

Start-up of First CDHydro[®]/CDHDS[®] Unit at Irving Oil's Saint John, New Brunswick Refinery

By Mr. Rob Gardner (Irving Oil Ltd.),
Messrs. Eric A. Schwarz, Kerry L. Rock (CDTECH[®])

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Introduction/Background

In 1999 Canada approved new regulations to provide cleaner air by placing limitations on the sulfur content of gasoline. Sulfur levels in gasoline had averaged 360 parts per million (ppm) in Canada, among the highest in the world. Levels in Ontario averaged 530 ppm in 1997, but levels in other regions of Canada averaged between 260 and 290 ppm. The proposed regulations would bring Canadian gasoline sulfur levels in line with those in California, Japan and the European Union. Irving Oil in Saint John, New Brunswick has been an exception to this trend; it has been a producer of less-than-150 ppm gasoline for some time.

Canadian government estimates project that over 20 years, low sulfur gasoline will prevent over 2100 premature deaths, 93,000 incidences of bronchitis in children, five million other health related incidents such as asthma attacks, and 11 million acute respiratory symptoms such as coughs, pneumonia and croup.

The new regulations will reduce the sulfur content in gasoline to an average level of 30 ppm with a maximum of 80 ppm. This is a 90% reduction from average levels today. To reduce the impact on industry, the requirement will be phased in. In 2002, the level will be lowered to an average of 150 ppm, with a maximum of 200 ppm. The 30 ppm level will come into effect in 2005.

The Canadian Vehicle Manufacturers' Association (CVMA) - comprising DaimlerChryslerCanada, Ford Motor Company of Canada, General Motors of Canada, Jaguar of Canada, Mazda of Canada, Saab of Canada, Saturn of Canada, and Volvo Cars of Canada -

launched a new fuel endorsement program called "Auto Makers' Choice™ Gasoline" in October 1999. At that time, Irving Oil of Saint John, New Brunswick became the first oil refiner to meet the stringent specifications of the program and currently offers this gasoline in New Brunswick, eastern Newfoundland and Prince Edward Island. The "Auto Makers' Choice" fuel endorsement is licensed to refiners or gasoline marketers whose gasolines meet all the criteria set out by the CVMA. These include the proper detergency levels to enhance emission performance. The approved gasolines must also have low sulfur levels and meet auto industry tests designed to ensure improved "driveability" requirements. Driveability includes excellent vehicle cold start, warm-up driving and emission performance. Irving Oil is the only Canadian refiner that has the "Auto Makers' Choice" endorsement.

Irving's Sulfur Reduction Program

In 1998, Irving began a refinery upgrade project that included a 70,000 BPSD Residue Fluid Catalytic Cracking Unit (RFCCU) to supplement the gasoline produced by the existing VGO FCC unit. The "King of Cats" (Figure 1) project was the largest refinery upgrade project in North America in the last decade.



Figure 1

Irving Oil recognized the need to maintain the low sulfur levels in gasoline products after completion of the "King of Cats" project. It also wished to position itself for the future 30 ppm specification. Irving saw this as an opportunity to continue to provide its customers with an environmentally improved product well ahead of the required regulations. After evaluation of the technologies available for desulfurization of FCC gasoline, Irving chose the combination of CDHydro®/CDHDS® technologies available from CDTECH based upon superior performance and comparable capital cost.

In May 2000 Irving Oil received a US environmental award. The company was awarded the Maine Earth Day 2000 Clean Energy Award by the Maine Coalition for Sensible Energy. The

award is presented to companies, organizations, or individuals that are working for wise energy choices to sustain future generations both environmentally and economically. Irving received the award in recognition of its “Auto Makers’ Choice Gasoline”, the first and only gasoline to earn the endorsement of automobile manufacturers for its low sulfur content. Irving’s “Auto Makers’ Choice” gasolines have also been endorsed by the Canadian Lung Association and the 4.1 million member Canadian Automobile Association (CAA). The “Auto Maker’s Choice” endorsement is granted to an energy provider whose gasolines meet all the criteria set out by the Canadian Vehicle Manufacturers’ Association. The approved gasolines must have sulfur levels that fall below 150 ppm.

Project Execution

The project was executed in world record time: technology selection was awarded to CDTECH and the project kick-off meeting was held in January 1999; basic engineering was completed mid June 1999; start-up began on November 11, 2000; and Irving accepted the *CDHydro/CDHDS* unit on December 7, 2000.

Process Overview

Following is a brief description of the *CDHydro/CDHDS* processing scheme at the Saint John Refinery. The FCCG and RFCCG are combined as full range catalytic naphtha (FRCN) and fed to the *CDHydro* column where it is fractionated to produce Light Catalytic Naphtha (LCN) and Medium plus Heavy Catalytic Naphtha (MCN/HCN) (Figure 2).

CDHydro Simplified Flow Diagram

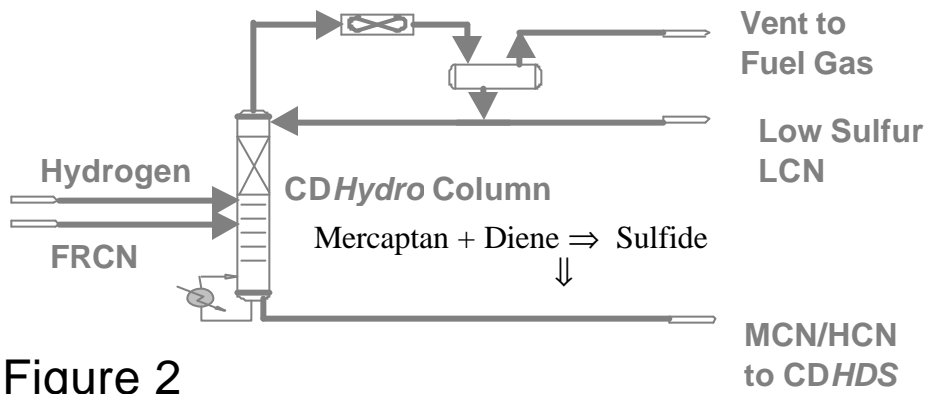
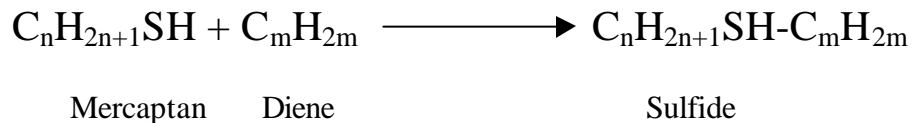


Figure 2

The top of the column holds a bed of nickel catalyst contained in structured packing that facilitates simultaneous reaction and distillation. Figure 4 is a cutaway view of the column, showing the catalyst bed. The structured packing has very high distillation efficiency, exceeding that of conventional trays.

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



The reaction goes essentially to completion, converting virtually all of the mercaptans in the light fraction of the FRCN into high boiling point sulfides that are removed with the MCN/HCN bottoms product. The LCN is produced as a sweet gasoline with very low sulfur content.

The bottoms of the CDHydro column is preheated and fed to the CDHDS column as shown in Figure 3. The feed is fractionated in beds of structured packing 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 catalyst 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 *CDHDS* column.

CDHDS Simplified Flow Diagram

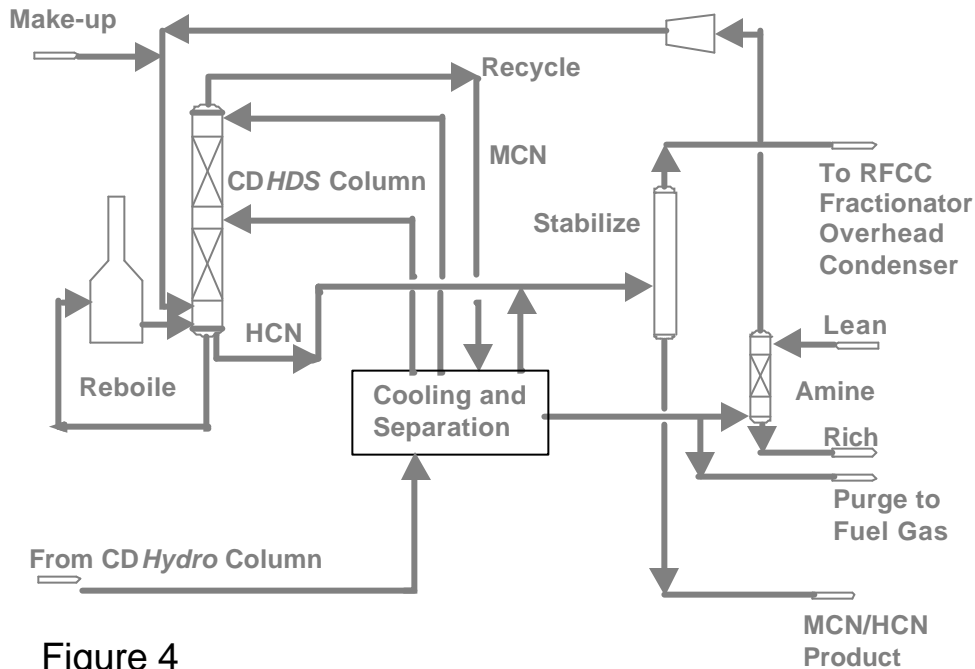


Figure 4

The cooled MCN is sent to the stripper 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 (sweet) MCN/HCN is sent to storage for final gasoline product blending. No further treatment of the stripper bottoms is required for sulfur or mercaptan reduction.

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 *CDHDS* 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 by the HDS catalyst. Therefore, a greater fraction of the sulfur leaves the *CDHDS* 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 *CDHDS* 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 *CDHDS* bottoms product is much lower than the corresponding conventional fixed bed HDS reactor product.

Design Basis

The feedstock is a combination of FCC gasolines produced by the RFCC and FCC units. The feedstock properties are:

| <u>Property</u> | <u>Combined FCC Gasoline</u> |
|------------------------|-------------------------------------|
| Flow rate, BPD | 58,047 |
| API gravity | 56.7 |
| Sulfur, ppmw | 1000 |
| Olefins, wt% | 37 |

Hydrogen is available at 84% purity.

Operator Training

In preparation for initial start up of the *CDHydro/CDHDS* unit, CDTECH prepared a training manual based in part on CDTECH's Basic Engineering Package. Using this document as reference material, CDTECH conducted a detailed training program for Irving's operating and

technical personnel at the refinery. The program covered such topics as normal operation and control, commissioning and start up, shut down and emergencies, safety and environmental issues, and analytical control. The course was conducted in two parallel classes to accommodate the entire operations staff, which was already working a shift schedule. The training took place less than two months before start up, when most of the construction was complete allowing the trainees to spend time after the course outside on the unit.

Commissioning & Catalyst Loading

The construction contractor and Irving personnel divided the plant into numerous test systems to allow tracking of construction progress and hydrostatic testing and flushing/blowing of systems. CDTECH provided an experienced operations expert to assist Irving personnel with precommissioning 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 column to protect the catalyst and distributors from extraneous materials. Following catalyst loading, the column was blinded and put under a nitrogen blanket to protect the column internals from ingress of such materials during the final stages of construction and pre-commissioning.

The catalyst structure is physically very similar to other commercial structured packing. The *CDModules*SM (the structured packing containing catalyst) are easily handled and loaded into the column in a specified pattern to maximize catalyst loading density.

Each bed of catalyst contains multiple levels (or layers) of *CDModules* arranged according to a predetermined loading diagram onto a catalyst support grid (Figure 4). Special perimeter structures are provided to fit the curvature of the tower wall. The *CDModules* are loaded to optimize the overall catalyst bed vapor-liquid contact efficiency for simultaneous reaction and fractionation.

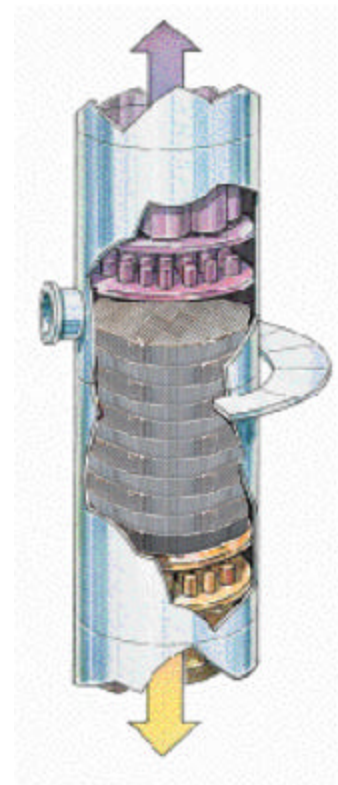


Figure 4

The *CDModules* for the *CDHydro/CDHDS* unit were stored in a warehouse off site, out of the weather. As needed, the *CDModules* containers were brought out to a staging area at the base of the columns. They were then placed into a loading basket, which was lifted by a crane to the loading platform.

There are loading manways located at each catalyst bed on the columns 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 *CDHDS* column was completed in September and the tower was put under a nitrogen blanket awaiting catalyst conditioning and start up.

Initial Start Up

The *CDHydro/CDHDS* unit was ready for start up in October; however, manpower was diverted to the new RFCCU to complete its construction and pre-commissioning activities. Since the *CDHydro/CDHDS* unit could be bypassed initially by the RFCCG and FCCG streams, emphasis shifted to preparing the RFCCU for start up. As progress on the RFCCU neared completion, work again shifted back to the *CDHydro/CDHDS* unit in order to have it ready for start up soon after the RFCCU. The *CDHydro/CDHDS* unit catalyst was conditioned in early November and feed was introduced to the unit on November 11, 2000.

Figure 5 shows the unit in the final stages of construction. The fired heater is in the foreground and the first tower is the *CDHDS* column. The second tower is the *CDHydro* column. The new RFCCU is seen in the background.



Figure 5

In addition to precommissioning, training, and catalyst loading services, CDTECH provided technical and analytical support 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, speciated sulfur and hydrocarbon gas chromatographs, and bromine number/mercaptans titrator). This support allowed the refinery laboratory to benefit from the experience of the CDTECH team and develop consistent analytical practices. This information was important to CDTECH's detailed analysis and comparison of plant operating data against commercial and pilot plant results.

Prior to the introduction of RFCCU gasoline (debutanizer bottoms) feedstock to the *CDHydro/CDHDS* unit (Gasoline Desulfurization unit), the selective hydrogenation and hydrodesulfurization 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 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 hydrodesulfurization 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 presulfiding, 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 presulfiding 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.

Full range RFCCU gasoline from the gas concentration section debutanizer bottoms was introduced to the unit on November 11, 2000 at about 50% of design rate. The feed rate to the *CDHydro/CDHDS* unit was later raised to about 85% of design rate with the introduction of the FCCG. The design capacity was not attained due to feedstock unavailability.

The start up of the *CDHydro* and *CDHDS* 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 unit start up was uneventful and no problems were encountered. Usual issues like controller tuning, sampling and developing a “feel” for the operation presented the main challenge during the initial few days of operation. Product was run down to tankage shortly after start up.

Unit Performance

Over the period of initial operation (November 11-December 7), the unit performance was checked at various operating conditions including low, mild and high levels of desulfurization. This was done to generate an operating envelope on the unit and to check the unit for any operating constraints. No constraints were found during these operations.

Low severity operation (maximizing octane retention at moderate desulfurization levels) was the most common operation over the initial start up period. Tests were done at higher severity operation to determine how low a sulfur product could be produced and the associated octane penalty.

Since initial start up, the unit has been operating steady at design throughput producing on-specification product. There has been one major upset thus far, resulting from a severe ice storm that shut down the entire refinery in late December. Although the unit experienced a sudden shut down, the results since the restart indicate no loss of performance or catalyst activity.

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 Figure 6.

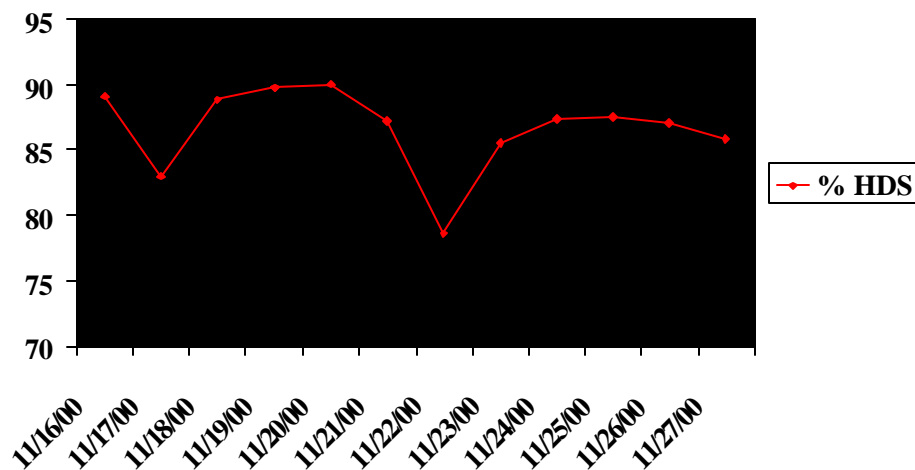


Figure 6

The HDS conversion across the unit was extremely high during initial operations, much above the design level of 68%. The HDS level was increased during the high severity test period at the request of Irving to determine the flexibility of the unit and the range of operation for planning, blending and production purposes. This was accomplished by increasing the pressure of the CDHDS column and varying the LCN draw from the CDHydro column. A lower CDHDS pressure operation coupled with a high CDHydro sidedraw rate resulted in less severe HDS conditions yielding slightly lower HDS conversion but higher octane retention as shown by the reduction in octane loss.

In general, the overall HDS conversion across the entire unit has been maintained in the mid 80% range during initial operation at the request of the Irving planning group. Average octane loss (R+M/2) has been around one number over this time period (Figure 7).

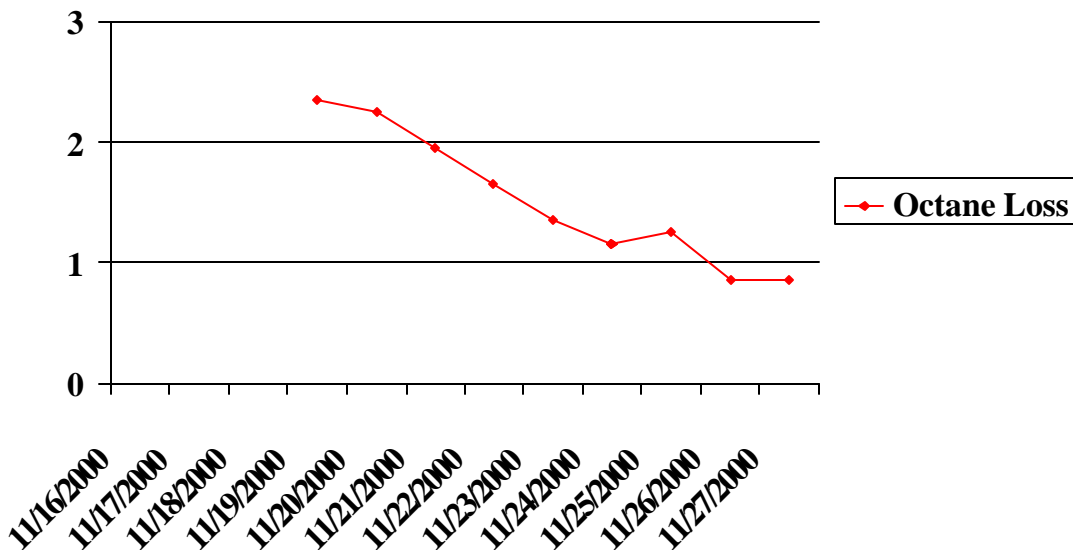


Figure 7

Since initial start-up, the unit has been operating steadily at design throughput producing a product meeting desulfurization and octane retention specifications.

The product has remained relatively sweet as shown by the weighted mercaptan level in Figure 8.

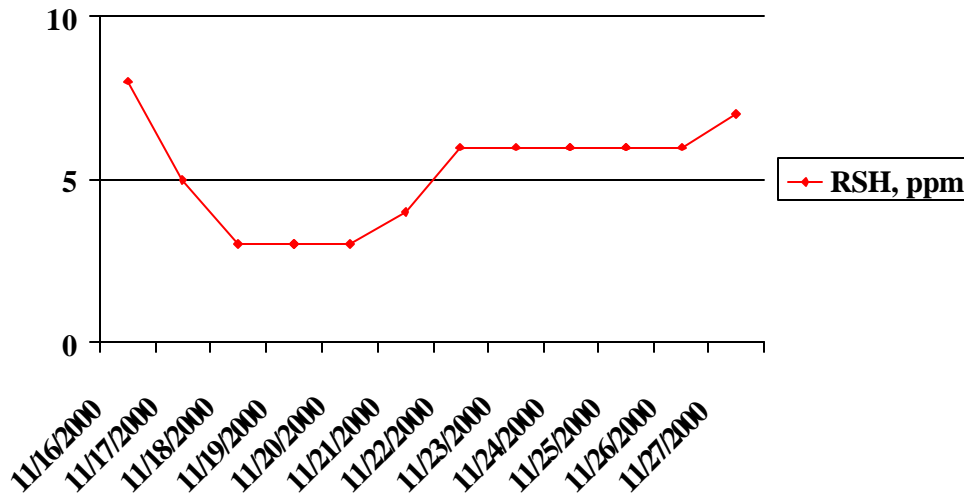


Figure 8

Future Work

The odor of the blended low sulfur gasoline is different from that of conventional high sulfur gasoline and previous “Auto Makers’ Choice” gasoline. The difference is easily detected by consumers who think it has a sweet diesel smell. This is a potential area for market differentiation.

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 a low probability of an emergency need to replace it 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 two existing commercial units. To address this issue, CDTECH has formed an alliance with Cat Tech. The unloading and reloading of the structured packing modules will be significantly improved by changing the design of the CDModules to make them easier and faster to load. These improvements will be utilized for the catalyst loading at the new Texaco Pembroke *CDHydro/ CDHDS* installation later this year.

Summary

Irving Oil has used this refinery expansion project to significantly increase its production of low sulfur gasoline well ahead of scheduled Canadian regulations. The project successfully commercialized CDTECH's *CDHydro* and *CDHDS* technologies for selective desulfurization of FCC gasoline. The whole gasoline desulfurization project was completed in less than two years from technology selection. The successful start-up and acceptance of the new units was accomplished in less than one month.

CDTECH

Tel: 713-821-5181

Fax: 713-821-3587

3010 Briarpark Drive

Houston, TX 77042