An Innovative Solution to Meeting Today's Diesel Specifications

by:

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Synopsis

Refiners are challenged to meet increasingly stringent fuel specifications even as the slate of available feedstocks becomes more difficult to process. Significant upgrades to existing facilities are often difficult to justify in an era of heavy capital restraint. Refiners must meet specific targets for long-term return on capital and product quality from middle and heavy distillate feedstocks for any investment to be attractive. IsoTherming® Hydroprocessing Technology provides a solution to the challenges refiners face to reduce sulfur in finished products to ultra-low levels while minimizing operating costs with competitive capital expenditures.

This presentation highlights the principles of the technology and demonstrates the versatility and robustness of a process that has been successfully implemented commercially in grassroots and revamp applications to improve margins and ensure a safe and sustainable operating environment. This presentation will focus on revamp applications, in which the efficient design of the process provides refiners a means of debottlenecking and improving performance with minimal modification and no additional recycle gas compressor capacity. Revamps using IsoTherming® technology can result in significant capital savings in comparison to a conventional trickle bed revamp, with considerably more operational flexibility.

Introduction

Today's refiners are facing an unprecedented number of challenges such as:

- Producing gasoline and diesel fuels to lower sulfur and increased combustion quality specifications
- More stringent environmental controls on emissions
- The need to process the lowest cost feedstocks available such as heavy, sour crudes
- Cost escalation in capital projects

One result of these challenges is the need for petroleum refiners to make significant investments to increase their hydroprocessing capabilities either through unit debottlenecks or via new unit construction. However, these investments must provide an acceptable long term return on capital while producing the desired product yields and qualities from cost advantaged feedstocks (FCC cycle oils, coker gas oils, shale oil, tar sands, etc.).

IsoTherming® Hydroprocessing Technology is a commercially proven, flexible, breakthrough technology that allows refiners to meet their hydroprocessing objectives at significantly reduced operating costs over conventional technologies with competitive capital expenditures.

IsoTherming® technology was first commercially proven at the Giant Industries refinery in Gallup, New Mexico in 2003. Since this time, the technology has been utilized in various other applications, including ultra-low sulfur diesel (< 10 ppm sulfur), FCC pre-treat, transmix, olefin saturation, GTL, and mild hydrocracking. Currently, there are 25 IsoTherming® units licensed globally, 12 of which are in commercial operation.

IsoTherming® Technology Background

Hydrotreating has been practiced by the refining industry for several decades. For hydrocarbon feedstocks in the heavy naphtha/light distillate boiling ranges, hydroprocessing units historically utilize a two-phase trickle bed reactor configuration.

In a trickle bed reactor, combined hydrogen make-up and recycle gases and liquid feed are mixed, heated to the desired reactor temperature and passed to a reactor fitted with an internal distribution device on top of the catalyst bed. The distributor serves two purposes: provides even distribution of the two phase mixture across the catalyst bed and promotes further mixing to ensure saturation of the feed liquid with hydrogen prior to entering the catalyst bed.

This reactor design has several fundamental shortcomings:

- As the reaction occurs at the catalyst surface between the dissolved hydrogen and the reactive species in the feed, the hydrogen is depleted from the liquid. In most refinery applications, the amount of hydrogen required for the reactions is greater than the solubility of hydrogen in the fresh feed alone. Thus, in order for the reaction to continue to completion, additional hydrogen must be replenished from the vapor phase. This in effect makes the rate of diffusion of hydrogen into the liquid phase a factor in the overall kinetics of the process.

- In order to overcome this diffusion limitation, excess hydrogen, often several times the quantity required for the reactions, is recycled back to the reactor to maximize the hydrogen partial pressure throughout the system. Hydrogenation reactions are highly exothermic. The mass flow of hydrocarbon feed and recycle hydrogen through the reactor has a limited capacity to adsorb the energy produced. Therefore, in applications that require large chemical hydrogen consumption, the reactor temperature increase can be significantly high. The larger the temperature rise, the more undesirable side reactions, such as cracking to light products (i.e. fuel gas and light naphtha), will take place. Cracking results in loss of valuable products and increased catalyst coking.

- Inter-bed hydrogen quenches, although providing supplemental hydrogen, offer limited means to minimize this temperature increase due to the limited mass flow of hydrogen that can be added to the system economically.

- Two-phase flow through a heterogeneous catalyst is prone to maldistribution. Any slight variations in pressure drop through the bed, even an unlevel catalyst bed, will result in liquid/vapor maldistribution. This results in inefficient use of the catalyst and, in worse cases, regions deficient in hydrogen that result in hot spots or coke formation. Ultimately, a premature unit outage and/or a catalyst dump/screen may be necessary.

IsoTherming® Hydroprocessing Technology was developed to address these shortcomings in the conventional hydroprocessing trickle bed design.

In IsoTherming® technology, the hydrogen required for the reaction is dissolved in the liquid before entering the catalyst beds. The appropriate supply of hydrogen is accomplished by saturating a combined feed and recycle stream of reactor effluent prior to entering the reactor. The liquid recycle rate is determined so that the amount of hydrogen dissolved in the combined (fresh and product liquid) feed is much greater than the reaction requirements. This design ensures a sufficient availability of hydrogen for the reactions at all points within the reactor.

With all the necessary hydrogen in the liquid, the overall reaction is now controlled by the intrinsic reaction rate (the combination of the effectiveness of the catalyst and the actual reaction rate). In addition, the heat capacity of the total reactor feed is considerably greater than that of the combined raw feed and the hydrogen recycle stream in conventional hydroprocessing configurations. As a result, the temperature rise across a given reactor bed is considerably less than that of a conventional design - hence the name “IsoTherming” [1]. This lower temperature rise eliminates the need for inter-bed cooling and the additional complexity it brings to the reactor operation and design.

When hydrotreating cracked stocks, such as coker gas oils or light cycle oils, in severe operating conditions, the considerably low temperature rise within the reactor minimizes undesirable side reactions. Hence, in the same service, an IsoTherming® reaction system will have increased yield of desired products compared to its conventional counterpart. In addition, the lower temperature rise results in lower coking rates and, therefore, longer catalyst life. This also practically ensures no large thermal excursions within the reactor and minimizes the chance of a runaway reaction. IsoTherming® reactors are consequently safer to operate.

The single liquid phase configuration ensures even flow distribution throughout the catalyst beds and complete wetting to minimize hot spots. In contrast, gas and liquid distribution considerations are critical within a conventional reactor, requiring complex designed distribution devices to prevent mal-distribution.

The IsoTherming® process delivers hydrogen in a liquid stream eliminating the recycle gas system and reduces required high pressure equipment. For example, hot and cold high pressure separators, high pressure condenser, recycle gas amine scrubber and the recycle gas compressor are not required. Therefore, capital savings may be achieved.

The impact of these design differences results in a process that has the following advantages over conventional hydroprocessing designs:

> Reduced Operating Expenses – Improved heat integration takes advantage of the recoverable heat of reaction from the liquid. The energy recovered can be used in other parts of the process or to generate steam. Frequently, lower charge heater duty is required, if needed, during normal operation.
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> Plot Space – Smaller plot plan advantages can be realized due to the elimination or reuse of high pressure process equipment. In addition, installing a reactor recycle pump that can either be skid mounted or hung from the piping replaces a potentially larger footprint of a recycle gas compressor. Lastly, smaller high pressure feed/effluent exchangers are needed due to superior heat integration by recycling the heat of reaction.
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> Robust, Reliable and Safe – An easier to operate process due to liquid full reactors enables reduced start-ups and shutdowns times. Lower hydrogen inventory in the system minimizes the potential for runway reactions during emergency shutdowns.

A simplified process flow diagram of the high pressure equipment in a grassroots IsoTherming® design is shown in Figure 1.

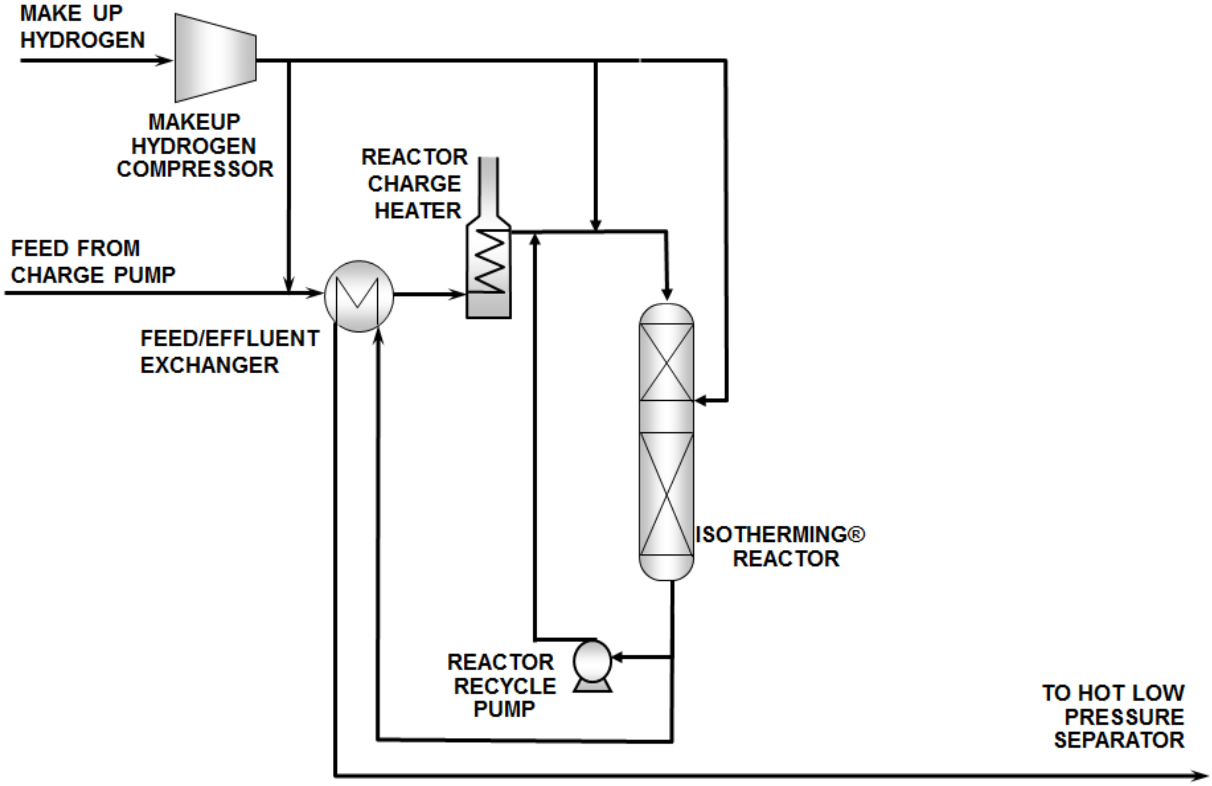

Figure 1. Simplified IsoTherming® High Pressure Equipment Flow Diagram

As depicted in Figure 1, additional high pressure equipment associated with separating the two-phase reactor effluent and recycling hydrogen are eliminated. The table below summarizes the high pressure equipment differences between a conventional design and a grassroots IsoTherming® configuration.

Table 1. Equipment Differences Between Conventional and IsoTherming® Technologies

	IsoTherming®	Conventional
Hot High Pressure Separator	No	Yes
Cold High Pressure Separator	No	Yes
Recycle Gas Compressor	No	Yes
High Pressure Off Gas Cooler	No	Yes
Hot Low Pressure Separator	Yes	No
High Pressure Amine Contactor	No	Yes
High Pressure Amine Pump	No	Yes
Stripper Preheat Exchangers	No	Yes
Reactor Recycle Pump	Yes	No

IsoTherming® Technology in Revamps

In the case of revamping a conventional unit that cannot currently achieve more stringent product specifications, IsoTherming® technology can easily be incorporated into the flow scheme to achieve the desired product requirements. Not only can significant capital savings be realized with this option versus a conventional revamp, but the net result is a unit that is considerably more flexible than a conventional revamp. Minimal capital investments in addition to reduced energy requirements are often feasible.

Consider a conventional unit that currently reduces sulfur in the diesel to 300 to 500 ppm is now required to produce less than 10 ppm with a desired increase in capacity. Normally, in order to achieve such objectives, a refiner may add a new reactor containing more catalyst to the system and typically an increase in recycle gas rate would be necessary. Additional makeup hydrogen compressor capacity may be necessary since hydrogen consumption will increase. An increase in pressure drop caused by a combination of increased catalyst volume and total recycle gas rate frequently requires new hydrogen recycle compressor capacity. New feed/effluent and separator off gas heat exchangers may be needed and potentially a new off gas cooler due to the increased flow of gas. The existing reactor internals may require modification or replacement to accommodate the higher gas flows. The amine treater also may need revamping to process the higher gas rate. Figure 2 depicts the main changes (indicated in red) when revamping for such application using conventional trickle bed technology.

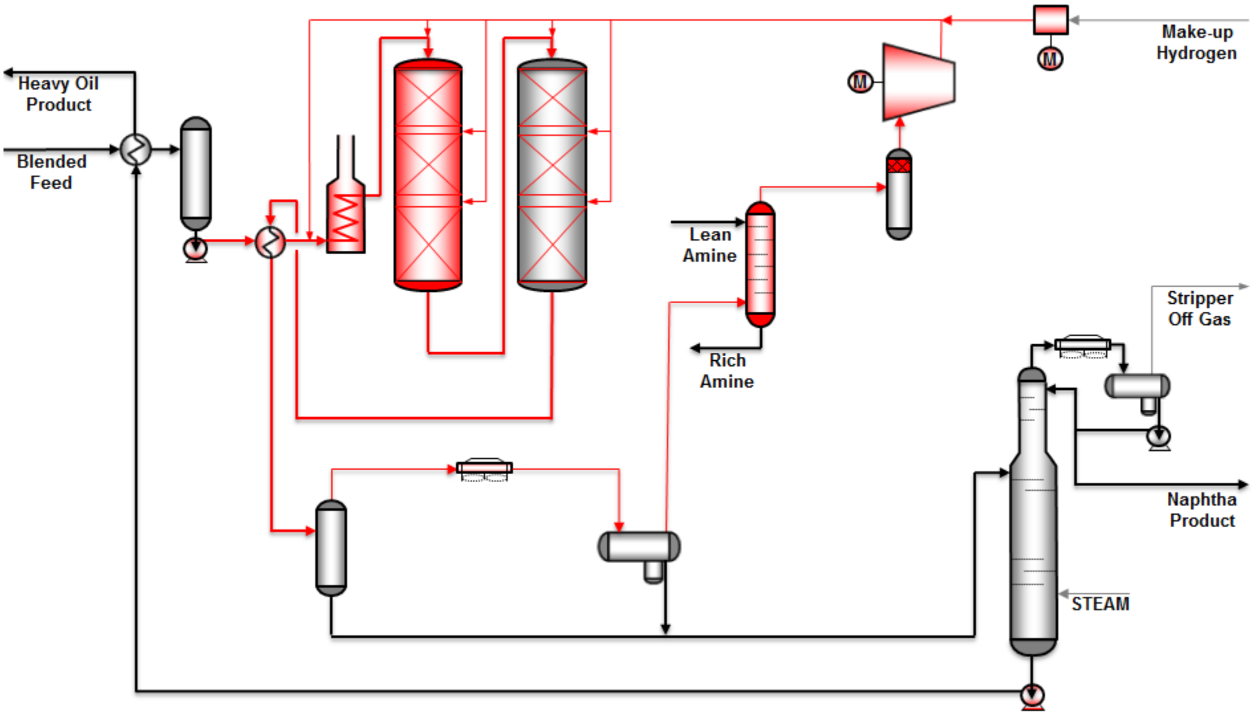

Figure 2. Typical Revamp with Conventional Technology

The same unit objectives can be accomplished by installing an IsoTherming® reactor system upstream of the existing trickle bed system. The IsoTherming® reactor removes the majority of the sulfur enabling the existing trickle bed system to complete the process to meet the desired sulfur specification. As a result, the trickle bed reactor and recycle gas loop now operate with a lower hydrogen demand and the existing equipment performance is greatly improved. In this scenario, the main changes, illustrated in Figure 3, in red, are the addition of the IsoTherming® reactor upstream of the existing reactor, a new recycle pump and the modification of the internals within the conventional reactor. Most of the high-pressure gas section can be reutilized and the existing recycle gas compressor is most often still adequate for the revamped service.

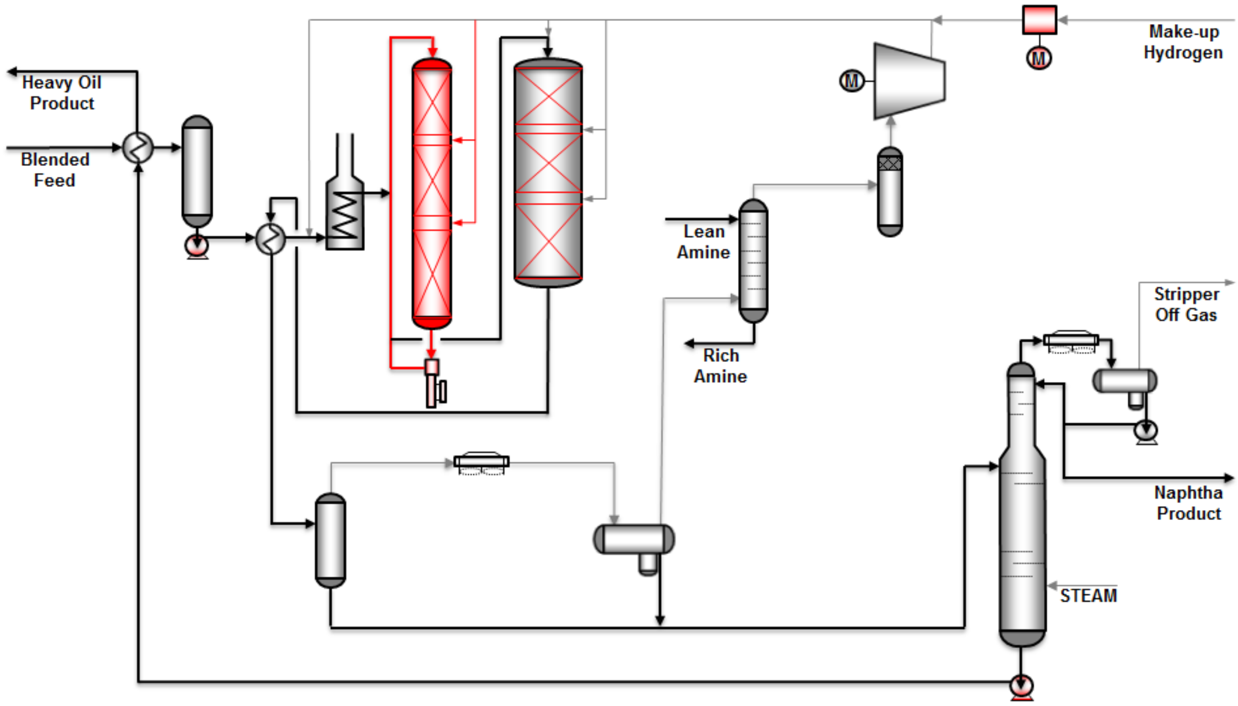

Figure 3. Revamping with IsoTherming® Technology for Conventional Units

Considering there are minimal tie-in connections with the existing system, revamp work can be conducted around the existing process ensuring minimal unit down time during turnaround activities to tie-in the new reactor system.

The main differences in process equipment when comparing conventional and IsoTherming® technology revamp solutions are shown in Table 2.

Table 2. Equipment Differences when Revamping Conventional Units with IsoTherming® Technology.

	Conventional	IsoTherming®
Reactors	New Required	May Retrofit Existing
Recycle Gas Loop		
Recycle Gas Compressor	Modify/Replace	No Modification
Reactor Recycle Pump	Not Required	Required
High Pressure Gas Loop		
Charge Heater	Modify/Replace	No Modification
Feed/Effluent Exchangers	New Exchanger	No Modification
Gas Liquid Separators	Modify	No Modification
High Pressure Piping	Modify/Replace	Some Tie-Ins
Project Timing		
Project Implementation	Longer	Shorter
Plot Space Requirement	Greater	Lesser
Project Cost		
Equipment Investment	Higher	Lower
Project Fees	Lower	Higher
Total Project Cost	Higher	Lower

Capital and Operating Cost Comparisons

Consider a diesel hydrotreater revamp where both a 35% capacity increase and achieving more stringent specifications (such as <10 ppm sulphur) are targeted. The capital cost requirement with IsoTherming® technology is very competitive due to the reduced equipment count and the re-use of existing equipment. Additionally, the reduced equipment count results in a smaller plot space required. The footprint of an IsoTherming® design could be up to 4 times smaller than a conventional design. Maintenance cost savings arise since there is less complex machinery to overhaul during a shutdown. Operating cost savings for a particular diesel hydrotreater revamp included a 20% reduction in power consumption, more than 25% decrease on fuel gas use, about 4% reduction in cooling water and neutral stripping stream when compared to a revamp with the conventional technology.

Similar benefits in capital expenditure competitiveness, operating cost savings, ease of operation, reduction of plot plan and a safer process may also be achieved in revamps for Mild Hydrocrackers and FCC Pretreaters. The actual benefits will depend on the application, the type of feed, the unit constraints and operating strategy for each individual project. Table 3 provide details of licensees using IsoTherming® technology to meet their revamp project needs.

Table 3. List of IsoTherming® Revamp Projects as of July 2015

Location	Capacity (KTPA)	Application	Feedstock	Primary Unit Objectives	Status/ Startup Date
USA	190	ULSD Hydrotreater	LCO, SRD	Expansion, Desulfurization	April 2003 - Startup
USA	2,600	FCC Pretreater	VGO, AGO, HCGO	Expansion, FCC Pretreat	December 2010 - Startup
India	2,500	ULSD Hydrotreater	SRD, LCO, HCN	Expansion, Desulfurization	July 2015 - Startup
China	3,900	ULSD Hydrotreater	SRD, LCO, LCGO, RDS Diesel, HCN	Desulfurization	Construction
USA	2,300	ULSD Hydrotreater	SRD, LCO, LCGO, HCN	Expansion, Desulfurization	Process Design

Conclusions

For a variety of reasons, petroleum refiners will continue to need or desire to install additional hydroprocessing capacity. This additional hydroprocessing capacity can be achieved in a shorter period of time and in a more cost effective manner utilizing DuPont's IsoTherming® technology. This technology is applicable for a broad range of hydroprocessing applications that include sulfur reduction and upgrading among others. The technology provides the refiner with a flexible and efficient hydroprocessing system while meeting processing objectives. IsoTherming® technology is a cost-effective solution to meet sulfur specifications in an increasingly competitive and demanding environment.

References

[1] Michael D. Ackerson, M. Steven Byars, and J.B. "Bob" Roddey, "Revamping Diesel Hydrotreaters for Ultra-Low Sulfur using IsoTherming® Technology", NPRA Annual Meeting, 2004.