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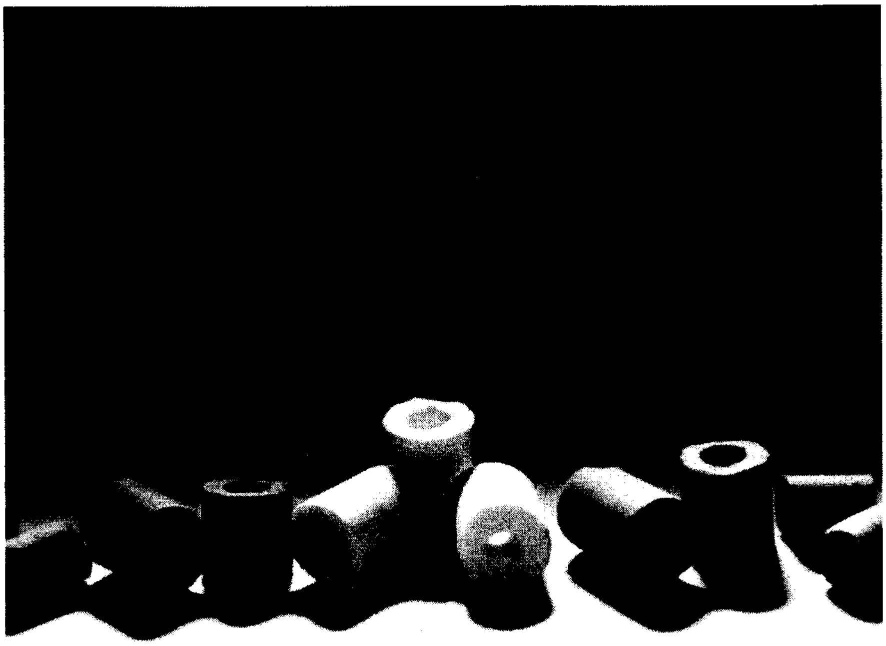
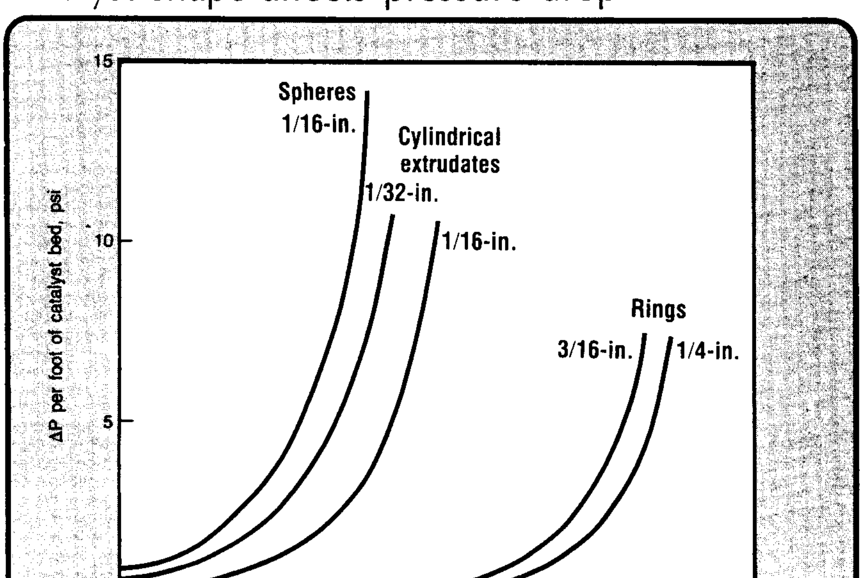
Raschig ring HDS catalysts reduce pressure drop



The Raschig ring hydroprocessing catalysts pictured range in diameter from 3/16-in. (extreme left & right) to 1/4-in., center (Fig. 1).

Fig. 2

Catalyst shape affects pressure drop*



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Many hydroprocessing units have a limit on their run length imposed by bed plugging. As opposed to catalyst deactivation, bed plugging can cause pressure drop over the reactor or first reactor in the train to develop rapidly.

For this reason many reactor designs call for the use of scale baskets together with grading of topping material and/or catalyst in the top bed of the lead reactor. Nevertheless, many plants have a history of unfavorable pressure drop development. Some refiners must regularly practice catalyst skimming operations. In such pressure drop limiting cases the use of Raschig ring catalysts as part of the reactor fill can markedly improve the pressure drop situation.

Plugging. Pressure drop is a limiting factor in many hydroprocessing schemes. Often run length is limited by plugging of the bed rather than catalyst deactivation.

Bed plugging may result from insufficient desalting of the crude, presence of tramp iron, insufficient feed filtering and carryover of scale or carbon from the heaters. Additionally, certain additives used upstream of the hydrodesulfurization (HDS) plant can complicate the problem. An example is the silicon based antifoaming additive sometimes found in coker streams. Furthermore, the metals present in resid feeds deposit in, on, and between the catalyst particles.

When such problems are encountered, use of ring-shaped catalysts will substantially extend cycle lengths. Catalyst rings have a lower resistance to flow, and the larger void volume provided by their shape allows for the deposition of greater amounts of interstitial matter before excessive pressure drop occurs.

Another contribution to the plugging of catalyst beds comes from metal sulfides. Catalyst pore plugging is caused by metals such as vanadium and nickel. In resids these metals are present as organic complexes which under hydroprocessing conditions readily react and deposit in the catalyst pores as metal sulfides. When

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these compounds can not enter the catalyst pore system they can deposit on and between the catalyst particles as interstitial matter. Normally, the amount of rings required for the topping layer will represent between 5 to 20% of the total catalyst charge. The required depth of Raschig ring catalyst for a given application will depend on a number of factors, including feedstock qualities, diameter of reactor and length of trash baskets. Despite the larger dimension of the rings, the drop in HDS activity is only slight because the large external surface area ensures relatively high effectiveness factors for Raschig ring catalysts, which are pictured in Fig. 1.

Void fractions. In many cases when the reactor is opened for catalyst skimming or changeout, a crust is found. This crust can vary in appearance, density, and characteristics, such as degree of compacting. But the crust is most often limited to the first few feet of the bed.

If it were possible to provide a larger volume for distribution of the crust forming material, an increase in run length would be obtained. Raschig ring catalysts offer that possibility because the void fraction of packed beds is a function of particle shape. In the range of particle diameter to reactor diameter relevant to the industry a comparison is shown in Table 1.

Pressure drop increases with the deposition of material between the catalyst particles (reduction of void volume). This is shown in Fig. 2 which depicts calculated pressure drop development as a function of particle shape in a hydroprocessing reactor running on atmospheric resid. These plots are representative of "trickle flow" operation. They show that pressure drop for rings is much less sensitive to contamination than it is for cylinders.

For gas phase operation, i.e. naphtha HDS, the trend is the same. This is illustrated in Fig. 3 where again use of the ring shape can be seen as beneficial to the operation.

Commercial experience. The concept of using ring-shaped catalyst is not new. Haldor Topsoe has employed this shape for many years in its sulfuric acid catalyst. Also the use of

Fig. 3

Pressure drop in a naphtha unit

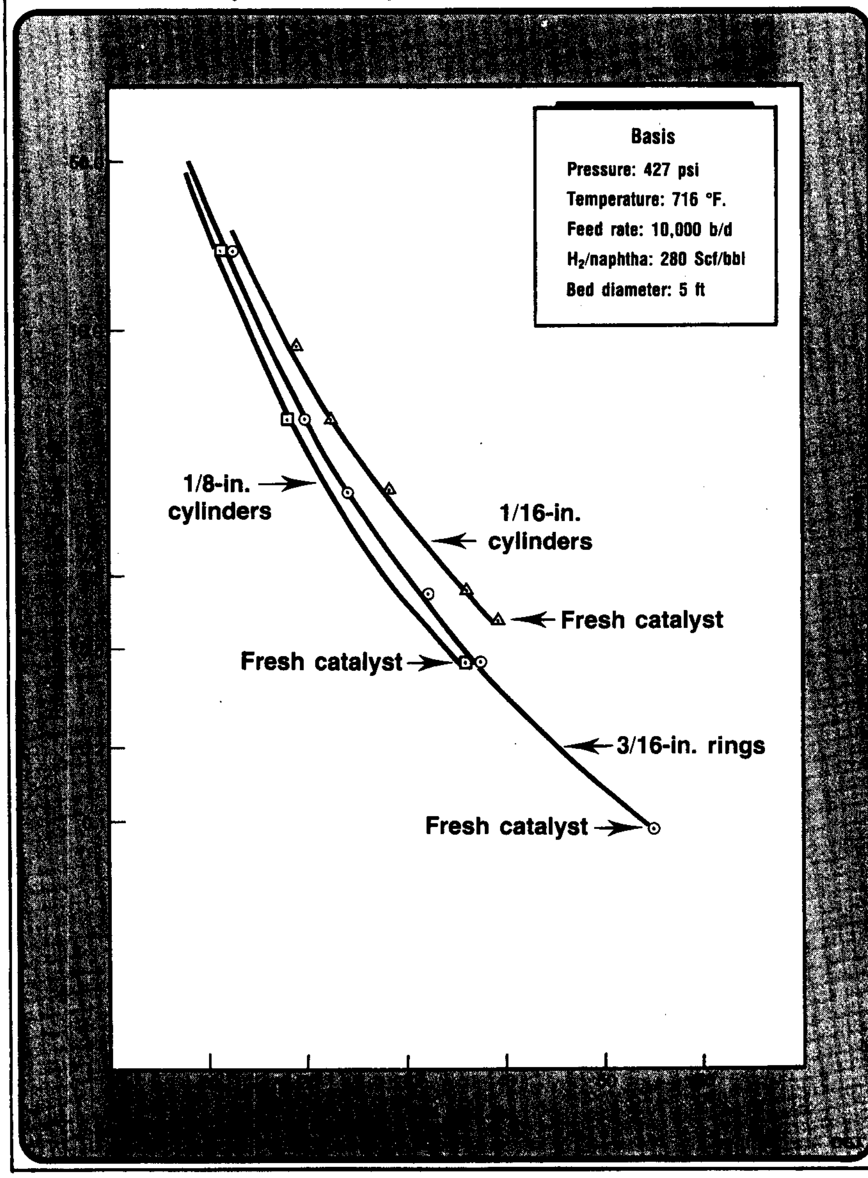


Fig. 4

VGO plant pressure drop before and after rings

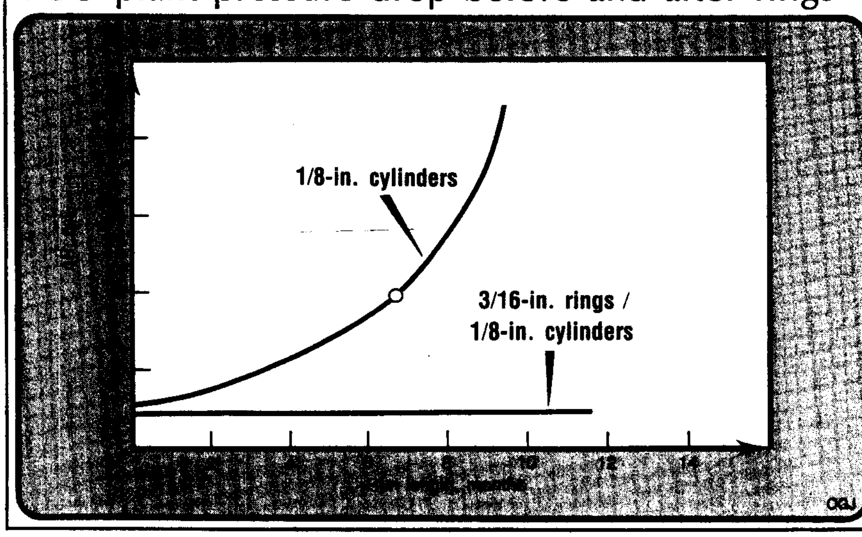


Table 1

Relation of shape to void

Particle Shape	Fraction Void
Rasching Ring	0.50-0.55
Cylinders	0.40
Spheres	0.30-0.33

rings is well known in tubular steam reformers for the production of hydrogen or synthesis gases.

But the use of Raschig-ring-shaped catalyst for hydro-processing catalysts was an innovative development when first commercially applied in 1979. We have obtained considerable experience since then. Following are examples of recent experience in two different applications of Raschig ring hydroprocessing catalyst.

VGO service. A vacuum gas oil (VGO) plant in the U.S. processes 45,000 b/d of material boiling up to about 1050° F., which is then fed to a fluid catalytic cracking unit.

The unit's one reactor contains two catalyst beds. During the annual shutdown in 1982, the first bed was topped off by about 7 ft of Raschig ring catalyst, on top of 14 ft of the regular 1/8 in. extrudate catalyst. Fig. 4 shows the pressure drop performance of the unit when it contained the single catalyst, then when it held the combination of rings and 1/8 in. extrudate.

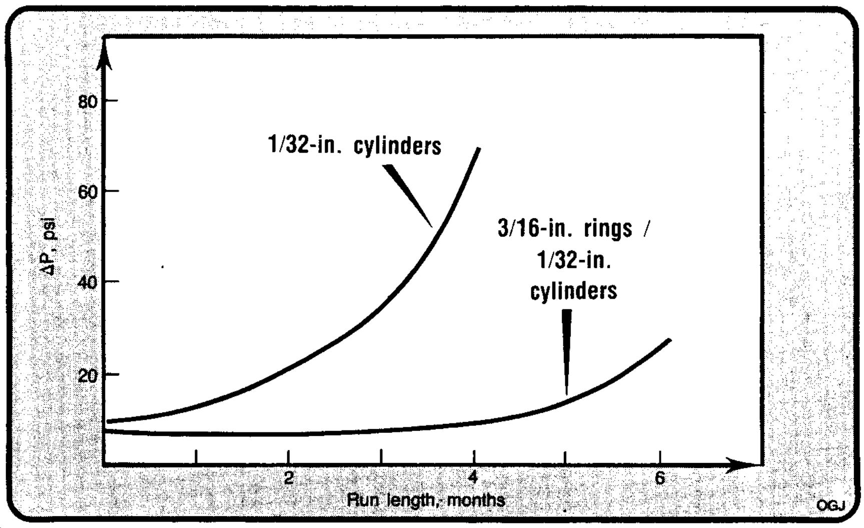
Apart from the lower pressure drop throughout the run which means no reduction in throughput towards end of run (EOR), other advantages were obtained. Distribution of material in the ring layer gives a more predictable pressure drop pattern for the run and the fact that no crust was formed, made an easier catalyst dump at the turnaround. Even though the Raschig ring catalyst has a lower bulk density than conventional extrudates, meaning that fewer pounds of catalyst are loaded per cubic foot, installation of the ring layer did not produce any detectable decline in activity or overall catalyst performance.

Resid service. In a large resid HDS plant situated in Japan installation of a topping layer of Raschig ring hydroprocessing catalysts solved the problems which this refiner experienced with high pressure drop development across the lead reactor. Feed stock to the plant is a heavy resid containing almost 220 ppm of metals and is of Arabian origin.

Desired run length for the plant is 6 months, which is quite possible with respect to catalyst activity. However, due to the build-up of deposits, mainly iron sulfide, on the 1/32 in. catalyst

Fig. 5

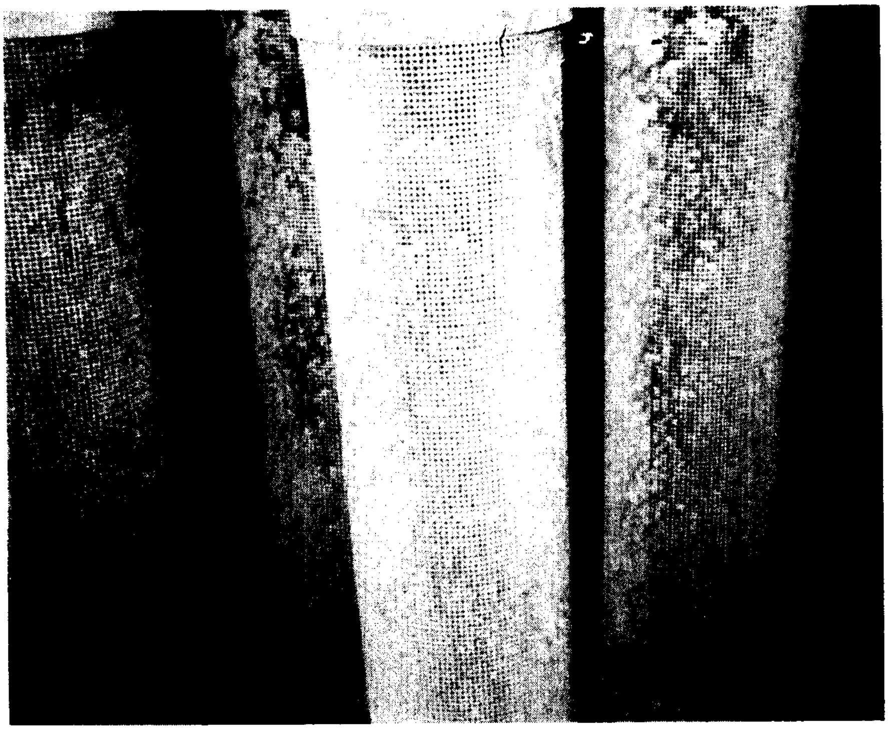
Resid plant extends run with rings



Trash baskets from reactor that had run with 1/20-in. regular catalyst (Fig. 6).

particles, the pressure drop across the first bed limited run length.

In fact, after 4 months on stream the pressure drop across the bed increased rapidly to the maximum of 70 psi. Because of this, it was necessary in some cases to reduce throughput towards EOR. Furthermore, the cata-



Same baskets as those in Fig. 6 after a run with 3/16-in. rings (Fig. 7).

lyst deposits caused poor flow distribution and resulted in severe problems when unloading the catalyst.

This refiner tried various solutions to these problems but without success. Only when the top 3-ft section of the catalyst bed was replaced by 3/16 in. OD Raschig ring catalyst did real improvement occur. Fig. 5 shows this.

As can be seen, the pressure drop development when using the rings remained relatively constant until about 5 months on stream. At this point, the pressure drop increased at a moderate rate, and at EOR was still below 30 psi. Catalyst unloading was considerably simplified because the deposits were distributed more evenly in the bed rather than being concentrated into a narrow area with the risk of crust formation.

Since the trial of the rings in one reactor train in 1982, this approach has now become standard operating procedure. Ring shaped catalyst is now utilized in both Resid HDS trains operated by this refinery.

There is also physical evidence that reveals the beneficial influence of Raschig ring topping layers. Figs. 6 and 7 show trash baskets from a plant which is hydroprocessing VGO. This plant has an iron problem. Fig. 6 shows the baskets as they came out during a catalyst skimming operation because the reactor's pressure drop limit had been reached. Catalyst employed was of the 1/20 in. variety. Note the deposits inside and outside the baskets.

In Fig. 7 the same baskets are shown, but in this case after operation with 3/16 in. Raschig ring catalyst.

Using hydroprocessing catalyst in Raschig ring form together with grading of a "composite catalyst filling" can, as these cases show, enable hydroprocessing operators to keep their units on stream longer.

The author . . .

Moyse

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Prior to joining Haldor Topsoe in 1969, Moyse worked for Shell for more than 10 years at the Shellhaven, U.K., refinery and as a member of the startup team for the Fredericia refinery in Denmark. He received his technical education at the King John School, Southend Polytechnic and within the Shell group of companies.

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