AM-05-23

EXPERIENCE WITH DESIGN, INSTALLATION AND OPERATION OF A SCR UNIT AFTER A FCCU

Presented By:

Shafiq Ahmad
Advisor
Shell Oil Products
Deer Park, TX

Peter I. Lindenhoff
Technology Manager
Haldor Topsoe, Inc.
Houston, TX

J. D. Slaughter
Project Manager
S&R Engineering
Houston, TX
EXPERIENCE WITH DESIGN, INSTALLATION AND OPERATION OF A SCR UNIT AFTER A FCCU

Introduction

The EPA has made nitrogen oxide (NOx) reduction from various sources a top priority. Most oil and electric power generation companies have had to enter into consent decrees with the EPA to reduce NOx emissions. Shell Oil Products was one of the companies that agreed to reduce NOx emissions from various sources in all its refineries.

In the fall of 2002 the project team from Shell selected Haldor Topsoe, Inc. as Technology and Catalyst provider for the SCR (Selective Catalytic Reduction) for the Deer Park Refinery FCCU. S & B Engineers and Constructors, LTD were chosen as engineering firm.

Background

The FCCU is a partial burn unit that operates at a normal capacity of 70MBPD. The feed slate is essentially vacuum and atmospheric gas oils. Only the vacuum gas oils are hydro-treated to 1% sulfur. There is no electrostatic precipitator on this unit. A 3rd Stage Separator removes most of the particulates from the flue gas. The Turbo Expander is used to recover energy and drive the Main Air Blower. Final flue gas treatment is obtained using Flue Gas Desulphurization using caustic scrubbing. Both the oil convection section and CO Boiler were replaced during the last FCCU turnaround in Fall 2002.

Key issues at Deer Park were:

- High SO₂ content of flue gas 1000+ ppmvd
- High solids loading – 40-50 PPH normal, 200 PPH maximum as there is no ESP in front of SCR.
- SO₃ content 3-12 ppmvd
- Available flue gas temperature was limited to about 550°F

Performance requirements imposed by EPA for outlet NOx were:

- 20 ppmvd @ 0% O₂ on 365 day average
- 40 ppmvd @ 0% O₂ on 3 hours average

The catalyst was guaranteed to remove 90% over a 5-year run-span which put the refinery right at the maximum limit of 20 ppm outlet NOx with 200 ppm Inlet NOx. Based on this the refinery decided to use both SNCR and SCR to achieve the final results.

An advantage of having the SCR/SNCR combination is that it is possible to reduce NOx even if it becomes necessary to bypass the SCR.

CFD studies were conducted to evaluate the effectiveness of SNCR technology, and it was concluded that in this case it could reduce NOx by 30-40%. During the CO Boiler
and Oil Convection Section replacement, the transition duct was enlarged to increase residence time. Also, one layer of tubes was removed from the oil box as well to increase residence time. Having the 30-40% reduction by SNCR would make it easier to achieve the final target.

![Figure 1: Catalyst Cracker Flue Gas Flow Path](image)

**Catalyst Cracker Flue Gas Flow Path**

In the Shell Deer Park catalyst cracker, flue gas from the catalyst regenerator first passes through a third (3rd) stage separator to knock out catalyst particles and then it flows to the expander which is used to recover power to drive the main air blower. From the expander outlet flue gas enters the CO combustor to oxidize the CO to CO$_2$. Hot flue gas from the CO combustor flows to the catalyst cracker feed preheater box via four transition ducts.

Ammonia injection facilities were added to each duct to implement the SNCR technology. Flue gas from the oil box passes through another box containing coils for 650 psig steam production and 200 psig and 650 psig steam superheating.

Flue gas from the steam box flows to the SCR. The flue gas temperature to the SCR is controlled by bypassing BFW around the preheater coil.

The SCR is designed for down flow with two catalyst beds with a provision to add a third bed. From the SCR the flue gas is routed to the caustic scrubber before exiting the 200-ft. high stack.

All the CEMS analyzers are in the stack. There are NOx, SOx and opacity analyzers in the duct before the SCR for checking the process performance. The SCR is also equipped with a bypass duct which is to be used in case of high pressure in the CO combustor or loss of activity of SCR catalyst. Bypass can also be used in case of excessive carryover of solids as determined by the opacity readings in the duct and high pressure drop in the SCR as a result of plugging with solids.
SCR Design Basis

The experience with SCR’s in flue gas from FCCU’s in a “high dust” and high sulfur service is very limited, but the experience with SCR’s from coal fired power stations is extensive.

Even though the dust level for this application is fairly high for an FCC unit, it is low compared to coal fired power stations. Typical dust loadings in an FCCU are 30 to 200 lbs/hr compared to 30,000 lbs/hr in coal fired power stations with the same flue gas flow.

The dust from a coal fired power station has similar particle size distribution and chemical composition. See Figure 2 for a comparison of the particle size distribution of FCC fines taken from an Electro Static Precipitator (ESP) and two typical types of dust from coal fired power stations.

Process Design Conditions

<table>
<thead>
<tr>
<th>Inlet</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue Gas Flow</td>
<td>1,000,000 lbs/hr</td>
<td></td>
</tr>
<tr>
<td>SO\textsubscript{2}</td>
<td>1,000 PPMVD</td>
<td></td>
</tr>
<tr>
<td>SO\textsubscript{3}</td>
<td>3 – 13 PMVD</td>
<td></td>
</tr>
<tr>
<td>NO\textsubscript{x}</td>
<td>100 – 200 PPMVD</td>
<td></td>
</tr>
<tr>
<td>Solids</td>
<td>40 – 50 PPH (Normal)</td>
<td>200 PPH (Max)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Outlet</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NO\textsubscript{x}</td>
<td>90% Removal</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10 – 20 PMVD</td>
<td></td>
</tr>
<tr>
<td>NH\textsubscript{3} Slip</td>
<td>10 PPMVD</td>
<td></td>
</tr>
<tr>
<td>Allowed DP</td>
<td>2” wc</td>
<td></td>
</tr>
</tbody>
</table>

The DeNO\textsubox Process

Selective Catalytic Reduction (SCR) is a widely used technology reducing nitrogen oxide emissions at high reduction efficiency. The abatement of nitrogen oxides results from injection of ammonia into the flue gas and subsequent passage through the catalyst, forming pure nitrogen and water.

Nitrogen oxides are primarily reduced according to the following stoichiometry:

\[
4 \text{NO} + 4 \text{NH}_3 + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O} \quad \Delta H_0 = -1,627.7 \text{ kJ/mol}
\]
\[
\text{NO + NO}_2 + 2 \text{NH}_3 \rightarrow 2 \text{N}_2 + 3 \text{H}_2\text{O} \quad \Delta H_0 = -757.9 \text{ kJ/mol}
\]
Typically the major part of the nitrogen oxides consist of nitrogen monoxide (NO); the first reaction is the most important one.

A minor amount of SO₂ is oxidized in accordance with the following reaction scheme:

\[
2 \text{SO}_2 + \text{O}_2 \rightarrow 2 \text{SO}_3 \quad \Delta H_0 = -196.4 \text{ kJ / mol}
\]

These reactions are exothermic due to the low concentrations the resulting temperature increase is less than 4°F.

The catalyst will also oxidize some hydrocarbons but not carbon monoxide.

The SCR process needs to have a temperature between 375°F and 950°F, but the presence of SO₃ makes it necessary to have a temperature above 500-600°F to avoid formation of AmmoniumBiSulfate(ABS).

The ABS dew point is determined by the partial pressure of SO₃, NH₃ and H₂O. The formation of ABS on the catalyst is dependent upon the capillary forces in the catalyst pores. Figure 3 shows the ABS temperature as a function of the SO₃ at two different inlet NOₓ concentrations (given two different NH₃ concentrations). The exact SO₃ concentration is often unknown; it is very difficult to correctly measure and it changes with the cracker feed and amount of combustion air.

The ideal temperature for the SCR would have been above 700°F. This could have been accomplished by splitting the steam convection section; however, there was neither time nor space available to implement this idea. Another option was to place the SCR downstream of the FGD and hereby reduce the SO₃ content; however, the cost of reheating the flue gas made it prohibitive. The SCR was therefore chosen to be installed in between the steam convection section and the FGD, the advantage being that the tie-ins could be completed during the 2002 turnaround. The temperature at this point can be controlled between 500 and 600°F, but there is a risk of ABS formation. The ABS formation is reversible; and in case of ABS formation on the catalyst, the inlet
temperature will be elevated to 600+°F which is sufficient to sublime the salts. This is done with a bypass on the boiler feed water to the convection section.

For the Shell Deer Park FCC 19% aqueous ammonia was selected as the ammonia source. The aqueous ammonia is vaporized before it is injected into the flue gas. To ensure a sufficient mixing of the ammonia and the flue gas, the point of injection of the ammonia into the flue gas must be as far away from the catalyst as possible. A proper location must be determined based on mixing and temperature. Proper mixing is even more critical when increased NOx conversion rates are required, and in a hybrid system with a combination of SNCR and SCR, there is a risk of having an uneven NH3/NOx distribution at the entrance to the reactor.

Ammonia injection is done through an injection grid containing many nozzles through which the reducing agent will flow. For this SCR a static mixer, turning vanes, and a flow rectifier were required.

**Flow modeling**

Flow modeling utilizing scaled (1:12) model and computational fluid dynamics were used to determine the shape of the ductwork. The static mixer is the best solution for combining the ammonia, NOx, and flue gas, and will ensure that the flue gas has a uniform temperature with only minor increase in pressure drop.

Flow modeling was done by FORCE/DMI. First, a computerized model was created. The first point of mal-distribution highlighted by this study (see Figure 4) was the tie-in to the steam convection section, a “T” that effectively becomes a 13’ x 9’, 90° elbow once flow is diverted to the SCR. A new elbow with turning vanes, based on recommendation from the DMI study, is to be installed during the next turnaround to reduce the pressure drop and improve the flow distribution.

*Figure 4*

*Velocity field at plane through centre line, Shell Deer Park, Existing and New 1-Piece, by FOWD Technology, Jan 2003*
Furthermore, the plot space available made it impossible to have a more typical direct entry into the SCR reactor.

After many trials, a solution was developed which required a 90° turn into the AIG and two static mixers followed by a 180° turn and drop into the main body of the SCR (see Figure 5).

A 1:12 scale plastic model was constructed based on the results of the CFD modeling and interaction with the engineering design firm for space availability. The advantage of the physical model is its ability to simulate two phase flow. Dust accumulation was modeled in various areas of the duct-work and the SCR using a suitable powder to represent the FCCU fines at the test conditions. The ability of the powder to represent the FCCU fines was ensured by evaluation of the Barth number, Euler number and Froude number, while maintaining high duct Reynolds numbers.

Dust accumulation tests were carried out at different dust loads corresponding to normal operation and a simulation of a major FCCU catalyst carry-over.

The use of the physical model greatly assisted in the determination of the position and shape of the turning vanes, mixers and the AIG. Sulzer supplied the scale model mixer and AIG components for the test as well as the full-sized components for the project.

![Figure 5](image)

In high dust applications, the dust must be evenly distributed across the catalyst surface, and provisions for cleaning should be made. Periodic use of soot blowers or sonic horns is necessary.

Sonic horns were selected for this project. Sonic horns can be operated at any defined interval of time, cost less than traditional soot-blowers, and are more easily maintained.
The DeNOx Catalyst

The vital part of the DeNOx unit is the catalyst. The catalyst is monolithic based on a fiber reinforced titanium (TiO₂) carrier impregnated by vanadium (V₂O₅) and tungsten (WO₃).

The design produces a flexible, thermal shock and erosion resistant catalyst with a high poisoning resistance, resulting in low deactivation rates and high mechanical durability. The openings in the corrugated structure are mainly determined by the particulate loading in the flue gas. The selected catalyst has a hydraulic diameter of 5.7mm, which is the same as a standard design catalyst for coal fired power stations (see Figure 6).

In order to facilitate handling, the catalyst is produced as cassettes which are assembled in modules. A standard electric or manual pallet lift can be used to handle the modules (see Figure 7). This alleviates the need for a complex, internal loading/unloading system.

NH₃ Vaporizers and Dilution Air System

Deer Park decided to use 19% Aqueous Ammonia as there are no restrictions on the quantity that can be stored. Aqueous Ammonia is vaporized in kettle type electric exchangers. Dilution air is also heated using electric heaters.

FCCU SCR Constructability Issues

There were many constructability obstacles that had to be recognized and resolved during the engineering phase of the Shell FCCU SCR Project.
The first of many obstacles was design timing itself. The FCCU Flue Gas Scrubber (for SOx) was required to be online in December 2003. However, the technology/catalyst provider was not selected until late 2002, when engineering for the Scrubber was well underway. Therefore, the system had to be designed to allow for the future tie-in of the SCR upstream of the Scrubber Unit.

Due to critical turnaround access and staging areas to the east and west, the balance of the FCCU Unit to the south and a major arterial pipe rack to the north, space was limited. In fact, there was only about 1000 square feet of usable footprint available for the SCR. Also, all material brought into the area for construction had to come underneath the northern pipe rack via an access area of only 29 ft wide by 24 ft tall and be staged to the SW of the SCR in a space of only 1300 square feet shared with a hydraulic crane and a 16" medium pressure steam line immediately overhead throughout the area (see Figure 8). Therefore, the SCR had to be built via panelized construction with panels small enough to get into the tight location but also large enough to minimize handling and welding costs. The SCR rough dimensions are 50'L x 20'W x 80'H. Tolerances are 6 inches from north wall of SCR to the centerline of a fuel gas line on the south side of the arterial pipe rack to the north. From the southern structure holding up the bypass duct, tolerances are less than 2 inches.

Another design consideration was the use of refractory. Refractory was not necessary due to the low operating temperatures of the flue gas downstream of the steam convection section. The entire system, both SCR and interconnecting ductwork, was built with a hot-wall design with slide plates and inlet and outlet fabric expansion joints for growth allowance and external insulation for corrosion protection.
FCCU SCR Start-Up Issues

Since the FCCU unit was online at the completion of the SCR, a pre-heating of the SCR was accomplished via a preheat vendor. Skin thermocouples and burner access ports were designed into the SCR to facilitate this preheat step.

The start-up of the SCR was slightly delayed by difficulty with the damper valves. All four damper valves were installed with external flag indicators as well as electronic limit switches to detect position of the gate. However, two of the damper valve indicators became disconnected and were lodged between the gate and the bonnet wall of the damper valve while the SCR was being brought online. This required the removal of the top panel of each bonnet and manual removal of the indicator rod while the SCR was in operation.

FCCU SCR Shutdown and Catalyst Change-out

The SCR catalyst was designed to last a minimum of 5 years at full design loading rates before change-out is required. This is also the normal turnaround schedule for the FCCU. However, should the SCR require a shutdown in between FCCU turnarounds, this can be accomplished.

The damper valves on the bypass are opened and those around the SCR closed and purged to divert the flow of the flue gas. A maintenance air purge line then flushes the SCR of trapped flue gas and heat. Finally, the inlet and outlet fabric expansion joints are retracted to allow the insertion of a blind plate or are simply removed altogether. This allows the inside of the SCR to be accessed without significant safety risks.

Platforms are stair-stepped to allow for catalyst change-out simultaneously on all levels. The original catalyst installation took approximately 1 shift per layer.

Performance

The SCR for the Shell Deer Park FCCU was commissioned in the fall of 2004. The unit was built with the FCCU in operation and started up within schedule.

When the unit came online it performed immediately; no tuning was necessary because of the way the SCR is designed. The pressure drop over the SCR is constant and lower than the guarantee. The NOx reduction has been higher than the guarantee. Since it is start of run for the catalyst It has been possible to bring the outlet NOx down to much lower numbers than the guarantee of 20 ppmvd. The outlet NOx is consistently controlled lower than 20 ppmvd, and the SNCR has therefore not been put in service. The inlet temperature to the SCR has been maintained between 525°F and 550°F. There has not been any measurable ammonia slip in the stack, which is not a surprise since it is downstream of the FGD. However, we have not found any measurable ammonia increase in the waste water from the FGD.

Operation of the SCR

Operation of the SCR is very simple and can be included in the daily work routine of the inside and outside operators. The inside operators have to monitor equipment status and emissions levels, but no physical adjustments are required for daily unit functions. The vaporized ammonia injection rates are controlled by stack NOx levels.
Conclusion

Experience with SCRs in FCCUs with high sulfur and high dust content is very limited. The design for our SCR is based on experience from SCRs in high dust, coal fired power facilities. With the help of CFD and scale modeling, the physical limitations were rectified. The project showed that it is possible to build and commission an SCR without interruption of the operation of the FCCU. Operating results to date from this SCR indicate that very low levels of NOx emissions are achievable, even with the SCR in a high dust and high sulfur service.