ew regulations for Ultra-Low Sulfur Diesel (ULSD) in Canada and the United States took effect in June 2006, reducing the on-road diesel sulfur content from 500 to 15 ppmw. Anticipating the new sulfur regulation, Irving Oil decided to convert the existing VGO Hydrocracker/LCO Desulfurizer at the Saint John refinery in New Brunswick, Canada to an LCO /heavy diesel ULSD unit.

Technical Requirements

Fluor Corporation provided engineering, procurement and supported technology selection. The project included increasing feed capacity from 30,000 to 45,000 BPSD while at the same time producing ULSD from a feedstock containing up to 50% LCO. Irving Oil wanted to make 7 ppm sulfur diesel and required at least 30°F improvement in cloud point for winter diesel. During the summer months they wanted to “turn off” the dewaxing function to maximize ULSD yield since low cloud point is not required at that time of year. Irving Oil also wanted to minimize the hydrogen consumption so that feed rate could be maximized within make-up hydrogen constraints.

In the summer of 2004, Irving Oil contacted several catalyst suppliers including ART and Süd-Chemie Inc. to begin the catalyst selection process for the revamped unit. ART is a supplier of top-tier hydrotreating catalysts, but does not have a dewaxing catalyst in its portfolio. Süd-Chemie offers premium dewaxing catalyst technology but does not have hydrotreating products. ART and Süd-Chemie joined together to offer a complete package.

The high level of LCO in the feed, combined with high unit operating pressure and the need to minimize hydrogen consumption made it a
challenge to design the appropriate catalyst system to meet the desired product characteristics. This was further complicated by the high level of nitrogen in the feed.

Hydrodesulfurization and saturation of olefins and aromatics are very exothermic reactions and bed activity must be controlled to avoid excessive temperature rise. The unit is equipped with inter-bed quench facilities to control the overall temperature levels. Hydrodewaxing (HDW) is endothermic and the dewaxing activity is controlled through the bed inlet temperature, using lower temperature to “turn off” the dewaxing catalyst activity.

It is easiest to control the temperature to the first bed which makes it a convenient position to place the HDW catalyst. However, there are several problems with installing the HDW catalyst in that location. Most dewaxing catalysts are sensitive to nitrogen compounds so they must be protected by a NiMo catalyst. LCO contains a high concentration of olefins, and that can deactivate the HDW catalyst quickly due to olefin polymerization and related coking. The required operating temperature window for the HDW catalyst is not compatible with management of the overall temperature profile, as the feed olefins and ‘easy’ sulfur react rapidly, producing a very high temperature rise. These constraints dictated that the HDW catalyst should be placed below at least one of the hydrotreating catalyst beds.

The key question became how to achieve the desired product specifications while minimizing hydrogen consumption. NiMo catalysts tend to have higher activity for saturating aromatics and removing nitrogen while CoMo catalysts tend to give lower hydrogen consumption through less aromatics saturation.

Hydrotreating Catalyst System

ART’s SmART Catalyst System® Series offers custom system design to meet individual refiner constraints and objectives. To help Irving Oil determine the expected hydrogen consumption and activity, ART pilot tested three catalyst systems: 100% NiMo, 50%/50% NiMo/CoMo SmART System® and 100% CoMo using Irving’s feed which is listed in Table XVII.

ART selected CDXi, a premium high activity CoMo catalyst for ULSD and AT505 which is a high activity conventional NiMo catalyst and predecessor to NDXi.

Figure 44 compares the HDS activity observed for each catalyst system. Under these conditions the all NiMo system is clearly the most active for sulfur removal, followed by the SmART System® and finally the CoMo catalyst, CDXi.

Figure 45 shows the hydrogen consumption for each catalyst system. Not surprisingly, AT505 exhibited the highest hydrogen consumption while ART CDXi has the lowest hydrogen consumption. The SmART System® falls between the CoMo and NiMo catalysts. Comparing Figures 44 and 45 it is apparent that the SmART System® Series provides the best combination of activity and hydrogen consumption; HDS activity was only slightly less than the all NiMo AT505 system and the hydrogen consumption was significantly lower.
Irving Oil also wanted to improve the aromatics content and cetane index of the ULSD product. These product attributes are summarized in Figures 46 and 47. There is a wide range in aromatics conversion between the NiMo and CoMo systems (about 15 numbers absolute) which explains the large difference in hydrogen consumption shown in Figure 45. The target aromatics level was <35 vol% which is easily achieved by AT505, but more of a challenge for the all CoMo system. The SmART System® resulted in product aromatics which were about three numbers (absolute) higher than the all NiMo system, and the target was readily achieved at a reasonable temperature.

The increase in cetane index tells a similar story. The cetane index for the CoMo system is roughly two numbers lower than achieved by the all NiMo catalyst, and the SmART System® resulted in a cetane improvement essentially equal to the all NiMo catalyst.

The pilot data summarized in Figures 44-47 clearly show that the staged catalyst approach is much more effective in meeting the objectives set out by Irving Oil. The SmART System® offers nearly the same HDS activity compared to the NiMo catalyst, but with lower hydrogen consumption. It also provided higher aromatics conversion relative to the CoMo catalyst, easily meeting the aromatics and cetane index targets. Using these data and performing additional modeling calculations allowed ART to determine the optimum SmART System® proportions which were ultimately used in the commercial unit.

**Dewaxing Catalyst and its Impact on the Process Design**

With the CoMo/NiMo ratio resolved, the design proceeded to the amount and placement of the HYDEX®-G HDW catalyst. This required a detailed evaluation of the overall system with respect to heat release, quench capabilities and catalyst requirements.
HDW does consume some hydrogen and will also generate some light ends which slightly reduce the diesel yield. The activity of the HDW bed can be controlled with the inlet temperature so during the summer a lower temperature turns down the degree of dewaxing.

As mentioned previously, most HDW catalysts are very sensitive to nitrogen poisoning and must be placed downstream of NiMo hydrotreating catalyst to protect the activity of the catalyst. Süd-Chemie’s HYDEX®-G is very nitrogen tolerant. In conjunction with its high activity, this gives much more flexibility in terms of its placement in the reactor. The HYDEX®-G can be placed in an optimal position in the reactor where the HDW bed inlet temperature is more readily controlled with inter-bed quench.

The position of the HYDEX®-G in the catalyst load was dictated by practical constraints and a sensitivity analysis. Practical constraints included:

- The catalyst bed volumes in the existing reactors are fixed
- The total available quench gas is fixed
- Individual quench gas rates must be compatible with the existing reactor internals hardware

- Peak catalyst bed temperatures must be limited to preserve catalyst activity

The sensitivity analysis investigated the impact of several parameters on the ability to manage the overall temperature profile (e.g., avoid overtreating in HDS catalyst and/or undesired dewaxing in the HDW catalyst). The parameters investigated were:

- Reduced heat release in the uppermost catalyst beds (e.g., due to catalyst deactivation)
- Variations in the required operating temperatures for both the HDS and HDW catalysts (e.g., to account for differences in deactivation rates)
- Selected combinations of the above.

The results of this analysis revealed that Bed 3 was the optimal location for the HDW catalyst.

Figure 48 shows a process flow scheme with a two-reactor system and an example for the location of the various catalyst layers and quench gas pipes to adjust for optimum bed temperatures.

The experiments that produced the data shown in Figure 49 were performed by an independent contractor on behalf of Irving Oil to understand the HDW catalyst operating temperature required to meet the target cloud point reduction. The experiments also quantified the light ends/naphtha production. These data were used in the sensitivity analysis, discussed above. The curve for the cloud point as a function of the HDW bed temperature also provides a means of predicting the extent of dewaxing that will occur during summer mode operation. The ability to effectively “turn off” the HDW catalyst depends upon the practical constraints and other parameters mentioned previously.

![Figure 48](image1)

ULSD/Dewaxing Process Flow and Catalyst Loading Scheme Example

![Figure 49](image2)

Pilot Plant Simulation to Confirm the Dewaxing Design Temperature
With the location of the dewaxing catalyst set, a second pilot plant test was completed by ART using the proposed SmART System® including the required volume of HYDEX®-G catalyst. The properties of the second feed provided by Irving Oil for the test are summarized in Table XVIII.

Figure 50 shows the sulfur conversion achieved by the SmART System® compared to the SmART System® + HYDEX®-G observed in the test. The product sulfur is the same for both catalyst systems indicating that sulfur conversion was not affected by the addition of the HDW catalyst. This was expected since HYDEX®-G contains only small amounts of base metals, and the metals function on this catalyst is to help keep the catalyst clean and prevent deactivation by excessive coking.

While HDS conversion was demonstrated in the first test, the second test focused on proving the viability of the entire design and the dewaxing performance. The cloud point was of specific concern. Figure 51 summarizes the Cloud Point Improvement (CPI) as a function of the operating temperature for the SmART System® + HYDEX®-G compared to the SmART System® alone. The CPI for the HYDEX®-G system shows a characteristic threshold temperature. Below the threshold the CPI is low, while above this initiation temperature the CPI increases substantially. At the temperature required to achieve <10 wppm sulfur the cloud point improvement is low, which is desired for "summer mode." Increasing the temperature will give the desired 30°F improvement for winter ULSD.

The quench capability in the commercial reactors is used to control the bed temperatures to avoid overtreating and achieve the ultimate goal of 7 ppm sulfur with control of the degree of dewaxing. The pilot plant data indicates that increasing the temperature by 40°F above the threshold temperature increases the

<table>
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<th>Type</th>
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<td>FBP</td>
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Figure 50
Product Sulfur Comparison

Figure 51
Cloud Point Improvement
CPI with HYDEX®-G to 90°F, much more than necessary. At this high level of CPI the yields of naphtha and light ends also increase which can have an adverse effect on the economics of the operation. However, this reserve of activity ensures the system is in balance with regards to stability of the HDS and HDW functions guaranteeing that all product specifications are met over the desired three year cycle life.

**Commercial Unit Performance**

The commercial unit started up in the Spring of 2006, and has been producing ULSD since the first day on stream. Figure 52 shows the normalized temperature for the operation thus far. It is apparent from the figure that the operation is quite stable especially considering the amount of LCO included in the feedstock. The unit came on stream with higher than expected activity, and the dewaxing activity has been exceptional.

All indications are that Irving Oil will be able to extend the cycle beyond the original 36 month cycle life estimate.

Figure 53 summarizes the dewaxing activity of the system. The feed varies quite a bit depending on crude source and the amount of LCO. These data have been sorted to demonstrate the performance on two different crude types at approximately equal LCO levels processed through the unit. As was observed in the pilot plant testing discussed above, the cloud point improvement is relatively low for low operating temperatures, and increases significantly as temperature is increased. Irving Oil has not needed to achieve the original CPI target of 30°F on a consistent basis, but as can be seen in the figure, the unit has achieved CPI’s of 35°F at reasonable operating temperatures.

The API increase has varied between 4-8 numbers depending on the crude source and the
amount of LCO being charged to the unit. This is shown in Figure 54 along with the product sulfur. The product sulfur has consistently been around 5 ppm with an average API uplift of 6+ numbers. The cetane uplift mirrors the API change, and thus, the unit is seeing a large increase in cetane compared to most ULSD units.

**Conclusions**

Based on the excellent performance of the Irving Oil unit, it can be concluded that the design work by ART, Süd-Chemie, and Fluor described in this paper was extremely successful. It prevailed over competitive offers in Irving Oil’s extended evaluation program and the commercial operation has exceeded expectations. Not only is the dewaxing temperature at a level for the catalysts to work as effectively and reliably as expected; the unit produced 7 ppm, low cloud point diesel from start of run, thus creating a new benchmark in the industry for low cloud point ULSD technology.

Optimal catalyst selection as well as precision design work is a prerequisite when it comes to meeting ultimate specifications and catalyst life time goals. The catalyst ensemble in the Irving Oil ULSD unit comprises ART’s high activity SmART Catalyst System® Series in combination with Süd-Chemie’s HYDEX®-G dewaxing catalyst. The stacked-bed configuration of high performance CoMo and NiMo catalysts provides the high HDS activity required for ULSD while minimizing hydrogen consumption. The HYDEX®-G catalyst takes advantage of its high activity, especially when it comes to processing heavier and difficult feeds with high nitrogen content as in the Irving Oil case.

Considering the complex requirements for Irving Oil’s ULSD unit, it is obvious that only an integrated approach to catalysts and unit design, as demonstrated by ART’s and Süd-Chemie’s collaboration with Fluor, leads to a successful commercial operation. The technology as implemented in Irving Oil’s ULSD unit offers tremendous potential to improve product quality and economics in many new and revamped ULSD units.