Revamping PKN Orlen AB Mažeikių Nafta LK-6u HDS units for “zero” sulphur diesel specification

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by

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Abstract
Topsøe has been the pioneer in the design of units for Ultra Low Sulphur Diesel (ULSD) of less than 10 wppm S and aromatics saturation to produce cleaner burning fuels. This paper presents a detailed illustration of the revamp approach for the LK-6u hydrotreating unit at PKN Orlen AB Mažeikių Nafta with the objectives to improve profitability and limit capital expenditures while producing ULSD. The objectives were successfully obtained by combining the market intelligence and technical expertise of PKN Orlen AB Mažeikių Nafta with the knowledge and expertise from Topsøe’s hydroprocessing experts. The revamped HDS unit was successfully started, and has produced ‘zero’ sulphur diesel or ULSD with less than 7 wppm sulphur content since October 2008. The revamp of similar hydrotreater units for ULSD production is a viable option and should be seriously considered.

Introduction
Many refineries consider revamping their existing hydrotreating units, designed by Leningrad Engineering Institute in order to produce ULSD. The success of such projects depends on whether the project team has the necessary catalyst, process and engineering knowledge to properly evaluate various project options. Furthermore, the project team must have a clear understanding of the interplay between catalyst and process solutions to arrive at the optimal solution from both a capital and operating expenditure perspective. The key decisions with major impact on project cost are made during the early scoping study phase. Therefore, the licensor’s participation during this critical phase is vital, as the licensor has a unique understanding of the key cost drivers based on experience and access to state-of-the-art catalyst and technology.
Case history

PKN Orlen AB Mažeikių Nafta in Lithuania initially selected Topsøe technology for revamp of an existing diesel unit, designed by Leningrad Engineering Institute. Topsøe revamped the unit to produce ULSD with less than 7 wppm sulphur and with a guaranteed first catalyst life cycle of 24 months. Topsøe’s scope of supply included

- Scoping study & pilot plant testing of feed
- Basic engineering design package including mechanical design of the new reactor
- Delivery of reactor internals
- Delivery catalyst.

Revamp procedure

The pre-revamp configuration of the HDS unit as illustrated in figure 1 is a conventional cold separator layout with recycle gas amine scrubber, but without hot separator or wash water injection facility. The purge from the high pressure section was used as stripping gas in the product stripper instead of ordinary steam, to avoid moisture in the hydrotreated diesel. The units operated at 55 barg reactor pressure and produced 50 wppm diesel with a catalyst life cycle of 12 months.
The revamp of the LK-6u No. 2 HDS unit was planned in three major phases, namely a scoping study, pilot plant test and execution of the basic engineering package. This approach allowed PKN Orlen AB Mažeikių Nafta to make an informed decision between the phases. Each of these phases is discussed in detail below.

**Scoping study**

During June 2005 Topsoe performed a fast-tract scoping study of the LK-6u No. 2 diesel hydrotreater and a report was submitted within four weeks. The primary objectives were to determine major bottlenecks, optimise reactor diameter and recommend catalyst type and size. It was also an objective to limit capital expenditure by reusing as much of the existing equipment as possible and provide cost estimates for new equipment. The scoping study phase allowed PKN Orlen AB Mažeikių Nafta to
make an informed decision regarding the possibility and economics of the revamp option.

The objective was pursued by a multi-pronged approach shown below in a log-book form in order to illustrate the main course of events during the scoping study.

24 May 2005: Letter of Intent issued for a scoping study

01 June 2005: Kick-off meeting addressing study methodology
- study report delivery within four weeks
- feedstock properties and design basis for study

02 June 2005: Hydraulic test run under Topsøe supervision
- obtain reactor-loop P-T profile
- interview with operational and technical personnel to identify operational problems
- obtain design information for existing equipment.
- establish “base case” simulation model to match actual operating conditions
- centrifugal recycle compressor performance
- reconciliation of test run measurement with original compressor performance curve
- system pressure drop vs. compressor differential head
- \( \text{H}_2 \) partial pressure and \( \text{H}_2 \) flow as data input for pilot plant

- optimisation of reactor diameter based on catalyst volume, catalyst type, catalyst size, system pressure drop and the corresponding flow and head the compressor would deliver
- optimum catalyst evaluation based on bottlenecks in the unit
- cost estimates with -20/+30% accuracy for revamp options

28 June 2005: Scoping study report submitted
Pilot plant test
The actual feed received from PKN Orlen AB Mažeikių Nafta was tested at Topsøe’s R&D centre in Copenhagen on different catalyst systems with the objective of verifying the LHSV, WABT and chemical hydrogen consumption in order make 7 wppm S diesel. This approach allowed a more accurate estimate of the catalyst volume and required operating conditions assuring that CAPEX and OPEX could be reduced to a minimum. The estimated operating conditions from the scoping study were used as a basis to get as close as possible to the final conditions.

Based on the results of the pilot plant test a customised ULSD kinetic model was developed allowing very accurate estimates to be made for a range of different revamp cases.

Major conclusions from the pilot plant tests in combination with the scoping study are that 7 wppm sulphur diesel can be made in the unit with the proposed feedstock.

Basic engineering
The scoping study and pilot plant results enabled PKN Orlen AB Mažeikių Nafta to make an informed decision on the optimum revamp path to follow based on the developed estimates for CAPEX and OPEX. The outcome of the evaluation was that the project was both economically and technically attractive using Topsøe catalyst and technology.

The basic engineering was therefore pursued on the basis of the scoping study and pilot test results with close cooperation with PKN Orlen AB Mažeikių Nafta engineering personnel. The recommendations and engineering judgment made during the scoping study were verified during the basic engineering phase. All existing equipment design conditions were rigorously evaluated and check rated for the new operating conditions in order to further minimize capital investment and maximize reuse of equipment as much as possible.
The feedstock properties used for basic engineering are shown in table 1.

<table>
<thead>
<tr>
<th></th>
<th>Basic engineering</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRGO/VGO/Visbr GO/HT</td>
<td>44.4 / 22.2 / 11.2 / 7.4 / 7.4 / 7.4</td>
</tr>
<tr>
<td>VGO/LLCO/SR Kero</td>
<td>7.4 / 7.4</td>
</tr>
<tr>
<td>Density, 15°C, kg/m³</td>
<td>865.4</td>
</tr>
<tr>
<td>Sulphur, wt%</td>
<td>0.9626</td>
</tr>
<tr>
<td>Total nitrogen, wppm</td>
<td>346.9</td>
</tr>
<tr>
<td>Bromine number</td>
<td>6.49</td>
</tr>
<tr>
<td>Total aromatics, wt%</td>
<td>40.0</td>
</tr>
<tr>
<td>Poly aromatics, wt%</td>
<td>13.1 / 1.8</td>
</tr>
<tr>
<td>ASTM D86 Distillation, °C</td>
<td>177 / 229 / 279 / 302 / 320 / 353 / 385</td>
</tr>
</tbody>
</table>

Table 1: Feedstock properties
The revamp configuration of the HDS unit and modifications made are illustrated in figure 2.

![Figure 2: Revamp configuration of LK-6u No. 2 HDS unit](image)

The main process issues encountered during the basic engineering and their solutions are discussed below:

1. A detailed analysis of the recycle gas compressor performance at revamp conditions was carried out. The new reactor was five times bigger than the existing reactor. Due to higher reactor pressure drop during EOR (due to fouling), the recycle gas compressor operated under surge conditions and resulted in lower hydrogen flow to the reactor loop. By providing a new pipeline that partially bypassed the recycle gas across the feed/effluent exchangers and fired heater, the pressure drop was reduced improving compressor performance. The recycle gas compressor could therefore be reused without any modifications.
2. As purge from the high pressure section was used as stripping gas in the product stripper, it affected the recycle gas molecular weight and in turn the compressor performance. More purge would improve the hydrogen purity but would reduce the recycle gas molecular weight and in turn the compressor flow. The purge rate was optimised for SOR/EOR conditions by making sure that the existing compressor could be reused while at the same time optimising catalyst performance. The extra stripping gas needed in the product stripper in order to obtain the diesel flash point was made available from purge stream from an existing naphtha/kero hydrotreater.

3. All the heat exchangers and air coolers in the reactor loop were check-rated for process conformity for the new operating conditions. Detailed evaluation of the reactor effluent air cooler AO-301 concluded that the heat transfer area was sufficient to cool the reactor effluent, but due to thermal expansion issues during the “heat wave” the air cooler had to be replaced.

4. A new wash water injection facility was required to wash the ammonium salts formed in reactor effluent lines in ULSD units, as the operating conditions were more severe. The existing cold separator was evaluated and found too small for water separation. It could only function as a 3-phase separator if the feed rate was reduced to less than 45% of the plant capacity. Replacing it with a big new separator was too costly, and plot space was limited.

5. The recycle gas water cooler AV-302 had corrosion and plugging issues and had frequently been out of service. Topsøe’s evaluation concluded that there were no chlorides in the reactor section, and the corrosion and plugging issue in AV-302 resulted from ammonium sulphide precipitation. Topsøe therefore incorporated a novel wash water injection facility in order to avoid the replacement of the high pressure cold separator and also solved the corrosion issues in recycle gas water cooler AV-302:
   a. the reactor effluent air cooler AO-301 outlet temperature was kept above the ammonium sulphide precipitation temperature.
   b. a continuous wash water injection facility was introduced on the cold separator SP-301 vapour outlet.
   c. the existing recycle gas water cooler AV-302 was relocated downstream the new water wash injection point.
   d. a new and very small cold separator was installed to separate the wash water from hydrocarbons.

6. The stripper feed/reactor effluent exchanger TK-304 design P and design T on the high pressure tube side was lower compared to those of the downstream heat exchanger in the reactor loop. The reason was an inconsistency in the original design which was discovered during the engineering phase. The exchanger TK-304 was replaced with new design conditions.
7. The plot space and site location of the new reactor and equipment was performed in coordination with PKN Orlen AB Mažeikių Nafta engineering personnel. As there were no major modifications to existing equipment, the suggested piping and equipment could be installed on site without affecting the operation of the existing unit and could be completed on line with minimum shutdown time.

The main course of events during the basic engineering phase is shown below in a log-book:

11 August 2005 Basic Engineering Contract signed covering
- license
- basic engineering
  • unit designed to operate for both CoMo or NiMo catalyst
- detailed engineering of reactor and reactor internals
- site supervision & technical services
- proprietary reactor internals
- initial charge of catalyst

Aug 2005-March 2006: Basic engineering phase
- PFDs, heat and mass balance pre and post revamp scenario
  • reconciliation of hydraulic test run data with simulation model
- detailed evaluation of scoping study recommendations
- check of design P and design T for equipment for post revamp
- use of ASME code for reactor and new equipment.
- detailed analysis of recycle gas compressor performance
  • recycle gas performance sensitive to molecular weight (or hydrogen purity)
  • gas molecular weight vs. hydrogen availability
  • purge rate vs. recycle gas molecular weight
  • hydrogen availability vs. system pressure drop
- capacity revamp of make-up gas compressors

Sept 2005 Reactor mechanical drawings submitted
Revamping PKN Orlen AB Mažeikių Nafta LK-6u HDS units for “zero” sulphur diesel specification

24 March 2006: Basic engineering design package submitted

Post basic engineering
23 October 2007: Purchase order confirmed and fabrication of proprietary reactor internals started.

13 June 2008: The proprietary Topsøe reactor internals were shipped from Europe.

20 June 2008: The catalyst was shipped from Topsøe’s catalyst plant.

Start-up and guarantee test run
The LK-6u No. 2 HDS unit was successfully started up on 24 October 2008. The guarantee test run was performed on 17 December 2008 and confirmed that the unit is able to produce ULSD with less than 7 wppm S. All process guarantees are satisfactorily met. Table 2 compares the feed and product properties measured during the guarantee test run.

<table>
<thead>
<tr>
<th></th>
<th>Feed</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphur</td>
<td>0.99 wt%</td>
<td>5.2 wppm</td>
</tr>
<tr>
<td>Total nitrogen, wppm</td>
<td>458</td>
<td>-</td>
</tr>
<tr>
<td>Bromine number</td>
<td>4.7</td>
<td>-</td>
</tr>
<tr>
<td>Total aromatics, wt%</td>
<td>32.2</td>
<td>-</td>
</tr>
<tr>
<td>Di/Tri aromatics, wt%</td>
<td>-</td>
<td>3.1 / 0.3</td>
</tr>
</tbody>
</table>

**Table 2:** Guarantee test run feed and product properties

HDS catalyst performance
The performance of the revamped LK-6u No. 2 diesel unit is illustrated in the graph below.
Revamping PKN Orlen AB Mažeikų Nafta LK-6u HDS units for “zero” sulphur diesel specification

Figure 3: Feed and product sulphur content vs. run days

*S content is measured after blending with hydrotreated kero with S content 20-30 wppm.

Figure 4: Normalized reactor average temperature vs. run days
The unit runs very satisfactorily and Topsøe’s catalyst has shown exceptionally high stability since start-up.

Repeat order: revamp of second HDS unit

PKN Orlen AB Mažeikių Nafta was satisfied with the basic engineering concerning revamp of LK-6u No.2 diesel unit and granted Topsøe to revamp their LK-6u No.1 diesel unit in March 2007. Since the two units are identical the design already completed for LK-6u No. 2 HDS unit was copied for LK-6U No.1 HDS unit. This eliminated the basic engineering phase and allowed for immediate placement of orders for equipment with the same vendors for both units, which resulted in a very compressed project schedule, minimum overall project lead time and costs.

The revamped LK-6u No.1 diesel unit was successfully started up on 22 April 2009.
Revamping PKN Orlen AB Mažeikių Nafta LK-6u HDS units for “zero” sulphur diesel specification

Revamp summary
The revamp project at PKN Orlen AB Mažeikių Nafta was very successful and demonstrates Topsoe’s hydroprocessing capabilities in high activity HDS catalysts, pilot plant testing, high efficiency reactor designs and execution of fast tract projects. In depth knowledge of deep HDS reaction kinetics and engineering design coupled with clear understanding of the interplay between catalyst and process solutions is the key to successful ULSD revamps in order to minimise CAPEX and OPEX. The knowledge of state-of-the-art catalyst, in-house R&D and process technology was effectively utilised in the execution of a fast-tract scoping study. During the scoping study important process decisions such as catalyst selection (type and size), effects of system pressure drop on treat gas flow, recycle gas compressor performance and reactor dimensions were made. Innovative process solutions such as bypassing gas around the heater to save pressure drop and new wash water injection scheme resulted in reuse of recycle gas compressor and high pressure separator.

The revamp can be summarised as follows:
- four weeks fast-tract scoping study
- reuse of recycle gas compressor and high pressure separator
- eight weeks for issue of reactor mechanical drawings
- amalgamation of ASME code with GOST standards
- integrated approach of hydroprocessing experts and team members from various cross-functional disciplines, namely process, catalyst, R&D and mechanical all in one house
- all product quality objectives were met or exceeded the specifications

Conclusion
The revamp of similar hydrotreater units for ULSD production is a viable option and should be seriously considered.

Refiners are and will continue to invest heavily in hydrotreating units as legislation for ULSD is adopted. ULSD revamps are unique, and early stage licensor participation is essential in order to customise simple and cost-effective revamps. To provide optimum design minimum new investment cost and optimal use of existing equipment, it is important that the licensor has a deep understanding of ULSD kinetics, the factors governing the removal of the most refractive sulphur compounds, state-of the art reactor internals and engineering knowledge together with access to state of the art high activity catalyst and technology obtained through in-house R&D.

Topsoe has supplied commercial ULSD catalyst and technology, demonstrating our engineering capability and experience in efficiently applying this technology to new units or the cost-effective revamp of existing HDS units.