89
C₇₊ naphthenes 0.48

C₇₊ total 2.37

C₆₊ total 48.30

Total 100.00

Fresh feed density, kg/l 0.655

Fresh feed flow, t/h 53

Stabilised isomerate

Yield, wt% 94.65

RON 88.01

MON 85.44

Density, kg/l 0.642

Table 3

Results of isomerisation processing of additional feed:

Isomerate blending RON (average): 89.5; isomerate blending MON (average): 85

Isomerate yield: 95 wt%

Isomerate density: 0.653

Isomerate volume: $11 \times 0.95/0.653 = 16.0\text{m}^3$.

Results of reforming processing (only 67 tons):

Reformate blending RON (average, as a consequence of the improved activity): 99; reformate blending MON: 88
Reformate yield: 81 wt% (turns out to average the same as Case A because the higher octane compensates the better quality of feed)

Reformate density: 0.804

Reformate volume: $67 \times 0.81/0.804 = 67.5\text{m}^3$.

In the two cases A and B the 22 lower boiling naphtha tons processed by the isomerisation remain unchanged and give the same results:

Isomerate blending RON (average): 89.5; isomerate blending MON (average): 85

Isomerate yield: 95 wt%

Isomerate density: 0.640

Isomerate volume: $22 \times 0.95/0.640 = 32.7\text{m}^3$.

Case results and differences**Case A**

Gasoline (reformate + isomerate) volume: $80.0 + 32.7 = 112.7\text{ m}^3$

Gasoline RON: 94.11; gasoline MON: 85.00

Gasoline density: 0.7465t/m^3

Litres contained in 1 ton of gasoline: $1000/0.7465 = 1339.6$

Gasoline yield on the 100 tons of naphtha feed: $112.7 \times 0.7465 = 84.13\text{ wt}\%$

Case B

Gasoline volume: $16.0 + 67.5 + 32.7 = 116.2\text{m}^3$

Gasoline RON: 95.02; gasoline MON: 86.74

Gasoline density: 0.7371t/m^3

Litres contained in 1 ton of gasoline: $1000/0.7371 = 1356.7$

Gasoline yield on the 100 tons of naphtha feed: $116.2 \times 0.7371 = 85.65\text{ wt}\%$.

Lower reformer severity in respect of Case A: equal reformer severity operating conditions would involve, as we have seen above, plus 3 octane points of reformate and equal feedrate and catalyst life; Case B exhibits instead plus 3 octane points and a space velocity (feedrate) lower than Case A by about 15 per cent, which is worth 15 per cent of additional catalyst life.

Differences (Case B minus Case A):

Gasoline volume: $116.2 - 112.7 = +3.5\text{m}^3$

Gasoline RON: $95.02 - 94.11 = +0.91$;

Gasoline MON: $86.74 - 85.00 = +1.74$

Gasoline (RON + MON)/2 = $(0.91 + 1.74)/2 = +1.325$

Gasoline density: $0.7371 - 0.7465 = -0.0094\text{kg/l}$

Litres contained in 1 ton of gasoline: $1356.7 - 1339.6 = +17.1$

Gasoline yield on 100 tons of naphtha feed: $= 85.65 - 84.13 = +1.52\text{ wt}\%$

Reformer catalyst life: + 15 per cent

The profit

We assume the underlisted revenues (per weight unit) relative scale:

Gasoline: 1

LPG: 0.75

Produced gas: 0.55.

We also assume the following revenue:

Gasoline: \$0.20/litre

As a result, the overall byproducts value is \$0.18/kg.

Scenario 1

As a premise, the energy consumption can be considered unchanged due to the two following factors which roughly compensate each other:

—Decrease of reforming recycle gas circulation power that diminishes exponentially with the reforming feedrate (the exponent being as high as 2.7)

—Increase (at equipment constant) of naphtha-splitting section energy consumption.

The profit gain, of Case B over Case A, includes the following effects (see under previous heading, The Balance):

1. More gasoline per m^3 : this effect is worth $+3.5 \times 0.20 \times 10^3 = +\700 per 100 tons of full-range naphtha = $+\$7$ per ton of full-range naphtha.

2. Lower byproducts weight yield: from figures under previous and present headings, this effect is worth $-\$1.52 \times \$0.18/\text{kg} \times 10^3 = -\274 per 100 tons of full-range naphtha = $-\$2.74$ per ton of full-range naphtha.

3. More octane: on the basis of an estimate of $\$3/\text{octane} \times \text{m}^3$, the RON + MON/2 of Case B, which is 0.875 points higher than Case A, is worth $+1.325 \times 3 = +\$4.0$ per gasoline m^3 or $+\$4.5$ per ton of full-range naphtha.

Summing up the above effects, we work out a profit gain of $\$8.7$ per ton of full-range naphtha, which is equivalent to $\$10.3$ per ton of gasoline (3.8 per cent of assumed gasoline revenue).

Moreover, we have increased by 15 per cent the reformer catalyst life.

Scenario 2

This second scenario takes advantage of the available spare capacity created in the reforming by subtracting the 11 tons quantity from the feed of Case A. Thus,

by assuming to buy on the market 11 tons of naphtha feed at a cost of \$0.20/kg, we realise, as a result of processing this naphtha in the reforming, a total profit of \$344 plus \$133 of octane credit.

The sum of \$477 referred to (divided by) the base (Case A) gasoline production is worth an additional \$5.7 per ton of base (Case A) gasoline.

Hence we arrive at an overall profit, at constant reforming severity, of $10.3 + 5.7 = \$16$ per ton of base case gasoline (5.3 per cent of assumed gasoline revenue).

We have now represented the case of the naphtha feed supplied from outside the refinery. However, the available spare capacity created in the reforming could also remove (fully or partly) a bottleneck in the refinery. Such a bottleneck is not unlikely because it is not rare for the reforming capacity to become insufficient due to the lead phase down-out combined with the demand increase. In this case, all the added value of the added processed crude is to be credited to the operational mode of Case B.

Additional profit

On top of the gains of both scenarios 1 and 2 it is necessary to add the savings coming from the solved problems, which we will consider thoroughly later on, relevant both to specifications imposed by state/national/international laws and directives and to unimposed quality improvements.

Remarks

Gasoline formulation resulting from Case B operation entails an RVP increase. Should this fact result in the RVP specification limit being touched, a minor fraction of butane can be switched to LPG with a probable, but modest, worsening of the indicated profit gain. We can neglect it as we did for the better value of byproducts in Case B (we assumed the value of the byproducts equal for the two cases).

For the realisation of our goal the necessary condition is an appropriate fractionation efficiency in the naphtha-splitting section. This condition could require minor interventions such as modifications of the splitting column internals. From the foregoing it is evident that the financial size of such interventions is negligible.

Marginal C₆ optimum

For values of C₆ content in the reforming feed lower than 0.8 vol%, we could not find any correlation between this parameter and reforming catalyst WABT, that is between C₆ content and reformate octane. Nevertheless economically optima C₆ concentrations in reforming feed do exist. A detailed discussion is not possible here for space reasons; instead

Isomerisation results vs marginally different feed C ₆ + / C ₇ + concentrations					
	Run A	Run B		Run A	Run B
Fresh feed compo., wt%					
Propane	0.10	–	Fresh feed density, kg/l	–	0.664
Butanes	1.06	0.26	Fresh feed flow, t/h	17	26
Dimethylpropane	0.01	–			
Isopentane	14.23	14.66			
Normal pentane	24.13	23.19			
Cyclopentane	1.66	1.72			
C ₅ - total	41.19	39.83			
2,2 Dimethylbut	0.30	0.45			
2,3 Dimethylbut	1.53	1.68			
2 Methylpentane	11.81	11.59			
3 Methylpentane	8.27	8.23			
Normal hexane	24.78	23.74			
Methylcyclopent	5.83	6.61			
Benzene	2.60	2.70			
Cyclohexane	2.53	3.43			
			Stabilised isomere		
C ₆ total	57.65	58.43			
C ₇ +	1.16	1.74			
C ₆ + total	58.81	60.17	Yield, wt%	96.09	96.39
			RON	86.1	87.3
Total	100.00	100.00	Density, kg/l	–	0.653

Table 4

we refer to the premises and the conclusion. A premise is that the definitely prevailing criterion for the last 8 per cent tenths of C₆ reforming feed content to be possibly shifted to the isomerisation is the one of the octane × barrels yield. On the other hand, the benzene Motor Octane Number is only a little higher than the isomere one [Unzelman G H, Fuel composition in 2000; *Fuel Reformulation, May-June 92*].

The conclusion is that the optimum reforming feed C₆ content is nil. The optimum level could be different (not higher than 0.5 vol%) in particular cases.

The solved problems

Octane

The new and clean octane reserve made available by the process we are talking about obviously can be spent in many ways, either alternatively or as additives.

For instance, it is quite clear that this octane reserve allows the lead-alkyl additives to be eliminated. This accomplishment, over and above legal requirements, would obviously be highly beneficial to health, due to all the well known effects of lead. Indeed the octane gains outlined under the previous heading, "Case results and differences", also if spread over a wide gasolines pool, largely allow the replacement of the leaded gasoline throughout Europe and most of the world. One of the interesting

aspects is that this replacement would be realised with a simultaneous reduction of the total aromatics concentration.

The new octane reserve in general favours the design of higher efficiency engines and according to a few sources [Nocca J L, Forestière A, Cosyns J; Diversify process strategies for reformulated gasoline; *Fuel Reformulation, Sept-Oct, 94*] favours a higher engine efficiency also independently from the engine design.

Gasoline production yield and capacity

The significance of the yield and capacity increases is fully valued by considering that, worldwide, these parameters, along with the octane, have become critical because of lead phase down-out combined with demand increase.

Moreover, the gain of octane number, yield, capacity and reforming catalyst life could improve the attractiveness of reforming units types which, although just limited in octane, yield and catalyst life, produce less aromatic reformates (the octane number being equal). For the existing units, marginal reductions of the reformates total aromatics concentration could be obtained by increasing the reaction pressure.

Gasoline quality

1. H/C ratio

The H/C ratio clearly increases, particularly in the Scenario 1 case. Roughly speaking in Scenario 1 the C/H ratio of

the isomerate plus reformat blend decrease is worth about 0.2 points. This entails an increase of gasoline energy content per weight and a decrease of weight consumption per kilometre of over 1 per cent.

The same decrease obviously applies to all types of emissions. However the carbon monoxide and dioxide emissions decrease, roughly speaking, by about 2 per cent, due to the fact that the carbon content per energy unit diminishes.

It is worth underlining that the CO₂ emissions decrease gives a substantial contribution to the fulfilment of the Kyoto requirements. This contribution could even be much higher in the case of using the new octane reserve for increasing the efficiency of the engines combustion.

2. Distillation curve

The process causes a shift of the distillation curve towards lower temperatures, particularly important in the Scenario 1 case. The considerable decrease of T₅₀ has the effect of a remarkable reduction of the exhaust VOC, including benzene.

The nitrogen oxides emissions slightly decrease, due to the general emissions reduction under the previous subheading (H/C ratio), and to an

inherent improving effect of the higher hydrogen content [Piel W J, Diversify future fuel needs with ethers; *Fuel Reformulation*, Mar-Apr 94]. These improving effects should outweigh a very small possible increase of the NO_x emissions due to the T₅₀ decrease.

As a result of the effects outlined in the last two paragraphs we get an important reduction of the ozone formation.

The driveability index:

$$DI = 1.5 T_{10} + 3 T_{50} + T_{90}$$

decreases, thus considerably improving.

3. Normal hexane content

Among the molecules composing gasolines the most toxic are considered to be benzene and MTBE, assessed by World Health Organisation's IARC as respectively A1 and A3 carcinogens. Of the other molecules the one having the lowest allowable exposure limit (Time Weighted Average) according to ACGIH, France, Germany, the Netherlands, Sweden and the UK [Exposure profile: crude oil; Concawe, Brussels, Apr 98] is the normal hexane, which, moreover, easily diffuses, due to its high vapour pressure.

Through the process the gasoline normal hexane content is minimised.

4. Benzene content

By removing the C₆ hydrocarbons from

catalytic reforming feed, the benzene content of reformat is radically reduced, simply because it is not formed. By having a C₆ content in the reforming feed at 0.5 vol%, the reformat benzene content does not exceed 1.5 vol% (which entails a benzene concentration of 0.87 vol% in Scenario 1 blend), while the benzene content of the isomerate plus reformat blend averages around 0.6 vol%, variations being mainly related to reforming pressure.

At the optimum target for the C₆ content of reforming feed, which is nil, the benzene content of the isomerate plus reformat blend should average around 0.3 vol%.

5. Total aromatics content

In the Scenario 1 case the total aromatics concentration of the isomerate plus reformat blend decreases about 3 percentage points on the blend quantity. In the case of Scenario 2, corresponding to an 11.1m³ addition of 99 RON reformat, the total aromatics concentration of the isomerate plus reformat blend decreases about 0.8 percentage points on the blend quantity.

Adding less than three octane points to the reformat, that is realising, partly or fully, the reforming catalyst activity and space velocity improvements

into reforming catalyst life and/or feedrate increases, as well as into a higher reformate yield, allows further proportional total aromatics concentration reductions.

A solution which could further reduce the reformate total aromatics content, thanks to the octane, yield, capacity and reforming catalyst life improvements realised by our process, is indicated under the previous heading, Gasoline yield and capacity.

6. Sulphur and olefins content

When the gasolines pool also contains cracked stocks, the increased yield of the isomerate plus reformate blend, which contains hardly any sulphur or olefins, obviously allows a diminution, by dilution, of the finished gasolines sulphur and olefins contents.

7. Effects of gasoline quality on the emissions

Listed below are the estimated effects on the emissions of the above described quality gasoline aspects (unless specifically indicated, we refer to a gasoline simply made by the Scenario 1 isomerate plus reformate blend, and for extending the estimate of the emissions reduction to the whole gasoline, where other components are present, it is necessary to proportionally decrease the indicated one):

According to paragraph 1 (H/C ratio), reduction of all the emissions but CO, CO₂ and NO_x by over 1 per cent, reduction of CO and CO₂ by about 2 per cent.

According to paragraphs 1 (H/C ratio), 2 (Distillation curve) and 6 (Sulphur and olefins content), reduction of the NO_x comprised between 0 and 0.8 per cent.

According to para 2 (Distillation curve), reduction of exhaust VOC emissions by about 7 per cent.

According to para 3 (Normal hexane content), reduction of evaporative normal hexane emissions by about 50 per cent.

According to paragraphs 2 (Distillation curve), 4 (Benzene content) and 5 (Total aromatics content), reduction of evaporative plus exhaust benzene emissions by over 50 per cent.

When cracked stocks are in the gasoline pool, according to para 6 (Sulphur and olefins content) a slight (further) reduction of all types of emissions is obtained, somewhat proportionally higher for the sulphurised components, the NO_x and the evaporative olefins. As long as light olefins have a high relevant reactivity factor, their reduction allows a further reduction of the ozone formation, on top of the one described in para 2 (Distillation curve).

Net benzene formation

According to the process the great majority of refinery benzene is not formed, which is the only means of fully avoiding benzene pollution. Moreover, the isomerisation minimises the run inside the refinery of the benzene contained in the crude by transforming it into naphthenes and isoparaffins.

The net benzene formation is the benzene quantity coming out of reforming plus cracking units, minus the one entering the refinery with the crude. The reduction of the net benzene formation (averaging at least 90 per cent) is even higher than the percentage of gasolines benzene content reduction. Accordingly, the benefit which the refinery obtains from the process is even higher than that obtained by the gasoline final consumer.

It is important to consider that the net benzene formation minimisation is a basic target in order to minimise benzene pollution in the workplace and to minimise the air and the refinery wastewater benzene content.

Roberto Amadei is an independent refining consultant, based in Genoa, Italy. He has worked for Shell and ENI, specialises in the fields of refining technology and planning, and has a PhD in chemical engineering from Genoa University.