Chevron Texaco CD*Hydro*®/CD*HDS*® Startup

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Introduction/Background

European legislation is targeting to reduce the sulfur content of gasoline. ChevronTexaco constructed a new gasoline desulfurization unit at their refinery in Pembroke, Wales (Figure 1) to meet these future targets and begin marketing low sulfur gasoline in the European Union. At Pembroke, as at most other refineries, the FCCU naphthas have a major impact on gasoline sulfur, being approximately 50% of the gasoline pool. The sulfur content of these streams, which can be as high as 2800 wppm, will be reduced to approximately 50 wppm in the new Ultra Low Sulfur Gasoline (ULSG) plant, which utilizes the CD*Hydro*®/CD*HDS*® technologies available from CDTECH. The ULSG plant was constructed in 2001 and began initial operations in early 2002.

Figure 1 – Site Photo

Project Execution

The project execution proceeded as follows: technology selection was awarded to CDTECH and the project kick-off meeting was held in September 1999; basic engineering was completed February 2000; start-up began on January 29, 2002; and ChevronTexaco accepted the CD*Hydro*/CD*HDS* unit on March 7, 2002.

Process Overview

Following is a brief description of the CD*Hydro*/CD*HDS* processing scheme at the ChevronTexaco Pembroke Refinery. The process unit consists of two catalytic distillation columns and one distillation column complete with reflux accumulators, pumps, fired reboiler, hydrogen recycle compressor, amine absorber and heat integration.

The CD*Hydro* Column removes mercaptans from the light distillate cut of the LCN from the overhead of the Naphtha Splitter. The CD*Hydro* Column bottoms are combined with HCN from the Naphtha Splitter bottoms and HHCN from the Main Fractionator Side Stripper in the Surge Drum located directly below the column sharing the same structure (Figure 2).

CD*Hydro* Simplified Flow Diagram

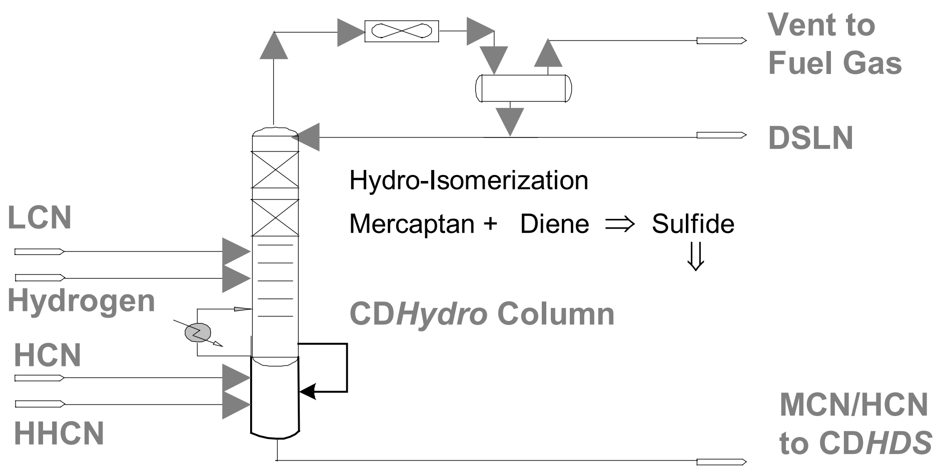


Figure 2

The technology involves the use of CD*Modules*[SM], which are units of structured distillation packing that contain catalyst and enable simultaneous reaction and distillation in a fractionation column. The top of the column holds two CD*Module* beds: a bed of nickel for thioetherification (mercaptan conversion) and a bed of Palladium for hydro-isomerization. Both nickel and palladium will also catalyze hydrogenation of diolefins that reduces catalyst fouling and gum formation in gasoline. The structured packing has very high distillation efficiency, exceeding that of conventional trays.

Hydrogen is fed to the column below the catalyst beds where it mixes with the vapor and flows up through the catalyst beds. In the Nickel bed, the liquid and vapor phases are in counter-current contact and react according to the following equation:

$$C_nH_{2n+1}SH + \quad \longrightarrow \quad C_nH_{2n+1}SH-$$

Mercaptan Diene Sulfide

The reaction goes essentially to completion, converting virtually all of the mercaptans in the light fraction of the LCN into high boiling point sulfides that fractionate into the column bottoms stream. In the Palladium bed, the counter-current contact of liquid and vapor phases promote the isomerization of primary olefins to secondary olefins according to the following equation:

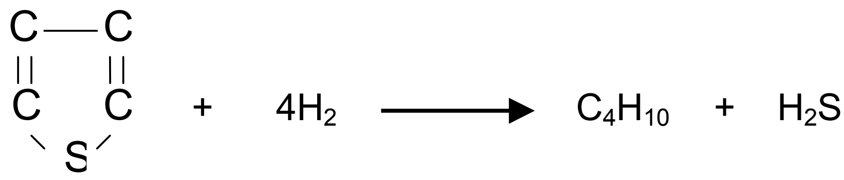
$$CH_2 = CH - CH_2 - CH_2 - CH_3 \rightleftharpoons CH_3 - CH = CH - CH_2 - CH_3$$

1-Pentene Cis and Trans-2-Pentene

The hydro-isomerization reactions are equilibrium reactions between normal-C_5 olefin isomers and also between iso-C5 olefin isomers creating a product with improved octane.

The desulfurized light naphtha (DSLN) product makes a sweet gasoline blending component with very low suflur content.

The bottoms of the CD*Hydro* column overflows to the surge drum where it is combined with HCN from the Naphtha Splitter bottoms and HHCN from the Main



Thiophene

Fractionator Side Stripper, is preheated and fed to the CD*HDS* column as shown in Figure 3.

CD*HDS* Simplified Flow Diagram

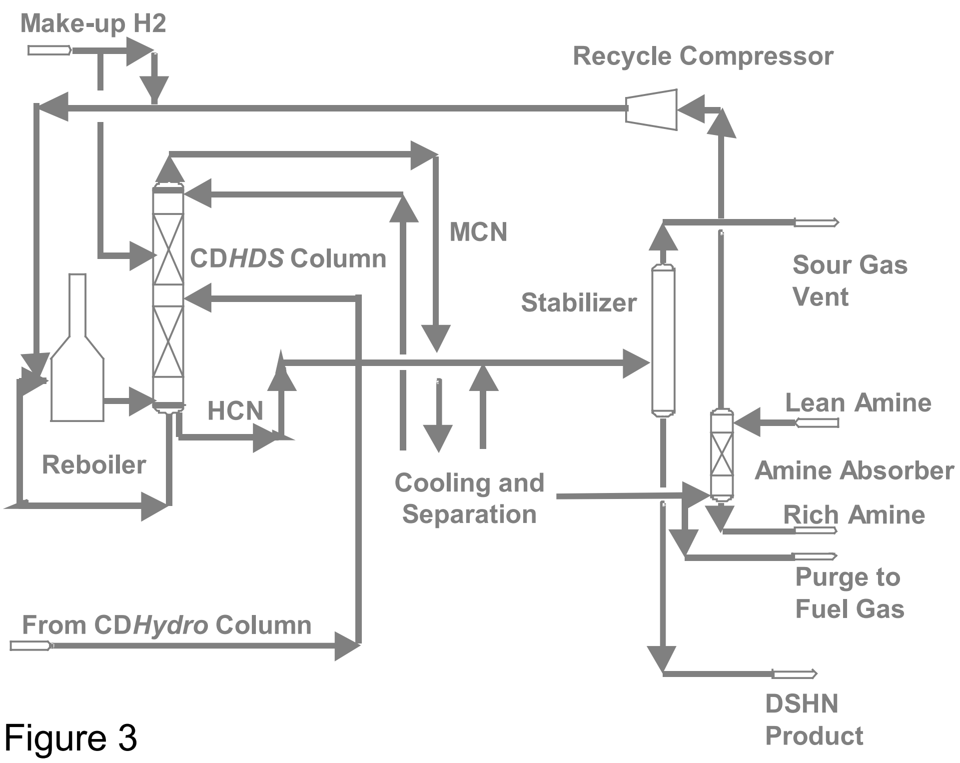


Figure 3

The HDS feed is fractionated in beds of CD*Modules* containing CoMo catalyst to produce a Medium Catalytic Naphtha (MCN) distillate and a Heavy Catalytic Naphtha (HCN) bottoms stream. A fired heater is used to reboil the column and hydrogen is added at the bottom, below the CD*Modules* beds. The sulfur contained in the feed is converted to hydrogen sulfide (H_2S), which is stripped overhead along with the MCN vapor. The MCN vapor is condensed to provide reflux as well as low-sulfur distillate. The vapor vented from the reflux drum contains the remaining hydrogen, H_2S and other light components from the make-up hydrogen. This stream is sent to the amine absorber where H_2S is removed and then to the recycle compressor before being returned to the CD*HDS* column.

The conditions in the catalyst section of the CD*HDS* Column form a strong hydro-desulfurization environment in which a majority of the sulfur compounds will react with hydrogen to form Hydrogen Sulfide.

The hydro-desulfurization reactions are rate limited. The rate of reaction is affected by the process operating temperature and hydrogen partial pressure in the “reactor”. The occurrence of other reactive components, like olefins, which could occupy catalyst sites, will also affect the reaction rate.

Under HDS conditions, some olefins will also hydrogenate via the following reaction:

$$CH_2 = CH - CH_2 - CH_2 - CH_3 + H_2 \text{ --(catalyst)}\rightarrow CH_3 - CH_2 - CH_2 - CH_2 - CH_3$$

1-Pentene + Hydrogen → n-Pentane

While olefin saturation is undesirable, it increases as percent desulfurization increases.

The cooled MCN is sent to the Stabilizer along with the HCN, where hydrogen and light make-up hydrogen components are stripped overhead to control the vapor pressure of the product. Low sulfur DSHN (MCN/HCN) is sent to storage for final gasoline product blending.

In conventional fixed bed reactors, there is a tendency for H_2S to combine with olefins to form mercaptans before the product leaves the reactor and to continue this reaction until the reactor effluent is cooled enough to stop the reaction. In some cases, this effect can result in a product with more than 200 ppm of mercaptans in spite of having reduced the other sulfur compounds to only a few ppm.

The mercaptans that are formed from the olefins have a much higher boiling point than the olefins from which they were formed. As a result, in the CD*HDS* column, the mercaptans tend to be separated from the distillate by fractionation. This effect keeps the mercaptans bottled up in the column where they are again separated into H_2S and hydrocarbon in CD*Modules*. Therefore, a greater fraction of the sulfur leaves the CD*HDS* overhead as H_2S instead of as mercaptans than in a conventional fixed bed reactor. The overhead vapor is quickly cooled in the condenser, thus quenching the reaction and stopping the formation of additional mercaptans. Meanwhile, the HCN is produced at the bottom of the CD*HDS* column where the H_2S and olefin levels are much lower than at the top of the column, hence it contains virtually no mercaptans. Therefore, the mercaptan content of the CD*HDS* bottoms product is much lower than the corresponding conventional fixed bed HDS reactor product.

Design Basis

The unit is designed for three modes of operation. The Base Case of operation is designed to desulfurize the LCN and part of the HCN and the HHCN feedstocks to meet a specification of 45 ppmw in the combined CD*Hydro*/CD*HDS* product. Overall sulfur desulfurization is 94.4% for the Base Case. The Alternate Case of operation is designed to process the LCN and the total HCN feed streams. The Low Sulfur Case processes a feedstock with the same composition as the Base Case, but containing a lower sulfur content. The LCN, HCN and HHCN feed streams are characterized as described below:

ASTM D86 (ºC)	LCN	HCN	HHCN
IBP	31	135	98
5 vol %	45	142	155
10 vol %	52	145	169
30 vol %	59	151	190
50 vol %	73	157	198
70 vol %	94	167	204
90 vol %	122	180	217
95 vol %	134	183	225
EP	154	195	245
Flow rate, Nm^3/h	260.4	17.3 (1)	33.0 (1)
S.G.	0.7126	0.8280	0.8632
MW	84.7	121.2	133.7
Bromine No.	80	22	18
Sulfur, ppmw	(2)	(2)	(2)

Notes: 1. HCN flow rate for the Alternate Case is 67.3 m^3/h. HHCN flow rate for the Alternate Case is 0.

2. Sulfur content of the feed streams for the Base Case are: 450 ppmw, 1200 ppmw, and 2860 ppmw for the LCN, HCN and HHCN streams, respectively. Sulfur content for the Alternate Case: 350 ppmw and 1100 ppmw for the LCN and HCN streams, respectively. Sulfur content for the Low Sulfur Case: 319 ppmw, 769 ppmw, and 1779 ppmw for the LCN, HCN and HHCN streams, respectively.

Operator Training

In preparation for initial start up of the ULSG unit, Pembroke Refinery and CDTECH personnel worked together on training the refinery technical and operations staff. As part of CDTECH's basic engineering, a supervisory operating manual (SOM) was prepared. Using this document as reference material, ChevronTexaco developed a detailed site-specific training manual. CDTECH conducted a "train the trainers" program at Pembroke. The training program covered such topics as normal operation and control, commissioning and start-up, shutdown and emergencies, safety and environmental issues, and analytical control.

The program formed the basis for two-week training courses provided to unit operators and engineers at site. Instructors were ChevronTexaco technical/operations personnel. The course was conducted in multiple classes to accommodate the entire operations staff, which was already working a shift schedule. The course was conducted a few months prior to start-up when most of the construction was complete, allowing the trainees to spend a portion of the "class" in the actual unit.

In addition, ChevronTexaco had a process simulator built by AspenTech to further aid in the training of the operations staff. All operators were required to spend a considerable time on the simulator to facilitate understanding of the new unit including reaction to emergency scenarios on the unit, e.g loss of feed, hydrogen, etc. The process simulator proved to be a useful training tool for shut down scenarios, normal operating deviations, warm start ups, and overall general comfort/familiarization with the unit and DCS system. It was not, however, set up for cold start ups nor DMDS influences.

Although CDTECH did not provide on site analytical support during start up, their analytical manager made a visit to site prior to start up to assess and review analytical procedures with ChevronTexaco laboratory personnel. This proved beneficial to both parties as test methods and procedures were reviewed and established. This was important as CDTECH provides on site analytical manpower and equipment support Services (as provided at the other two CD*HDS* units). Although these services are optional to the licensee, CDTECH recognizes the importance of analytical control of the unit and therefore, is proactive in establishing communication and review of the licensee's analytical capabilities prior to start up.

Commissioning & Catalyst Loading

The construction contractor and ChevronTexaco personnel divided the plant into numerous test systems to allow tracking of construction progress and hydrostatic testing and flushing/blowing of systems. Over 100 systems were defined with over 1000 instrument loops. In addition to following standard operating procedures for leak testing, ChevronTexaco contracted Air Products to conduct Helium testing of the piping systems to ensure the smallest of leaks would be identified. CDTECH provided input as required to Pembroke on their 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 columns to protect the catalysts and distributors from extraneous materials. Following catalyst loading, the columns were blinded to protect the column internals from ingress of such materials during the final stages of construction and pre-commissioning.

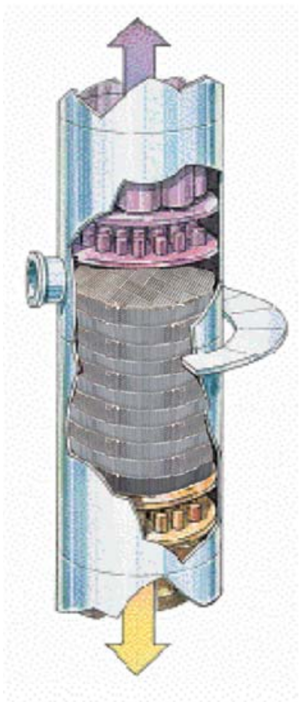


Figure 4

The CD*Modules* beds form an integral part of the catalytic distillation towers. The catalyst structure is physically very similar to other commercial structured packing. The CD*Modules* are loaded into the column in a specified pattern to maximize catalyst loading density.

Each CD*Modules* bed contains multiple levels (or layers) of packing arranged according to a predetermined loading diagram onto a CD*Modules* support grid (Figure 4). Special perimeter structures are provided to fit the curvature of the tower wall. The CD*Modules* are loaded to optimize the overall catalyst bed, vapor-liquid contact efficiency for simultaneous reaction and fractionation. The CD*Modules* for the CD*Hydro*/CD*HDS* unit were stored in the original shipping sea-tainers within the refinery near the unit and out of the weather. As needed, the individual CD*Modules* cartons/pallets were brought to a staging area at the base of the columns using a forklift. Each carton was color-coded to allow easy identification and transfer of the material from the sea-tainers to the column. The pallets were then directly placed into an elevator that was erected alongside the columns for this very purpose (Figure 5). This temporary lift structure facilitated loading and will be reinstalled during future catalyst replacements. The column platforms were designed to accommodate this elevator system. Side-by-side lifts provided the flexibility to work on the CD*Hydro* and CD*HDS* columns simultaneously and eliminated extra handling of the CD*Modules* at grade.

Figure 5 - Elevator System

There are loading manways located at each catalyst bed on the columns between the catalyst support grid and the chimney-collector tray. The distributor supplier's field services personnel provided the labor for loading the catalyst structure under the supervision of CDTECH personnel. One pallet of catalyst, in its original shipping carton, was placed adjacent to the man way. Modules were then placed on a set of rollers and moved inside the column. A ginny wheel was used to lower the modules to the loading level inside the column. A complete layer was loaded in just over an hour.

Catalyst loading of the CD*Hydro* and CD*HDS* columns started in mid August and was completed in early September working primarily one shift per day. The towers were closed, blinded and placed under a nitrogen blanket following installation of the distributors awaiting catalyst conditioning and start up.

Initial Start Up

In addition to training and catalyst loading services, CDTECH provided technical support around-the-clock during the commissioning and initial start up of the plant. The CD*Hydro*/CD*HDS* unit was ready for start up in December; however, start up was delayed until after end of the year holidays to provide refinery personnel some much needed vacation time.

Prior to the introduction of FCCU gasoline feedstocks to the CD*Hydro*/CD*HDS* unit, the selective hydrogenation and hydro-desulfurization catalysts had to be activated or "conditioned". The selective hydrogenation catalyst must be reduced in the presence of hydrogen at a minimum operating temperature. The reduction procedure consisted of first circulating a sweet hydrocarbon stream (sweet, heavy straight run naphtha) through the column at a mild temperature, increasing the temperature to a higher level and injecting hydrogen to reduce the nickel catalyst.

As loaded, the fresh hydro-desulfurization catalyst is in an oxide form. In this form, the catalyst is not active for the desired HDS reactions. A thorough presulfiding was needed to convert the metal oxides into active substoichiometric sulfides. Prior to sulfiding, the catalyst had to be dried to remove moisture absorbed from the atmosphere during handling and packaging into the structured packing. Drying was 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 sulfiding procedure consisted of soaking the catalyst with hydrocarbons containing DMDS and sulfiding at elevated temperatures. Once finished, the unit was kept under nitrogen pressure until reactive feedstock was available.

No special conditioning is required for the Palladium-based hydro-isomerization catalyst.

The start up of the CD*Hydro* and CD*HDS* columns was like a start up of conventional distillation columns with one exception, the additional hydrogen feeds (for reaction) are not started until column reflux is well established. The start-up period, which began in January 2002, was completed during February. LCN feed was introduced to the ULSG unit on the 29th of January with HCN feed on 30th of January. An issue with the recycle gas compressor hydrogen seals delayed the introduction of HHCN to the unit until the 5th of February.

The skin-point temperatures on the fired heater were a constraint to the unit feed rate and correct operation of the CD*HDS* tower during the period February 4-7. The unit feed rate was constrained to approximately 260 m^3/h during this period. Following discussions with the Detailed Engineering Contractor the high temperature alarms on the skin points were increased and the constraint to unit operation removed.

The feed was increased to the unit design rate of 310 m^3/h on the 8th of February in order to test the unit hydraulic performance. The naphtha feeds to the unit were reduced to 260 m^3/h on the 11th of February due to a reduction in FCCU feed rate as a result of operating issues unrelated to the ULSG plant in another operating unit. The feed was increased back to 310 m^3/h on the 20th-21st February in preparation for the test run. The feed rate was maintained at this figure until the 26th February for the unit test run and was then reduced to 230 m^3/h for economic reasons.

The ULSG unit was able to produce naphtha to within the 50 ppm total sulphur specification from early in the start-up process and maintained this performance throughout initial operation. There was no off specification product produced once the product rundowns were routed to on specification tankage shortly after start up.

A test run was conducted at the design feed rate of 310 m^3/h from the 23rd to 26th February in order to evaluate the performance of the unit versus design and the unit was formally accepted from the process licensor, CDTECH, in early March.

Following is a chronological summary of key milestone dates during initial operation:

01/04/2002 – Started catalyst conditioning.
01/29/2002 – Started LCN feed to unit.
01/30/2002 – Started HCN feed to unit.
02/04/2002 – Started recycle compressor.
02/05/2002 – Started HHCN feed to unit.
02/23/2002 – Started Acceptance Test Run.
02/26/2002 – Completed Acceptance Test Run.
03/05/2002 – ChevronTexaco formally accepts unit.

There were numerous problems with the pumps on the unit resulting in the large time gap between catalyst conditioning and actual start up.

Figure 6 shows the unit during the initial stages of operation. The fired heater and the CDHydro and CDHDS towers are clearly shown along with the support structure for the exchangers and drums.


Figure 6 – ULSG Unit

Unit Performance

The unit operation and control follows conventional distillation practices with few exceptions related to the reaction performance and catalyst activity maintenance. The operating data over the initial start up period of operation is shown in Figures 7-8.

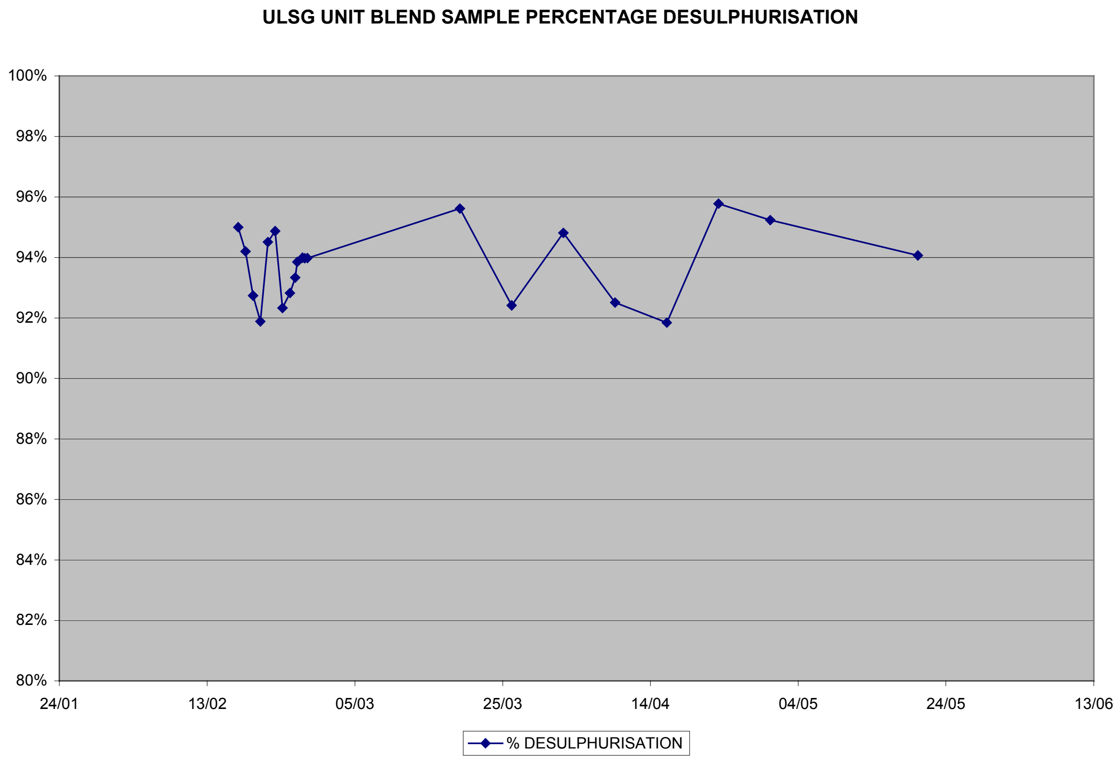


Figure 7

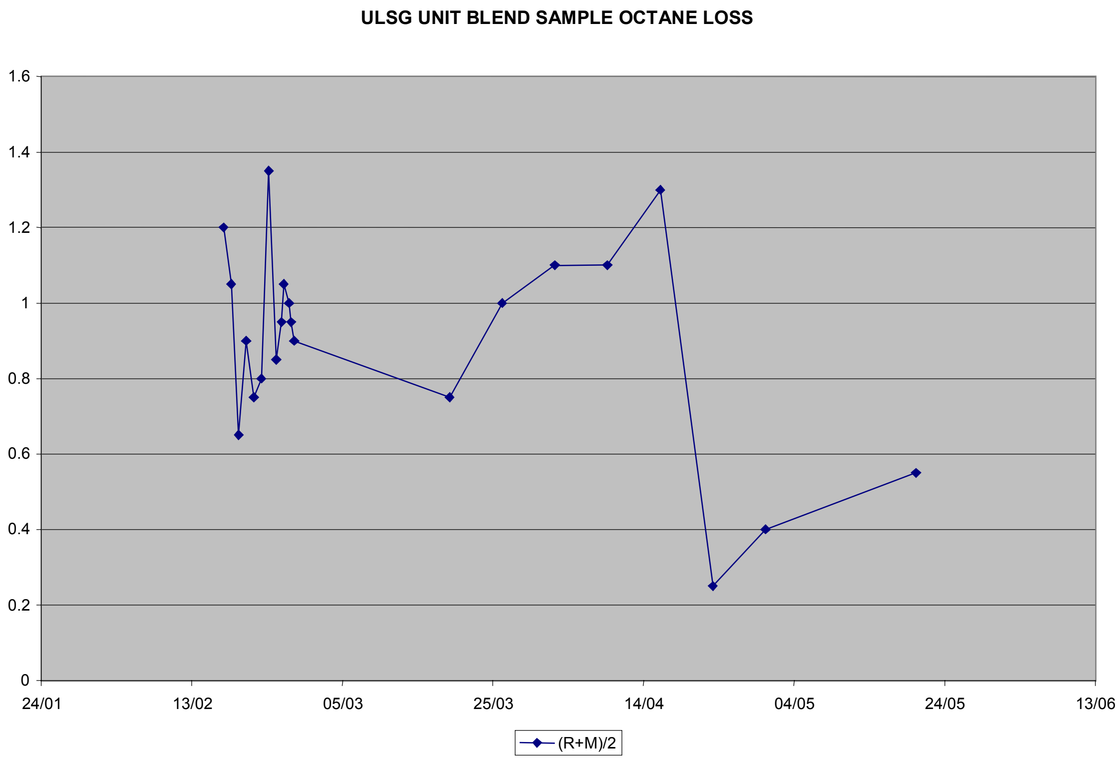


Figure 8

Over the period of initial operation (January 29 – February 28), the unit performance was checked at various operating conditions including low and high feed sulfur levels.

The HDS conversion across the unit was extremely consistent during initial operations at the design level of 94-95% (Figure 7). In general, the overall HDS conversion across the entire unit has been maintained in the mid 90% range during initial operation at the request of the ChevronTexaco planning group. Average octane loss (R+M/2) has been less than one number and more recently, around one half a number since initial start up (Figure 8).

Since initial start-up, the unit has been operating steadily at design throughput producing a product meeting desulfurization and octane retention specifications. There has been one upset on the unit thus far, resulting from a high liquid level in the fuel gas knock out drum causing the fired heater to shut down.

Future Work

In order to produce 10 ppm gasoline pool for the European market, ChevronTexaco Pembroke has approved Phase II design which incorporates a Polishing Reactor and associated cooling and separation equipment. The basic engineering design for Phase II is complete and Detailed Engineering is in progress. Pembroke expects to commission Phase II before 10 ppm sulfur gasoline is mandated in the European Union, expected to be by January 1, 2005.

Other Issues

Feedback from refiners has highlighted a concern about the need to replace the unique structured packing catalyst system on short notice. Although the catalyst itself is robust and appears to have a long life, there remains the potential for emergency catalyst replacement, such as by Acts of God. As a result, CDTECH has committed to keep a stand-by supply of the catalyst in inventory, to be available on emergency notice.

Another item of concern for refiners is the time required for replacement of the catalyst. Although the normal time required would be within the period available in a typical FCC major turnaround, an emergency replacement would necessitate a much faster rate than demonstrated during the initial catalyst loading at the existing commercial units. To address this issue, CDTECH has optimized loading equipment and technique to speed up loading and unloading. The unloading and reloading of the structured packing modules has significantly improved by changing the design of the CD*Modules* to make them easier and faster to load. These improvements were utilized for the catalyst loading at ChevronTexaco Pembroke CD*Hydro*/ CD*HDS* installation. Pembroke is monitoring catalyst activity with CDTECH in order to establish whether to change the catalyst in the fall of 2003 in connection with a FCCU turnaround. Recent loading experience at Pembroke and other CD*Hydro* units confirm we are able to unload and reload within a typical FCCU turnaround cycle.

Other Commercial Experience

It has been two years since the first CDTECH CDHDS unit started up at Motiva's Port Arthur refinery in Texas. Performance over these first two years has met or exceeded expectations. The unit is operating at design rates at 90-95% desulfurization and less than one octane number loss. The figure below plots the HDS catalyst activity maintenance over time. The Port Arthur results fall on a line showing only marginal loss of usable catalyst activity with a projected catalyst life exceeding guarantee level. As a result, they do not plan to replace the catalyst in January 2003 as originally scheduled. Although the unit has experienced some feed outages, etc. due to normal refinery upsets, the only major emergency shut down was related to a faulty oxygen sensor on the fired heater coupled with poor quality fuel gas which caused a small explosion within the furnace.

The first integrated CD*Hydro*/CD*HDS* unit was started up at Irving Oil in Saint John, New Brunswick, Canada. This unit has been in operation for 1.5 years. Performance has been very good with product quality exceeding the licensee's requirements. A recent test run on the unit showed the relative CD*HDS* catalyst activity at 90% of fresh catalyst. The CD*HDS* activity maintenance is in line with Port Arthur (as shown in Figure 9) and catalyst life is expected to exceed initial projections. To put this in perspective, Irving Oil's unit has experienced a multitude of shut downs since initial start up as a result of various problems on the new resid catalytic cracking unit and still, the performance and catalyst activity have not been altered. This is a tribute to the robustness of the technology and sound shut down procedures and operator training.

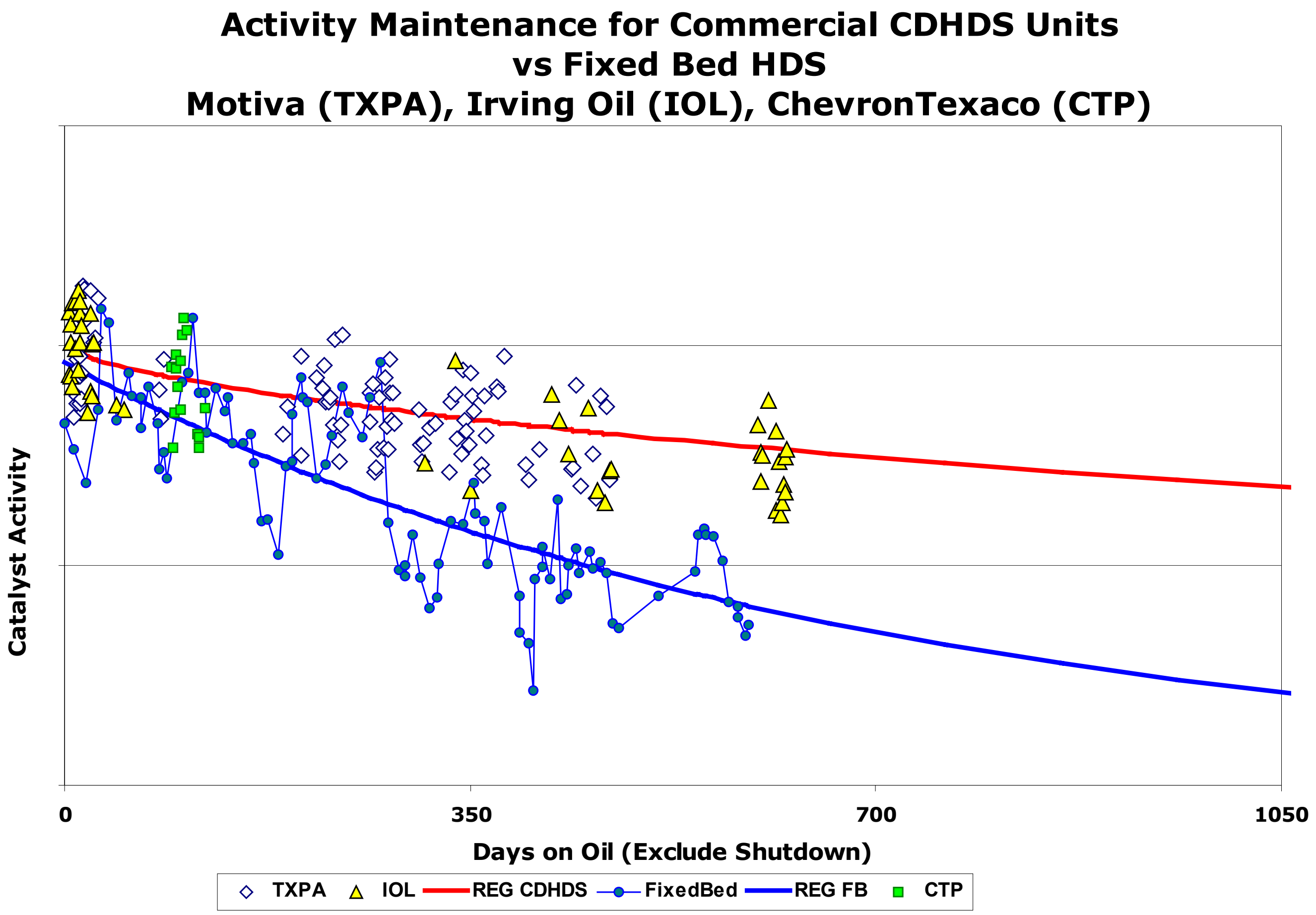


Figure 9

Figure 9 shows the HDS activity maintenance over time for the CDTECH operating units as compared to conventional technology. From the data collected thus far, CD*HDS* catalyst life is expected to exceed FCCU turnaround cycles while the fixed bed technology will probably fall short.

Summary

ChevronTexaco has used this refinery expansion project to significantly increase its production of low sulfur gasoline well ahead of scheduled European regulations. The project successfully commercialized CDTECH's CD*Hydro* and CD*HDS* technologies for selective desulfurization of FCC gasoline. The whole gasoline desulfurization project was completed in roughly two years from technology selection. The successful start-up and acceptance of the new units was accomplished in a timely manner consistent with the previous two unit start ups at Irving Oil and Port Arthur.