Start-up of First CD*HDS*® Unit at Motiva's Port Arthur, Texas Refinery

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Introduction/Background

In 1998, Motiva Enterprises LLC's Port Arthur Refinery approved funding to proceed with a project to design and construct a cracked naphtha desulfurization process to desulfurize heavy FCCU naphtha. The unit had to provide the refinery with the ability to economically produce reformulated gasoline meeting the Phase II Complex Model requirements of the 1990 Clean Air Act Amendments (CAAA). In particular, to meet the NOX emission standard for Port Arthur Refinery's RFG and to continue to meet the NOX emissions requirements for conventional gasoline, the gasoline sulfur content had to be reduced. The technology selected had to be consistent with future requirements to further reduce sulfur in gasoline products. Port Arthur Refinery's target was to drop the gasoline pool sulfur by 20-25 percent following implementation of this project.

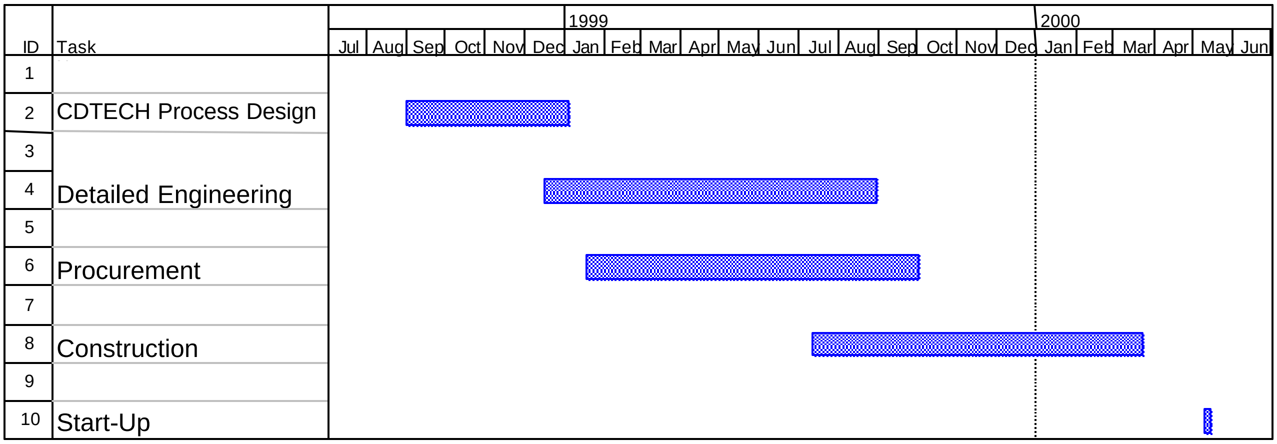
Although Motiva had experience with a CDTECH competitor's technology in the same service at Port Arthur Refinery and a related technology within its own organization, it selected the CD*HDS*^{â} process from CDTECH due primarily to lower capital costs, superior octane retention, and ability to operate at reduced severities without encountering high mercaptan levels in the treated gasoline. The lower operating pressure of the CD*HDS* technology when compared to conventional processes was also an attractive parameter in the technology selection. Moreover, it was anticipated the aforementioned technology would not provide the necessary performance to meet the more stringent sulfur levels required by the Phase II CAAA regulations while minimizing octane loss.

The unit design was "kicked off" in the fall of 1998. Matrix Engineering, located in Beaumont, Texas, was selected to perform detailed engineering and procurement services.

Conex International, also out of Beaumont, was the general contractor responsible for the construction phase of the project.

The project was completed on schedule and on budget. Figure 1 summarizes the schedule of the main project activities:

Figure 1



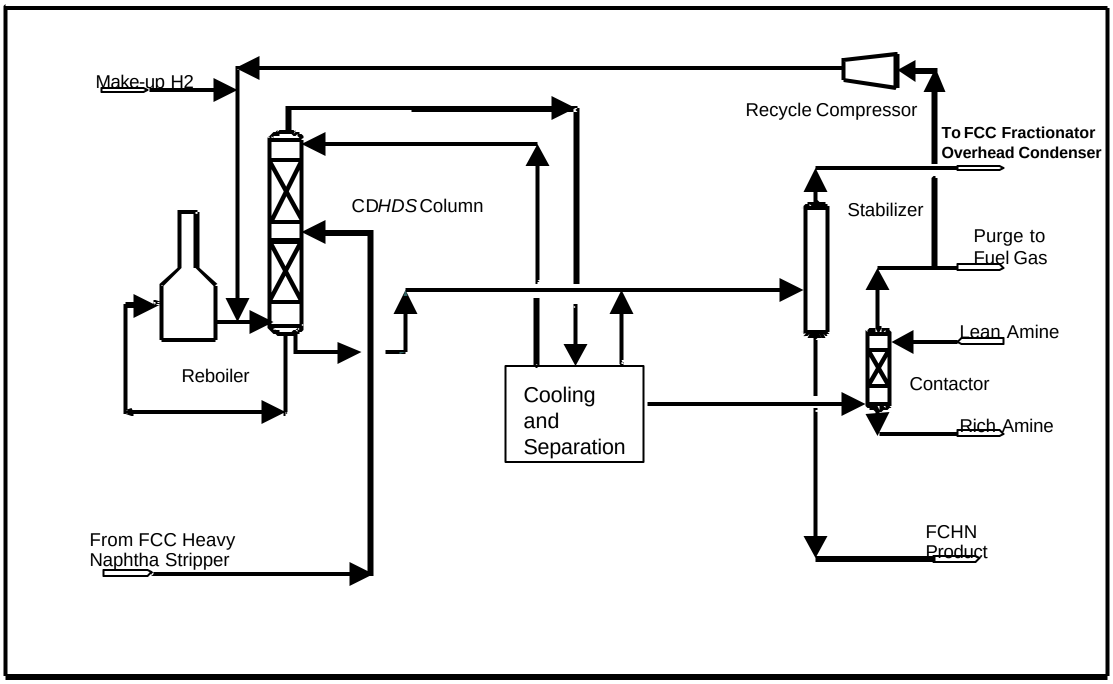
The unit was mechanically complete in March 2000 but start-up was delayed until May due to an unplanned shutdown of the fluid catalytic cracking unit (FCCU). Heavy cracked naphtha (HCN) was introduced to the unit on May 14 and since then, the plant has been operating steadily at design rates, with the exception of two short FCCU outages, producing on-specification desulfurized gasoline product.

Process Overview

Following is a brief description of the CD*HDS* processing scheme at the Port Arthur Refinery. The unit design maximizes heat integration in order to conserve energy.

The source of the HCN feedstock is the existing Heavy Cat Naphtha Stripper off the FCCU main fractionator. Figure 2 is a simplified flow diagram of the process. The HCN feeds the CD*HDS* unit via a feed preheat train (not shown) consisting of several exchangers maximizing heat integration within the unit. The feed enters the CD*HDS* column on flow control.

Figure 2



The CD*HDS* column contains the hydro-desulfurization catalyst embedded in CDTECH-proprietary structured packing. This arrangement facilitates simultaneous distillation and hydrodesulfurization.

The conditions in the CD*HDS* column form a selective hydrodesulfurization environment in which the sulfur compounds will react with hydrogen to form hydrogen sulfide (H_2S) while preserving olefins. The greater portion of the desulfurized naphtha leaves with the overhead vapor.

Make-up hydrogen supplements the recycle hydrogen to provide the total hydrogen requirement.

The CD*HDS* column reboiler is a fuel gas fired heater. A temperature controller, located on the column, controls the boil-up by regulating fuel gas to the burners.

The overhead vapor from the CD*HDS* column is partially condensed and sent to an accumulator that operates at moderate temperature. A portion of the liquid from this drum is pumped back to the column as reflux while the remainder feeds the stabilizer. The vapor containing H_2S is routed to an amine contactor.

The sour vapor from the cooling and separation section is contacted with lean amine to remove H_2S. The vapor leaving the contactor is recycled back to the process by a recycle compressor on flow control. A purge is taken to fuel gas to control non-condensables in the process.

The function of the stabilizer is to remove hydrogen, H_2S and light hydrocarbons from the desulfurized naphtha. The vent from the stabilizer is returned to the FCC Fractionator Overhead Condenser for reprocessing. The bottom stream from the stabilizer is the HDS naphtha product (FCHN) that is routed to offsite blending.

Process Design

The unit is designed to process HCN with the following characteristics:

ASTM (D-86), °F	
IBP	124
5 %	229
10%	263
20%	297
30%	319
40%	339
50%	353
60%	368
70%	384
80%	401
90%	422
95%	437
FBP	451

Sulfur, wt%	0.52

The unit uses available pipeline hydrogen with a purity of 99 percent at a rate of 1.5 MMSCFD. The process does not require high purity hydrogen, so it is possible to use lower purity hydrogen such as reformer hydrogen.

Operator Training

In preparation for initial start up of the CD*HDS* unit, Port Arthur Refinery and CDTECH personnel worked together on training the refinery technical and operations staff. As part of CDTECH's basic engineering package, a supervisory operating manual was prepared. Using this document as a guide, Motiva developed training modules that were finalized in a joint CDTECH/Motiva review at CDTECH's R&D facilities in Pasadena, Texas. The overall program covered such topics as normal operation and control, commissioning and start-up, shutdown and emergencies, safety and environmental issues, and analytical control. The modules formed the basis for a one-week training course provided to unit operators and engineers at site. Instructors were Motiva technical personnel, assisted by CDTECH. This was conducted within a few months of start-up when most of the construction was complete, allowing the trainees to spend a portion of the "class" in the actual unit.

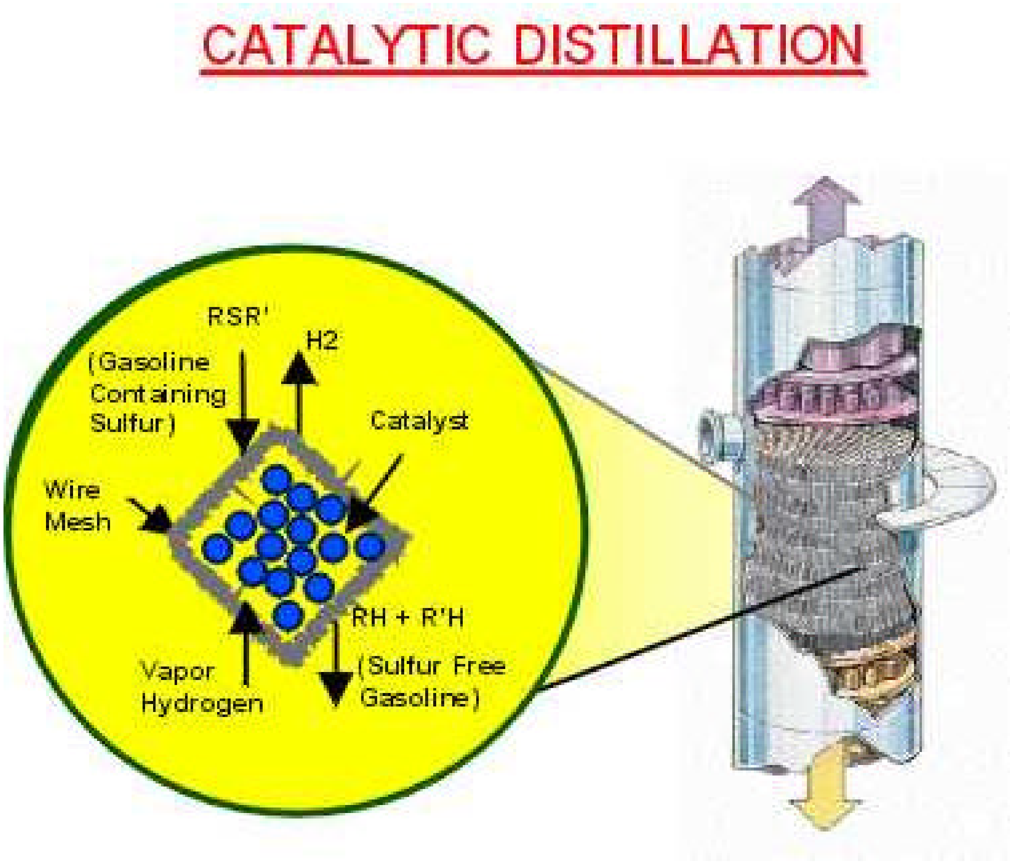
Commissioning & Catalyst Loading

The construction contractor and Port Arthur Refinery personnel divided the plant into more than 100 test systems to track construction progress, hydrostatic testing and flushing/blowing of systems. CDTECH provided an experienced operations expert to assist Port Arthur Refinery inspectors with these pre-commissioning activities. Most of the hydrostatic testing and flushing of the unit systems was done with water. Special care was taken with lines that were tied into the CD*HDS* column to protect the catalyst and distributors from extraneous materials. The column was blinded and put under a nitrogen blanket following catalyst loading to protect the column internals from ingress of such materials during the final stages of construction and pre-commissioning.

The hydrodesulfurization catalyst used in the CD*HDS* unit is a commercially available catalyst that is contained in a proprietary catalytic distillation structure provided by CDTECH. Physically, the structure is very similar to other commercial structured packing and loading it into the column is the same process. It is placed into the column in a specified pattern to maximize catalyst loading density.

Each bed of catalyst contains multiple levels (or layers) of structure (Figure 3) arranged according to a predetermined loading diagram onto a catalyst support grid. Special perimeter structures are provided to fit the curvature of the tower wall. The catalyst packing is loaded to optimize the overall vapor-liquid contact efficiency for simultaneous fractionation and reaction.

Figure 3



There is a loading manway located at each catalyst bed on the column between the catalyst support grid and the chimney-collector tray. The construction contractor's personnel provided the labor for loading the catalyst structure under the supervision of CDTECH personnel.

Catalyst loading of the CD*HDS* column was completed in March and the tower was put under a nitrogen blanket awaiting catalyst conditioning and start up.

Initial Start-Up

The CD*HDS* unit was ready for start-up in late March; an unplanned shutdown of the FCCU delayed commissioning of the CD*HDS* unit. After repairs and startup of the FCCU the CD*HDS* unit was commissioned in May.

In addition to pre-commissioning, training, and catalyst loading services, technical and analytical support were provided around-the-clock during the commissioning and initial start-up of the plant. The analytical support included on-site laboratory equipment (total sulfur/nitrogen analyzer and bromine number/mercaptans titrator). This information was important for detailed analysis and comparison of plant operating data against pilot plant results.

Prior to the introduction of heavy naphtha feedstock to the CD*HDS* unit, the hydrodesulfurization catalyst has to be “conditioned.” The fresh catalyst as loaded is in an oxide form that is not active for the desired hydrodesulfurization reactions. A thorough sulfiding is needed to convert the metal oxides into active substoichiometric sulfides. The sulfiding procedure consists of soaking the catalyst with hydrocarbons containing DMDS and sulfiding at elevated temperatures. Prior to presulfiding, the catalyst has to be dried to remove moisture absorbed from the atmosphere during handling and packaging. Drying is accomplished by circulating hot hydrocarbons through the column and injecting nitrogen to act as a sweeping gas to carry the moisture-laden vapor overhead.

The catalyst conditioning steps took four days to complete. Once finished, the column was kept under nitrogen pressure until reactive feedstock was introduced.

HCN from the FCCU heavy naphtha stripper was introduced to the unit on May 14 at about 50 percent of design rate. A hydraulic restriction in the line from the HCN stripper to the feed surge drum initially limited capacity to about 80 percent of design rate. The start up of the CD*HDS* column is similar to the start up of conventional distillation columns with one exception, the additional hydrogen feed (for reaction) is not started until the column reflux is well established.

Following is a brief chronology of the key activities during the commissioning and initial start up of the plant:

- May 10: Dry-out of HDS catalyst started with N_2 injection and heat up
- May 11: Dry-out completed. Sulfiding procedure started with Injection of DMDS to provide initial “soak” of catalyst.
- May 12: Started H_2 and heat up of catalyst to first sulfiding “hold” step at 450°F. Await H_2S breakthrough at these conditions.
- May 13: Breakthrough of H_2S confirmed. Heat catalyst to second “hold” step at 600°F. Await second H_2S breakthrough.
- May 14: Sulfiding of catalyst completed. Feed introduced to unit at 09:00 hrs. Unit lined out by 14:00 hrs. Sample of product taken at 22:00 hrs. showed it meeting desulfurization specification. Charge rate limited to 80 percent of design due to hydraulic limitations on tie-in to HCN Stripper.
- May 15: Recycle Compressor started – ran for eight hours then tripped on high motor amps. Unit returned to once through H_2 operation.
- May 16: HDS product sent to normal rundown line as restart of compressor delayed to modify anti-surge piping.
- May 20: Charge rate increased to design rate following modifications to remove hydraulic restriction in piping from HCN Stripper to Feed Surge Drum.
- May 21: Started stripping steam to HCN Stripper. Water collecting regularly in Surge Drum boot. Some water carryover noted.
- May 23: Compressor modifications completed – machine restarted. Recycle gas rate limited by molecular weight and check valve restriction.
- May 30: Lowered HDS column pressure to reduce HDS conversion to determine unit flexibility and to approach design severity. HDS conversion lowered to design level of 90 percent.
- September: Recycle compressor check valve has been repaired and hydrogen recycle is at design rate.

Unit Performance

Figure 4

Since initial start-up, the unit (Figure 4) has been operating steadily at design throughput producing a product meeting desulfurization and octane retention specifications. There have been two upsets thus far, both involving electrical trips of the recycle gas compressor. In both cases, the operation of the unit was unaffected, with smooth transition from recycle to once-through hydrogen operation.

The feedstock composition has changed significantly at times, e.g. sulfur levels in the HCN feedstock have varied up to as high as 0.75 wt percent. Even so, the unit control remained unchanged and the product continued to meet desulfurization and octane retention specifications. The unit operation and control follows conventional distillation practices and the reaction parameters are easily controlled within normal column operation.

The operating data over the first six months of operation is shown in Figures 5 through 7.

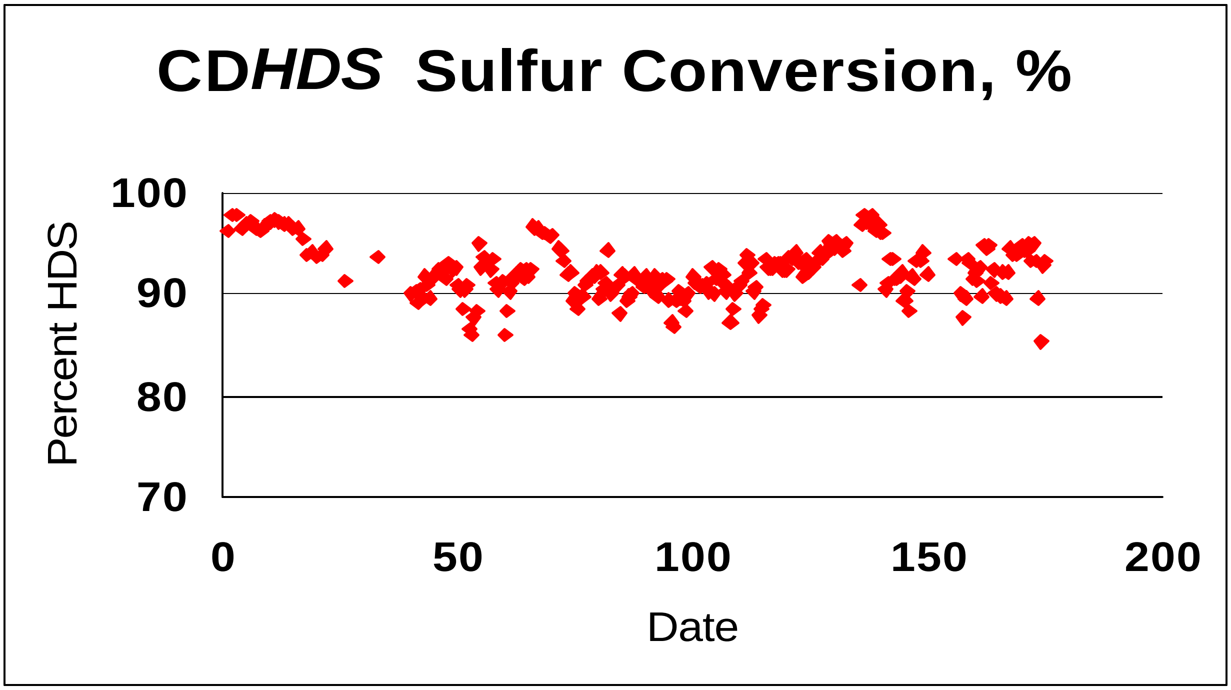


Figure 5

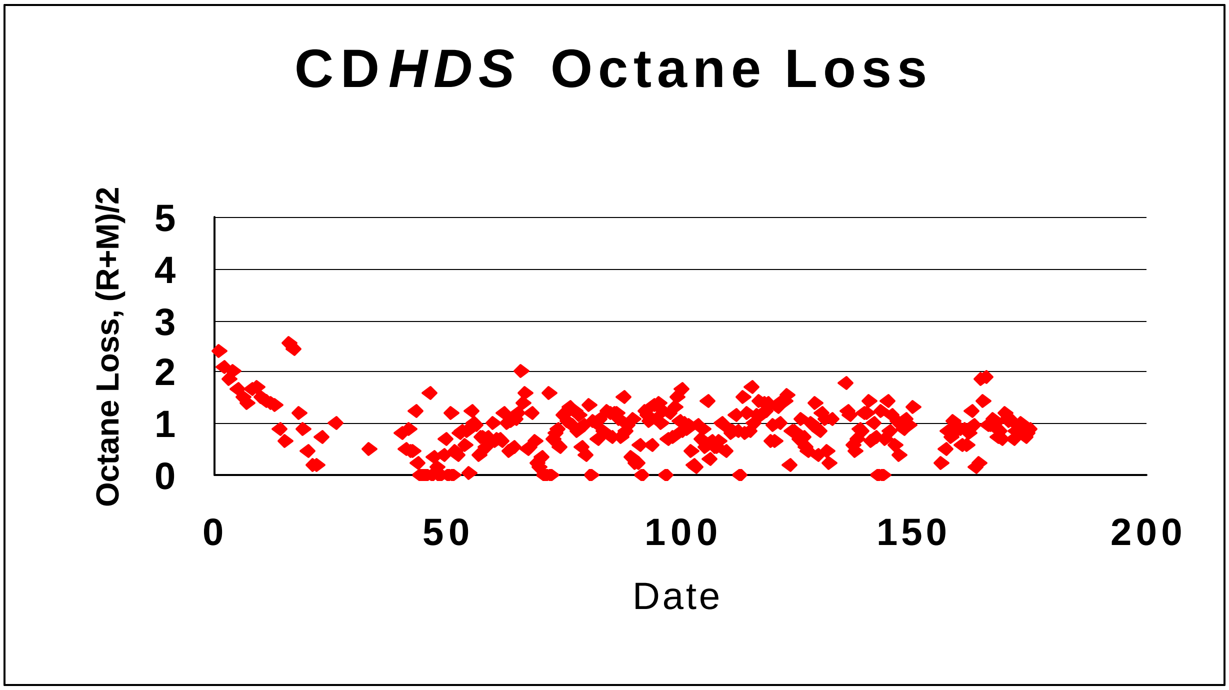


Figure 6

The HDS conversion across the unit was high during initial operations. The HDS level was deliberately lowered to the design HDS condition. This was accomplished by reducing the pressure of the CD*HDS* column, which resulted in less severe hydrodesulfurization conditions within the column, yielding lower HDS conversion. At the same time, the saturation of olefins declined as shown by the reduction in octane loss.

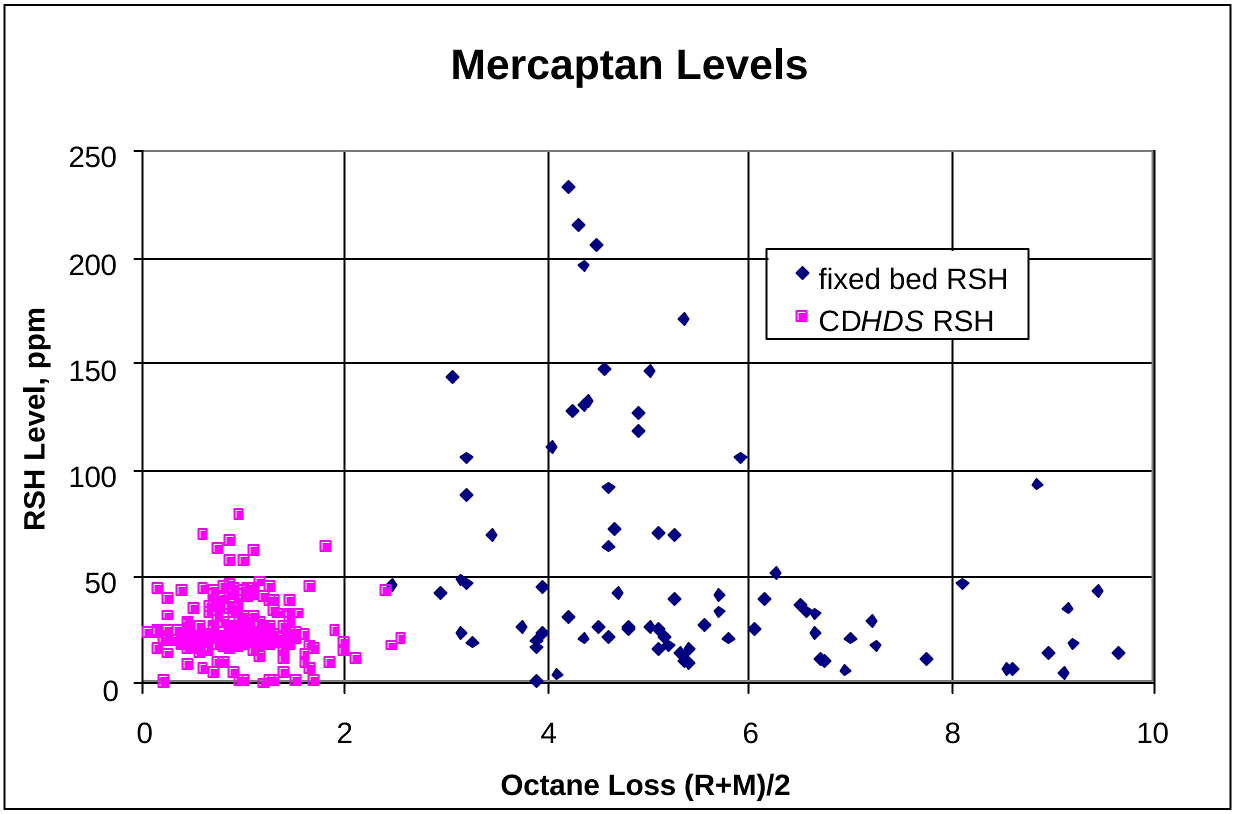


Figure 7

During the past few months, the HDS conversion has been maintained within the design range over a wide range of feed sulfur levels. Average octane loss has been at or below one number over this time period.

The mercaptan levels in Port Arthur's CD*HDS* treated Heavy Cat Naphtha have been low enough that the refinery has been able to blend and ship gasoline with no further treatment required. The data from the fixed bed unit (see Figure 7) were gathered during a prior run on the same Heavy Cat Naphtha feedstock. While acceptable RSH levels could be achieved on the old unit, octane losses at the necessary operating conditions were extremely high, typically 4-6 numbers (vs. current loss of 1 number with the CD*HDS* process).

The unit has been operating smoothly since start-up in May. Little operator attention is required to control the unit and no gasoline blends have been produced off-specification for sulfur or octane.

Additional Work

The CD*HDS* unit was shut down early in 2001 during a scheduled FCCU maintenance turnaround. At that time, the only work planned on the CD*HDS* unit was to modify the feed surge drum to include a coalescer element to mitigate water carryover from the feed surge drum.

Based on the successful performance and operations of the CD*HDS* unit Port Arthur Refinery has authorized CDTECH to begin work on the basic engineering of a second phase, low sulfur gasoline project. The project will provide additional facilities to treat the entire FCCU cracked naphtha stream using CD*Hydro*®/CD*HDS* technologies.

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