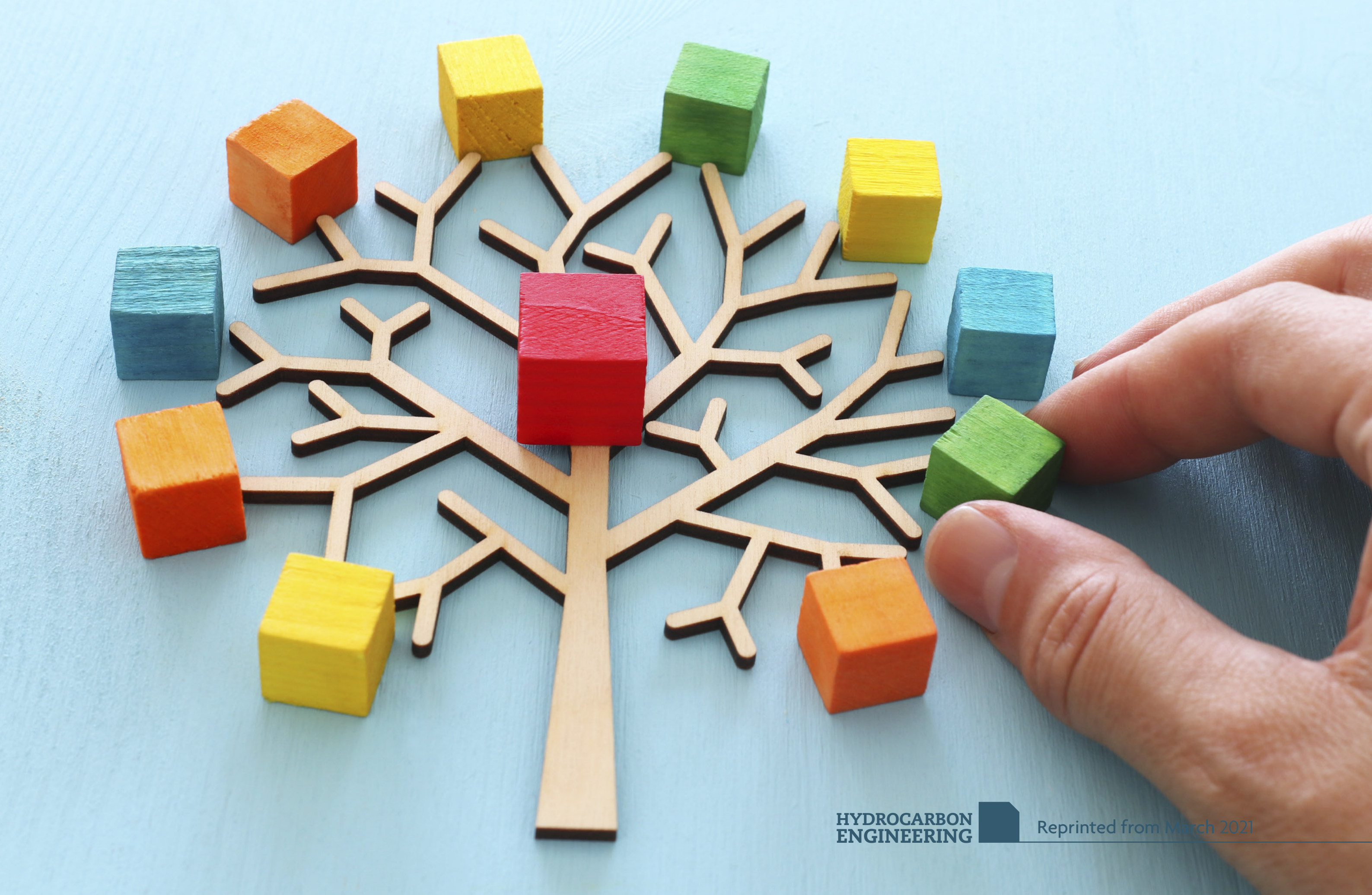
OCTANE IMPROVEMENT IN FCC UNITS: AN OPEN CHOICE

Hernando Salgado and Melissa Clough Mastry, BASF Refining Catalysts, offer a review of octane improvement methods in an FCC unit and assess each method's advantages and disadvantages.

Octane number is one of the most important properties of gasoline and the most typical product differentiation factor at a fuel station. From the refining economy's point of view it is important to maximise the octane of certain streams, including fluid catalytic cracking (FCC) naphthas, to optimise their blending with lower octane streams and therefore maximise the value creation in the final gasoline pool. This is particularly important for an FCC unit, since naphtha (or FCC gasoline) is one of its premium products and often the main reason for its existence in fuel-oriented refineries.

There are several methods for improving the research octane number (RON) of FCC gasolines – and with this the associated refining economics – which are described in this article. Among these methods, there are quick solutions that include simply increasing the reaction temperature (ROT) or



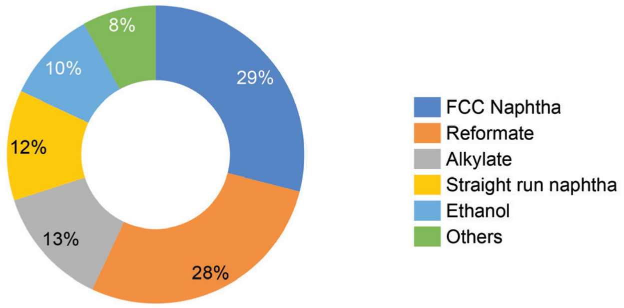


Figure 1. Average gasoline pool consumption in the US.[1]

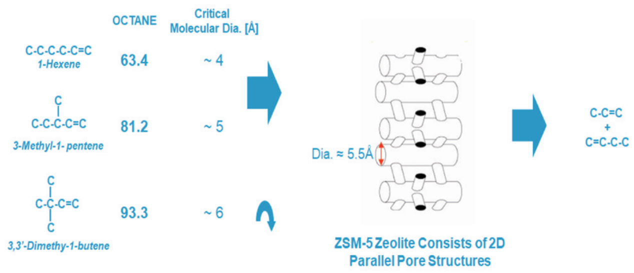


Figure 2. ZSM-5 zeolite mechanism in the FCC unit.

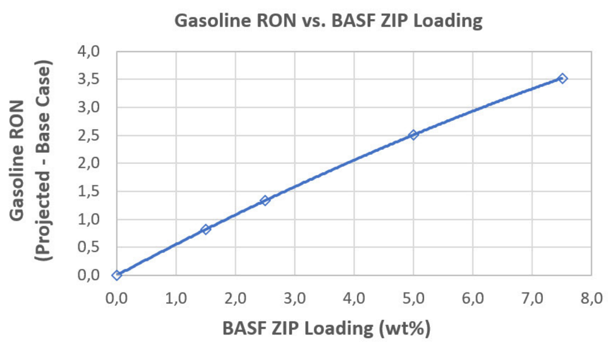


Figure 3. Effect of olefins additive (ZIP) additions on FCC gasoline RON.

the addition of an olefins additive (based on ZSM-5 zeolite). Longer-term solutions involve catalyst reformulation or combinations of two or more methods.

In this article, these methods are presented along with their corresponding pros and cons by using a refinery case study as an example. In addition, kinetic simulations are included to show the impact of applying each method in a refinery setting. The most efficient and economical method, or combination thereof, will depend on each unit and refinery configuration.

Octane number in gasoline and the FCC unit

Worldwide, one of the main components of the final gasoline pool is the FCC naphtha. While some FCC units produce one single naphtha stream, others might produce two or three cuts (light, middle, and heavy), depending on the unit configuration and economics.

Other components used in the refinery gasoline pool include reformate, alkylate, isomerate, straight run naphthas, and ethanol (Figure 1).

The property that most defines the final gasoline product is the octane number, which is a measure of the knock resistance of gasoline and describes the behaviour of the fuel in an engine during combustion. The octane number is defined as a numerical value from 0 to 100 and is a function of the chemical composition of the gasoline. Aromatics, iso-paraffins, iso-olefins and cyclo-paraffins are octane boosters, while linear paraffins are octane depressors.

When determining the octane number, a distinction is made between the RON and the motor octane number (MON). While the RON describes the behaviour of the fuel in the engine at relatively low temperatures and speeds, the MON does so at relatively high temperatures and speeds.

FCC naphthas are rich in iso-olefins (light FCC naphtha) and aromatics (heavy FCC naphtha). Such streams are valued as high-octane components, especially in terms of RON, since MON is promoted more by iso-paraffinic components such as alkylate, which is mostly comprised of iso-octane isomers (it should be kept in mind that 2,2,4-trimethylpentane, commonly called iso-octane, has by definition RON and MON ratings of 100).

Methods for improving octane in FCC gasolines

The methods for improving octane in gasoline depend on changing its chemical composition. The concentration of iso-olefins and aromatic molecules should be increased, since FCC reactions have little impact on cyclo-paraffins, while on the other hand FCC naphthas are poor in iso-paraffinic molecules. Consequently, methods to increase octane of FCC naphthas are more focused on increasing RON rather than MON, as will be discussed in the following sections.

There are three main methods to increase the content of iso-olefins and aromatics, and therefore RON, in FCC naphthas:

- Adding an olefins selective additive (ZSM-5 zeolite based) to the catalyst inventory.
- Increasing ROT.
- Decreasing the REO/zeolite ratio of the base catalyst.

Each of these methods will be explained in the following sections. Moreover, a combination of these methods can also be applied, depending on the conditions and configuration of each unit and refinery.

It must also be noted that an important factor that determines the gasoline RON in an FCC unit is its feed quality. It might be particularly challenging to increase RON in certain units that process highly paraffinic feeds, leading to relatively low octane in the FCC gasolines. This is an important factor to consider, since it might reduce the effect of the methods previously mentioned.

Effect of adding an olefins selective additive

The use of an olefins selective product (based on ZSM-5 zeolite) is one of the most popular methods to improve

Table 1. Yield and operating variables projection with 5% ZIP as a percentage of fresh catalyst loading

Parameter	Base catalyst	Base catalyst +5 wt% ZIP	Delta
Fresh cat addition (kg-cat/t-feed)	2.43	2.52	0.10
BASF ZIP dosage (wt%)	0.0	5.0	5.0
Ecat activity (wt%)	70	70	0
Ecat total surface area (m^2/g)	107	109	2
ROT (°C)	510	510	0
RegenT (°C)	661	662	1
Catalyst to oil ratio	11.9	12.1	0.3
Ex-reactor yields			
H_2S (wt%)	0.04	0.04	-0.01
H_2 (wt%)	0.06	0.06	0.00
Methane (wt%)	0.15	0.15	0.00
Ethylene (wt%)	2.50	2.58	0.09
Ethane (wt%)	2.57	2.62	0.05
Propylene (wt%)	1.62	2.67	1.04
Propane (wt%)	0.42	0.52	0.09
iC4 (wt%)	1.20	1.41	0.21
nC4 (wt%)	0.43	0.44	0.01
C4= (wt%)	2.18	3.05	0.87
1,2-C4= (wt%)	0.04	0.07	0.03
Gasoline (wt%)	62.81	60.64	-2.18
LCO (wt%)	11.37	11.12	-0.26
Slurry (wt%)	2.43	2.28	-0.15
Coke (wt%)	12.15	12.34	0.19
Std conversion (wt%)	86.20	86.60	0.40
Delta coke (wt%)	1.02	1.02	-0.01
Total dry gas (wt%)	5.28	5.42	0.14
Total LPG (wt%)	5.87	8.09	2.22
C3=/total C3	0.79	0.84	0.04
C4=/total C4	0.57	0.61	0.05
RON gasoline	90.5	93.0	2.5
MON gasoline	82.6	84.0	1.4

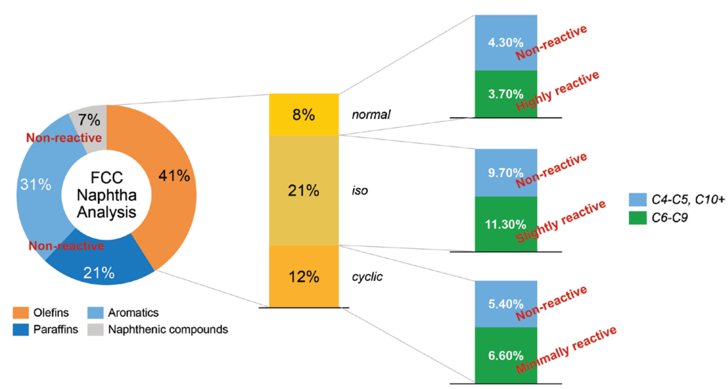


Figure 4. PIONA analysis of FCC naphtha.

RON in FCC naphthas. Indeed, the ZSM-5 zeolite was invented by Mobil Oil Corp. (now part of ExxonMobil) in 1975 as an octane booster additive to be used in FCC units, although currently it is widely used to improve light olefins yields.

Olefins additives improve RON by imparting the ZSM-5 zeolite shape selectivity to convert the linear and slightly linear (i.e. mono-branched) olefins present in the light naphtha into lighter olefins, while rejecting the highly branched and high-octane olefins, therefore preserving these high-octane molecules in the gasoline product (Figure 2).

Since part of the olefins in the FCC gasoline are converted to propylene and butylenes, one of the effects of the olefins selective product is an increase in LPG yields, more or less to the same extent as gasoline decreases.

Because the ZSM-5 zeolite effect results in a reduction of gasoline yield, the aromatic molecules and branched olefins present in the FCC gasoline are concentrated, improving its RON. If the FCC gasoline is split into several fractions the RON in the lighter fraction is increased by the greater concentration of branched olefins, while in the heavier fractions the RON is improved by the higher concentration of aromatics.

In addition, it has been observed that conversion of light olefins (mainly propylene) to aromatics can also be promoted by the presence of ZSM-5 zeolites at temperatures higher than 600°C, increasing RON further.[2,3] However, this phenomenon is hardly seen at conventional FCC process conditions.

A kinetic simulation was performed to determine the effect of adding BASF ZIP (ZSM-5 based product) on the gasoline RON of an RFCC unit located in a Mediterranean refinery. It must be noted that this particular unit only has a full range naphtha product with a target to increase RON by 2.5 points. The results are shown in Figure 3.

The target to increase RON by 2.5 points is achieved after having a 5 wt% loading of BASF ZIP in the circulating Ecat. Expected results in yields and main operating variables based on the kinetic simulation are shown in Table 1.

In Table 1, it can be seen that the drop in gasoline yield is comparable with an increase in LPG and dry gas due to the increase in light olefins.

Since olefins additives (such as BASF's ZIP or ZEAL) do not crack the heavy molecules present in vacuum gas oil (VGO) and resid feeds, it is important to mention that the catalytic activity to crack these molecules is impacted when the selective additive concentration of the olefins is increased, particularly when olefins additive (containing ZSM-5 zeolite) is added separately from the catalyst. To overcome such an activity decrease, Ecat activity must be compensated for with higher fresh catalyst additions in order to maintain the target conversion in the FCC unit. Alternatively, an olefins selective additive can be pre-blended with an in-situ catalyst in such a way to avoid dilution effects.

For ZSM-5 zeolite to be effective, there must be precursors available in the FCC naphtha stream to crack. To this end, an effective olefins selective additive management strategy involves a detailed

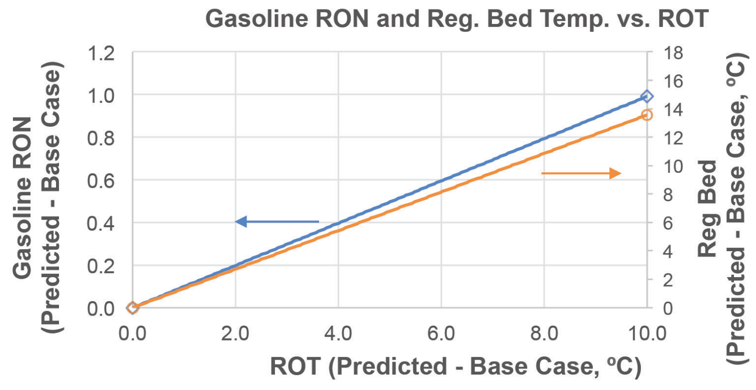


Figure 5. Effect of ROT on FCC gasoline RON and regenerator bed temperature.

Table 2. Yield and operating variables projection for higher ROT (+10˚C)

Parameter	Base case	ROT + 10˚C	Delta
Fresh cat addition (kg-cat/t-feed)	2.43	2.43	0.10
Ecat activity (wt%)	70.0	70.0	0.00
Ecat total surface area (m^2/g)	107	107	0.00
ROT (˚C)	510	520	10
RegenT (˚C)	661	675	14
Catalyst to oil ratio	11.9	12.1	0.2
Ex-reactor yields			
H_2S (wt%)	0.04	0.03	-0.01
H_2 (wt%)	0.06	0.06	0.00
Methane (wt%)	0.15	0.17	0.02
Ethylene (wt%)	2.50	3.00	0.50
Ethane (wt%)	2.57	2.83	0.26
Propylene (wt%)	1.62	1.78	0.15
Propane (wt%)	0.42	0.48	0.05
iC4 (wt%)	1.20	1.24	0.04
nC4 (wt%)	0.43	0.46	0.03
C4= (wt%)	2.18	2.35	0.17
1,2-C4= (wt%)	0.04	0.06	0.02
Gasoline (wt%)	62.81	62.27	-0.54
LCO (wt%)	11.37	10.77	-0.60
Slurry (wt%)	2.43	2.14	-0.29
Coke (wt%)	12.15	12.36	0.20
Std conversion (wt%)	86.20	86.60	0.40
Delta coke (wt%)	1.02	1.03	0.00
Total dry gas (wt%)	5.28	6.06	0.78
Total LPG (wt%)	5.87	6.30	0.44
C3=/total C3	0.79	0.79	0.00
C4=/total C4	0.57	0.57	0.01
RON gasoline	90.5	91.5	1.0
MON gasoline	82.6	83.3	0.7

analysis of the naphtha. The most effective tool for this work is a paraffins, iso-paraffins, olefins, naphthenes, and aromatics (PIONA) analysis.

This analysis can identify what type and quantity of molecules are present in the FCC naphtha in order to determine if additive precursors are available. In the following example, an FCC naphtha sample was analysed for this purpose.

As can be seen in Figure 4, the FCC naphtha contained 41% olefins. However, even more information is required to understand the olefins additive potential. Normal olefins are the most reactive, while iso-paraffins are the next reactive group. The more branched the molecule, the less reactive it is. Cyclic paraffins can also be reactive, although very minimally. Long side chains containing a double bond can be cracked in activated ZSM-5 zeolite that is part of an olefins additive, while the cyclic portion mostly remains outside of the ZSM-5 channel.

Furthermore, C6-C9 molecules are the most reactive with a ZSM-5 zeolite. In this example, 3.7 wt% of the gasoline is still highly reactive, while 11.3 wt% is slightly reactive. The rest of the gasoline is minimally or non-reactive. In this example, this FCC had some, albeit very little, room for further olefins selective additive optimisation.

Effect of ROT

ROT has a strong effect on FCC gasoline RON. Since branched olefins are more stable than linear olefins, at higher ROT, linear olefins in gasoline are more susceptible to secondary cracking reactions, which is a phenomenon often called over-cracking. In addition, aromatic molecules in gasoline are refractory and are preserved.

Therefore, higher ROT means that more gasoline over-cracking is occurring, resulting in a higher RON due to the concentration of branched olefins and aromatic molecules. Furthermore, higher ROT will significantly impact other variables such as the regeneration temperature due to a higher coke yield, as well as higher dry gas due to an increase in thermal cracking, with potential impacts in both the main blower and wet gas compressor.

A kinetic model was used to illustrate this point and is depicted in Figure 5. As can be observed in Figure 5, after increasing ROT by 10˚C, RON in gasoline is expected to increase by only 1.0 point. In this particular case study, an increase in ROT by 10˚C was not enough to meet the refinery target. In addition, the regenerator bed temperature would increase by 14˚C, increasing dry gas yield by 0.8 wt%, with negative impacts on the wet gas compressor operation.

Predicted results in yields and main operating variables, based on the kinetic simulation, are shown in Table 2.

Effect of rare earths (catalyst reformulation)

Another variable that impacts RON in FCC gasoline is the rare earth oxides (REO) content in fresh catalyst per unit of zeolite (i.e. the REO/zeolite ratio). Besides having a function of stabilising the catalyst due to hydrothermal conditions in the regenerator and metallic contaminants from the feed, REO also affects the cracking mechanism by increasing hydrogen transfer reactions.

Hydrogen transfer reactions play a fundamental role in catalyst selectivity since they promote the saturation of olefinic molecules to their paraffinic counterparts, therefore reducing iso-olefins content in gasoline and the amount of linear olefins to be further cracked to LPG molecules.

As a result, a high REO on zeolite catalyst will end up producing relatively low gasoline RON and low LPG yield (with low olefinicity), due to the increase in hydrogen transfer reactions (Figure 6). Conversely, a catalyst with high REO on zeolite will give higher gasoline yields.

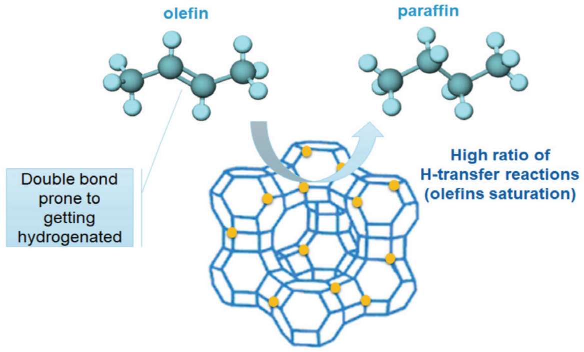


Figure 6. Effect of hydrogen transfer on olefins saturation.

In the case of the RFCC unit studied in this article, it uses a catalyst with 3 wt% REO, which has been suitable for supporting the high gasoline yield requirement. However, if an increase in RON is desired with similar gasoline yield, then a catalyst reformulation needs to be considered.

By using a kinetic model, an alternative catalyst with 2 wt% REO and improved active matrix to increase bottoms conversion was evaluated. As seen in Table 3, by decreasing the REO content from 3 wt% to 2 wt% (and thereby the REO on zeolite), an increase of 1.0 point in RON can be achieved. In this case, a further decrease in REO content is not advisable because the catalyst must be protected from hydrothermal and vanadium deactivation, since the unit processes residual feeds.

A second case that combined multiple approaches was therefore evaluated by using the lower REO catalyst while also adding BASF ZIP to

Table 3. Yield and operating variables projection with reduced REO and BASF ZIP

Parameter	Base case: 3% wt REO base catalyst	Case 1: 2% wt REO reformulated catalyst	Case 2: 2% wt REO reformulated catalyst +3.3 wt% ZIP	Delta case 2 - base
Fresh cat addition (kg-cat/t-feed)	2.42	2.42	2.55	0.13
BASF ZIP dosage	0.0	0.0	3.3	3.3
Ecat activity (wt%)	70	69	69	-1
Ecat total surface area (m^2/g)	107	116	117	10
ROT (°C)	510	510	510	0
RegenT (°C)	661	675	14	-6
Catalyst to oil ratio	11.9	12.1	0.2	0.8
Ex-reactor yields				
H_2S (wt%)	0.04	0.04	0.04	-0.01
H_2 (wt%)	0.06	0.07	0.07	0.01
Methane (wt%)	0.15	0.15	0.16	0.01
Ethylene (wt%)	2.50	2.39	2.45	-0.05
Ethane (wt%)	2.57	2.64	2.68	0.11
Propylene (wt%)	1.62	1.68	2.40	0.78
Propane (wt%)	0.42	0.35	0.42	0.00
iC4 (wt%)	1.20	1.13	1.26	0.06
nC4 (wt%)	0.43	0.39	0.39	-0.04
C4= (wt%)	2.18	2.25	2.79	0.61
1,2-C4= (wt%)	0.04	0.05	0.07	0.03
Gasoline (wt%)	62.81	62.79	61.37	-1.45
LCO (wt%)	11.37	11.67	11.47	0.09
Slurry (wt%)	2.43	2.16	2.06	-0.36
Coke (wt%)	12.15	12.23	12.37	0.21
Std conversion (wt%)	86.20	86.17	86.47	0.27
Delta coke (wt%)	1.02	0.98	0.98	-0.05
Total dry gas (wt%)	5.28	5.26	5.36	0.08
Total LPG (wt%)	5.87	5.80	7.27	1.40
C3=/total C3	0.79	0.83	0.85	0.06
C4=/total C4	0.57	0.59	0.62	0.05
RON gasoline	90.0	91.0	92.5	2.5
MON gasoline	82.6	83.0	83.8	1.2

increase RON to the desired target. Unlike the purely olefins additive addition discussed previously, in this case the required dosage of the olefins selective additive to meet the refinery target is much lower (35% less, as can be seen in Table 3).

By applying both approaches – a catalyst reformulation to a lower REO content catalyst and adding an olefins selective additive based on ZSM-5 zeolite – the RON target of +2.5 can be achieved, whereas gasoline yield is not dramatically affected.

Discussion and economic considerations

After evaluating the three approaches to increasing gasoline RON at the RFCC unit in this study, the best option is a combination of catalyst reformulation and BASF ZIP additions. When it comes to catalyst reformulation, depending on the unit turnover, it can take time to fully see the desired results. Typically, this can take one to three months or as long as 12 months.

Therefore, if the target to improve the gasoline RON needs to be achieved in a short time period, a quick solution needs to be implemented. Under such a scenario, the quickest way to effectively boost the gasoline RON is purely the addition of an olefins selective additive, such as BASF ZIP. Furthermore, this addition is a flexible way to influence RON and yields since the additive dosage can be adjusted on a daily basis, depending on refinery targets. For a long-term solution, a catalyst reformulation and the flexibility to add or pre-blend an olefins selective additive is an attractive option from the economic point of view, since other benefits might simultaneously be achieved, such as an optimised gasoline yield and bottoms upgrading to LCO.

Conclusions

The optimal strategy for increasing gasoline octane greatly depends on the refinery configuration, operating constraints, and octane targets.

If an increase in RON is needed in a short time scale, the addition of an additive such as BASF ZIP, designed with activated ZSM-5 zeolite, is the best approach. Depending on the unit turnover and inventory, the effect can be noticed in a matter of weeks. Another short time scale approach to increase gasoline RON is to increase the ROT. This alternative must be weighed with the other effects however, including a higher temperature in the regenerator dense bed and increased dry gas and coke yields.

As a long-term solution, a combined approach involving a catalyst reformulation to lower REO content and the use of an olefins selective additive (based on ZSM-5 zeolite, such as BASF ZIP) is the best option.

References

1. TAMM, D.C., et al, 'Analysis of gasoline octane cost', Report for the US Energy Information Administration (October 2018), https://www.eia.gov/analysis/octanestudy/pdf/phase1.pdf
2. MOHIUDDIN, E., MDLELENI, M., and KEY, D., 'Catalytic cracking of naphtha: The effect of Fe and Cr impregnated ZSM-5 on olefin selectivity', *Applied Petrochemical Research*, Vol. 8, No. 2 (June 2018), pp. 119 – 129.
3. HOU, X., et al, 'Reaction pathways of n-pentane cracking on the fresh and regenerated Sr, Zr and La-loaded ZSM-5 zeolites', *Chemical Engineering Journal*, Vol. 349 (October 2018), pp. 297 – 308.