Meeting low sulphur diesel challenges

Liquid stream hydroprocessing technology enabled a refiner to meet fast-changing diesel sulphur specifications and process a wide variety of feedstocks

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Diesel is the predominant fuel used for shipping goods and moving freight across the country and around the world. Increasing global demand for cleaner burning transportation fuel (particularly diesel fuel) is driving refiners to look for ways to increase low sulphur diesel production capacity. At the same time, refiners are looking to process larger amounts of low cost sour and heavy feedstocks to increase profitability. With increasingly strict fuel quality regulations being rolled out across the world, meeting this increased demand for cleaner burning diesel fuel is a significant challenge.

To meet increased demand for cleaner burning fuel while simultaneously maintaining or increasing profitability, refiners need to increase their hydroprocessing capacity and capabilities to produce more diesel and remove more sulphur while minimising capital investment and operating costs. Hydroprocessing involves chemically treating a petroleum stream with hydrogen in the presence of a catalyst at elevated temperatures and pressures. Hydroprocessing units allow refiners to improve product quality, comply with government regulations, and increase profitability by converting low valued streams into high margin and high quality products. Refiners can increase hydroprocessing capacity by constructing new grassroots hydroprocessing units or debottlenecking and revamping existing units.

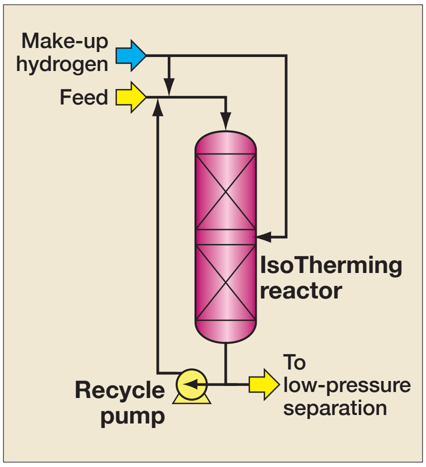

Figure 1 Hydrogen delivery options for IsoTherming technology

IsoTherming technology

Hydroprocessing has been part of the typical refinery configuration since the mid-20th century, and it has essentially been done the same way since that time – using conventional, two-phase trickle bed reactor technology. Approximately 10 years ago, a disruptive hydroprocessing innovation, IsoTherming technology, was finally brought to the marketplace, challenging the norms associated with conventional trickle bed technology. The core of IsoTherming technology is the ability to provide the hydrogen necessary for hydroprocessing reactions using a liquid stream, rather than a recycle gas stream. To satisfy hydrogen requirements within the reactor, fresh reactor feed is saturated with hydrogen. Additional hydrogen can be added to the feed by means of a saturated product recycle stream (using a reactor recycle pump) and by hydrogen injection to resaturate the liquid within or between catalyst beds. These different hydrogen addition options eliminate the need for a recycle gas compressor. **Figure 1** illustrates these different hydrogen delivery options for an IsoTherming reactor.

The technology also employs a novel reactor system with a single liquid phase that uses hydrogen and catalyst more efficiently. Regardless of the method of hydrogen delivery, all of the hydrogen needed for the hydroprocessing chemical reactions is dissolved in a single liquid phase. Applications in which the technology has been commercially deployed include kerosene and diesel hydrotreating, fluid catalytic cracking (FCC) pretreating, and mild hydrocracking. IsoTherming technology has commercially processed a wide range of straight run and cracked feedstocks, including 100% light cycle oil (LCO), at capacities ranging from 2000 b/d to 78 500 b/d (13 m^3/hr to 520 m^3/hr).

The technology has other commercially proven advantages compared to conventional trickle bed technology. They include the following.

Increased catalyst performance and improved yields

A conventional trickle bed reactor depends on near perfect feedstock distribution throughout the catalyst bed to maximise reaction efficiency and to avoid overheating and coking. In addition, the quench stages in a trickle bed reactor are meant to manage temperature rise and require the injection of large volumes of additional hydrogen into the reactor. With an IsoTherming liquid full reactor, the catalyst is completely wetted. This draws the heat of reaction away from the catalyst surface and eliminates local hot spots that would otherwise promote coking and catalyst deactivation. All commercially operating IsoTherming gasoil hydrotreating units have experienced catalyst life in excess of four years, demonstrating the technology's ability to achieve lower catalyst deactivation rates than conventional trickle bed technology. In addition, uniform liquid flow throughout the catalyst bed in an IsoTherming reactor results in a uniform radial temperature profile and acts as a heat sink for exothermic chemical reactions. This results in a lower temperature rise across the reactor and minimises light ends generation.

Reduced operating expenses and capital cost savings

IsoTherming technology's approach to hydrogen delivery eliminates the need for a recycle gas compressor (and associated high pressure separation equipment). **Figure 2** shows a visual comparison of the equipment differences between IsoTherming technology and conventional trickle bed technology. IsoTherming commercial units have noticeably less equipment and smaller plot space requirements compared to conventional trickle bed units.

Electricity usage is lower for IsoTherming technology due to the use of a lower power reactor recycle pump for delivering hydrogen instead of a higher power recycle gas compressor. In addition, the direct heat transfer resulting from the recycle of hot reactor product to the inlet of the reactor reduces the required fired heater duty needed to achieve the target reactor temperature. For units with low hydrogen requirements, the ability to supply hydrogen using only feed saturation (and no saturated product recycle) means even fewer pieces of high pressure equipment are required. The technology has been shown to have 40-60% utility savings and up to 30% capital cost savings compared to conventional trickle bed technology in evaluated units.

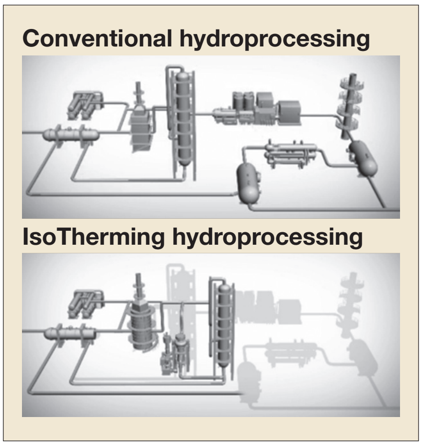

Figure 2 Conventional trickle bed vs IsoTherming equipment configurations

Robustness, reliability, and safety

One unique feature of IsoTherming technology is the reactor recycle pump. As mentioned previously, the reactor recycle pump recycles a portion of the reactor product to the inlet of the reactor. This additional liquid volume is then saturated with hydrogen to ensure that sufficient levels of hydrogen are delivered to the reactor for all required hydroprocessing chemical reactions. This particular service requires low head and high flow to pump high pressure and high temperature liquid. Conventional pumps with mechanical seals do not offer the necessary safety and reliability, so a canned motor pump is the only viable type of pump to use for this service. Canned motor pumps are often an anomaly in the refining industry, but are very commonplace in the chemical industry. They are used because the high suction pressure and temperature make a conventional shaft sealing system unreliable, and the design guarantees there are no leaky seals. DuPont engaged rotating equipment experts to develop a complete specification for the IsoTherming reactor recycle pump, which has resulted in robust reactor recycle pump designs well known for their commercial reliability.

The technology is also an inherently safer hydroprocessing technology. Elimination of the recycle gas compressor and associated treating equipment not only removes a large amount of high pressure equipment from the system, but also significantly reduces the hydrogen inventory in the unit. There is also no potential for reactor runaway (and associated catalyst deactivation) in the IsoTherming reactor. This is illustrated in **Figure 3**, which shows operating data from a commercial unit that experienced a four hour power failure.

With a conventional trickle bed unit, a power failure would cause the unit to lose make-up hydrogen and would trip the reactor charge pump and heater. To eliminate the potential for reactor temperature runaway and increased catalyst deactivation, operators would need to quickly depressurise and drain the conventional trickle bed reactor to remove excess hydrogen and reactants. Once power was restored, the conventional trickle bed unit would need to be refilled, reheated, and repressurised. This process would take multiple hours (if not days), resulting in additional unit downtime.

For the reactor power failure event shown in **Figure 3**, the reactor vents and pressure control valve on the reactor outlet were completely closed so that liquid volume was maintained in the reactor vessel at

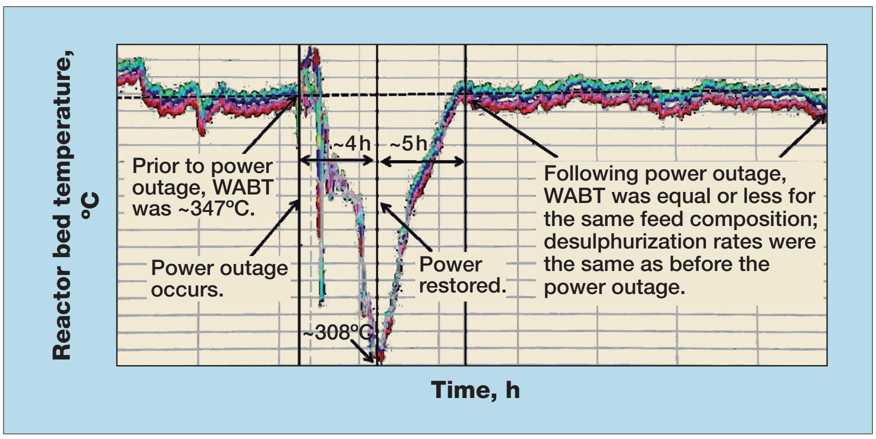

Figure 3 IsoTherming reactor bed temperature during an unplanned power failure

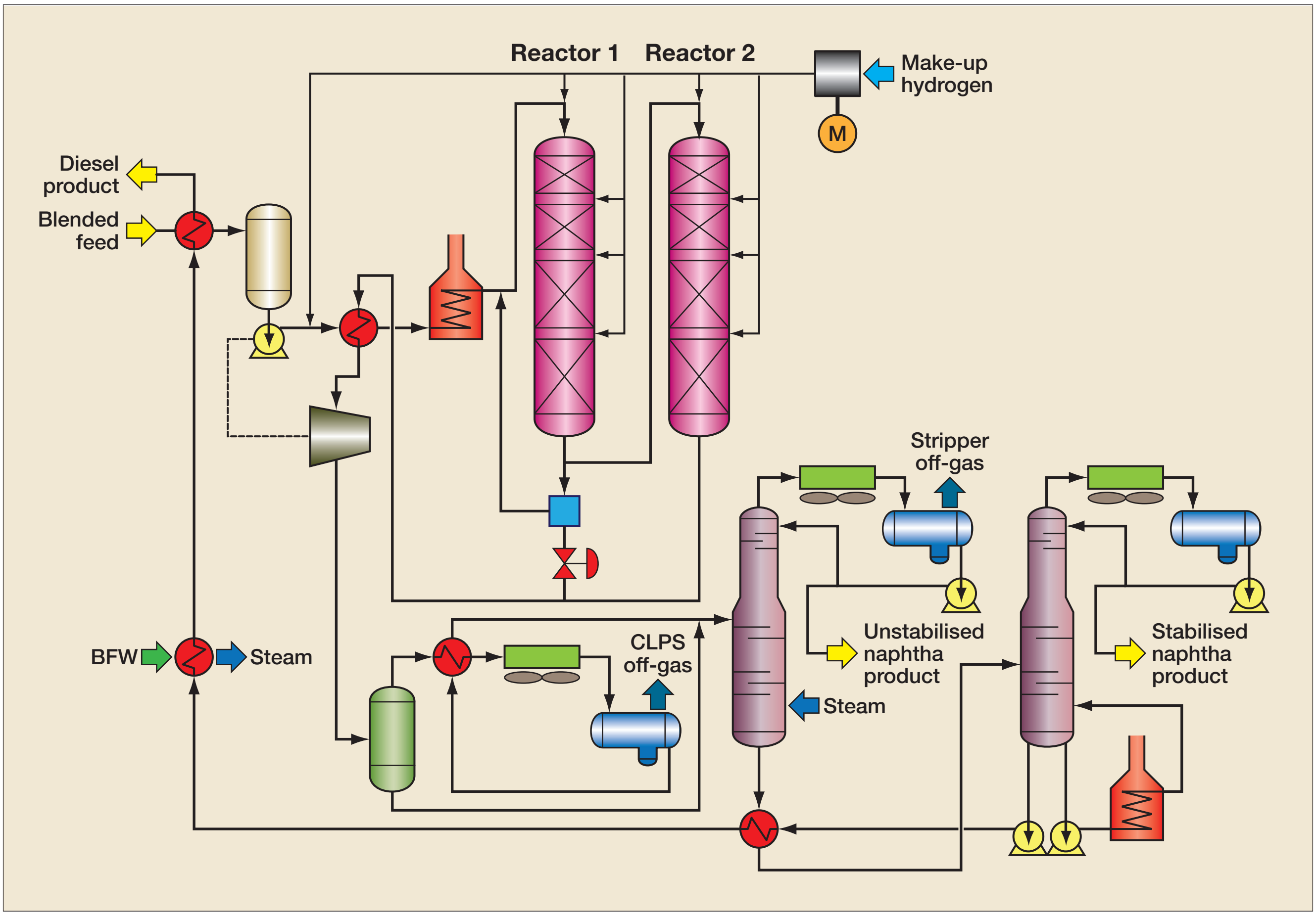

Figure 4 Process flow diagram of the IsoTherming DHT unit

a pressure close to normal operating conditions. The cooling over the four hour outage period was due to natural heat losses and a lack of hot liquid entering the system.

With IsoTherming technology, hydrogen content in the liquid full reactor is limited by solubility. While the liquid maintained in the reactor still contained dissolved hydrogen, hydrogen solubility limitations significantly reduced the number of hydroprocessing chemical reactions (and associated heat release) that could occur. Also, the liquid full catalyst bed acted as a heat sink for the exothermic chemical reactions, which limited undesired temperature rise and eliminated any potential for runaway in the reactor.

Within five hours of regaining power, the commercial IsoTherming unit shown in **Figure 3** returned to stable operation, producing an on-spec diesel product at similar operating temperature and with no apparent catalyst deactivation. This quick return to original operating conditions without any long-term damage (and without having to refill, reheat, and repressurise the reactor) demonstrates the technology's robustness and inherently safer operation compared to conventional trickle bed technology.

A grassroots IsoTherming DHT unit

In April 2014, DuPont commissioned and brought online the world's largest capacity grassroots IsoTherming diesel hydrotreating (DHT) unit (78 500 b/d, 520 m^3/hr) at a refinery in Asia. The unit utilises DuPont proprietary hydroprocessing catalyst and was designed to process a feed blend containing 60% straight run diesel (SRD) and 40% cracked feedstocks consisting of light coker gas oil (LCGO), light cycle oil (LCO), desulphurised resid (RDS), and coker naphtha (CN). Capital cost advantages, decreased energy consumption, and reduced utilities requirements and operating costs were the key drivers for the refiner's selection of IsoTherming technology over conventional trickle bed technology.

Unit design

When the DHT unit was originally licensed in 2010, it was designed to produce a Euro IV equivalent (<50 wppm sulphur) diesel product ('Phase 1') to meet impending government fuel regulations. During the detailed design and construction phase, however, the government announced plans to implement even more stringent Euro V equivalent (<10 wppm sulphur) diesel fuel regulations to address air quality issues. To address the rapidly changing regulations, DuPont worked with the customer to develop a plan to meet the new product specifications. To minimise the overall project cost and schedule impact, DuPont launched a 'Phase 2' process design phase in parallel with the original Phase 1 detailed design and construction activities. During the Phase 2 design phase, DuPont designed and integrated an additional IsoTherming reactor into the previous Phase 1 design. The additional catalyst volume within the new reactor would enable the customer to produce a Euro V equivalent diesel fuel prod-

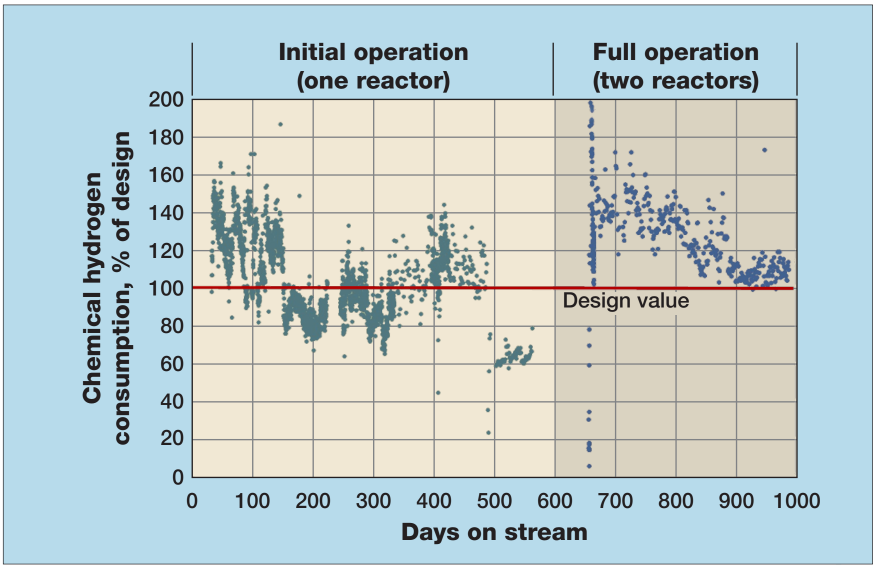

Figure 5 Chemical hydrogen consumption data during commercial operation of the IsoTherming DHT unit

uct compliant with the upcoming regulations. To expedite fabrication and commissioning of the Phase 2 reactor, DuPont and the refiner agreed to procure a duplicate of the Phase 1 reactor design. With detailed engineering and fabrication already complete on the first reactor, design duplication allowed the refiner to reduce the second reactor's delivery time. By early 2014, however, the refiner had completed construction activities associated with the Phase 1 design and decided to start up the IsoTherming DHT unit without the second reactor. The Phase 1 design was successfully commissioned in April 2014 and the DHT unit met all Phase 1 performance requirements. Due to the wide operability range afforded by the Phase 1 DHT unit design, the customer was able to produce a wide variety of products to meet local demand, and chose to continue operation rather than commission the second reactor. In February 2016, the Phase 2 reactor was commissioned and the DHT unit demonstrated continuous production of Euro V equivalent diesel product in compliance with government regulations. A complete process flow diagram of the grassroots DHT unit is shown in **Figure 4**.

DHT unit operating performance

Upon initial start-up of the IsoTherming DHT unit in April 2014, a wide range of diesel fuel regulations were being phased in, providing the refiner with multiple outlets and markets for the DHT unit diesel product. As the 'Initial Operation' phase in **Figure 7** shows, the refiner was able to selectively produce diesel products ranging from 10-150 wppm sulphur. The key factor allowing the customer this operational flexibility was the design of the DHT unit reaction zone.

The final DHT unit reaction zone is configured in two separate sections. The first reaction zone (Phase 1 design) features a single IsoTherming reactor (Reactor 1) which utilises a reactor recycle pump to recycle a portion of the reactor product to the inlet of Reactor 1. The reactor product recycle stream is saturated with additional hydrogen, which provides sufficient hydrogen for the required hydroprocessing chemical reactions and provides the DHT unit the flexibility to operate with large variations in feed flow and composition. This operating flexibility is demonstrated in the DHT unit's hydrogen consumption (see **Figure 5**, days 0-600), which varies from 60% to over 160% of the design hydrogen consumption. This flexibility allowed the refiner to process a wide variety of feeds in order to maximise refinery profits.

By 2015, Euro IV equivalent diesel fuel regulations had been widely implemented and the refiner had shifted operation of the DHT unit almost exclusively to Euro IV equivalent (<50 wppm sulphur) diesel production (see **Figure 7**, days 300-600). With the impending implementation of Euro V equivalent diesel regulations, the refiner decided to commission the second (Phase 2) IsoTherming reactor in February 2016. The second reaction zone (Phase 2 design) features a single reactor (Reactor 2) installed downstream, and in series with the first reactor (Reactor 1). Reactor 2 is a polishing reactor designed to convert the Euro IV equivalent diesel from Reactor 1 into Euro V equivalent diesel product. Unlike Reactor 1, Reactor 2 does not utilise a saturated product recycle stream, and instead operates in the plug flow

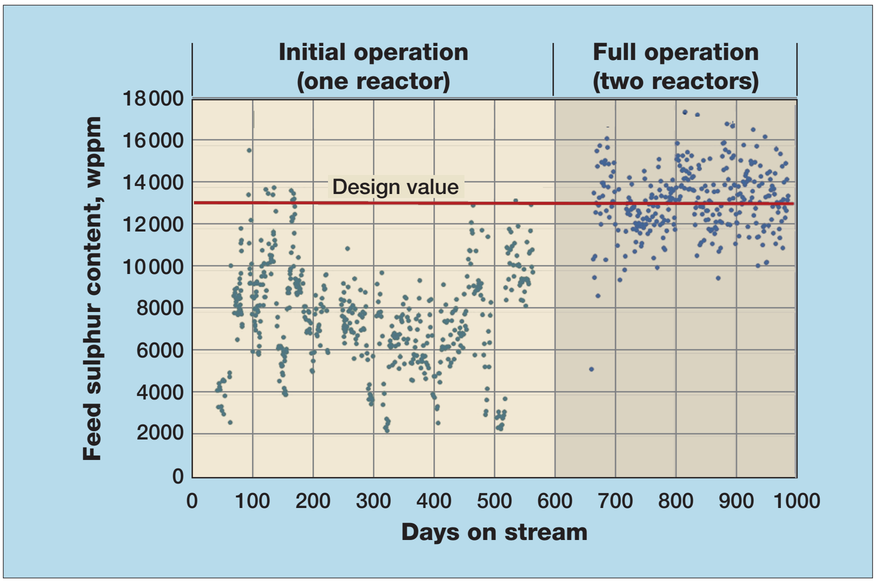

Figure 6 Feed sulphur content data during commercial operation of the IsoTherming DHT unit

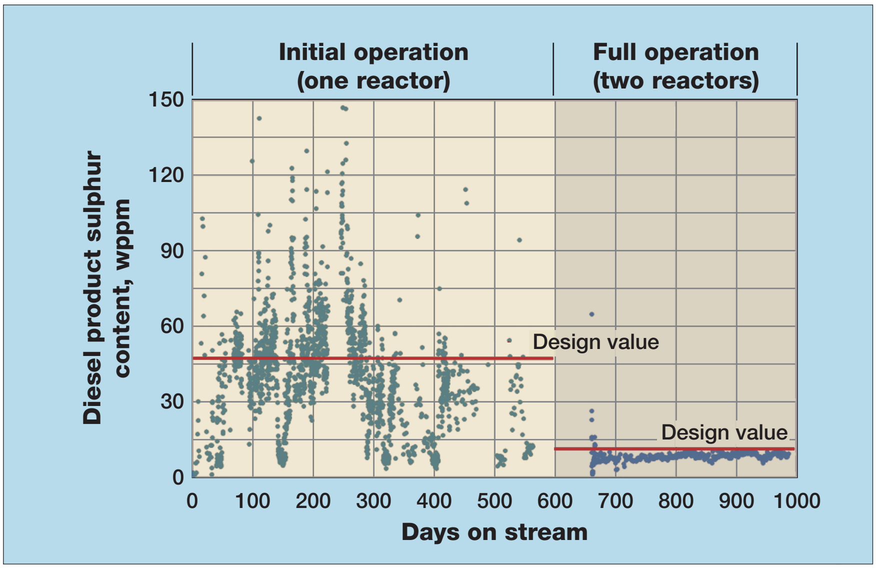

Figure 7 Diesel product sulphur content data during commercial operation of the IsoTherming DHT unit

regime (with once-through liquid). Elimination of the saturated product recycle stream (and its associated dilution effect) in Reactor 2 allows the overall DHT unit to produce Euro V equivalent diesel product (see **Figure 7**, days 650-1000) with reduced catalyst volumes.

Since the start-up of Reactor 2, the DHT unit has continuously produced Euro V equivalent diesel product. The capabilities of IsoTherming technology continue to provide the refiner with a wide range of operating flexibility. As **Figures 5**, **6** and **7** show, the refiner is able to process a wide variety of feedstocks with sulphur levels and hydrogenation requirements well in excess of the DHT unit design, while still consistently producing Euro V equivalent diesel product.

Conclusion

IsoTherming hydroprocessing technology from DuPont has many commercially proven advantages compared to conventional trickle bed technology. These include increased catalyst performance, improved product yields, reduced operating expenses, capital cost savings, and inherently safer operation. In addition, the successful start-up and ongoing operation of the world's largest capacity grassroots IsoTherming DHT unit using DuPont proprietary catalyst shows that IsoTherming technology alone can consistently produce Euro V equivalent (<10 wppm sulphur) diesel product, even with significant variability in feed properties and operating performance.

DuPont is continuously optimising its liquid full IsoTherming reactor design to process increasingly severe feedstocks at a lower capital cost. The company is also actively identifying and evaluating opportunities for the technology in new and emerging markets and applications and licenses the technology and offers products and services throughout the life of the unit. With 24 licensed commercial units worldwide, IsoTherming technology is an innovative and commercially proven technology that is changing the way refiners are looking at hydroprocessing.

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