

REVAMPING DIESEL HYDROTREATERS FOR ULTRA-LOW SULFUR USING IsoTHERMING TECHNOLOGY

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ABSTRACT

Just over two years remain before refiners must meet the new ultra-low sulfur diesel (ULSD) specifications. Much has been learned about the chemistry of ULSD production since the EPA began discussing the new requirements.

This paper discusses the kinetic and hydrogen requirement barriers to ULSD production and the impact these barriers have on the design of a conventional unit revamp. Conventional revamps often require much of the existing equipment to be replaced due to hydraulic limitations associated with the necessary increase in total treat gas.

This paper also shows how the new IsoTherming^{TM1} technology can overcome the barriers to ULSD production in the most cost efficient way. Installed in a pretreat mode, IsoTherming allows the unit to be revamped without encountering hydraulic limitations in the existing conventional unit; thus, the refiner can minimize the capital required to meet ULSD specifications.

INTRODUCTION

Refiners have considered many options for producing on-road diesel to meet the new EPA mandate of <15 ppm sulfur:

- Construct grassroots facilities, typically at higher pressure;
- Revamp existing units: additional catalyst volume, high activity catalysts, new liquid distributors;
- Reducing straight run and cracked stock endpoints to reduce the difficult to remove sulfurs;
- Combination of revamp and endpoint reduction.

Some of the design issues associated with revamping a unit including high activity catalysts, increased reactor volume, increased hydrogen requirements and increased reactor exotherm, compound one another resulting in very costly revamp options. Even in a revamp, much of the existing equipment will need to be replaced.

In this paper will discuss the issues associated with revamping a diesel hydrotreater, with particular attention to the use of low pressure units, to maximize the utilization of existing equipment will be discussed. Also shown is how a new hydroprocessing technology, IsoTherming, can be utilized in a unit revamp and avoid most of the problems associated with the conventional processes.

REACTION BARRIERS TO PRODUCING ULSD

Much attention has been given to the difficulty in desulfurization of the 4,6 substituted dibenzothiophenes. The reaction rates for the sterically hindered 4,6 substituted dibenzothiophenes are extremely low. Therefore, to accomplish the desulfurization of these molecules with a reasonable volume of catalyst, a two-step approach to the desulfurization is more likely. The first step is the hydrogenation of one of the aromatic rings in the molecule, the second is the desulfurization of the saturated molecule which is much faster than the direct hydrodesulfurization on the sterically hindered 4,6 substituted dibenzothiophene.²

Catalyst vendors and others have also come to realize that many other factors influence the rate at which these difficult sulfurs are removed. Many of these factors are discussed by others.^{2,3,4} Some are important enough to the production of ULSD to warrant discussion here, including:

- Organic nitrogen content of feed
- Hydrogen consumption
- Aromatic equilibrium

Organic Nitrogen in ULSD Production

Organic nitrogen compounds are known to adsorb on the catalyst's active sites, blocking the sites from other hydroprocessing reactions because the hydrodenitrofication reactions are slow at typical diesel hydroprocessing conditions. This hydrodenitrofication rate is a very strong function of hydrogen concentration in the oil.^{2,9} In the production of LSD (<500 ppm), the blocking of a large fraction of the active sites is not a significant problem because the rate of direct hydrodesulfurization of most sulfur containing molecules is fast. However, the rate of desulfurization of the 4,6 substituted dibenzothiophenes and other related compounds either by direct hydrodesulfurization or hydrogenation of the aromatic followed by hydrodesulfurization is extremely slow. This slow reaction rate is compounded by the blocking of the catalytically active sites by the organic nitrogen compounds. Removal of the organic nitrogen can dramatically improve the activity of hydrotreating catalysts.^{2,7}

The hydrodenitrofication (HDN) reaction rates are dependent on the catalyst, the concentration of the reactive species (organic nitrogen and hydrogen), and reaction temperature. The Ni/Mo catalysts generally have higher denitrofication activity than the Co/Mo catalysts. The affinity of the organic nitrogen compounds for the catalytic sites has been reported as extremely high, and if the organic nitrogen concentration exceeds 20 ppm as much as 90 percent of the catalyst sites may be occupied.² Thus, the effect on the reaction rate for denitrofication by the organic nitrogen compounds is small since the compounds are already present on the active site blocking them from availability. This trend is shown in Figure 1.^{2,7}

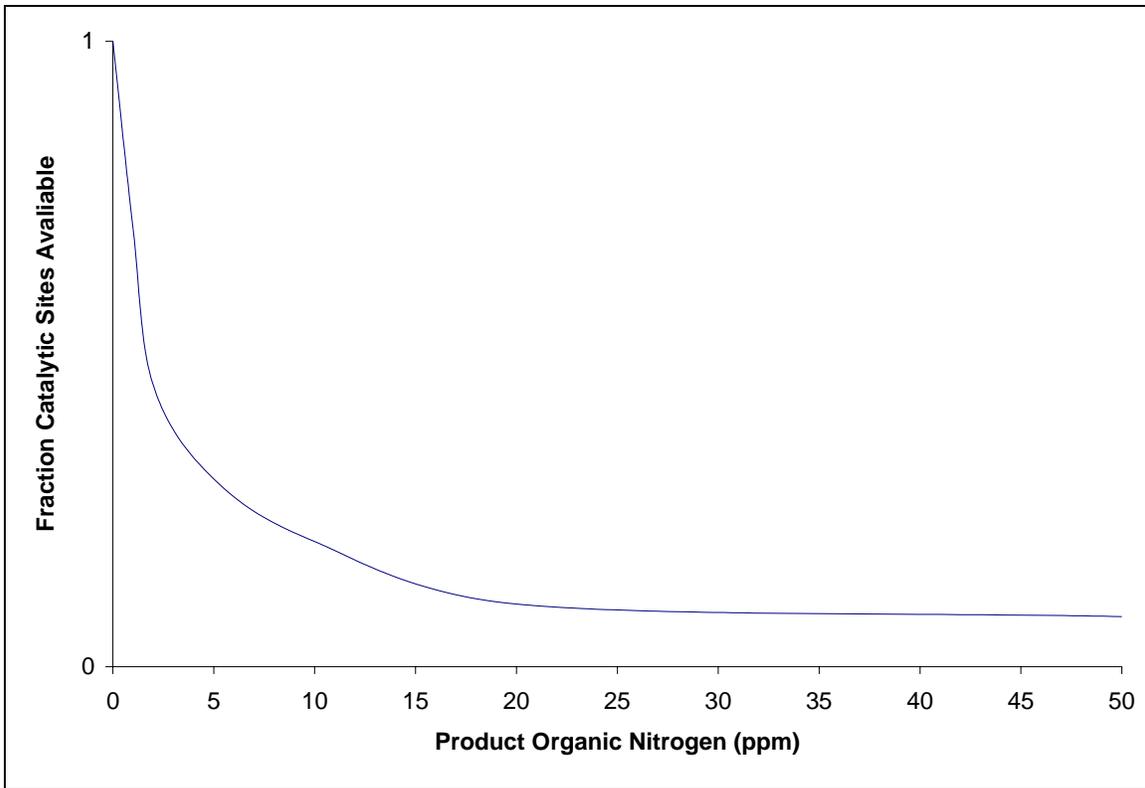


Figure 1: Catalytic Sites Available vs Product Nitrogen Content^{2,9}

The effect of temperature on reaction rates is well understood. The reaction rate increases exponentially with temperature.

The effect on the reaction rate of the dissolved hydrogen concentration is second order or greater. That is, doubling the hydrogen concentration in the liquid at the active site will increase the rate of hydrodenitrofication by a factor of 4 or more. This relationship is shown in Figure 2.^{2,9}

Reaction inhibition from the organic nitrogen is a severe problem for distillate hydrotreaters in ULSD service. The organic nitrogen in the feed and the partial pressure of hydrogen in the reactor greatly influence the performance of the catalyst utilized in ULSD production.

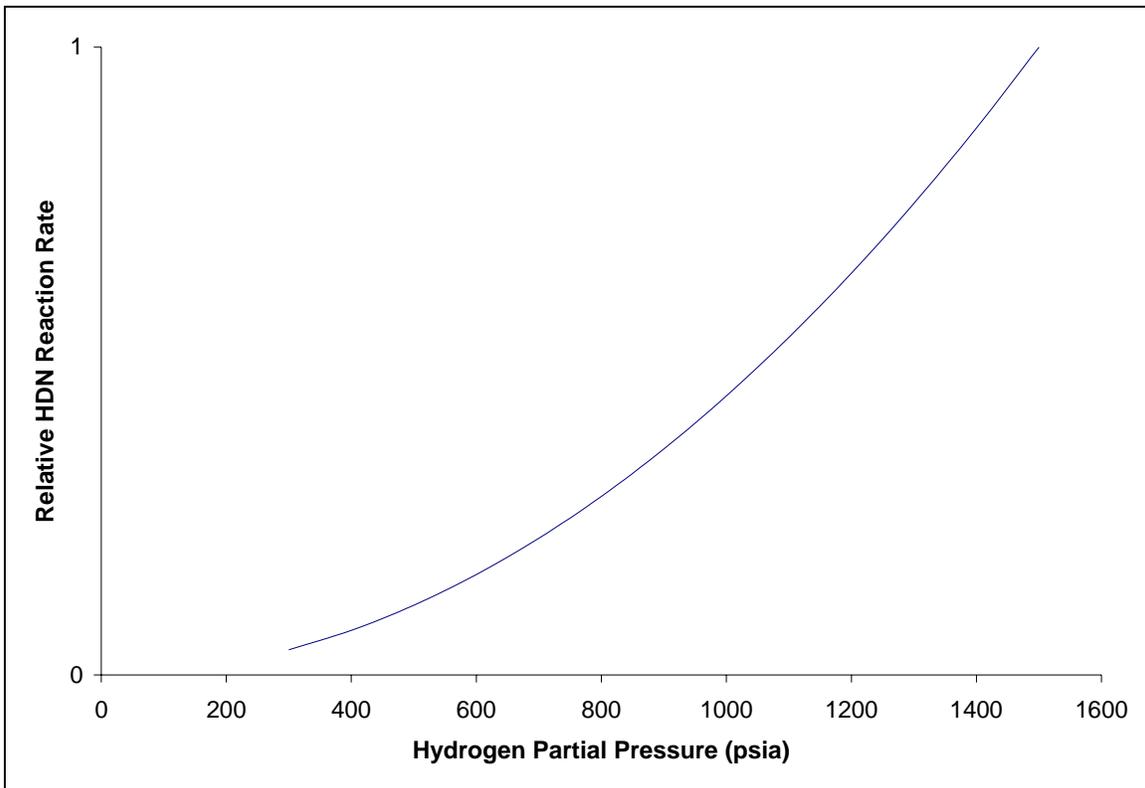


Figure 2: HDN Activity as a Function of Pressure^{2,9}

Hydrogen Consumption in ULSD Production

The chemical hydrogen consumption for the production of ULSD will be significantly higher than the consumption for low sulfur diesel production. Several factors influence the amount of the increased hydrogen consumption including:

- Catalyst selection for LSD vs ULSD
- Amount of cracked material boiling over 620° F in the feed
- Unit pressure
- LHSV

Many refineries chose to use Co/Mo catalyst in the production of LSD. The Co/Mo catalyst provided an effective route to sulfur removal in lower pressure units with the added benefit of lower hydrogen consumption since the Co/Mo catalysts have lower hydrogenation activity compared to the Ni/Mo catalyst. Moreover, the Co/Mo catalysts actually have higher activity for direct hydrodesulfurization and less organic nitrogen inhibition. Refiners with feed that contains a high amount of high boiling cracked material currently using Co/Mo catalyst will experience a large increase in hydrogen consumption when switching to Ni/Mo catalysts for ULSD production.

The amount of hydrogen required to remove the last 500 ppm sulfur is small, even considering the hydrogenation route to desulfurizing the substituted dibenzothiophenes with saturation followed by desulfurization. However, the other aromatics in the feed will be saturated along with the target molecules. In general, the level of aromatic saturation that is necessary to provide enough of the target molecule in the hydrogenated form for the removal of the sulfur to be accomplished is the same for any catalyst at any given reactor condition.

There is a balance between reactor temperature, which affects both reaction rates and the aromatic equilibrium (the fraction of the substituted dibenzothiophenes in the hydrogenated form), the liquid hydrogen concentration, aromatic concentration in the feed, and the residence time in the reactor (LHSV) which must be sufficient to accomplish the required desulfurization for ULSD. In designing a reactor this balance must be taken into account.

Incremental chemical hydrogen consumption is dependent on many factors, some of which were mentioned above. However, the increase in hydrogen consumption could be as little as 5 to 10 percent for a feed with little cracked stocks and little heavy material, to more than 150 percent for a feed with a great deal of heavy cracked material with typical increases between 40 to 100 percent.^{2,5}

Aromatic Equilibrium in ULSD Production

As previously mentioned, the direct route to hydrodesulfurization for the substituted dibenzothiophenes is extremely slow and not practical in general. The fact that the route is so slow gives rise to a “sulfur floor,” a sulfur amount which cannot be overcome by increase in temperature. Considering the effect of equilibrium on the fraction of substituted dibenzothiophenes in the hydrogenated form, the aromatic form is more favored at higher temperatures; at some temperature the increase in reaction rate is more than offset by the decrease in the hydrogenated form on the remaining aromatic sulfurs, so for a given reactor operating with a set hydrogen partial pressure and a given feed, there can be a point where increases in temperature will no longer produce a product lower in sulfur due to aromatic equilibrium competing with sulfur removal. This point is highly dependent on the concentration of the substituted dibenzothiophenes, the unit pressure, hydrogen partial pressure, catalyst activity, nitrogen content of feed, reactor exotherm and catalyst volume.²

DESIGN IMPACT OF REACTION BARRIERS IN ULSD PRODUCTION

Any technology that is to be successful producing ULSD must overcome the reaction barriers discussed above. As a result, the design must consider:

- Necessary nitrogen removal requires high pressure, large catalyst volume, or the elimination of difficult sulfurs from feed
- Increased hydrogen consumption requires additional make-up gas
- Additional catalyst volume is required
- Additional hydrogen quench is required
- Additional recycle gas is required
- Aromatic equilibrium and “sulfur floor” requires
 - increased catalyst volume
 - increase hydrogen partial pressure

REVAMP DESIGN BASIS

This revamp is for an existing unit processing 30,000 bbl/day of a feed consisting 55 percent straight run diesel (SR), 25 percent light cycle oil (LCO), and 20 percent light coker gas oil (LCGO). A summary of the feed is shown in Table 1. As seen in the table, the total sulfur and basic nitrogen in the blended feed are 1.17 weight percent and 148 ppm respectively. The 95 percent point is relatively high at 705° F.

Table 1: Design Feed Properties

	SR	LCO	LCGO	Blend
BPSD	16,500	7,500	6,000	30,000
API Gravity	34.5	14.8	32.7	28.5
Total Sulfur Wt. %	1.094	1.260	1.651	1.171
Basic Nitrogen ppm	14.5	261	334	148
D86 Distillation, ° F				
5%	472	436	368	441
10%	492	457	389	468
50%	552	569	529	557
90%	616	716	668	667
95%	635	756	699	705
Cetane Index	50.5	25.9	45.4	41.8
Sulfur Species, ppm				
Thiophenes	—	—	1,498	301
Benzothiophenes	5,978	4,805	10,984	6,413
Dibenzothiophenes	1,273	572	666	847
Methyl Dibenzothiophenes	2,391	1,694	1,250	1,710
Dimethyl Dibenzothiophenes	837	2,261	1,325	1,182
Trimethyl Dibenzothiophenes	453	1,664	692	777
Tetramethyl Dibenzothiophenes	20	1,623	89	480
Unidentified Volatile Sulfur				168

The unit is to be revamped to produce a product containing <8 ppm sulfur. The catalyst for the revamp is a high activity, new generation Ni/Mo catalyst. The revamp required catalyst life is two years.

A simplified process flow diagram of the existing unit is shown in Figure 3. Currently, the unit operates at 750 psig reactor inlet pressure and a LHSV of 2.3. The total treat gas rate is 1,600 SCF/bbl with a hydrogen purity of 78 percent. Make-up hydrogen purity is 89 percent. Current hydrogen consumption is 480 SCF/bbl when producing 350-400 ppm sulfur product.

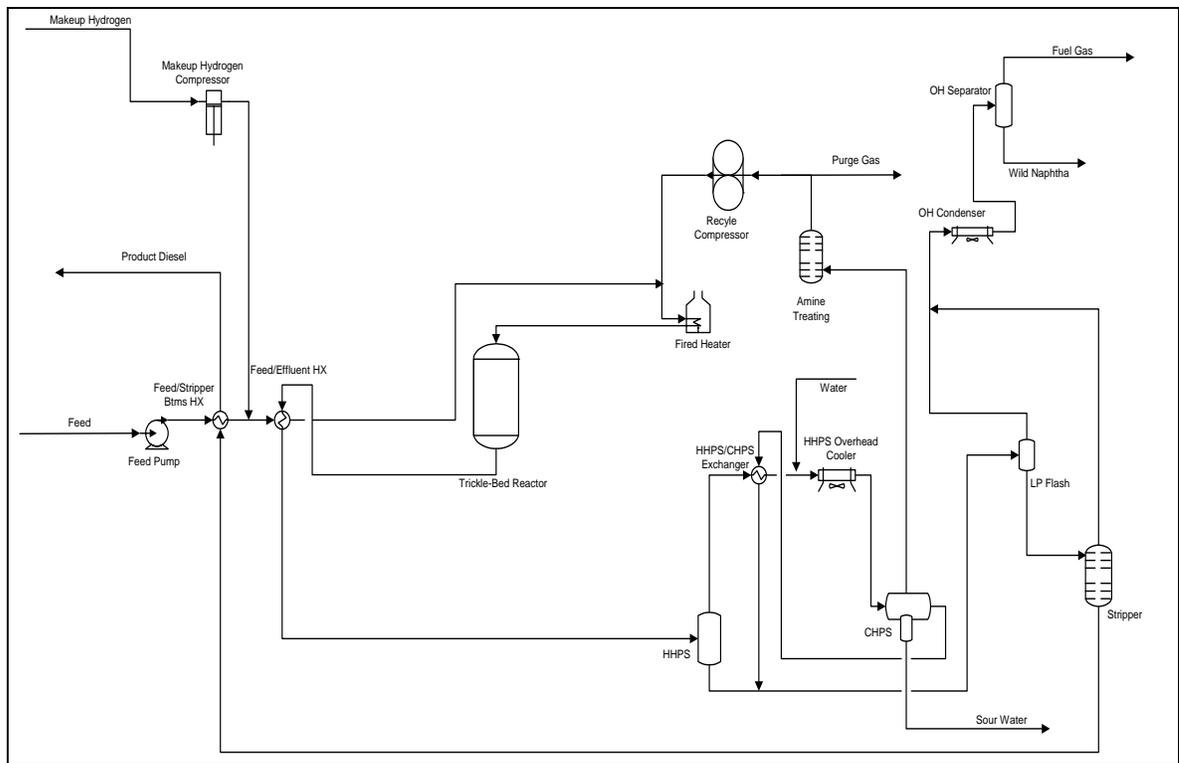


Figure 3: Simplified PFD of Existing Unit

CONVENTIONAL UNIT REVAMP

Reactor Volume

A number of recent publications discuss the increase in catalyst volumes necessary for producing ULSD.⁶ For this unit revamp a total LHSV of 0.6 was recommended by the catalyst vendor. A LHSV of 0.6 requires the addition of a second reactor containing 8,600 ft.³ of catalyst, 2.8 times greater than the existing reactor catalyst volume.

Hydrogen Consumption

Published data from catalyst vendors indicate that the hydrogen consumption increases significantly when producing 10 ppm sulfur product vs. 500 ppm sulfur product. Increases in chemical hydrogen consumption from 40 to 100 percent can usually be expected.^{6,7}

Estimated hydrogen consumption of 750 SCF/bbl, an increase of 56 percent, was provided by a catalyst vendor. Pilot plant studies were carried out in Process Dynamics' pilot facilities using the recommended LHSV. The measured hydrogen consumption was 780 SCF/bbl to achieve 10 ppm sulfur product.

Higher hydrogen consumption requires higher treat gas rate. Typical recommended treat gas rates are 3 to 4 times chemical hydrogen consumption. In addition, the higher consumption results in higher heat release. The increased heat release requires more quench gas to limit the temperature rise. The total treat gas rate for the unit revamp increased from 1,200 SCF/bbl to 2500 SCF/bbl at the reactor inlet. In addition, 950 SCF/bbl quench gas is required.

Major Equipment

Reactor

Figure 4 is a simplified process flow diagram of the unit revamp. The new equipment items are shown in red. In addition, the existing reactor internals were modified for more efficient reactor performance. Additionally, the amine treating was modified for the additional gas rate.

An additional trickle-bed reactor containing 8,600 ft.³ of catalyst must be added to provide sufficient catalyst for a LHSV of 0.6.

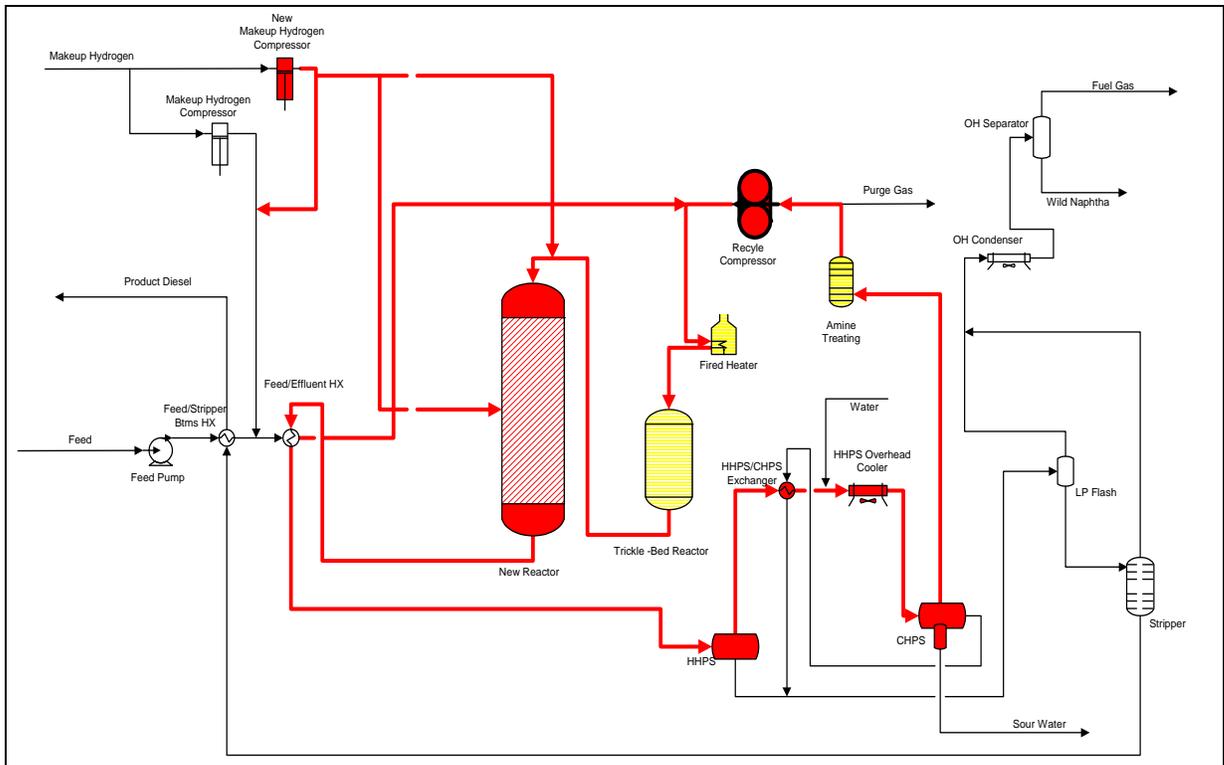


Figure 4: Conventional Unit Revamp

Makeup Compressor

A second makeup compressor was added due to the increased hydrogen consumption. The compressor was designed for 13.5 MMSCFD with a suction pressure of 265 psi and discharge pressure of 760 psi.

Recycle Compressor

Due to the increased pressure drop caused by a combination of increased catalyst volume and total recycle gas rate, a new hydrogen recycle compressor is required. The new compressor will handle 61.4 MMSCFD with a design suction pressure of 650 psi and discharge pressure of 760 psi.

Heat Exchange

Due to the increase flow in treat gas, new feed/effluent and HHPS/CHPS heat exchangers must be added along with a new HHPS offgas cooler.

Vessels

Due to hydraulic issues, new vessels will be required for both the hot high pressure separator and the cold high pressure separator.

Table 2 is a summary of the new equipment items. The estimated total cost for the conventional unit revamp is \$39 million (\$1,300/bbl).

Table 2: New Equipment for Conventional Unit Revamp

Equipment Item	Size
Reactor	19' diameter x 58' T/T
Makeup Compressor	13.5 MMSCFD
Recycle Compressor	61.4 MMSCFD
Feed/Effluent Exchanger	163 MMBTU/hr
Hot High Pressure Separator	10' diameter x 30' T/T horizontal
Cold High Pressure Separator	8' diameter x 24' T/T horizontal

ISO THERMING TECHNOLOGY REVAMP

Process Dynamics' IsoTherming is being used successfully in a 3,800 bbl/day diesel unit at Giant Industries' Gallup, N.M., refinery. The IsoTherming unit has been in operation since April, 2003.

Although developed by Process Dynamics, the technology has been commercialized by the consortium composed of Process Dynamics (Fayetteville, Ark.), Linde BOC Process Plants (Tulsa, Okla.), and Roddey Engineering Services (Shreveport, La.).

Because the IsoTherming technology has been discussed in some detail previously¹, only a brief overview will be presented here. The essence of IsoTherming technology is that all the hydrogen needed for the hydroprocessing reactions is dissolved in the liquid before contact with the catalyst. For most feed stocks, the hydrogen required is greater than the amount soluble at reactor conditions. Recycled product is used to dissolve the additional required hydrogen.

This technique has two main advantages as a stand-alone technology. First, there is no need to add all the processing equipment required to ensure good liquid distribution over the catalyst and a good mass transfer environment. Second, with the additional heat sink due to the liquid recycle the temperature rise across the reactors can be greatly reduced allowing for operation nearer to isothermal conditions. The closer a reactor operates to isothermal conditions, the longer the catalyst life.⁸

The IsoTherming technology has additional advantages as an add-on unit. For example, in a diesel hydrotreater revamp the IsoTherming section can be added as a pretreat unit at higher pressure since it can be completely isolated from the existing unit. The operation of the IsoTherming pretreat at higher pressure allows for the reduction in organic nitrogen and the saturation of the substituted dibenzothiophenes, and other aromatics. This allows the conventional reactor following the pretreat unit to operate in a low hydrogen demand environment, greatly improving its performance. Another advantage to IsoTherming as an add-on unit is that it can, for the most part, be constructed independently which results in less down time for the tie-ins of the revamp.

For an IsoTherming revamp, the IsoTherming unit is designed so that only minimal changes will be made to the existing equipment. The IsoTherming section must produce an intermediate product that meets organic nitrogen, sulfur, and aromatic content design targets. The IsoTherming pressure, catalyst volume, and hydrogen requirement are specified to satisfy these targets.

Hydrogen Consumption

Hydrogen consumption to meet ULSD for the design has been determined to be 800 SCF/bbl. In designing the unit the consumption is split with 600 SCF/bbl consumed in the IsoTherming unit and 200 SCF/bbl in the conventional unit. The exotherm associated with the hydrogen consumption is controlled by the feed temperature to the IsoTherming

unit, the recycle liquid rate, and the hydrogen addition. The unit is designed for a 30° F temperature rise across the IsoTherming reactors. The modest hydrogen consumption in the trickle-bed reactor produces an exotherm across the reactor of about 40° F so that no additional quench or treat gas is needed.

IsoTherming Reactor Volume

The IsoTherming catalyst volume and operating pressure are determined by the extent of reaction needed to produce the desired intermediate product that is fed to the conventional reactor. For the design case, the unit operating pressure is 1,350 psi with 1,400 cubic feet of catalyst split between two IsoTherming reactors.

The IsoTherming design conditions and intermediate stream properties are shown in Table 3.

Table 3: IsoTherming Design

Unit Pressure	1,350 psi
Total LHSV	5
Makeup Gas to IsoTherming	750 SCF/bbl
Catalyst	High Activity Ni/Mo
IsoTherming Liquid Product	
API	>33
Organic Nitrogen	<5 ppm
Total Sulfur	<500 ppm

Major Equipment

Figure 5 is a simplified PFD of the unit revamp with the new equipment marked in red and the minor modification marked in yellow. The IsoTherming section consists of a new makeup hydrogen compressor, a new feed heater, a booster pump with installed spare, two new IsoTherming reactors, and a new liquid recycle pump with installed spare. Modifications to the existing trickle-bed reactor distributor and trays are required. The major equipment items are summarized in Table 4. The total estimated cost for the IsoTherming unit revamp is \$21.8 million (\$750/bbl).

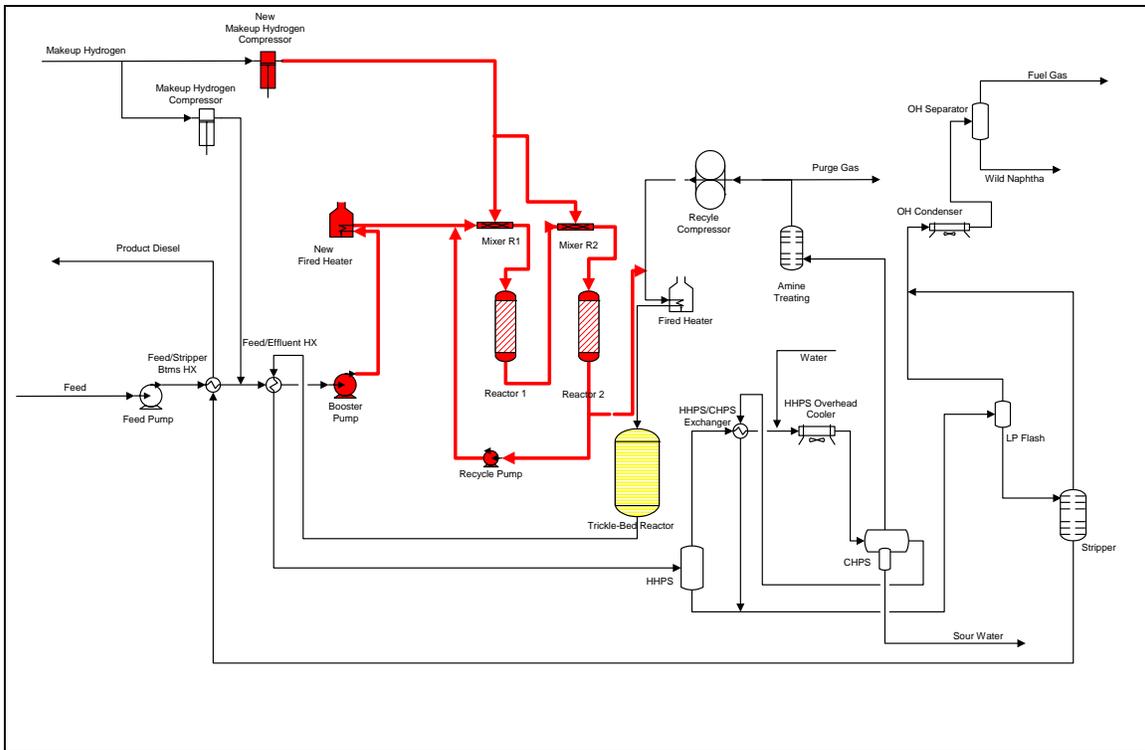


Figure 5: IsoTherming Unit Revamp

Table 4: New Equipment for IsoTherming Revamp

Makeup Hydrogen Compressor	265-1,500 psi	25 MMSCFD
(2) Booster Pump	750 psi-1,500 psi	30,000 bbl/day
Fired Heater	1,500 psi	37 MM BTU/hr
(2) Recycle Pump	1,450-1,500 psi	90,000 bbl/day
(2) IsoTherming Reactors	1,500 psi	7' diameter x 25' T/T
(2) Static Mixers		Inline 10'

SUMMARY

Some of the initial thinking on how to approach conventional unit revamps for producing ULSD was to simply add more catalyst volume to deal with removing the slow reacting and difficult 4,6 dibenzothiophene and related compounds. Although the statement is simple and has some merit, the practical application of the concept leads to a relatively complicated and expensive revamp. Much of the existing equipment must be replaced. Although the ultimate goal is ULSD, issues such as nitrogen inhibition, hydrogen consumption, and significant increased heat release actually determine the revamp design.

In this paper the integration of an IsoTherming unit into an existing conventional reactor to produce ULSD has been shown. The IsoTherming technology is the most efficient, low-cost approach to dealing with the barriers to ULSD production. The total cost of an IsoTherming revamp is 60 percent of a conventional revamp and can be integrated with less down time since there are only minor modifications to the existing system. Hydrogen consumption, nitrogen removal and heat removal are all accomplished by carrying out the reactions in a kinetically-limited liquid full reactor scheme. The existing conventional reactor is left for polishing. The IsoTherming approach allows the refiners to maximize the use of their existing equipment even when revamping low pressure units.

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