Investigate Your Options

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ABSTRACT

This paper will investigate how computer aided simulation tools may be used to evaluate the existing acid gas handling systems as well as potential modifications in these units. In particular, the benefits of changing amines, debottlenecking sulfur plants, oxygen enrichment, tail gas treatment options and general rules for optimizing these units will be reviewed. As a rule, it is always wise to determine the operational efficiency for each unit before any major modifications are initiated. This will hopefully prevent a new design from failing due to previously undetected internal or other problems.

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INTRODUCTION

Today's refiners face the daunting task of complying with recently issued regulations set forth to ensure the production of ultra-low sulfur diesel fuel (ULSD). A majority of the efforts thus far to ensure compliance with these standards has been focused on the technology available for the removal of the additional sulfur from the fuel. Although the incremental amount of additional sulfur removed is small compared to the total, an equally important issue is the manner in which this additional sulfur is processed since the sour gas treating facilities at most refineries are at or near capacity. The costs associated with producing ULSD will be substantial in most cases; however, through the use of simulation technology, refiners may investigate and implement optimal operating conditions in the amine sweetening and sulfur recovery facilities. This paper will investigate how computer aided simulation tools may be used to evaluate the existing acid gas handling systems as well as potential modifications in these units. In particular, the benefits of changing amines, debottlenecking sulfur plants, oxygen enrichment, tail gas treatment options and general rules for optimizing these units will be reviewed. As a rule, it is always wise to determine the operational efficiency for each unit before any major modifications are initiated. This will hopefully prevent a new design from failing due to previously undetected internal or other problems.

BACKGROUND

Emissions regulations are not foreign to the petroleum industry. In fact, for the past three decades refiners have been forced to significantly alter gasoline formulations in an effort to reduce tailpipe emissions. With the ever-increasing popularity of diesel engines in the commercial and personal sectors, diesel fuel is now being scrutinized and regulated with much of the same fervor. The most commonly recognized diesel sulfur specification worldwide is 500 ppm1. However, according to the United States Environmental Protection Agency (EPA), this standard will not suffice when high-efficiency catalytic exhaust emission control devices are implemented in 2007. Ultra-low levels of sulfur in diesel fuel will be necessary for these devices to function properly2. As a result, the United States along with many other industrialized regions are proposing and implementing revised sulfur specifications.

- The United States EPA will require a 97 percent reduction in the sulfur content of highway diesel fuel from its current level of 500 ppm to 15 ppm. The fuel provision will go into effect in June 2006 and will be phased-in through 20093.

- The European Union (EU) indicates that a specification of 50 ppm will be imposed in 2005.
- Over the next ten years, Japan will gradually reduce the sulfur content in diesel fuel to 50 ppm.
- Swedish Class 1 diesel is already at a limit of 10 ppm1.

To comply with these regulations, refiners are being forced to make a number of changes. The National Petrochemical & Refiners Association predicts that refineries will invest approximately $11 billion in capital expenditures to comply with on and off-road diesel sulfur specifications4. Since the costs of compliance are enormous compared to the potential return, it is essential that refiners thoroughly investigate any and all options, including the sour gas handling system, to make the transition to ULSD as economical as possible.

The relative amount of additional sulfur to be produced from current levels down to 15 ppm for a known produced quantity of diesel is very small in terms of volume of liquid sulfur product. However, the ability to recover the additional H2S and process it to liquid sulfur may require significant changes in operational variables. The overall impact on a specific refinery varies based on the throughput and sulfur content of crude processed. For refineries that process high sulfur crude, the increase may be minimal versus current production. However, for refiners that are at capacity in their sour gas facilities or that process sweet crude, these changes could substantially increase the total sulfur recovery rate. It is for these refiners that the largest strides must be taken to ensure future compliance.

WHAT ARE THE OPTIONS?

In the sour gas handling system, the major units which may be impacted include the amine sweetening units, sulfur recovery plants and tail gas cleanup units. The options for processing the additional loads in each of these units are discussed below. One of the first items to consider when evaluating the sour gas handling system is the hydrogen loop.

- Is there sufficient capacity or volume to effectively manage the hydrotreating requirements? This single item has a direct impact on the amine system and subsequent sulfur recovery and handling equipment.
- If possible, can the hydrogen loop be operated at a higher pressure to obtain more volume or throughput of hydrogen.
- If no additional volume of hydrogen is available, then what alterations are possible relative to the amount of hydrogen that is treated by the amine?

Typically, refiners prefer to process a higher percentage of hydrogen with the amine system to reach an overall sulfur specification in the hydrotreated fuels. To accomplish this, the capacity and efficiency of the current amine system should be carefully studied.

For any amine system (Figure 1) there are process parameters that govern the range of use and applicability. Every refiner typically has its own set of best practices regarding acceptable rich and lean loadings for proper operation. Before any changes are made upstream of the amine unit, it is an absolute necessity to ensure that the unit is operating efficiently and as expected for the current conditions. Every step must be taken to evaluate and verify performance in order to avoid any costly mistakes. Even if a unit is currently meeting specification, it may be operating well below its optimal level.

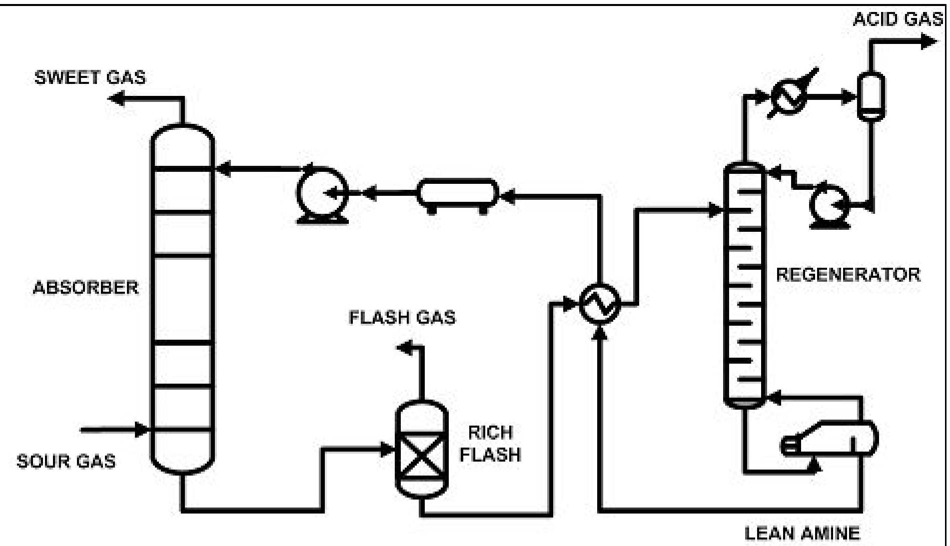

Figure 1- Simple Amine Sweetening Facility

Assessing an existing unit can be quite difficult. A good process simulation program offers significant assistance when studying existing facilities and diagnosing problems within a single unit or network of units. The simulation program should be capable of predicting the performance of a unit for a known set of operating parameters. The simulator should also be of assistance in determining the difference between predicted versus actual performance of the facility. Tower internal problems or bottlenecks that are not apparent are often culprits of sub-optimum operation. Through computer simulation, refiners have the ability to investigate all facets of the units in detail and adjust operating parameters so that optimal levels may be readily achieved.

For example, in a case where a facility is processing larger volumes of hydrogen recycle gas; there are a number of factors to consider. The first concern is the capacity of the current absorption towers and their ability to process the larger volume of recycle gas. If the towers are too small to handle the additional volume, a new tower will be needed. Similarly, you must have the equipment capacity on the liquid side to accommodate potentially higher volumes of amine solvent, particularly with respect to the cross exchangers, reboilers, and coolers.

Another option that could yield extended benefits beyond the amine system is to explore different amine solvents. While all amines have their place and may be adequate for a number of applications, some are definitely more attractive than others if the luxury of choice is available. Monoethanolamine (MEA) and diethanolamine (DEA) have been staple amines for most refiners for many years. Over the past 10 years, the use of methyldiethanolamine (MDEA) based solvents has grown significantly due to its lower economic impact and decreased circulation rates. These favorable attributes are due largely to the MDEA based solvent's ability to operate at a higher weight percent and to slip CO2. Because there is more amine per given volume of solution, the total volume of solvent required is effectively reduced. Tertiary amines such as MDEA also require less heat duty for stripping the acid gas, which provides significant economic returns over the primary and secondary amines. In addition to the proven economic benefits, tertiary amines also offer lower solution degradation rates, which translate into reduced solvent make up rates that further impact the bottom line. Switching to an MDEA based amine solution also enhances the acid gas absorption by rejecting CO2, thus lowering the volume of acid gas to the sulfur plant. This single item alone provides additional benefits for the sulfur plant and subsequent tail gas treatment unit. If either of these downstream units is bottlenecked under the current operating conditions, more capacity is now available to reduce the load.

If unable to choose an alternative amine, there are other options to consider that may increase the acid gas carrying capacity. Operating the current amine system at higher overall rich loadings will provide some incremental capacity. Additional margin may also be found by increasing the strength of the amine solvent. By increasing the weight percent amine, you can also gain some processing capacity. Other operational issues such as lean amine temperature can also help to load the solvent to higher levels, again providing some incremental processing capacity. It is truly an incremental change in the amount of acid gas removed from the diesel. Given that fact, one should give significant thought to these seemingly small areas as places to gain capacity. These options are all very favorable when compared to the capitol cost of building another unit.

In the sulfur recovery unit (Figure 2) there are also a number of concerns. Again, a thorough investigation of the current system is imperative before any system changes are implemented. The existing equipment has capacity limitations that should be determined for each sector. Is the unit capable of handling the new feed compositions from the amine system? Can the unit process the new volume and composition of the acid gas stream? Again, a thorough investigation of the facility with a computer simulation tool will help in determining these limitations. Upon completion of this task, one may begin to investigate scenarios for improvement. Some of the available enhancement options include: the addition of another catalyst bed, oxygen enrichment of the air feed to the burner, and better control of reheater and condenser temperatures. A process simulator can easily determine the reheater temperature necessary to maintain the best possible reactor bed temperature, resulting in optimal H2S conversion. Another benefit of using simulation tools for optimizing or troubleshooting sulfur plants is their ability to calculate the sulfur dew point in every piece of equipment. This enables precise determination of catalyst bed exit temperatures to obtain the best possible H2S conversion and subsequent liquid product. Depending on the type of tail gas cleanup unit employed, if any, the H2S to SO2 ratio in the tail gas is extremely important. It is very common in refineries today to find ratio controls in the sulfur plant tail gas for maintaining the proper air feed to the Claus plant, resulting in efficient and optimum conversion. Each of these items must be considered to ensure the best overall solution and hopefully prevent the need for building another plant.

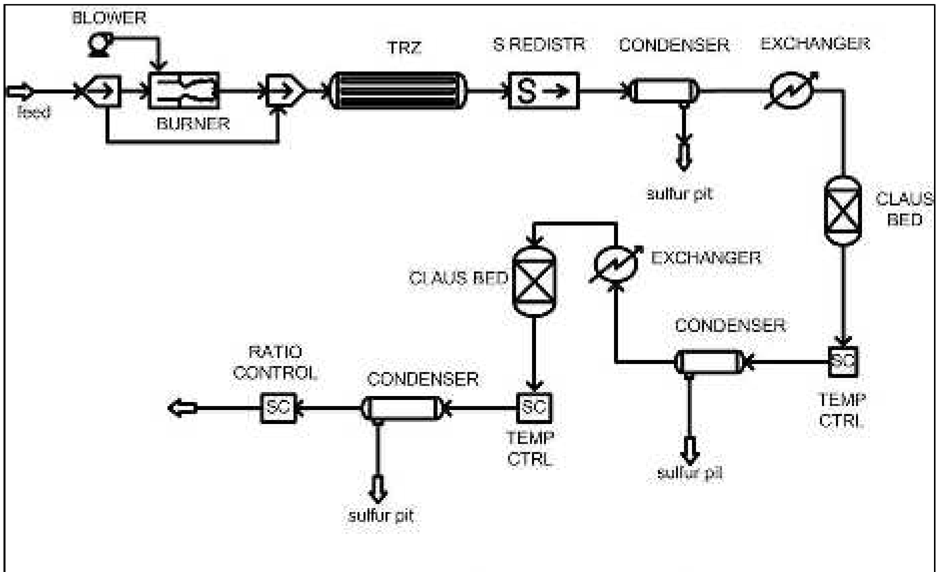

Figure 2 - Two Bed Sulfur Recovery Plant

The final conversion step in the tail gas treatment unit is equally important. The purpose of this step is to polish the remaining acid gas stream of H2S. Most prevalent in industry are direct oxidation and amine based systems. Direct oxidation units convert the remaining H2S from the Claus plant directly to sulfur via a specialty catalyst. For this system, much of the same discussion for Claus plants also applies to the operation of this specialty bed.

Also important to the amine based systems (Figure 3) is proper operation of the sulfur plant to prepare the feed to the tail gas unit as best as possible. For systems with very high required sulfur recovery, a hydrogenation unit prior to the amine system may be necessary for complete conversion of sulfur species back to H2S. Some common historical practices at refineries have been ones of little concern for optimum performance of the sulfur plant due to the presence of the tail gas cleanup unit. It should be an area of great attention. Operating each subsequent unit at a defined optimum provides benefit to all downstream applications. Small improvements in Claus performance yields increased capacity for the downstream tail gas unit. This is true from the primary amine system forward.

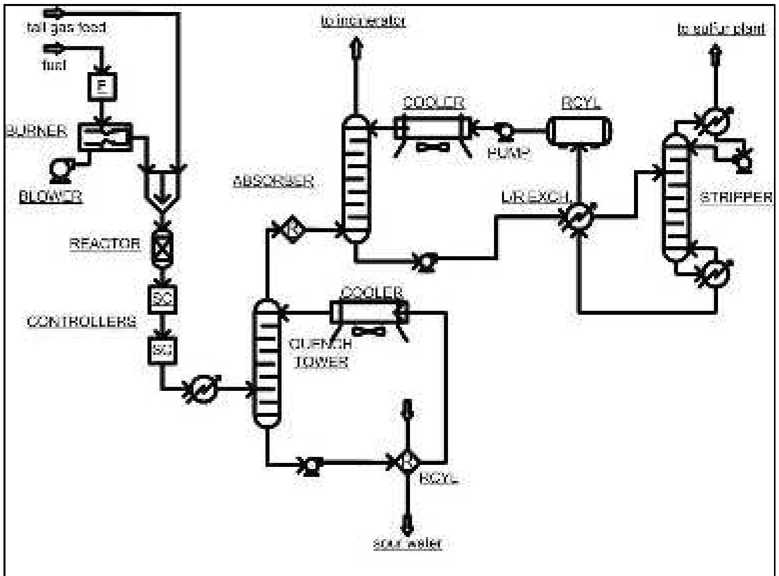

Figure 3. Tail Gas Cleanup Unit

CONCLUSION

While most written text to date on ULSD fuels has been on methods for removal of sulfur from fuel, there are other important processes impacted that must be investigated. This paper has shown some ways to increase system capacity without significant capital expenditure. Particularly in refining applications, it is important to operate the amine and sulfur systems in a most efficient manner due to the increasing loads placed on them. Granted, the technology for sulfur handling systems may not be as glamorous, it is equally important. For if you are unable to process the additional sulfur removed, what have you accomplished? The two seemingly very different processes are indeed directly linked.

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