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ISOTHERMING – A NEW TECHNOLOGY FOR ULTRA LOW SULFUR FUELS

Presented By:

Ron D. Key
Director, Process
Engineering and
Technology Development
Linde BOC Process
Plants LLC
Tulsa, OK

Michael D. Ackerson,
Ph.D.
M. Steven Byars, Ph.D.
Process Dynamics
Fayetteville, AR

John Laurent
Technical Manager
Giant Refining Company
Gallup, NM

Jim Hallock
Project Manager
Giant Refining Company
Gallup, NM

National Petrochemical & Refiners Association

1899 L Street, NW
Suite 1000
Washington, DC
20036.3896

202.457.0480 voice
202.429.7726 fax
www.npra.org

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By:
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INTRODUCTION

In light of the new diesel sulfur requirements, and possible future requirements, the refining industry is faced with making decisions that affect its ability to stay in business and remain profitable. New concepts and technologies have been introduced to remove difficult sulfur species that make reaching the near zero sulfur requirements attainable. The proper technology selection depends on a number of factors. Many of these factors are unique to a given refinery.

Process Dynamics and Linde BOC Process Plants LLC (LBPP) have developed a new technology (1), IsoTherming. Analysis of the fundamentals of hydrodesulfurization in the context of trickle-bed reactor performance has led to this new technology that provides lower levels of sulfur in the diesel product stream at both reduced capital and operating costs when compared to competing technologies.

DRIVERS FOR TECHNOLOGY SELECTION

As new regulations are written, many projects must be undertaken simply to stay in business. However, to remain healthy, a business must make a profit. Unfortunately, producing ultra low sulfur diesel is usually not considered for its high rate of return on investment. Therefore, the best technology selection is a technology that allows the refiner to meet the mandated sulfur requirements at a total cost (capital and operating) that has the lowest negative impact on the refinery's profitability.

Refiners have indicated a few recurring points that are critical to their evaluation of technologies for production of ultra low sulfur diesel. These points are discussed below.

Meets Mandated Sulfur Requirements

Any technology selected must be able to meet the current sulfur regulations and provide an appropriate level of contingency such that ultra low sulfur diesel can be consistently produced.

Minimal Capital Investment

Refineries have had to spend capital resources on a recurring basis to remain operational. Over the last few years, the projects that are done to improve rate of return are far exceeded by projects that are required to become or remain environmentally compliant. Margins have been reduced and discretionary projects have virtually been eliminated thus reducing total available capital for any project. To be successful, an ultra low sulfur diesel technology must be able to be implemented with a reasonable, preferably low, capital cost relative to other alternatives. If this hurdle can not be met, then a refiner may have to make a serious decision about the future of the facility.

Minimum Plot Requirements

Most refineries are in locations where the boundaries are well established. There is often not plot space available for new equipment without demolition of existing units.

Minimum Impact on Operating Cost

- Minimum Additional Hydrogen Requirement

  In a hydroprocessing scheme, hydrogen is a necessity. The optimal hydrodesulfurization process will consume sufficient hydrogen to remove the necessary sulfur quantities and provide Cetane Index improvements with minimal increases in hydrogen demand. A significant increase in hydrogen demand will have to be compensated by either hydrogen stream upgrading (e.g. PSA or membrane unit) or the addition of an additional hydrogen-generating source either as a capital project or an over-the-fence purchase of hydrogen.

- Minimal Additional Staffing/Training Requirements

  The optimum technology will be more readily understood by operating personnel with minimal training and will not require significant (if any) additions to the operating crews.

Minimum Impact on Current Operation

The optimum technology will allow modifications/retrofits to be done with minimal downtime of the existing equipment and systems.

Product Improvement Where Possible

After some discussion, it appears sulfur removal is the most critical mandated fuel improvement. However, it is clear additional improvements will be required at a later date. A favorable technology will provide product improvements such as a reduced aromatic content and increased Cetane Index.

CHALLENGES OF DEEP DESULFURIZATION

Many authors (2, 3, 4, and 5) have written about the difficulties associated with deep desulfurization of diesel. Many factors influence the quantity and type of sulfur in the feedstock. Main factors that influence the degree of difficulty in removing sulfur include:

- Crude Source
- FCC Performance
- Quantity of the Light Cycle Oil (LCO)
- End Point of the Straight Run and Light Cycle Oil

The relative reaction rates of various sulfur species are shown in Table 1 (6). As seen in the table, the more difficult species, the substituted dibenzothiophenes, have the highest boiling points and are more prevalent in streams with high end points.

Table 1 (6)
Relative Reaction Rates and Boiling Points Of Various Sulfur Species

Sulfur Species	Relative Reaction Rate	Boiling Point, F
Thiophene	100	185
Benzothiophene	30	430
Dibenzothiophene	30	590
Methyl Dibenzothiophene	5	600-620
Dimethyl Dibenzothiophene	1	630-650
Trimethyl Dibenzothiophene	1	660-680

There are many ways to achieve sulfur removal of the more difficult molecules. Some of the most currently popular suggested and proven methods are (7):

- Replacing Current Catalyst with More Active Catalyst
- Higher Operating Temperature
- End Point Adjustment of the Feed
- Higher Purity Hydrogen Make-up or Increased Hydrogen Partial Pressure
- Adding Additional Reactor Volume (one or more reactors)
- H_2S Removal from the Recycle Gas
- Improving the Feed Distribution to the Trickle-bed (Conventional) Reactor

Depending on the needs of the refinery some of these alternatives may be economically viable to consider either individually or in combination. Another approach is to recognize the above as viable solutions, but also to step back and look at the mechanisms that really control hydrodesulfurization.

The basic hydrodesulfurization reactions are as follows:

Mercaptans: $RSH + H_2 \rightarrow RH + H_2S$
Sulfides: $R_2S + 2H_2 \rightarrow 2RH + H_2S$
Disulfides: $(RS_2) + 3H_2 \rightarrow 2RH + 2H_2S$

Thiophenes: $C_4H_4S + 4H_2 \rightarrow C_4H_{10} + H_2S$

Aromatics: $ArS + 2H_2 \rightarrow Aromatic + H_2S$ (excludes ring saturation)

Most of the hydrodesulfurization reactions are considered to be irreversible (8, 9, 10, 11, and 12). Aromatic ring saturation is a reversible reaction that is controlled by equilibrium (12).

Trickle-bed reactors, originally developed in the last century, have been used for a number of years in the hydrodesulfurization of diesel. Reactors are operated with large quantities of hydrogen circulating over the catalyst bed, up to 10 times the hydrogen required for chemical consumption. The vapor and liquid are mixed and passed through a distributor; as a result they are in equilibrium as they enter the catalyst bed. As the reaction occurs at the catalyst surface between the dissolved hydrogen and the reactive species in the feed, hydrogen is depleted from the liquid and must be replenished from the vapor phase.

DEVELOPMENT OF ISOTHERMING

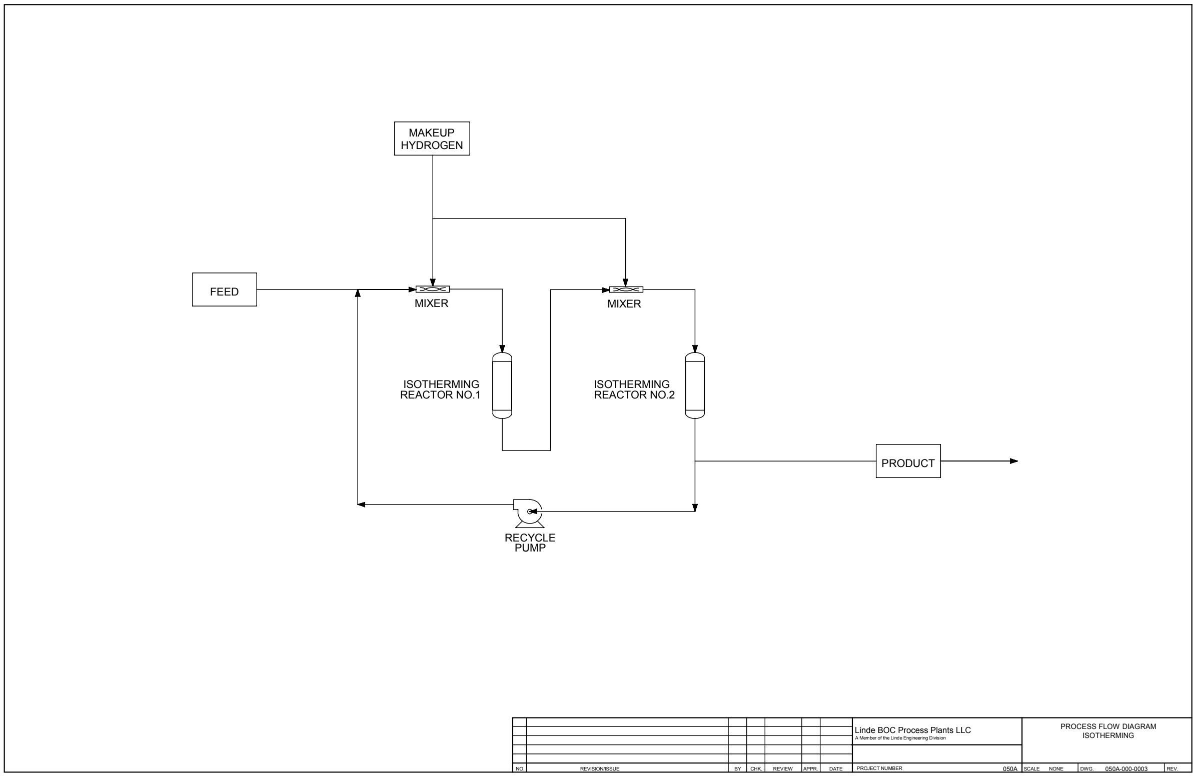
Understanding the important design and operating issues of a trickle-bed reactor led to the development of a concept for a process that moves the reactor performance more toward kinetic constraints. The hydrotreating process can be enhanced if all the hydrogen needed for the reaction is dissolved in the liquid before the liquid enters the catalyst bed. The supply of hydrogen is accomplished by saturating a combined feed and recycle stream, of previously hydrotreated liquid, with hydrogen. With all the necessary hydrogen in the liquid, the combined feed and recycle enters the catalyst bed where the reactions occur. The overall reaction is controlled by the intrinsic reaction rate (the product of the effectiveness factor of the catalyst and the actual reaction rate). An added benefit to the recycled product is its ability to contain the heat of reaction, hence the name IsoTherming.

Installed in the pre-treat position in an ultra low sulfur diesel application, the IsoTherming unit will account for 90-98 percent of the sulfur removal and 70-90 percent of the hydrogen consumption while containing only 15 to 30 percent of the total catalyst volume.

One important characteristic of an IsoTherming pre-treat retrofit is that it is disconnected from the existing reactor loop. Since the IsoTherming unit is not contained within the existing hydrogen recycle system, the pre-treat IsoTherming unit can be operated at higher pressure than the existing unit. The pre-treat IsoTherming configuration allows refiners with low-pressure units to add the enhanced performance of a high-pressure unit without having to upgrade the entire hydroprocessing unit to a higher pressure.

To test the IsoTherming process, a laboratory scale pilot plant was built. Figure 1 shows the basic process flow configuration of the pilot plant.

Figure 1
Pilot Plant Process Flow Configuration



Over the past six years, the theory has been tested and refined. Process Dynamics and Linde BOC Process Plants LLC decided that the technology was ready for demonstration on a commercial scale, and a commercial IsoTherming unit was planned.

APPLICATION OF ISOTHERMING

Once the IsoTherming technology was proven on a pilot scale, and to meet the fast approaching regulatory requirements, the need to quickly have a commercial scale unit operating with the IsoTherming technology was recognized. After careful consideration, Giant Refining was approached about installing an IsoTherming unit at their Ciniza Refinery in Gallup, New Mexico. Giant was a logical choice because Pro-Quip (predecessor of LBPP) had installed a 3,000-bbl/day diesel hydrotreater approximately ten years ago. Some of the same personnel along with all of the original drawings were available to make the retrofit of the IsoTherming technology into the existing unit easier.

Giant agreed to participate in the commercial development of IsoTherming. However, Giant greatly desired to increase the existing unit from its nameplate capacity of 3,000 bbl/day to 3,800 bbl/day and meet a 10 ppmw diesel product sulfur specification. The Giant feed is typical of many refineries, a 60/40 mix of straight run and LCO with a total sulfur content of approximately 2,100-ppm by weight.

The Giant unit has a few features the make achieving a 10 ppmw product sulfur specification difficult. The unit is a low pressure unit (900 psig design pressure, 705 psig separator operating pressure) and the unit does not currently remove the hydrogen sulfide from the recycle gas. The authors are not aware of any projects where a low pressure diesel hydrotreater unit has been retrofitted to not only meet 10 ppmw sulfur specification but also increase unit capacity without modifying the existing conventional trickle-bed reactor and support equipment (except for catalyst change out). Table 2 below summarized the original design conditions and variables along with the expected performance of the unit after it had been retrofitted with an IsoTherming pre-treatment unit.

Table 2

Comparison of Original Giant Design with the IsoTherming Retrofit

	Original Design	**Expected After Retrofit with IsoTherming**
Feed Rate, bbl/day	**3,000**	**3,800**
Trickle-Bed, LHSV	**2.3**	**3.0**
IsoTherming Unit, LHSV	**-**	**4.5**
Pressure at Cold Sep., psig	**705**	**665**
Make-up H_2 Purity, mol percent	**80.5**	**80.5**
H_2 Partial Pressure at Reactor Inlet, psia	**478**	**430**
IsoTherming, SOR inlet, °F	**-**	**620**
IsoTherming, SOR outlet, °F	**-**	**630**
Trickle-bed, SOR inlet, °F	**645**	**585**
Trickle-bed, SOR outlet, °F	**705**	**630**
Hydrogen Consumption, SCF/bbl	**250**	**350**
Product Sulfur Content, ppmw	**<500, normal 260 to 350**	**6**
Product Nitrogen Content, ppmw	**Not Available**	**2**
Cetane Index	**Not Available**	**53.6**

Samples of the straight run and light cycle oil feeds were forwarded to Process Dynamics who mixed the feeds in the appropriate 60/40 volume ratio and then performed pilot plant tests to predict the performance of the commercial unit. These results are also the basis for scale-up and design of the commercial equipment. The feed and product inspections are shown in Table 3 and the results of the pilot study are summarized in Table 4.

Table 3
Feed and Product Inspections of the IsoTherming System for Giant Refining

Description		SR	LCO	Feed	IsoTherming Product	Final Product
D-86, °F						
	IBP	386	433	414	387	389
	5 %	450	443	447	443	447
	10 %	482	449	469	462	467
	50 %	554	513	538	542	545
	90 %	634	629	632	638	637
	95 %	657	655	656	662	660
	EP	686	685	686	692	687
API Gravity, 60°F		37.1	25.4	32.8	33.9	35.6
Sulfur, ppmw		937	3,819	2,105	275	6
Nitrogen, ppmw		57	380	186	25	1
Cetane Index (D-4737)		58.7	33.0	47.4	49.5	53.6
Contaminants, ppmw						
	Tetramethyl Thiophenes	1	14	6	<1	<1
	Benzothiophene	<1	98	39	<1	<1
	Methyl Benzothiophenes	<1	449	180	<1	<1
	Dimethyl Benzothiophenes	15	630	261	1	<1
	Trimethyl Benzothiophenes	75	500	245	4	<1
	Tetramethyl Benzothiophenes	164	361	243	10	<1
	Dibenzothiophene	53	198	111	11	<1
	Methyl Dibenzothiophenes	167	535	314	66	<1
	Dimethyl Dibenzothiophenes	187	500	312	74	1
	4,6 Dimethyl Dibenzothiophene	39	74	53	32	2
	Trimethyl Dibenzothiophenes	135	250	181	55	2
	Tetramethyl Dibenzothiophenes	39	52	44	15	1
	Unidentified Sulfur	60	153	97	6	<1

Table 4

Pilot Test Results for a 60/40 SR/LCO Blend

Description	IsoTherming Unit	Trickle-Bed Reactor
LHSV, hr^{-1}	4.8	3.4
Pressure, psig	600	600
Temperature, °F	625	625
Feed Sulfur, ppmw	2,105	275
Product Sulfur, ppmw	275	6
Feed Nitrogen, ppmw	186	25
Product Nitrogen, ppmw	25	1
Hydrogen Consumption, SCF/bbl	275	75

Upon completion of the pilot plant studies, engineering began with several challenges to be met. Some of the more critical challenges were:

- Selection and Purchase of a High Temperature, High Pressure Recycle Pump
- Proper Injection and Mixing of the Hydrogen with the Diesel Stream
- IsoTherming Reactor Design
- Control Scheme to Provide Adequate Hydrogen
- The time of implementation of the new regulations is near, so a decision was made to go directly from the laboratory unit to the commercial unit. The commercial unit is 162,000 times larger than the laboratory unit.

Figure 2 presents a simplified process flow diagram of the diesel hydrotreater prior to the retrofit with IsoTherming technology.

Figure 2- Hydrotreater Prior to Retrofit with IsoTherming Technology

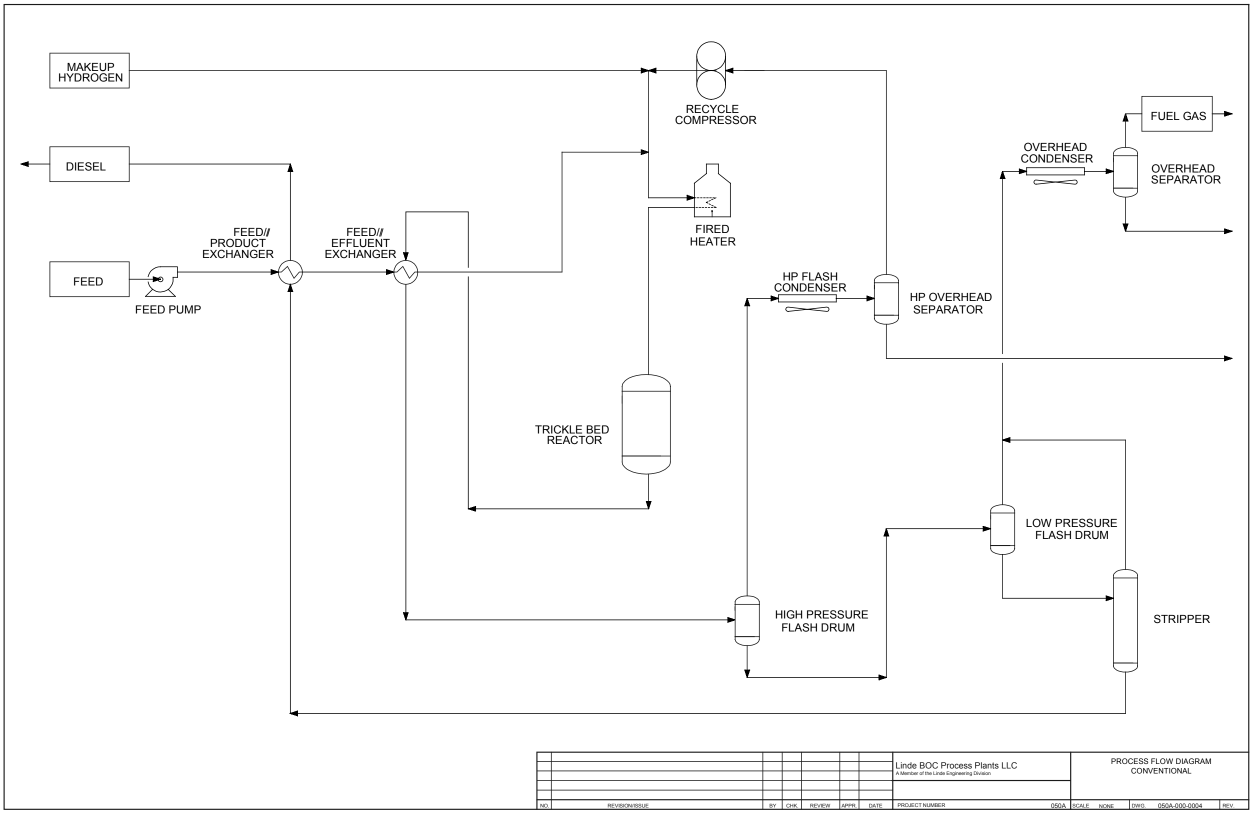
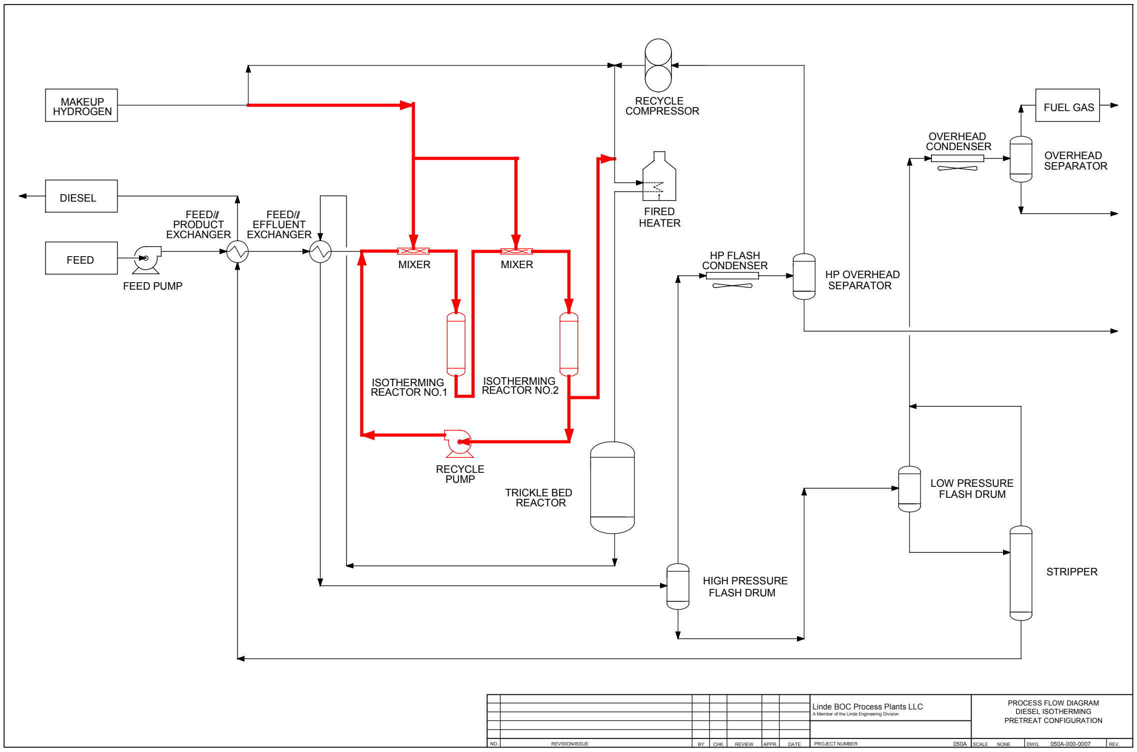


Figure 3 presents a simplified process flow diagram of the diesel hydrotreater after the retrofit with IsoTherming technology.

Figure 3 – Hydrotreater after Retrofit with IsoTherming Technology



The unit was engineered, designed and constructed in less than 12 months from the date of contract award. The plant is now in the start-up phase. Results of the effort will be forthcoming in the near future.

The following photographs below indicate the relative size of the IsoTherming unit at Giant's Ciniza Refinery.

Figure 4
The IsoTherming Unit Ready to be Set

Figure 5
The Reactors of the IsoTherming Unit

Figure 6
A View of the IsoTherming Unit Integrated into the Ciniza Refinery

HOW DOES ISOTHERMING STACK UP AGAINST THE DRIVERS FOR TECHNOLOGY SELECTION

Minimal Capital Investment

Based on the experience with Giant and detailed cost estimates, the estimated cost to the refiner (including catalyst and installation) of an IsoTherming retrofit to convert an existing 15,000 bbl/day diesel hydrotreater from a product outlet sulfur specification of 500 ppmw to 10 ppmw is about $300/bbl.

Minimum Impact on Operating Cost

Any hydrotreating process will require more hydrogen to meet the ultra low sulfur requirements. IsoTherming is no different. The Giant unit requires an increase of 100 SCF/bbl of hydrogen to meet the ultra low sulfur specification.

The additional operating cost of the IsoTherming unit is summarized in Table 5 below.

Table 5
Summary of Incremental Utility Requirements
For the Retrofit Giant IsoTherming Unit

Description	**Assumed Unit Cost (13)**	**Annual Cost, $/year**	**Percentage of Annual Cost**
Hydrogen	**$4.00/MSCF**	**$547,200**	**92**
Electricity	**$0.045/kWH**	**15,552**	**3**
Cooling Water	**$2.00/1,000 Gallons**	**10,368**	**2**
Annualize Catalyst Replacement	**-**	**20,000**	**3**
Total Incremental IsoTherming Cost	**-**	**$593,120**	**100**
Credit for Increased Volume	**$30.00/bbl**	**($205,200)**	
Total Incremental IsoTherming Cost		**$387,920**	
Total Incremental IsoTherming Cost		**$0.284 per barrel of feed**	

Of the total incremental cost increase, 92% of the cost is for hydrogen consumption. Additional hydrogen consumption will occur with any hydroprocessing unit to reach 10-ppmw sulfur from the original 500-ppmw of sulfur specification.

The IsoTherming technology was readily accepted and understood by operating personnel with minimal training and did not require any additions to the operating crews.

Minimum Plot Requirements

The 3,800-barrel per day IsoTherming retrofit required a plot space of 14 X 20 feet. It is estimated a 15,000-barrel per day IsoTherming retrofit will require a plot space of approximately 600 square feet.

Minimum Impact on Current Operation

The expected down time for the Giant refinery retrofit was less than one week plus the usual time for catalyst sulfiding.

Product Improvement Where Possible

The Cetane Index of the Giant product increased by a nominal 5 to 7 points over that of the feed, while the nitrogen content was reduced to nearly zero.

Meets Mandated Sulfur Requirements

The entire team is convinced the modified IsoTherming unit will exceed the requirements for ultra low sulfur diesel.

CONCLUSION

It is clear the IsoTherming technology has merit for consideration in refinery retrofits for the production of ultra low sulfur diesel. For Giant, IsoTherming provided the opportunity to meet the mandated sulfur requirements for a low pressure hydrotreater while simultaneously increasing capacity.

The IsoTherming technology allows the engineering, design, construction and operation of a unit that:

- Minimizes Capital Investment
- Minimizes Impact on Operating Cost
- Minimizes Plot Requirements
- Minimizes Additional Hydrogen Requirement
- Minimizes Impact on Current Operation
- Provides a Product Improvement Over Previous Operation
- Minimizes Additional Staffing/Training Requirements
- Meets Mandated Sulfur Requirements
- Ability to Retrofit a Low Pressure Unit with a High Pressure Retrofit

ACKNOWLEDGMENT

The authors wish to thank all of the many participants who worked to make the IsoTherming process viable for today’s needs.

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