



IsoTherming[®]

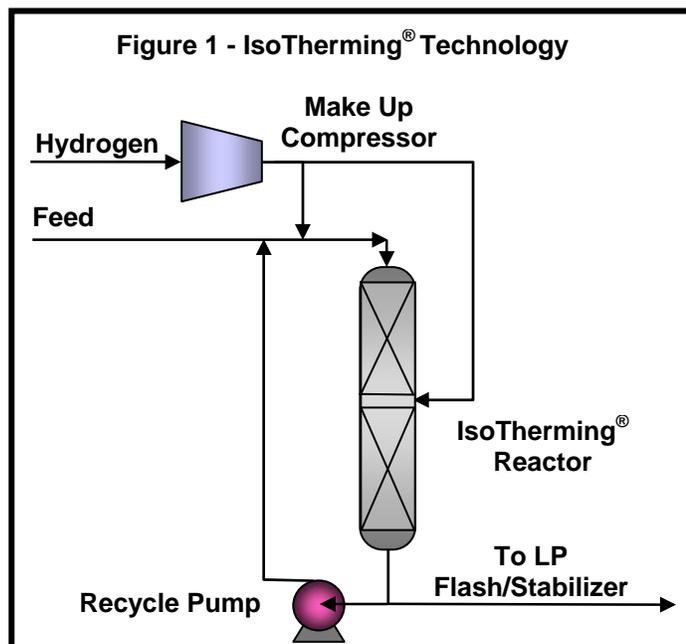
hydroprocessing technology is a commercially proven breakthrough process which provides petroleum refiners a more economical and flexible means to produce today's ultra low sulfur transportation fuels. DuPont acquired the technology from Process Dynamics, Inc., a technology development firm based in Arkansas, USA in August 2007.

In conventional technology for hydroprocessing, the reactions occur in the liquid phase. A large volume of hydrogen rich recycle gas is fed along with the reactor

feed to ensure that the required hydrogen for the reactions can be transferred to the liquid phase. The heart of IsoTherming[®] technology, Figure 1, is the ability to provide the hydrogen necessary for the reactions through a saturated liquid recycle stream. This eliminates the need for a recycle gas compressor. Flow through the reactor is now a single, liquid phase.

The hydrotreated liquid recycle stream is used to deliver the required hydrogen to the reactor. It also acts as a heat sink and results in more isothermal reaction conditions reducing uncontrolled cracking reactions and thus less light ends make.

By removing the need for hydrogen dissolution in the reactor, the process has removed the mass transfer limitation of the overall reactions. The reaction rate is now kinetically limited and proceeds faster than before. As a result, the reactor can now be sized for the hydroprocessing reactions themselves rather than for dissolving of hydrogen in the reaction mixture. This change in reactor design has a number of very attractive benefits to a refiner including:





Lower Total Investment

Lower catalyst volumes to achieve the same process objectives result in correspondingly smaller reactors. Not only are capital savings realized in reactor cost and catalyst, but the elimination of the need for a recycle compressor loop and the required associated ancillary equipment (Amine Absorbers, Knock Out Drums, Heat Exchangers) results in reductions of ISBL cost by 20% to 40%, depending on the application.

Reduced Equipment Delivery Lead Times

The delivery lead time for heavy wall reactors is now 2 to 4 years and there are very few shops worldwide capable of fabricating these large high pressure reactors. Delivery lead times for centrifugal compressors are now nearly 3 years. The smaller IsoTherming® reactor size often allows for reduced wall thickness and therefore potentially increases the number of fabrication shops able to manufacture these vessels. The elimination of the recycle compressor removes the delivery of this piece of equipment as a project-critical schedule milestone.

Reduced Light Ends Make

The lower temperature rise across the IsoTherming® reactor allows the refiner to achieve their desired product specification while minimizing undesired cracking reactions. This reduces the yield of light ends that have limited value within many refineries. In addition, the reduced cracking reactions decrease hydrogen consumption to meet the same product specification. The degree of improvement, of course, will vary depending on a number of factors (feedstock, service, operating conditions, and catalyst to a name a few). For highly unsaturated feedstocks such as Light Cycle Oil (LCO) or Coker Gas Oil (CGO), the reduced temperature rise across the IsoTherming® reactor system provides a distinct advantage not only due to decreased cracking, but the lower average temperature allows for effective treatment of hard-to-remove nitrogen compounds without the adverse effect of sulfur recombination reactions.

Increased Catalyst Life

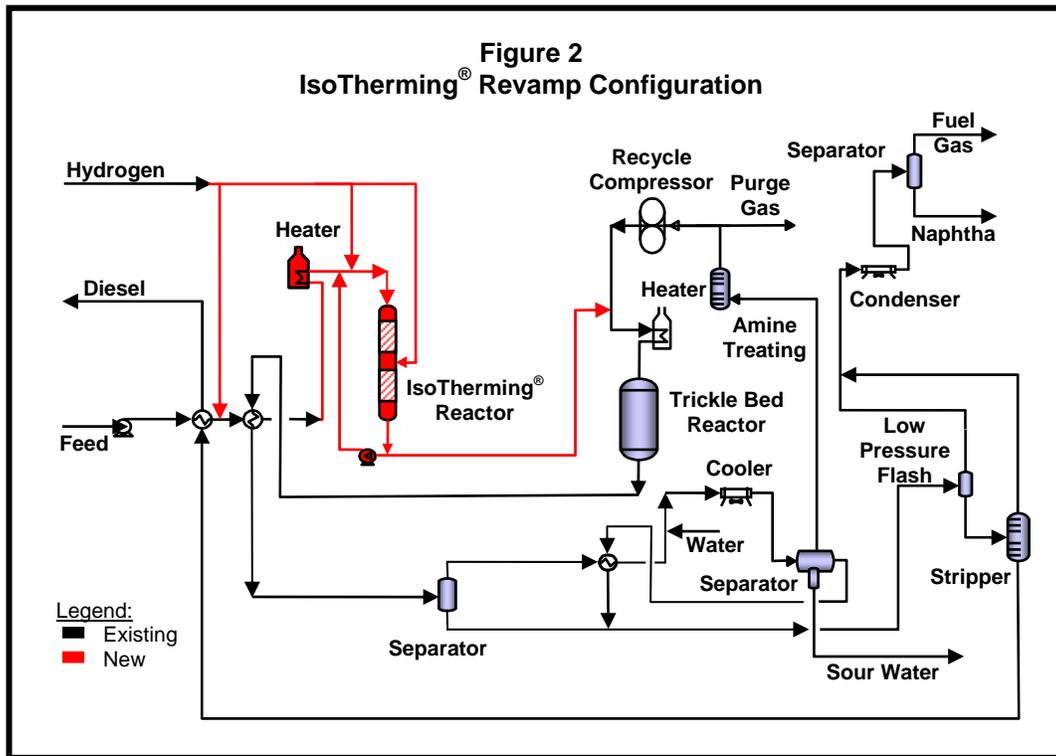
Minimization of cracking reactions minimizes coke deposition on the catalyst, often a limiting factor in catalyst life. Increased thermal mass and complete surface wetting also aid in extending catalyst life.

Reduced Maintenance and Operating Cost

By eliminating the hydrogen recycle loop, considerable maintenance cost savings can be realized. Lower catalyst volumes and increased catalyst life reduces replacement catalyst cost and associated metals/waste disposal cost. In addition, for feeds that contain a reasonable amount of cracked stocks, IsoTherming® recovers the heat of reaction and recycles the hot hydrotreated product back to the inlet of the reactor. Therefore, the feed heater is normally only fired for startup and sulfiding. Under normal operating conditions, the feed heater is not needed, resulting in substantial savings in fuel gas costs and a dramatic reduction in stack emissions.

Configuration Flexibility

For refiners contemplating a revamp of existing hydrotreating assets, IsoTherming® offers the option of utilizing an IsoTherming® reactor system as a pretreatment unit. If there is an existing hydrotreater, the IsoTherming® hydrotreating technology can be installed as a simple pretreat unit ahead of the existing hydrotreater, Figure 2.



The pretreat configuration can be installed at a fraction of the cost of competing low sulfur technologies. The IsoTherming[®] pretreat reactors do most of the hydrodesulfurization leaving less work for the existing conventional reactor, which now operates in a polishing mode. The mass transfer limitation of the conventional trickle bed reactor is no longer a constraint due to the fact the IsoTherming[®] reactors have already transferred the bulk of the hydrogen to the oil. Because of this, catalyst deactivation due to coking in the conventional reactor is also drastically reduced. For existing low pressure units, a higher pressure IsoTherming[®] loop can be installed, maximizing the use of existing assets and minimizing overall cost.

Frequently Asked Questions

When discussing IsoTherming[®] hydroprocessing technology with prospective users, certain questions are often asked, which aid in comparing IsoTherming[®] operations with conventional practice. Some of these are:

1. **What catalysts are used? Do you have your own catalysts?** DuPont specifies a given catalyst load depending upon the application, operating conditions and feeds being processed. We have both CoMo and NiMo catalysts at our disposal for rebranding and supply an optimized first catalyst load to each of our licensees.
2. **How do I load and pre-sulfide the catalyst in your process? Is it necessary to use pre-sulfided catalyst?** The catalyst is dense-loaded and sulfided according to the supplier's procedures for liquid sulfiding agents. Pre-sulfided catalyst is not required, but if selected may affect the design somewhat.
3. **How do I monitor and predict catalyst life? What data came from pilot testing, and what about full scale experience?** An accelerated catalyst aging test performed for one client showed essentially no aging under controlled pilot conditions. Actual data from operating sites is being



analyzed for WABT vs. time to track activity and deactivation trends.

4. ***When will you have a commercial ULSD unit without a trickle bed? What about full conversion hydrocracking?*** One commercial IsoTherming[®] unit is producing ULSD in a single loop on kerosene feed. Two mild hydrocrackers have been commissioned and can produce ULSD without a trickle bed on the back end. Given the operating conditions associated with full conversion hydrocracking, there are technology changes that will be required. As a result, DuPont has elected to focus the application of IsoTherming[®] technology on hydrotreating and mild hydrocracking.
5. ***What guarantees are you offering?*** DuPont will provide performance guarantees similar to those offered by other hydroprocessing technology licensors.
6. ***What will you tell me without a Confidentiality Agreement? How much of the equipment is proprietary? Is it possible to visit existing units easily?*** Reactor size, process configuration, an un-sized equipment list, product quality, and yields can be disclosed without a Confidentiality Agreement. The reactor internals are proprietary and are available only from DuPont. Numerous potential licensees who have signed a Confidentiality Agreement have visited operating sites.
7. ***What are the current limitations of your design?*** The system has a limit on how much hydrogen can be added to the reactor determined by pressure and recycle rate. Changes in feedrate and/or catalyst may affect this limit. We currently require sub-critical conditions within the reactor, although we are investigating supercritical reactor operation and may be able to accommodate these conditions in the near future.
8. ***How is hydrogen dissolved in the reactor feed? What about between successive beds?*** Intimate mixing by static mixers is used to saturate these liquids. Hydrogen dissolution between successive beds is considered part of the proprietary reactor control scheme and will only be disclosed on a project specific basis.
10. ***What sort of pump is used for recycle service? What capacity is available?*** Currently there are two options to consider for the recycle pump service. Suppliers include Teikoku who offers a “canned” motor type pump as well as Flowserve who offer a sealed type PR pump. Flow ranges up to 5,000 US gpm (1135 m³/hr) are available.
11. ***How do you configure a depressurizing valve when there is no HP separator? What are the principles and procedures for protecting the catalyst in an emergency?*** Depressurizing details are part of our proprietary control scheme, which require a CA to disclose. Emergency procedures are similar to a conventional unit, except that the design gives more protection against a runaway than does a conventional unit.
12. ***What is the maximum liquid mass flux and maximum bed depth in the reactor? Do you find any erosion associated with the inter-bed injection system?*** Mass flux and bed depth can be greater than a trickle bed, but are not direct design parameters. We do not experience any erosion at the velocities used in the design.
13. ***Multi-bed reactors can take a long time to load and unload. Your internals may make this more difficult. What comments do you have on this topic?*** DuPont has worked extensively on procedures with a specialist catalyst handling contractor during construction of several units, and have made some modifications to ease these operations. Multi-bed configuration is not a requirement if catalyst handling remains a concern.
14. ***Without a recycle compressor, how do I strip the catalyst of hydrocarbon prior to a catalyst dump?*** The makeup gas compressor or vent gas compressor may be used. A rental machine for planned shutdown is another option. Connections should be discussed during detailed engineering.

15. ***Dilution of heavy sulfur molecules by your recycle scheme lowers the diffusion driving force in ULSD operation. You also recycle H₂S and ammonia. Do these affect catalyst activity and kinetics?*** Diffusion is not controlling if the catalyst (pore size in particular) is well chosen. Reduced driving force for diffusion and recycle of reaction products do impact the catalytic reactions, but these effects are mitigated by the increased hydrogen driving force due to soluble hydrogen and increased wetting of the catalyst surfaces. Our kinetic models take these effects into account during design.
16. ***Mass transfer between vapor and liquid phases is thought to be very fast and not usually considered to affect overall reaction rates significantly. You claim that elimination of this step within the reactor allows the reactors to be smaller. Do you somehow achieve faster reaction kinetics with liquid phase only?*** Mass transfer is very fast if the liquid and vapor phases are in intimate contact. This may not necessarily be the case in a trickle bed with incomplete wetting and segregation/channeling. Hence the continued emphasis on catalyst shapes, radial redistribution, and other means of enhancing vapor/liquid contact in conventional trickle beds. The reaction kinetics (and catalysts) for IsoTherming[®] are the same as conventional systems, only the removal of mass transfer as a limitation allows the full capability of the catalyst to be realized.
17. ***What are the process conditions? Are they different from trickle bed operations? What process variables do I tune if, for example, I add more LCO to the unit feed?*** Temperature and pressure will be similar to a trickle bed on the same feed. Changing feed composition may call for changes in liquid recycle ratio and/or operating temperature.
18. ***What about utility consumption compared to conventional design?*** The recycle pumps typically use about 10% of the electric power of a recycle gas compressor. The fired heater duty will be less at SOR conditions. Other factors are dependent on specific design conditions.
19. ***What is the impact of water generated from oxygenates in the feed? What is the impact of silicon from coker feeds? What about hydrogen consumption?*** All these are about the same as conventional design, as the catalysts and operating conditions are the same. Unless the oxygenate contamination is very large, free water will not form. Chemical hydrogen consumption will be similar to a trickle bed using the same catalyst.
20. ***Does the recycling of product create more light ends from cracking?*** No, we find that fewer light ends are generated due to more uniform contacting with the catalyst and the heat sink effect of the increased liquid mass in the bed. These act to decrease unwanted cracking.
21. ***Do you have a limit on nitrogen content for hydrocracking? Any added problems with ammonia salt formation in hydrocracking service?*** In general, IsoTherming[®] handles nitrogen as well as or better than conventional designs. We have operating experience with nitrogen levels as high as 1750 ppm in the feed, and pilot testing as high as 4000 ppm without trouble. Ammonia salts are handled as in conventional units, with a water wash.
22. ***How does aromatics saturation compare with trickle beds?*** IsoTherming[®] is at least as good if not better than trickle beds. The aromatics saturation equilibria favor saturation at lower temperatures, so any process which enables other product criteria to be achieved at lower temperature will show better saturation.
23. ***Can you make Euro-5 diesel with <10 ppm S and <11% polyaromatics? What about the future specs which may move down to <6% or <7% polyaromatics?*** We have operating experience at current Euro-5 standards, and pilot plant tests producing diesel at <6% polyaromatics.
24. ***Do you have pilot studies on upgrading FCC light cycle oil? How about FCC heavy cycle oil?*** Both these feeds have been tested for upgrading in either diesel or hydrocracking operation and the IsoTherming[®] process performed well in every case.

Commercial Experience

The first full-scale commercial IsoTherming® unit was started up in April 2003 to produce ULSD at the Western refinery near Gallup, New Mexico. The unit was configured as a pretreating unit ahead of the existing conventional diesel hydrotreater processing a feed that contained a 40/60 mix of LCO/Straight Run (SR) Diesel. The process produced an ULSD product with a sulfur content of less than 5 ppm. This allowed the refinery to process all their LCO and SR diesel and produce ULSD without the need for undercutting or bypassing of feed.



A comparison of light ends make was done when producing a 10 ppm ULSD product in a conventional reactor versus a conventional reactor with an IsoTherming® pretreat section. The light ends make when operating the conventional trickle bed reactor dropped significantly when the IsoTherming® pretreat section was added.

The unit at Western Refining was operated over a wide range of conditions to test the limits of the technology and the sensitivity to feed variations. It proved to be able to produce a ULSD product even when the feed end points were raised nearly 25°F and also when the percentage of LCO in the feed was increased substantially.

As a result of the initial commercial success, the unit was modified two years later to expand the refinery's ULSD capacity to treat the total refinery diesel production.

The following is a summary of IsoTherming® licensing activity to date:

Operating Units:

<u>Company</u>	<u>Location</u>	<u>Application</u>	<u>Startup</u>
Western Refining	Gallup, NM	ULSD Revamp	April 2003
Western Refining	Gallup, NM	Grassroot Kerosene Hydrotreater	April 2006
Western Refining	Yorktown, VA	Grassroots ULSD Hydrotreater	May 2006
Holly Refining	Woods Cross, UT	VGO Mild Hydrocracker	March 2009
Holly Refining	Artesia, NM	VGO Mild Hydrocracker	May 2009
Frontier Refining	El Dorado, KS	Revamp VGO Hydrotreater	Dec 2010
Proper Year	China	Grassroots Mild Hydrocracker	May 2011

In Design or Under Construction:

<u>Company</u>	<u>Location</u>	<u>Application</u>	<u>Startup</u>
Zhejiang Meifu	China	Grassroots LSD Hydrotreater	2Q2011
Jiangsu Jurong	China	Grassroots LSD Hydrotreater	3Q2011
Jinao Hubei	China	Grassroots LSD Hydrotreater	4Q2011
Purneftpererabotka	Russia	Grassroots LSD Hydrotreater	2Q2012
Unipet	China	Grassroots LSD Hydrotreater	3Q2012
PetroChina	China	Grassroots LSD Hydrotreater	4Q2012
Sinochem	China	Grassroots LSD Hydrotreater	1Q2013
Mei Shan Shi Ao Xin	China	Grassroots Mild Hydrocracker	2Q2013
To Be Announced	New Jersey	Revamp ULSD Hydrotreater	On Hold



DuPont Clean Technologies

STRATCO® Alkylation Technology

BELCO® Technology

IsoTherming® Hydroprocessing Technology

MECS® Technology



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