Pamela Pryor and Richard Cooper, DuPont Clean Fuel Technologies, USA, introduce IsoTherming® technology, an alternative to traditional desulfurising methods.
DuPont™ IsoTherming® hydroprocessing technology is a breakthrough process that offers petroleum refiners a more economical and flexible means for producing 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 2) 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 becomes 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 fewer light ends are made.

By removing the need for hydrogen dissolution in the reactor, the process removes the mass transfer limitation of the overall reactions. The reaction rate becomes 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 hydrogen in the reaction mixture. This change in reactor design has a number of 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 realised 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 - 40%, depending on the application.

**Reduced equipment delivery lead times**
The delivery lead time for heavy wall reactors is now 2 - 4 years, and there are very few shops worldwide capable of fabricating these large high pressure reactors. Most are currently operating with a significant backlog of work. Delivery lead times for centrifugal compressors are now nearly three 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**
The lower temperature rise across the IsoTherming® reactor allows the refiner to achieve its desired product specification while minimising 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**
Minimisation of cracking reactions minimises 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 realised. 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. The recycle pumps typically use approximately 10% of the electric power of a recycle gas compressor. Other factors are dependent on specific design conditions.

**Configuration flexibility**
For refiners contemplating a revamp of existing hydrotreating assets, IsoTherming® technology presents the option of utilising an IsoTherming® reactor system as a pretreatment unit ahead of the existing hydrotreater (Figure 3).

The pretreatment configuration can be installed at a fraction of the cost of competing low sulfur technologies. The IsoTherming® pretreatment reactors do most of the hydrodesulfurisation, 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, maximising the use of existing assets and minimising overall cost.

**Catalyst and chemistry considerations**
Using IsoTherming® technology, there is no difference in the chemistry from conventional practice. Both CoMo and NiMo catalysts from a variety of suppliers have been used in pilot studies and in commercial operation, and no preference is made among catalyst suppliers. Pilot plant runs on candidate feeds can be made to assist in catalyst selection.

The selected catalyst is dense loaded and sulfided according to the supplier’s procedures for liquid sulfiding agents. Presulfided catalyst is not required, but if selected, may affect the design. An accelerated catalyst ageing test conducted for one client showed essentially no ageing under controlled pilot conditions. Actual data from operating sites is being analysed for WABT versus time to track activity and deactivation trends.

**Proprietary process design**
Reactor size, process configuration, an unsized equipment list, product quality, and yields can be disclosed for a prospective application without a confidentiality agreement. The reactor internals are proprietary and are available from DuPont. Intimate mixing by static mixers is used to saturate the reactor feed with hydrogen. Hydrogen dissolution between successive beds is considered part of the proprietary reactor control scheme and will only be disclosed on a project specific basis.

The system has a limit on how much hydrogen can be added to the reactor, determined by pressure and recycle rate. Changes in feed rate and/or catalyst may affect this limit. At present, subcritical conditions are required within the reactor, although supercritical reactor operation is being investigated and these conditions may be accommodated in the near future.

Liquid mass flux and catalyst bed depth can be greater than a trickle bed, but are not direct design parameters. With the proprietary internals installed, bed erosion is not experienced at the velocities used in the design.

**Safety**
Due to safety considerations, a ‘canned’ motor type pump is used in recycle service. Individual flow ranges up to 5000 gal./min (1135 m³/hr) are available.

Emergency procedures are similar to a conventional unit, except that the design gives more protection against a runaway than a conventional unit does. Depressuring details and sizing for depressurising valves are part of the proprietary control scheme, and require a CA to disclose.

**Operating conditions**
Process conditions, such as temperature and pressure will be similar to a trickle bed on the same feed. Changing feed composition may call for changes in the liquid recycle flowrate and/or operating temperature.

Diffusion of heavy sulfur molecules 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. Kinetic models take these effects into consideration during design.

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**Figure 1.** IsoTherming® ULSD hydrotreater located near Gallup, New Mexico, USA.
Mass transfer is very fast if the liquid and vapour phases are in intimate contact. This may not be the case in a trickle bed with incomplete wetting and vapour phase segregation/channelling. Hence the continued emphasis on catalyst shapes, radial redistribution, and other means of enhancing vapour/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 realised.

Operating experience
Chemical hydrogen consumption will be similar to a trickle bed using the same catalyst. It is evident 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 with liquid recycle. These act to decrease unwanted cracking.

In general, IsoTherming® handles nitrogen removal and aromatics saturation as well as or better than conventional designs. DuPont has operating experience with nitrogen levels as high as 1750 ppm in the feed, and pilot testing with up to 4000 ppm without any trouble. Ammonia salts in hydrocracking service are handled as in conventional units, with a water wash. The aromatics saturation equilibria favour saturation at lower temperatures, so any process that enables other product criteria to be achieved at lower temperature will show better saturation.

Further process development
DuPont has operating experience at current Euro-5 diesel standards of <10 ppm S and <11% polyaromatics, and pilot plant tests producing diesel at <6% polyaromatics against possible future standards. Other development efforts have shown that LCO and/or heavy cycle oil from the FCC can be upgraded in either diesel or hydrocracking operations, and the IsoTherming® process performed well in every case.

Commercial experience
The first full scale commercial IsoTherming® unit 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 a ULSD product with a sulfur content of less than 5 ppm. This allowed the refinery to process all of its LCO and SR diesel and produce ULSD without the need for undercutting or bypassing feed.

A comparison of light ends generated was carried out when producing a 10 ppm ULSD product in a conventional reactor versus a conventional reactor with an IsoTherming® pretreatment section. The amount of light ends made when operating the conventional trickle bed reactor dropped significantly when the IsoTherming® pretreatment 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 capable of producing 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.

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Table 1. A summary of IsoTherming® licensing activity to date

<table>
<thead>
<tr>
<th>Operating units</th>
<th>Company</th>
<th>Location</th>
<th>Application</th>
<th>Startup</th>
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<td>Western Refining</td>
<td>Gallup, NM</td>
<td>ULSD revamp</td>
<td>April, 2003</td>
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<td></td>
<td>Western Refining</td>
<td>Gallup, NM</td>
<td>Grassroots kerosene hydrotreater</td>
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<td>Revamp ULSD hydrotreater</td>
<td>May, 2006</td>
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<td>Western Refining</td>
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<td>Grassroots ULSD hydrotreater</td>
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<td>Holly Refining</td>
<td>Woods Cross, UT</td>
<td>VGO mild hydrocracker</td>
<td>Q1 2009</td>
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<td>In design or under construction</td>
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<td>Artesia, NM</td>
<td>VGO mild hydrocracker</td>
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<td>Revamp VGO hydrotreater</td>
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<td>TBA</td>
<td>New Jersey</td>
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