Increasing diesel production from the FCCU

FCC naphtha desulphurisation technology produces low-sulphur heavy catalytic naphtha as a separate product for blending into the diesel pool

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Sulphur concentration in the gasoline pool is being reduced in many parts of the world. In Europe, Euro V regulations, implemented in 2009, require less than 10 ppm sulphur in gasoline. Since 2008, the gasoline sulphur specification in the US and Canada has been less than 30 ppm on average, and a further reduction to 10 ppm is under consideration in the US. In Europe and North America, diesel with a sulphur content in this range is referred to as ultra-low sulphur diesel (ULSD). In Russia, the gasoline sulphur content will be reduced to 10 ppm by 2015. It is likely the sulphur specification in the rest of the world will also become more stringent over time.

Gasoline is a complex product, with many important parameters determining its quality, aside from sulphur concentration; these include vapour pressure, benzene concentration, boiling range and octane rating. In some regions, such as the EU and India, demand for diesel is higher than for gasoline. In others, including the US, demand for diesel is projected to grow while gasoline demand declines, as shown in Figure 1, which also illustrates the future projected change in the global gasoline-to-distillate ratio.

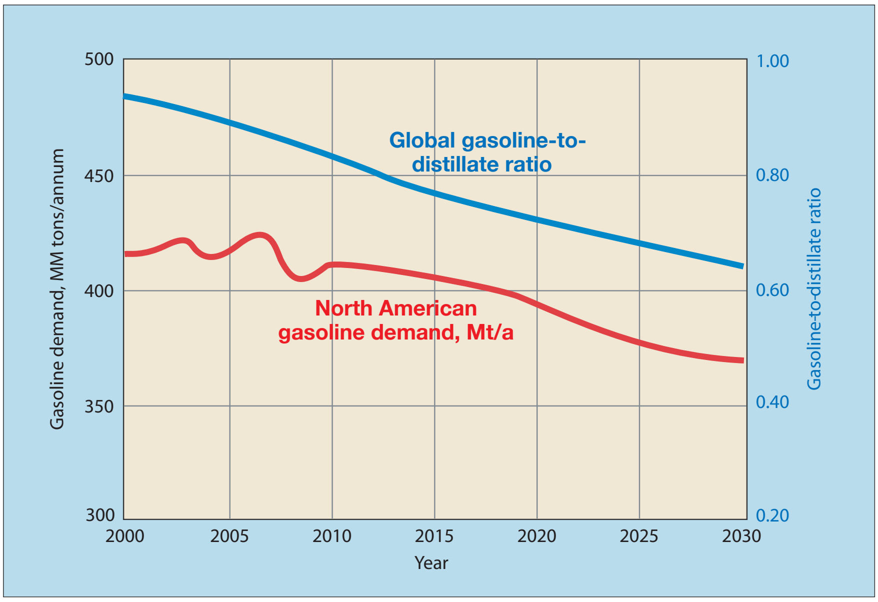

Figure 1 Decline in gasoline demand

To reduce gasoline product and increase diesel product, some refiners produce lower end-point gasoline, routing the heavier cut of the full-range gasoline to the diesel pool. This results in higher capacity requirements for the diesel hydrotreaters, which are often already fully utilised.

To remove sulphur from FCC gasoline, CDTECH offers the commercially proven LCN (light catalytic naphtha) CDHydro and CDHDS processes. These processes, which employ the principle of catalytic distillation, conduct selective hydro-desulphurisation in a distillation environment. The full-range gasoline is split into three different cuts, giving the refiner blending flexibility. It is possible to use the CDHDS process to tailor the sulphur content of the distillate and bottom product, making it feasible to produce 10 ppm low end-point gasoline and a separate heavier cut that meets the less than 10 ppm sulphur specification for blending into the diesel pool. This flexibility can provide significant value by debottlenecking the diesel hydrotreater.

Properties of FCC gasoline

Figure 2 shows a plot of the concentrations of total sulphur, mercaptan sulphur (RSH) and olefins (measured via bromine number) as a function of the boiling point of the FCC gasoline. At the light end of the gasoline, the olefin concentration is high and the total sulphur concentration is relatively low. Nearly all the total sulphur is in the form of RSH. As the boiling point increases, the sulphur concentration begins to increase quite significantly, while the RSH concentration actually declines. At the heaviest end, most of the sulphur is contained in compounds such as benzothiophene and methyl benzothiophene. Conversely, the olefin concentration profile follows the opposite trend: the lighter end of gasoline is olefin-rich, while the heavier end contains very few olefins.

The data plotted in Figure 2 illustrate the challenge involved in treating the light end of the

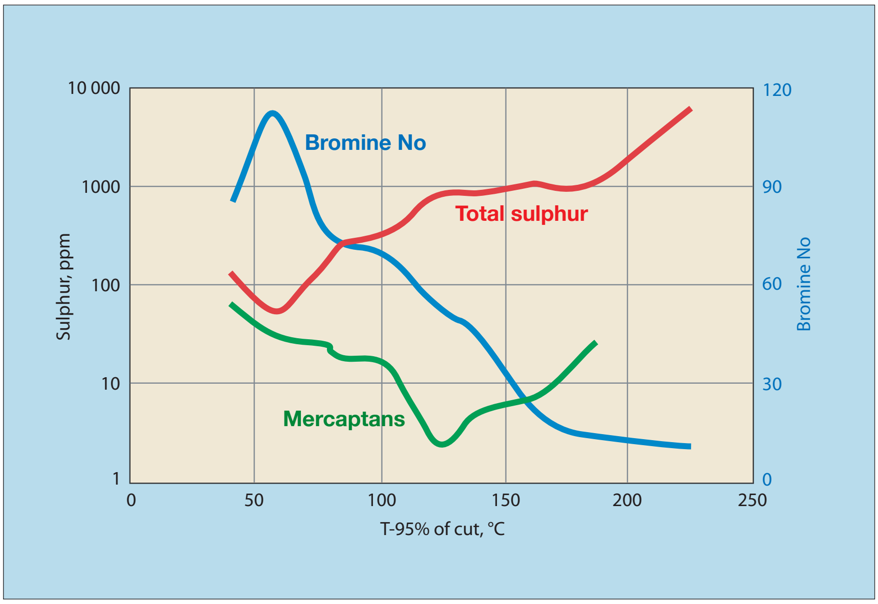

Figure 2 Concentration profiles of total sulphur, mercaptans and olefins (as bromine number) in FCC gasoline

gasoline through to the heavy end. To meet a 10 ppm sulphur specification, the light cut requires only 90% conversion of sulphur; the middle cut (near 135°C) requires 99% conversion, while the heaviest cut requires 99.8% sulphur conversion.

The preservation of olefins is vital to reducing hydrogen consumption and minimising octane loss. Olefin saturation, although inevitable in a hydrodesulphurisation process, is minimised when sulphur conversion is kept to a minimum. With this fact in mind, an ideal desulphurisation process would provide an environment where the highest severity is applied only to the heavy fraction of the gasoline, which has high sulphur and low olefin concentrations. The olefins in the heavy fraction also have a lower octane content than the olefins in the light fraction. Reaction severity would be decreased for the lighter fractions, which have lower sulphur and higher olefin concentrations. Treating the lighter fraction at lower severity limits the saturation of valuable olefins in this olefin-rich region.

Process overview

CDTECH has developed a selective treatment method for full-range FCC gasoline, which optimises the severity of treatment for different cuts of gasoline to maximise sulphur removal while minimising olefin loss. As Figure 3 shows, the first step is to treat the lightest fraction of the gasoline in a LCN CDHydro unit, where the RSH is non-destructively removed. The LCN CDHydro unit is not a hydrodesulphurisation step. It operates at very mild conditions, resulting in no measurable olefin loss.

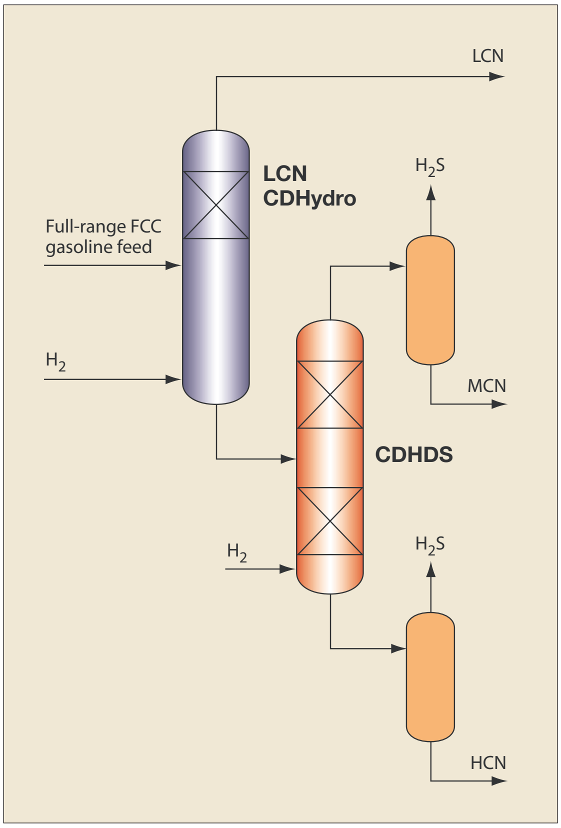

Figure 3 A proposed flow scheme to maximise blend flexibility

Part of the rectification section of the LCN CDHydro column contains catalyst packed in a distillation structure. The rest of the column contains conventional distillation trays. The LCN CDHydro unit works by performing an additional reaction between the RSH and the contained diolefins over the catalyst to form a heavier sulphide (RSR). The heavy sulphide goes to the bottom of the LCN CDHydro column and exits with the bottom product.

The light product from the LCN CDHydro column has a very low RSH content, very high olefin concentration, a high octane rating and a relatively high Reid vapour pressure (RVP). Some refiners choose to isolate this fraction in order to increase flexibility in the blending operation.

The LCN CDHydro column bottoms go to the CDHDS column. This is the hydrodesulphurisation step that converts sulphur in the gasoline to H_2S. The CDHDS column also contains a hydrodesulphurisation catalyst packed in a distillation structure. Since the process is based on distillation, the catalyst structure below the feed point operates at much higher temperatures than the catalyst structure above the feed point. This has the effect of increasing reaction severity for the heavy portion of the gasoline, where the requirement for sulphur conversion is the highest and the olefin content is the lowest. Simultaneously, the medium catalytic naphtha (MCN), which contains higher olefin levels and fewer refractory sulphur compounds, goes up the column, where conditions are less severe than they are at the bottom. Thus, the reaction conditions in the CDHDS unit are ideally suited to the goals of preserving olefins and minimising octane loss.

Since the CDHDS unit performs distillation, there is an opportunity to isolate two additional FCC gasoline fractions to increase blending flexibility and control the end point of the product. The CDHDS column distillate product (MCN) makes an ideal low end-point blendstock for the gasoline pool.

End-point flexibility

The CDHDS column bottom product (heavy catalytic naphtha, or HCN) can also be isolated and is a high end-point product; however, it is important to realise that this product has a very low sulphur concentration. The HCN can be desulphurised to sulphur concentrations that are lower than those required for the gasoline pool without sacrificing olefins and octane in the MCN bound for the gasoline pool. This increases its number of potential uses, while maintaining good economics for the treatment of the MCN. The HCN can be blended into the gasoline pool if desired. If low end-point requirements become constraining, the HCN can be sent into a low-sulphur or an ULSD pool without requiring any further sulphur removal, making it ideal for blending into the diesel pool. Thus, the HCN will not occupy capacity in the refinery's diesel hydrotreater (DHT), which otherwise could potentially cause a DHT bottleneck.

The ability of the CDHDS column to produce a higher sulphur distillate and lower sulphur bottom product is unique and cannot be replicated by installing a gasoline splitter downstream of a fixed-bed FCC gasoline hydrodesulphurisation (HDS) unit.

The product from a fixed-bed FCC gasoline HDS unit contains heavy sulphur components such as benzothiophenes. When the gasoline produced from a fixed-bed unit is distilled, the bottom product will contain more sulphur than the distillate product. To meet the sulphur specifications required to send this bottom product into the diesel pool, two options exist:

- Send it for further treatment in the DHT, which may restrict diesel production in the refinery
- Treat the entire gasoline stream to reach a sulphur level well below the desired diesel specification, which will result in a very large octane loss in the gasoline pool, but will not restrict diesel production.

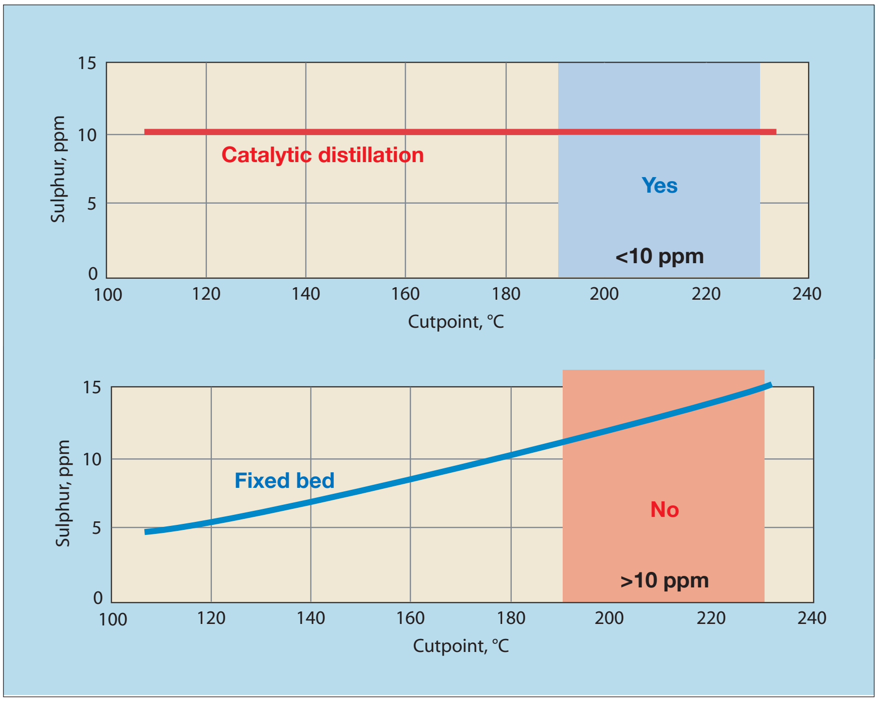

Figure 4 Comparison of sulphur content in FCC gasoline fraction

The refiner may opt to undercut the gasoline and send only a low end-point feed through the fixed-bed FCC gasoline HDS unit, but this still requires running the heavy gasoline-range material through the DHT. The CDTECH flow scheme does not take up capacity in the DHT and therefore gives refiners an opportunity to debottleneck diesel production. However, some CDTECH licensees operate their units in this manner on a seasonal basis to satisfy changing market conditions. By taking advantage of the HCN as a separate product, the refiner avoids having to treat this material in a separate hydrotreater. This mode of operation commercially demonstrates the flexibility of the technology to operate on feedstocks of variable boiling range.

The modifications required to maximise diesel production are negligible. A typical configuration of a CDHydro/CDHDS unit, together with the DHT, is shown in Figure 5. In this configuration, it is assumed that H_2S stripping of the MCN

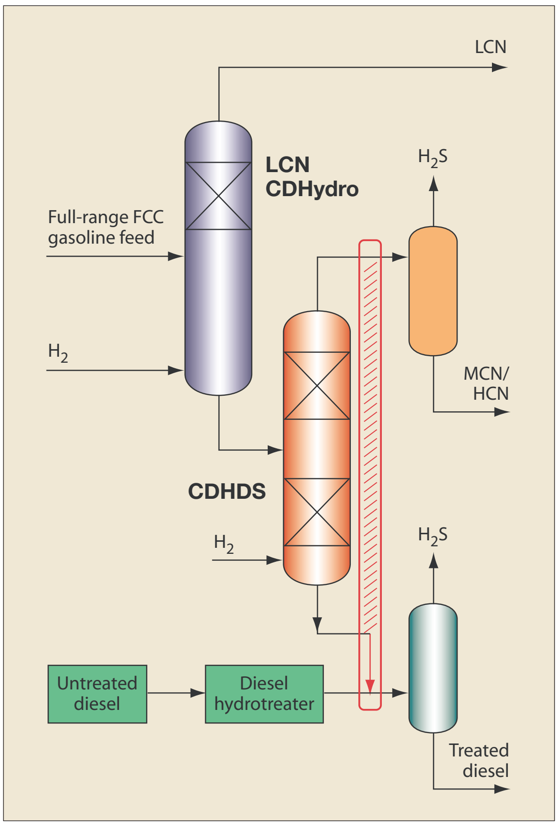

Figure 5 Conceptual configuration for maximising diesel production

and HCN streams is performed in a single stripper column. Refiners who aim for maximum blending flexibility usually have separate MCN and HCN stripper columns, as depicted in Figure 3. In that case, the HCN stream can be directly blended to the diesel pool.

If separate MCN and HCN stripper columns are not available, the bottom product must be routed to the H_2S stripper column in the DHT unit. Generally, the HCN stream is small relative to the diesel product, so the additional load can be handled in the H_2S stripper column. Hence, the only hardware modification needed is to install piping between the CDHDS column and the H_2S stripper column in the DHT unit.

Treatment of the HCN fraction in the CDHDS column has very little impact on the relevant properties of the diesel fraction.

Flashpoint

The MCN/HCN cutpoint is usually set by the flash point requirement, which is typically set at 55°C minimum. This corresponds with a D86 10% point of approximately 180°C, and is easily controlled in the CDHDS column.

Cetane number

The cetane number of the diesel fraction from an FCCU (light cycle oil) is rather low, generally in the order of 20. Some improvement in cetane number is achieved by hydrotreating the diesel fraction, which converts the aromatics into naphthenes. The resulting cetane number after hydrotreating is generally in the order of 40. Given that the amount of diesel from the CDHDS unit is small relative to the total diesel pool, the impact on the cetane number is negligible.

Long catalyst life

Treating cracked streams in fixed-bed FCC gasoline HDS units can result in catalyst coking and fouling, which in turn can cause substantial pressure drop. These problems are addressed by periodically shutting down the units to vacuum out the upper layers of catalyst. To help reduce fouling, these units require a selective hydrogenation unit (SHU) upstream to significantly reduce reactive dienes from the feed.

The CDHDS process is very selective in minimising olefin saturation and maximising octane retention

An added benefit of conducting the HDS reaction in a catalytic distillation environment is the significantly longer catalyst life. The reflux in the CDHDS column provides a sink for the heat of reaction, so catalyst hotspots are virtually eliminated. The reflux also provides a washing action, where coke precursors are removed from the surface of the catalyst before they have an opportunity to develop into larger formations that deactivate the catalyst or plug the catalyst bed. Inspections of many CDHDS units over the past 15 years have confirmed the validity of this mechanism. CDHDS units, which do not require an upstream SHU, have been in operation for more than six years with no apparent loss of catalyst activity.

The CDHDS technology is unique, in that the desulphurisation step does not limit the run length of the FCCU, even as refiners press for FCC cycles of up to six years and eventually more. For refiners employing shorter FCC turnaround cycles, the catalyst in the CDHDS column can last for multiple cycles.

Hydrogen usage

The CDHDS process is very selective in minimising olefin saturation and maximising octane retention. As a result, hydrogen consumption is moderate. In addition, the CDHDS column is designed to run at modest hydrogen recirculation rates, which results in a smaller recycle compressor with less power consumption. Since the hydrogen recirculation rates are low, the CDHDS process can run with lower purity hydrogen than a typical fixed-bed unit. Given the tight supply of hydrogen in most refineries, these can be significant operating factors.

Another consideration is the refiner's fallback position in the event that the hydrogen recycle compressor goes down unexpectedly. Given the modest hydrogen requirements of the CDHDS unit, it is possible to run it on once-through hydrogen until the repair is completed. In a typical fixed-bed unit, it is impractical to attempt to match the recirculation rates on a once-through basis due to the much higher required hydrogen rates.

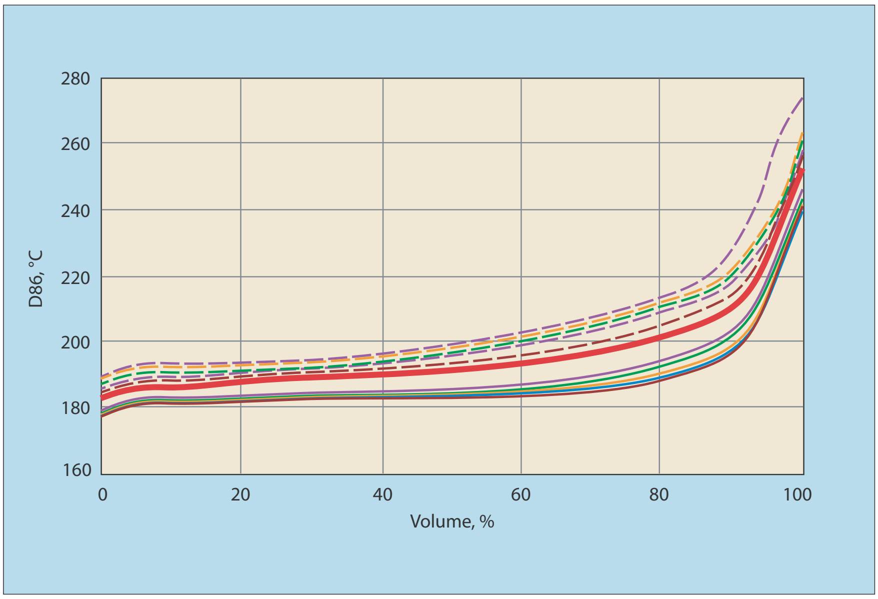

Figure 6 Boiling range of heavy catalytic naphtha (HCN)

Therefore, it will be necessary to shut down not only the fixed-bed FCC gasoline HDS unit, but also the FCCU until the compressor repair is completed. The ability of the CDHDS process to operate on once-through hydrogen means it does not have to shut down for a recycle compressor outage.

Case study

A refinery using CDHydro/CDHDS will soon be ready to produce HCN as a separate ULSD blendstock. The stream, already containing less than 10 ppm sulphur, is currently being sent to the gasoline pool until piping modifications are completed. The stream will then be sent to an existing DHT product stripper, where H_2S will be removed to meet the final blending specifications for ULSD. As a result, about 10% of the total FCC gasoline will then be diverted to the diesel pool. Figure 6 shows the typical distillation range of the HCN over several days of operation. The 180–190°C initial boiling point (IBP) and 240–275°C endpoint will fit well within the normal diesel boiling range of 175–325°C.

Summarising, the CDHDS bottom product could be used to blend to gasoline (typically C_5–230°C), diesel (typically 180–360°C), kerosene (typically 180–280°C) or white spirit product (typically 140–200°C), all with a sulphur content of less than 10 ppm.

Wholesale pricing of diesel vs gasoline is seasonally dependent, as is clear from Figure 7. While the price difference between diesel and gasoline is (in October 2009) minimal, this price difference is expected to return to traditional levels (typically €50/tonne) due to increasing demand for diesel.

For 2400 tonnes per day (20 000 bpsd) FCC gasoline capacity, the economic advantage of routing CDHDS bottom product to the diesel pool is in the order of €4 million per year, assuming a future €50/tonne margin between diesel and gasoline. Also, when the refiner has the flexibility to export the CDHDS bottom product as a white spirit product, margins are even better.

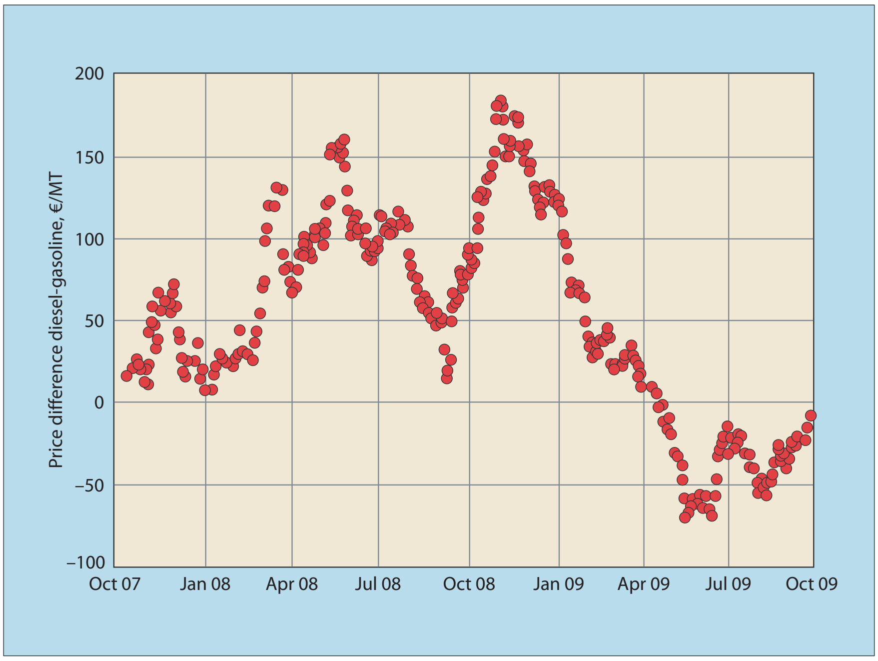

Figure 7 Price difference diesel-gasoline (Western Europe)

Conclusion

The LCN CDHydro and CDHDS processes, which employ catalytic distillation for the hydrodesulphurisation of gasoline, offer significant advantages over fixed-bed hydrodesulphurisation processes. The selective treatment of the full-range gasoline fractions ensures maximum octane retention with low hydrogen consumption. In addition to lower utility consumption, these processes offer an extremely long catalyst life. They provide the refiner with operating reliability, blending flexibility and the potential to debottleneck the DHT capacity, and thus maximise diesel production. The economic advantage of this flexibility embedded in CDHydro/CDHDS technology is significant and will be in the order of €4 million per year for a 20 000 bpsd FCC gasoline desulphurisation unit.

The CDHDS bottom product could be used to blend to gasoline, diesel, kerosene or white spirit product, all with a sulphur content of less than 10 ppm

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