Hydrotreater revamps for ULSD fuel

Scope and capital investment for revamping an existing diesel hydrotreater to meet the 15wppm sulphur standard. The base design is typical of hydrotreaters commissioned in the early 1990s to meet on-road specifications of 500wppm sulphur

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In mid-2006, thanks to the US Environmental Protection Agency (EPA), 80% of refiners' on-road diesel pool will have to meet a new ultra-low sulphur diesel (ULSD) specification of no more than 15wppm sulphur. To ensure this target is not exceeded at the ultimate point of distribution, and to allow for some manufacturing flexibility, revamped or new facilities will need to achieve a desulphurised product sulphur level significantly below the mandated target. Sulphur limits and regulations of similar severity are being implemented in other areas of the world such as Europe and certain parts of Asia.

For an existing diesel hydrotreater, a number of options will directionally improve sulphur removal, including:
— Higher activity catalyst
— Increased reactor temperature
— Installation of high-efficiency reactor feed distributors
— Increased catalyst volume
— Recycle gas scrubbing to remove hydrogen sulphide.

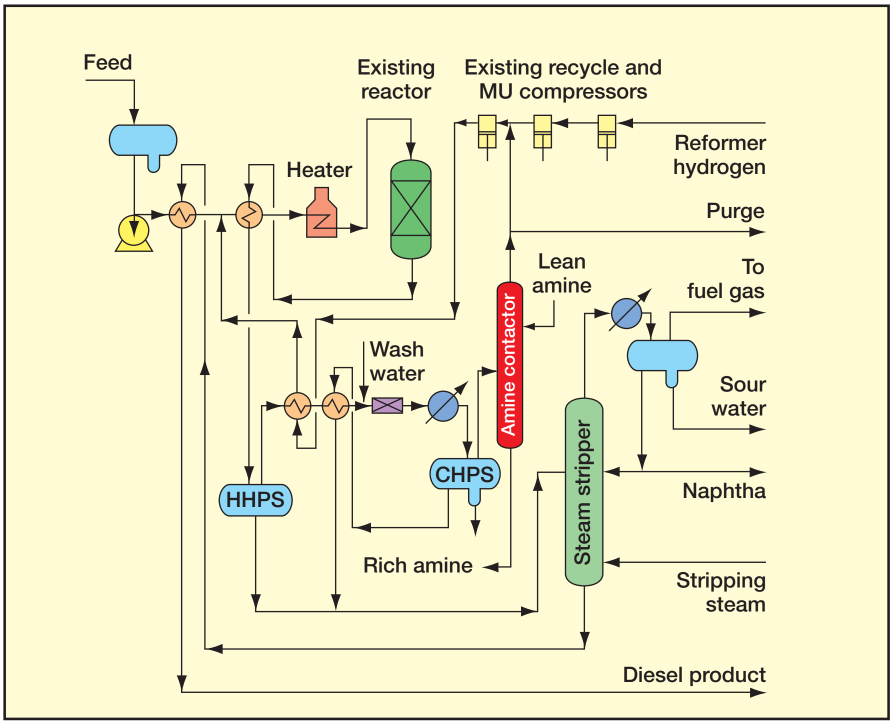

Figure 1 *Base case process flow diagram*

Revamp design basis

The feed basis for this study is identical to the original design and consists of a blend of two-thirds straight-run gas oil and one-third light-cycle oil (LCO). Table 1 shows the feed constituents and blended properties. Key design criteria for the original facility are shown in Table 2. This includes existing reactor operating pressure, catalyst volume and treat gas rate. The design product sulphur for the original design was 470wppm.

A simplified flow diagram of the base cases is shown in Figure 1. Other study basis criteria were:
— Product sulphur content of 8wppm
— Utility systems such as steam, cooling water, power, instrument/plant air, and the pressure relief system have sufficient capacity for the revamp
— The existing DCS has capacity to

Feed properties

Feed property	SRGO	LCO	Blend
BPSD	20 000	10 000	30 000
API	34.5	20.0	29.4
Sulphur, wt%	0.8	2.0	1.2
N, wppm	100	500	242
Total aromatics, vol%	20.0	65.0	35.0
Mono-aromatics, vol%	12.8	23.0	16.2
Poly-aromatics, vol%	7.2	42.0	18.7
Bromine number	1.0	10.0	4.2
D86 90 vol% Temp, °F	640	640	640
Cetane index	49.9	30.3	42.6

Table 1

Base case reactor conditions

Base design condition	Base case
Charge rate, BPSD	30 000
Number of reactors	1
Reactor inlet pressure, psig	760
LHSV, hr^{-1}	1.5
Catalyst volume, ft^3	4680
Reactor outlet H_2, psia	348
Chemical H_2, SCF/bbl	250
SOR WABT, °F	670
Cycle length, months	18
Make-up hydrogen, SCF/bbl	290
Treat gas rate, SCF/bbl	1400
Quench rate, SCF/bbl	0
Product sulphur content, wppm	470
Recycle gas scrubber	Yes

Table 2

accommodate all new instrumentation

— Plot space is available near the hydrotreater unit for new equipment

— The refinery is currently consuming all available reformer hydrogen. Incremental hydrogen will be purchased from a pipeline

— Hydrotreating kerosene for cloud point control in the winter is not required

— The existing hydrotreators are not operating at charge rates significantly above the original design.

The original design treat gas rate of 1400 SCFB was assumed for this study. Higher recycle rates, if hydraulically feasible, would extend the catalysts cycle or allow higher throughputs. For this study, Criterion Catalysts provided the reaction conditions in Table 3 for several options required for the production of ULSD. All reaction conditions are based on an assumed distribution of higher boiling sulphur compounds. For a definitive design, pilot testing of the feedstock is recommended. The base case reaction parameters are also shown for comparison.

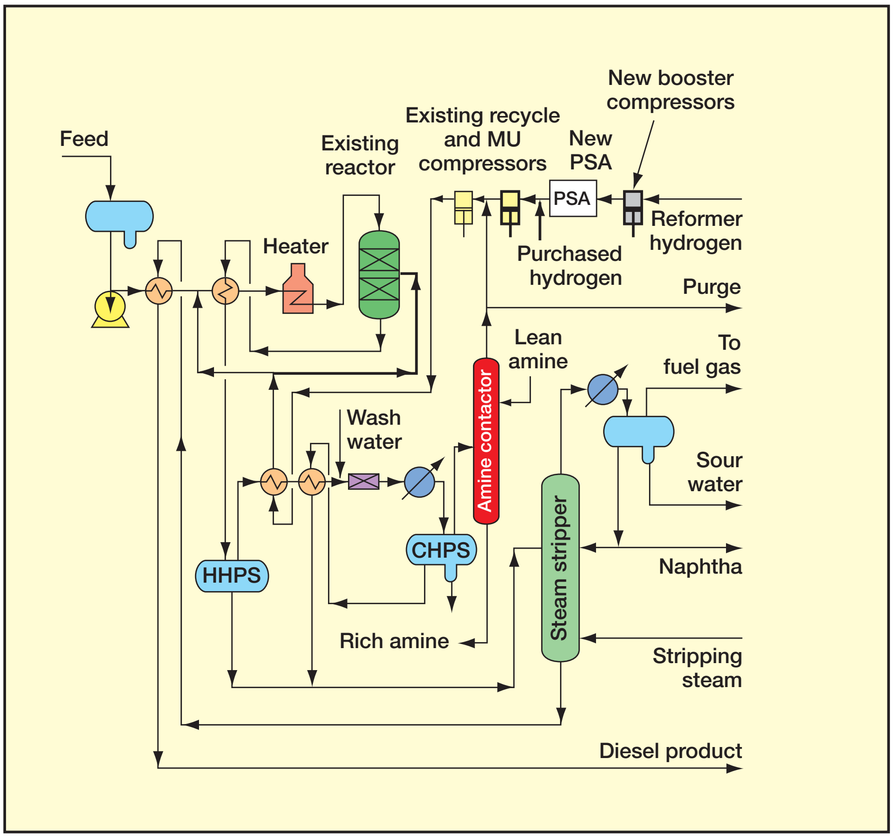

Figure 2 *Revamped hydrotreater with two new packed beds added to existing reactor, new MU compressor and introduction of purchased hydrogen*

In all revamp cases, the current catalyst was replaced with Criterion's most active desulphurisation catalyst, DC-2118. Three options were considered. The first (Revamp A) consisted of purifying the reformer hydrogen with a pressure swing adsorption (PSA) unit. Combined with the purchased hydrogen, this resulted in the total make-up volume having a purity of 99.9 vol%. Revamp cases B and C consisted of adding incremental catalyst volume to the base case design. The incremental hydrogen volume was also supplied by pipeline purchases. Purification of the reformer make-up was not considered.

Base case and revamp reaction conditions

Reaction condition	Base 1	Revamp A	Revamp B	Revamp C
Charge rate, BPSD	30 000	30 000	30 000	30 000
Reactor inlet, psig	760	760	760	760
LHSV, hr^{-1}	1.50	1.70	1.00	0.75
Catalyst volume, ft^3	4680	4150	7020	9360
Catalyst type (Criterion)	448	DC-2118	DC-2118	DC-2118
SOR WABT, °F	670	709	688	674
Cycle length, months	18	10	18	27
Chemical H_2, SCF/bbl	250	33	284	323
Treat gas rate, SCF/bbl	1400	1400	1400	1400
Product sulphur content, wppm	470	8	8	8
Recycle gas scrubber	Yes	Yes	Yes	Yes

Table 3

Simulation results

Simulation results	Base case	Revamp 1A	Revamp 1B	Revamp 1C
Reactor outlet H_2 PP, psia	348	575	403	430
Make-up as 100 % H_2, SCF/bbl	290	364	334	374
Make-up purity, mole % H_2	83.9	99.9	88.0	87.9
Treat gas purity, mole % H_2	70	93	76	76
Quench rate, SCF/bbl	0	400	400	400
Purge gas rate, SCF/bbl	14	0	38	38
Reformer hydrogen, SCF/bbl	346	346	346	346
Purchased hydrogen, SCF/bbl	0	74	44	84
Total make-up, SCF/bbl	346	420	390	430

Table 4

Using the reaction conditions specified, computer simulations were developed for each revamp alternative. Hydrogen make-up rates were calculated based on the sum of chemical hydrogen consumption, solution losses and purge gas, if any, from the simulations. Additional process information for each revamp is presented in Table 4.

The simulation results were used to rate existing equipment and determine what modifications were required as well as the size and other design information for new items. All shell and tube exchangers, air coolers, pumps and fired heaters were rigorously rated. Pressure drop across each catalyst bed was calculated using the Ergun(1) equation with the Larkin(2) two-phase correction parameter. An allowance was also included for fouling. The resulting information was used to develop hydraulic calculations across the reactor loop to establish an operating/design pressure and temperature profile, check the performance of the recycle compressor, and to identify other limitations within the system.

Table 5 summarises the detailed

revamp scope for each case. Process flow diagrams of the hydrotreater revamps are shown in Figures 2 and 3 (equipment and lines shown in bold are new or modified).

Revamp requirements

Each revamp case shares the following common requirements, including state-of-the-art high-activity catalyst, increased hydrogen make-up compression capacity and the addition of reactor quench.

All cases take advantage of the latest advances in catalyst technology and are based on using Criterion's DC-2118 CoMo catalyst. Catalyst beds were assumed to be dense loaded with 1/20" catalyst to provide maximum cycle length and to ensure even contacting between the catalyst and oil. Also to ensure maximum cycle length, the existing feed distributors were upgraded. Good feed distribution and proper catalyst installation is critical for the production of ULSD. Design and cost information for new feed distributors and inter bed quench internals was provided by Shell Global Solutions.

Producing ULSD requires a significant increase in chemical hydrogen consumption compared to what is needed to make diesel meeting the 500wppm specification. This is due to additional, marginal saturation of aromatics and the removal of sulphur from aromatic sulphur compounds. To provide the incremental make-up capacity, a new spared reciprocating booster compressor is added upstream of the existing first-stage make-up cylinders. Due to design pressure limitations, the existing first-stage make-up compressor intercooler and knock-out drum were re-piped to service the new booster compressor. A new intercooler and knock-out drum designed for a higher pressure were specified to replace this equipment. The existing make-up cylinders also required replacement because of the higher capacity and operating pressure.

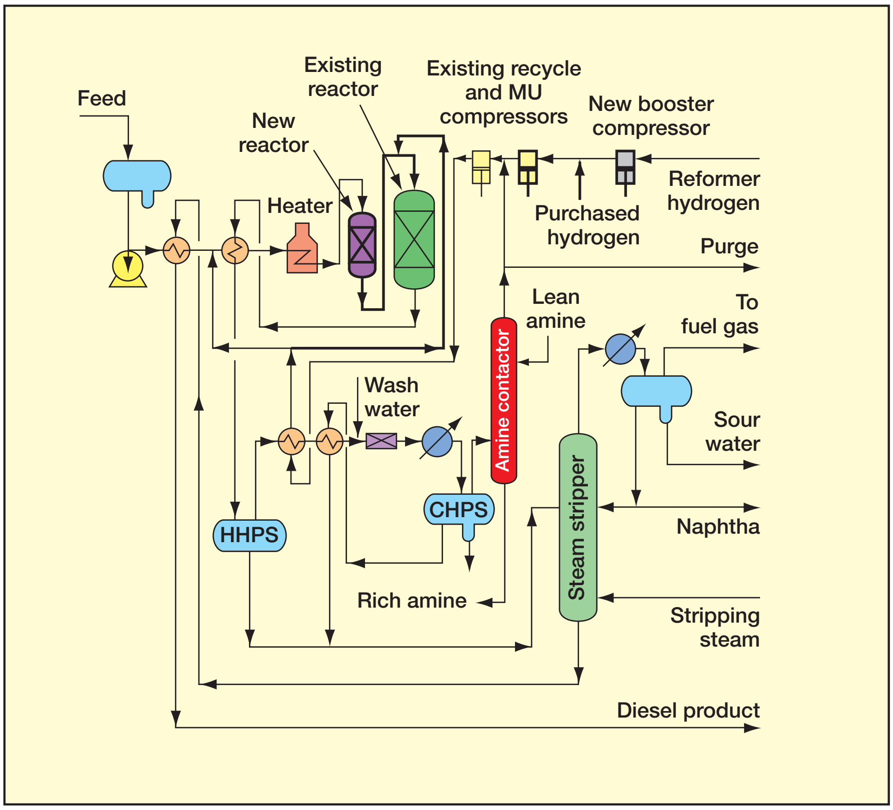

Figure 3 *Base revamp Case B and C flow diagram with modified flow from recycle compressor into existing reactor*

Another option to consider for providing increased make-up is to add new compression capacity in parallel with the existing make-up compressors. The new machine would handle purchased hydrogen, while the existing compressors would still be dedicated to reformer off-gas. The new compressor would require three stages, however, to comply with API Standard 618, which recommends a maximum discharge temperature of 275°F for reciprocating compressors in high-purity hydrogen service. This is a result of the increased heat capacity ratio associated with the higher-purity hydrogen.

This would also be an issue for the existing make-up compressors for Case A, where the reformer hydrogen is purified in a PSA unit. With the new compressor installed in series with the existing make-up machines, the total supply to the hydrotreater could be furnished with high-purity purchased hydrogen when the reformer is out of service for catalyst regeneration or maintenance. Due to the discharge temperature limitations previously noted, this flexibility would be lost with a parallel make-up compressor installation.

The higher hydrogen consumption results in a significant increase in reaction heat for all cases and, thus, quench was added to limit the temperature rise in the reactor and extend catalyst cycle life. In revamp Case A, the existing reactors were modified to include inter-bed quench by splitting the catalyst volumes into two beds. In the other cases where a new reactor is added in series, quench gas is added between the reactors. Modifying the existing reactors for inter-bed quench requires four vertical feet that otherwise would have been occupied by catalyst. The loss of catalyst volume is more than offset by quenching the reaction and limiting the overall temperature rise of the reactor.

Revamp scope

Case A * Install Criterion DC-2118 catalyst
* Add hydrogen booster compressor and replace cylinders in the existing make-up compressor
* Add quench to reactor
* *Add PSA Unit with tail gas surge drum and compressor*
* *Revamp cost: $108 000 000*

Case B * First three items in Revamp 1A plus
* *50% more catalyst in a new reactor*
* *Revamp cost: $8 100 000*

Case C * First three items in Revamp 1A plus
* *100% more catalyst in a new reactor*
* *Revamp cost: $8 660 000*

(Items in Italics are unique to that revamp option)

Table 5

Utilising reactor quench directionally lowers the reactor loop pressure drop and heater duty for all revamp cases, because quench gas bypasses the feed/effluent exchangers and charge heater. This may allow for some increase in the recycle gas rate by operating the spare recycle compressor and further extending the cycle length. A more detailed analysis of the reactor loop hydraulics and unloading capabilities of the existing compressors would be required to determine the magnitude of this improvement.

Upgrading the catalyst alone is not sufficient to meet the lower sulphur specification. As noted previously, in revamp case A the reformer make-up hydrogen is purified using a PSA unit, which concentrates the hydrogen from 83.9–99% with a hydrogen yield of 86%. High-purity hydrogen from the pipeline is used to satisfy the incremental demand. The combined make-up gas has a hydrogen concentration of 99.9 vol%, which increases the purity in the treat gas (compared to the base case) from 70–93 vol%. As a result, the hydrogen partial pressure at the reactor outlet increases from 348–575psia. The resulting catalyst cycle length, however, is reduced to 10 months.

The PSA unit could be installed outside the hydrotreater plot area, which may have particular appeal if space inside the unit is limited. Installation at a remote location allows for construction to be completed while the hydrotreater is operating, leaving only minimal piping tie-ins for a unit shutdown. In addition to the PSA unit, a knock-out drum and tail gas compression system are required. Also, additional purchased hydrogen is required to make-up for hydrogen yield losses across the PSA.

The catalyst volumes are increased in revamp options B and C in lieu of purifying the reformer make-up hydrogen. New reactors in series with the existing reactors were sized to increase the catalyst volume by 50% and 100% in cases B and C, respectively. Direct hydrogen quench is added between reactors. The additional volume of catalyst more than compensates for the less pure make-up hydrogen and increases the cycle life to 18 and 27 months for cases B and C, respectively.

Other considerations

Manufacturing ULSD will require the consideration of a number of other factors, including(3) :

— Dedicated feed storage to minimise feed quality variability

— Rapid response to routine operational upsets, including product stripper performance

— Segregation of offsite product handling systems to minimise contamination with other streams

— Handling and reprocessing of off-spec product

— Equipment reliability.

The specific revamp scope costs for these issues have not been addressed in this article.

Conclusions

Most hydrotreaters that were installed to meet the 1993 low sulphur diesel requirements (500wppm) can be modified to meet the future specification for ULSD of 15wppm for a modest on-site capital investment. The key alternatives to consider for the revamp design are:

— Installation of the most active commercially available hydrotreating catalyst

— Increased catalyst volume

— Removal of hydrogen sulphide via recycle gas amine scrubbing

— Improved reactor hydrogen partial pressure.

For all designs, the use of high-efficiency reactor vapour/liquid feed distributors is essential.

For revamp case A, even though the hydrogen partial pressure was increased substantially, the loss of catalyst volume associated with the reactor quench required an unusually high start-of-run WABT, which in turn limited the cycle length to just 10 months. This may not be acceptable to many refiners.

The revamp designs presented in this study, although sufficient to meet the future requirements of ULSD, only marginally improve other product properties such as cetane number, polynuclear aromatics, total aromatics and gravity. Improvement of these quality specifications, which are the subject of regulations in certain areas of North America and Europe, requires another stage of treating for the reduction of aromatics and possibly partial destruction of polycyclic saturated compounds. It may be possible to integrate this equipment into the existing hydrotreater; otherwise, a new grass roots facility is required.

The offsite revamp scope and cost was not addressed in this work, but could substantially increase total project cost. This includes modifications to product rundown, storage and shipping systems to prevent contamination with other middle distillate streams. Also, infrastructure systems for hydrogen supply and utilities could be impacted. Further, the revamp designs, although theoretically capable of meeting the more stringent sulphur specification, will lack some of the robust design features of a new grass-roots facility custom designed for this purpose.

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