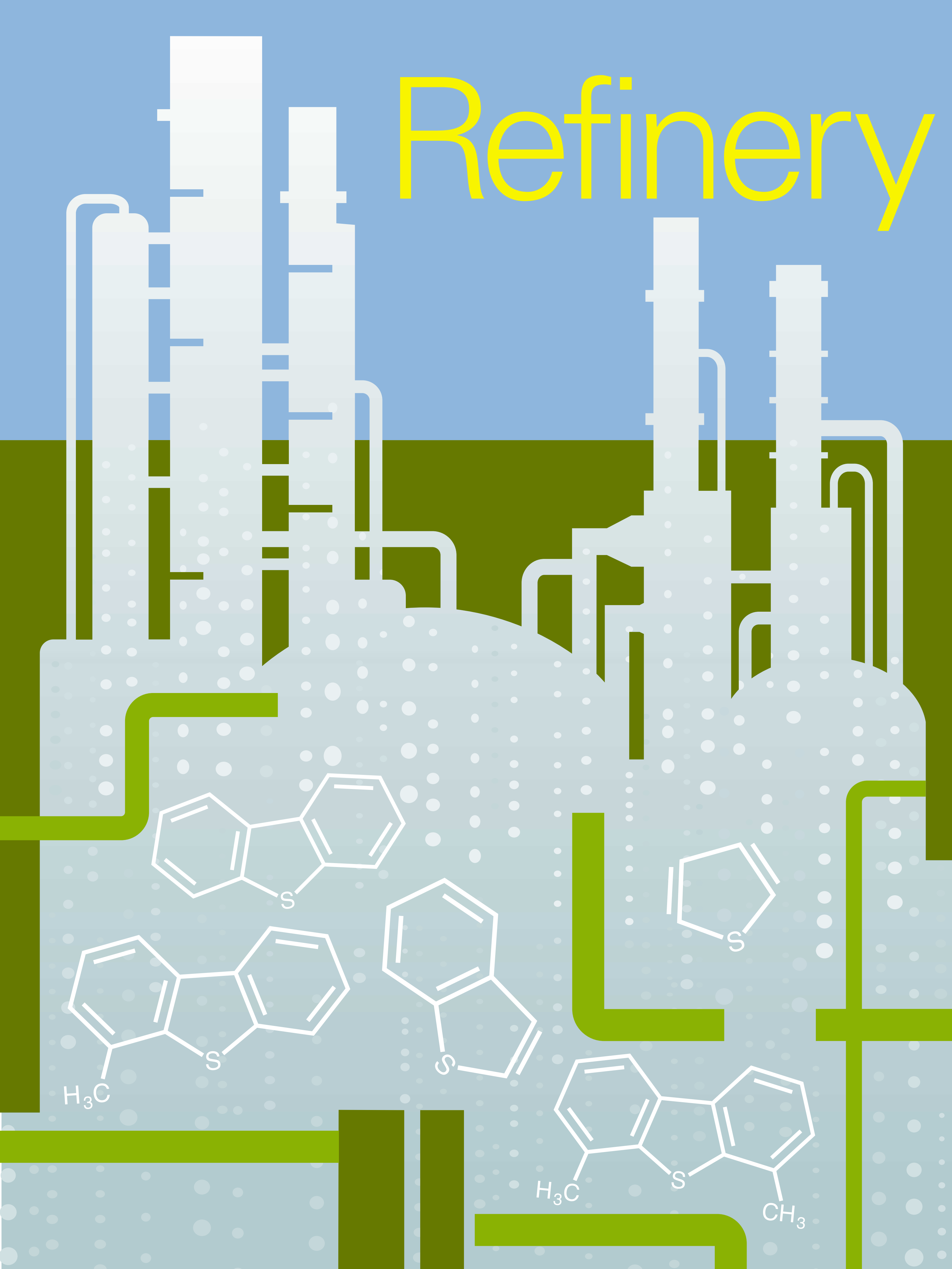
Refinery



rejuvenation

As part of its commitment to deliver cleaner fuels around the world, BP's refinery technologists are breathing new life into the hydrotreatment process for removing sulphur from diesel, as *Tom Seslar* discovers

An observation often dressed up to appear respectable among young engineers is the notion that technology in the oil business – particularly refining – has a grand past but a less exciting future. Don't buy into that myth before you listen to some up-to-the-minute reality from BP's John Yates and Paul Ziegelaar regarding what's happening to the hydrotreater, an example of how old refining technology can be adapted to perform new wonders. They point out that the effectiveness of hydrotreating and computing have improved at roughly the same rate during the past decade.

Yates is manager of refining advisors for BP's worldwide collection of refineries, and Ziegelaar a hydroprocessing advisor. Both are based at BP's technology centre in Naperville, Illinois.

Long regarded rather unglamorously as a 'refinery workhorse unit', a hydrotreater removes sulphur from fuels such as diesel. Much of Ziegelaar's work life centres on hydrotreaters, with good reason as the world races ever faster toward an age of legally mandated, sulphur-free diesel. Within the next few years, it's expected that most of the major markets BP serves around the globe will have enacted laws requiring sulphur-free diesel. The main drivers for this change are environmental, calling for reductions in emissions of particulates, nitrogen oxides and sulphur to the atmosphere. Furthermore, the latest vehicle exhaust after-treatment systems – catalytic converters – for reducing hydrocarbons, particulates and nitrogen oxides are less tolerant to sulphur, as this reduces the activity of the catalyst.

The term 'sulphur-free diesel' generally refers to diesel containing less than 15 parts per million (ppm) sulphur by weight in the USA, and less than 10ppm in Europe and the rest of the world.

Hydrotreatment is a generic process which reacts hydrocarbon compounds with hydrogen in the presence of a catalyst, to obtain a change in the characteristics of the hydrocarbons – in the refinery context, hydrotreatment is most commonly used for removing sulphur from the hydrocarbon components that make up diesel and gasoline. The majority of diesel is produced by hydrotreating middle distillate feedstocks coming from the crude oil distillation unit. Such feedstocks normally contain high levels of sulphur or aromatic compounds.

Now comes the surprising reality that hydrotreating, a long-established process in the refining industry, has re-emerged as a breakthrough technology. Over the last 20 years, the level of sulphur in finished diesel has fallen by two orders of magnitude, even though the sulphur content of the 'raw' diesel feed has barely changed. Over the same period, BP has found ways to bring down the cost of removing sulphur from a barrel of diesel product by 40%.

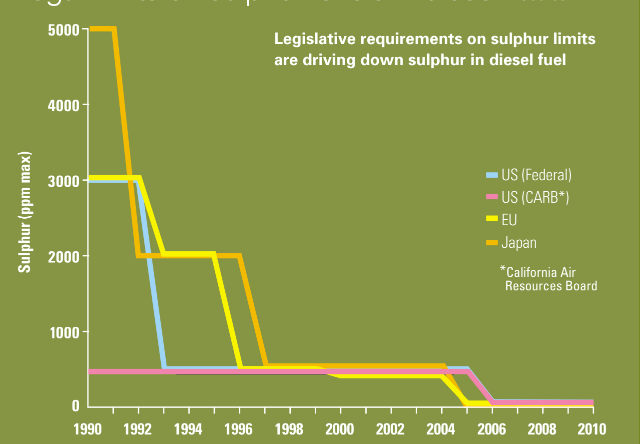
'As far as I know there is almost no other technology that comes close to this rate of improvement in performance over the last decade,' observes Yates. 'If you have something that improves by a factor of 100 over a period of 10 years, that is quite extraordinary. Computers are said to double – in terms of power – every 18 months. Moving from 1000ppm of sulphur in diesel down to 10ppm is a similar rate of improvement.'

Opportunity seized

BP spearheaded this performance improvement with the company's early commitment in the mid-1990s to making cleaner fuels, and by being proactive about finding the technology needed to achieve this. In part, the latter has come from shopping around among hydrotreating technology suppliers, using the best ideas from each and challenging them to improve still more. In addition, within BP, there is a strong community involved with hydrotreating – process engineers at the refineries as well as technology specialists focused on catalyst selection and process modelling.

External relationships also played a part. By participating in industry research >>

Legal limits on sulphur levels in diesel Source: BP



A hydrotreater at BP's refinery in Grangemouth, UK. Improvements in catalyst technology and process configuration have allowed existing hydrotreaters to reach new high levels of efficiency

>> and development (R&D) projects, BP's refining business contributes its expertise through its New Technology team and its Community of Practice (CoP), at the same time gaining access to the very latest technology (*Frontiers*, August 2003).

'The opportunity was there for anyone to make ultra low sulphur diesel,' Ziegelaar points out. 'BP was one of the first to recognise that the technology was available and moved quickly to use it. This is a story about how we understood that improvements in different technologies had created the opportunity to produce clean fuels at an acceptable cost, followed by assembling the technologies quickly and deploying them in our refineries.'

Most refineries include several hydrotreating units. For many years, industry practice was to hydrotreat some of the higher sulphur-content feedstocks, while others bypassed the hydrotreaters. But with the trend toward lower sulphur fuels, moving from the 10,000ppm of sulphur of 30 years ago to the 10ppm of today, it is necessary to treat almost all the streams, and do this to a far greater degree of sulphur removal than before, demanding both more treatment capacity and a better process.

The conventional alternatives for improving hydotreater performance are changing the catalyst or modifying the unit to enable it to treat higher throughputs of feedstock. Constructing a new hydrotreater is another solution, but is normally the least economic option. As a basic 'rule of thumb', if the existing hydrotreating unit has a reactor operating pressure above 35 bar, it is normally economic to modify the unit – known as 'revamping' it – using existing technology such as booster pumps to force more feedstock and more hydrogen through it. If the pressure is below this level or the unit is expected to process a large percentage of difficult feedstocks, such as those containing hard-to-treat aromatic compounds or very high sulphur oils, then a new unit may be necessary.

The prospect of producing 'zero-sulphur' diesel triggered lots of innovative thinking in the industry, particularly around ways of avoiding the construction of new hydrotreaters. To evaluate the new ideas, the refining business's New Technology group and the CoP worked together, maintaining awareness of technology developments and arranging trials at BP refineries.

Catalyst performance has increased at an exponential rate – and BP is a front runner in using them in its hydrotreaters

Catalyst action

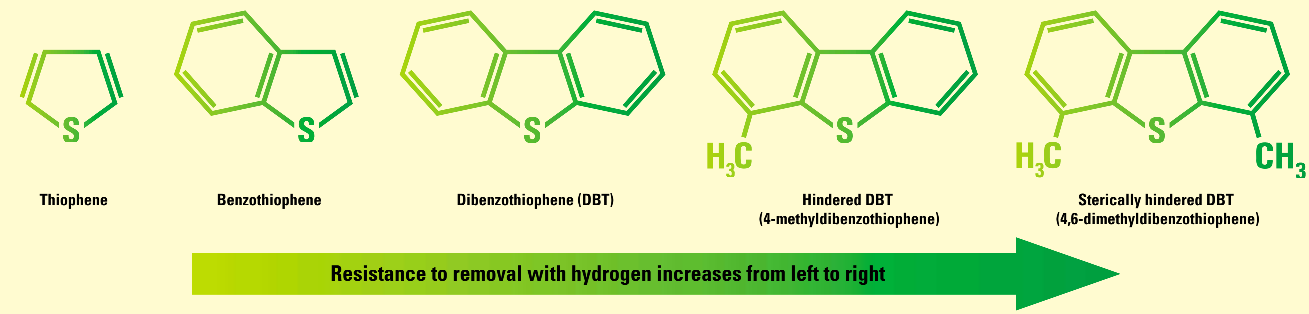
Catalysts were a key focus in BP's efforts to improve hydrotreaters, potentially offering the most economic solution for boosting performance. There are two main types of commercially available hydrotreating catalyst – one based on cobalt-molybdenum (CoMo), the other on nickel-molybdenum (NiMo). Hydrotreating is not a simple process and encompasses several possible chemical pathways, all of which depend on catalyst design. For example the pathways include hydrodesulphurisation (HDS), for the removal of organic sulphur; hydrodenitrogenation (HDN), for the removal of organic nitrogen; and hydrodearomatisation (HDA), for breaking down aromatic compounds. To make things even more complex, these pathways interact with one another. For example, HDN removes impurities that inhibit the HDS process. All of the catalysts promote all three reactions, but to different degrees. Also, the different types of catalyst respond differently to different feedstocks and operating conditions.

'For several decades there was little improvement in hydrotreater catalyst performance, measured by their chemical "activity" in promoting reactions,' says Tom Knox in the New Technology team at Sunbury in the UK. (See graph on page 15.) 'Then, in the mid-1990s, activity began to improve at an exponential rate. In a few years, CoMo activity doubled – and BP was a front runner in using the new catalysts in many of its hydrotreaters.'

In 2000, during BP's evaluation of emerging catalyst technologies, a new breed of catalyst appeared – the proprietary 'Nebula' catalysts made by Akzo Nobel. The Nebula catalysts doubled activity again, with BP becoming the first major refiner to use the new catalyst commercially, the result of close R&D co-operation between BP and Akzo Nobel at the Nerefco refinery in the Netherlands, which BP jointly owns with ChevronTexaco.

The Nebula catalysts have many advantages, one of which is removing some of the remaining 'stubborn' bits of sulphur below the 50ppm level, known as sterically hindered dibenzothiophenes (DBTs). In times as recent as ten years ago, when diesel

Sulphur compounds present in diesel feedstock



sulphur levels typically were in the range of 2000-5000ppm, there was a widely held view that 50ppm was a fundamental barrier in sulphur removal, due in part to the presence of DBTs, which required – it was then thought – expensive catalysts and two-stage reactions to remove them. But the advent of the high-activity Nebula catalysts means that existing hydrotreaters can be upgraded simply by changing out the old catalyst.

In addition to the appearance of a new catalyst – the market is increasingly competitive in this area – BP's work has also shown that DBTs will react to hydrotreatment with conventional CoMo catalysts, given sufficient time to react with the hydrogen. This extra time is provided by increasing the volume of the reactor in the hydrotreater, a relatively low-cost move – doubling reactor size usually adds less than 10% to a new project's overall capital cost, says Yates. The larger reactor means more catalyst volume inside, and this can often avoid the need for high pressure operation, making the unit less costly to build.

'There are also a host of other positive measures we worked to develop,' Yates adds. 'Process designs can now be simplified to reduce the amount of equipment involved. One large reactor is usually more economical than multiple reactors in series, and improved reactor internals ensure that all of the diesel feedstock contacts all of the catalyst, making the catalyst utilisation far more effective and also preventing the flow from bypassing some areas of the reactor. And process efficiency can be moved on still further by mixing the hydrogen with the diesel feedstocks before they enter the reactor.'

Diesel diversity

Finally, BP has become very smart about integrating the hydrotreater with the rest of the refinery. Diesel is normally the product of blending several liquid streams, so the way a refinery chooses to make the blend has a big impact on the final product. This means that making clean diesel carries implications right across the refinery, hence most BP refineries have shaped their clean diesel strategies with the help of 'peer assist' teams drawn from engineers and planners from other BP refineries, along with input from the company's central technology and strategy groups. According to Ziegelaar, the approach has been highly effective in propagating best practices to most of the company's business units that needed to build new capacity for diesel desulphurisation.

BP now has dozens of diesel hydrotreaters 'from all walks of life', and from the various heritage oil companies that came together through merger or acquisition in recent years. 'It has been possible to gather and exploit the best ideas from everywhere,' says Ziegelaar.

Apart from catalyst design, hydrotreating technology is essentially an 'open art', meaning there is little need to license a proprietary technology other than perhaps for project execution convenience. In a distinct move away from past practice, integrated site-based project teams combining site, contractor and process chemistry personnel can often discover more economic solutions than traditional licensor approaches.

In the regions of the world where BP operates refineries, the company is well positioned relative to its main competitors to make sulphur-free diesel. Because BP has a richly diverse heritage of hydrotreating units, options will differ from site to site, backed up by the knowledge of how to make exciting use of catalysts, revamp existing hydrotreatment units, or to design new ones.

Thus in just a few years, diesel hydro-desulphurisation within BP has moved from a 'dull and static' technology to one that is sleek, fast-moving and intriguing, with a large and positive impact on the profitability of BP's refining business. It is also making a highly valuable contribution to the atmosphere of the planet that we all share. ■

Improvements in hydrotreating catalyst activity

Source: Akzo Nobel

Performance of CoMo catalysts remained broadly static for many years. In the mid to late 1990s, Akzo Nobel's Stars catalyst doubled catalyst activity, followed by another doubling with the advent of the Nebula catalyst