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Thermal DeNOx Optimization: A Case Study in Fluid Catalytic Cracking

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THERMAL DENOX OPTIMIZATION:
A CASE STUDY IN FLUID CATALYTIC CRACKING

by: David E. Rozier III

A thesis submitted to the faculty of the University of Mississippi in partial fulfillment of
the requirements of the Sally McDonnell Barksdale Honors College

Oxford
May 2017

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Reader: Dr. Wei-Yin Chen
This thesis is dedicated to my late grandfather, David E. Rozier, Sr., who was fond of saying, “A job worth doing is a job worth doing well.”
Acknowledgments

First and foremost, my completion of this thesis would not have been possible without the love and support of my family and friends, especially my parents, Dave and Jackie Rozier. I would like to thank Dr. Adam Smith, Dr. John O’Haver, Dr. Wei-Yin Chen, and Mr. David Carroll for their feedback and encouragement. I would also like to thank ExxonMobil for affording me the opportunity as an intern to conduct this project work and granting me permission to publish technical details. Finally, I must thank all of my coworkers in Operations Support at the Baton Rouge Refinery for their assistance with the project discussed here.
Abstract

This thesis will first provide background information on fluid catalytic cracking (FCC), a highly important unit operation to the process of petroleum refining, and a description of Thermal DeNO\textsubscript{x}, an environmental treatment system common to FCC units and other process units where high temperature furnaces are used. Next, this thesis will detail a project which I had the chance to lead as a process engineering intern at ExxonMobil’s Baton Rouge Refinery in the fall of 2016. The objective of the project was to optimize Thermal DeNO\textsubscript{x} systems installed on two FCC units at the refinery. Experiments were conducted on these units at different chemical injection rates and temperatures, in order to determine the operating parameters at which the Thermal DeNO\textsubscript{x} systems were as efficient and economical as possible. A control scheme was implemented on the unit to maintain operation at these experimentally determined parameters, with a projected economic benefit of $250,000 per year for the refinery. This thesis also includes a discussion of my personal learnings and takeaways from this experience, including the challenges one can face when leading an engineering project in an industrial manufacturing setting.
# Table of Contents

Introduction.........................................................................................................................1

Case Study: FCC Thermal DeNO\textsubscript{x} Optimization.................................................11

  Background......................................................................................................................11

  Methods.........................................................................................................................12

  Results and Discussion...............................................................................................16

Conclusion.......................................................................................................................24

Bibliography....................................................................................................................25
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1</td>
<td>A Typical High-Conversion Refinery: Simplified Process Flow</td>
<td>3</td>
</tr>
<tr>
<td>Figure 2</td>
<td>Simplified FCC Process Flow</td>
<td>4</td>
</tr>
<tr>
<td>Figure 3</td>
<td>Regenerator Flue Gas Treatment: General Layout</td>
<td>6</td>
</tr>
<tr>
<td>Figure 4</td>
<td>Temperature Effect of H$_2$ on Thermal DeNO$_x$</td>
<td>10</td>
</tr>
<tr>
<td>Figure 5</td>
<td>PCLA CO Furnace Process Flow</td>
<td>11</td>
</tr>
<tr>
<td>Figure 6</td>
<td>Effect of Regenerator CO Percent on Thermal DeNO$_x$ Efficiency</td>
<td>17</td>
</tr>
<tr>
<td>Figure 7</td>
<td>Effect of Hydrogen Injection on Thermal DeNO$_x$ Efficiency</td>
<td>17</td>
</tr>
</tbody>
</table>
## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>COF</td>
<td>carbon monoxide furnace</td>
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<tr>
<td>DeNO$_x$</td>
<td>nitrogen oxide removal/destruction</td>
</tr>
<tr>
<td>FCC</td>
<td>fluid catalytic cracking</td>
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<tr>
<td>KGO</td>
<td>coker gas oil</td>
</tr>
<tr>
<td>LPG</td>
<td>liquefied petroleum gas (primarily propane)</td>
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<tr>
<td>NH$_3$</td>
<td>ammonia</td>
</tr>
<tr>
<td>NO$_x$</td>
<td>nitrogen oxides</td>
</tr>
<tr>
<td>OPEX</td>
<td>operating expenses</td>
</tr>
<tr>
<td>PCLA</td>
<td>powdered catalyst unit of Louisiana (ExxonMobil FCC unit)</td>
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<tr>
<td>PGO</td>
<td>process gas oil</td>
</tr>
<tr>
<td>SNCR</td>
<td>selective non-catalytic reduction</td>
</tr>
<tr>
<td>SO$_x$</td>
<td>sulfur oxides</td>
</tr>
<tr>
<td>Vppm</td>
<td>volumetric parts per million (measure of concentration)</td>
</tr>
<tr>
<td>WGS</td>
<td>wet gas scrubber</td>
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<tr>
<td>WHB</td>
<td>waste heat boiler</td>
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</tbody>
</table>
Introduction

The development of the fluid catalytic cracking (FCC) process was critical to the success of the petroleum refining industry in the 20th century, and the process remains important today. Following the Industrial Revolution, including the invention of the automobile, petroleum refiners faced a challenge – to match the volume demand for petroleum products with the volume composition of crude oil. The volume demand for gasoline had begun to increase much more rapidly than the volume demand for fuel oil, making the heavier fractions of crude less valuable. Interestingly enough, refiners faced the opposite problem in the 19th century, and it was common practice then to dump excess gasoline while processing the crude oil required to meet fuel oil demand. With petroleum refiners seeking a solution that limited waste of crude oil resource, engineers worked to develop methods to convert the heavier fractions of crude into gasoline-range molecules [2].

The first commercial operation that successfully addressed this economic challenge facing the petroleum industry was the Houdry unit, started up in 1937 by Sun Oil [4]. Named after the French inventor, Eugene Houdry, this unit relied upon a semi-batch catalytic cracking process, enabling the large, heavier crude oil molecules to be cracked into smaller gasoline-range molecules in the presence of a powdered catalyst. The catalytic cracking reactions deposited coke (carbon) onto the catalyst and required manual removal and restoration of the deactivated catalyst for each batch. Soon after the startup of the Houdry unit, Standard Oil began an effort to develop a continuous catalytic
cracking process, culminating in 1942 with the startup of the first ever commercial FCC unit, PCLA-1, in Baton Rouge, LA. This continuous process was made possible by fluidizing the powdered microspherical catalyst via the addition of sufficient gas, allowing the catalyst particles to flow as a fluid and be continuously regenerated. Following this success, refiners worldwide began utilizing and improving upon similar processes. The success of this FCC unit in converting the lower volume demand fractions of crude into higher volume demand fractions (gasoline) became a key factor in profitability for petroleum refiners. Today, nearly 50% of all gasoline produced comes through FCC and ancillary units [4].

In order to understand how an FCC unit fits into the refining process, it is helpful to understand the general process flow of a typical modern refinery. The refining process begins with the crude unit, where crude oil (raw feed) is separated via distillation into various fractions according to boiling point, before being sent to intermediate units for further processing (see Figure 1). The FCC is typically fed process gas oil (PGO) from the crude unit as well as coker gas oil (KGO) from the coker, a thermal cracking unit. Gas oil is typically defined as the fraction of crude oil with a boiling point between 450\(^\circ\)F and 800\(^\circ\)F [2]. Again, the value of the FCC is in its ability to selectively convert these low-value feeds into high-value products. The final products from the FCC and ancillary units include LPG, gasoline, and various fuel oils. Conveniently, adjustments to FCC product fractionation can be made in order to shift product yields in accordance with seasonal demand, a common practice for modern refiners [2].
Fig. 1. A Typical High-Conversion Refinery: Simplified Process Flow [4]
A simplified process flow for a typical FCC unit is shown in Figure 2. The main components of the FCC include the riser, disengaging vessel (“reactor”), regenerator, and fractionator. As fresh feed enters the unit, it is mixed with recycle from the fractionator (cycle oil) and fresh catalyst from the regenerator. Cracking reactions take place in the riser as soon as the feed contacts the hot regenerated catalyst. The main driving force for the catalyst traveling up the riser is, interestingly enough, the expanding volume of the hydrocarbon gas [4]. The riser essentially acts as a plug-flow reactor as the gaseous hydrocarbon feed and fluidized powdered catalyst travels through. Upon reaching the disengaging vessel, the desired cracking process has nearly reached completion. This vessel is also commonly referred to as the reactor, though today that is a bit of a misnomer (in older designs significant cracking did take place in this vessel). In the disengaging vessel, the spent catalyst is separated from the cracked hydrocarbon gas, usually via multi-stage cyclones. The gaseous hydrocarbon product is routed to the

![Simplified FCC Process Flow](image)

Fig. 2: *Simplified FCC Process Flow [2]*
fractionator, where it is cooled, liquefied, and distilled into various fractions. The lighter fractions are sent downstream for further processing, and the residual hydrocarbon (cycle oil) is recycled to the FCC feed.

One key characteristic of the FCC is the ability of the catalyst to be continuously regenerated. During the cracking process, coke is deposited on the catalyst, which inhibits active sites, and the catalyst is considered spent. Coke is made up of mostly carbon, though other components include hydrogen, sulfur, and nitrogen compounds [4]. Conveniently, this coke is combustible and can be burned off in the regenerator, thus restoring catalyst activity. Air blowers are used to supply the necessary combustion air, as well as the air necessary to re-fluidize the spent catalyst as it flows to the regenerator. Following regeneration of the catalyst by removal of the coke through combustion in the regenerator, the catalyst is routed to the riser, where it is once again mixed with the feed at the start of the process cycle. The driving force for this flow is usually the pressure differential between the regenerator and the disengaging vessel, and steam is typically added to aid in fluidization at the mixing point of the regenerated catalyst and hydrocarbon feed. The regenerated catalyst, being around 200°F – 300°F hotter than the feed, provides the heat necessary for both feed vaporization and cracking reactions to take place in the riser [4].

In this manner, the catalyst is continually circulated within the unit, and the catalyst circulation rate can be astoundingly large, about 70 tons per minute for larger units! This metric provides a good idea of the size and scope of FCC units. Circulating regenerated catalyst within the unit is referred to as equilibrium catalyst or “e-cat.”
Refiners must add fresh catalyst, however, to make up for catalyst losses and to replace e-cat that is periodically withdrawn to maintain catalyst activity [4].

The final relevant piece of the FCC to discuss is the regenerator flue gas treatment system. In addition to the stream of fluidized regenerated catalyst, a flue gas stream also exits the regenerator. A general layout for flue gas treatment units is shown in Figure 3. The nature of flue gas treatment is highly dependent on the mode of operation for the regenerator, which can be designed for either complete combustion or partial combustion. The level of combustion achieved in the regenerator is an economic decision for refiners, depending on feed quality/consistency, environmental restrictions, and utility costs, although some older units will be incapable of complete combustion [4]. Although complete combustion is a more energy efficient mode of operation and requires a lower capital investment in flue gas treatment, partial combustion also has its advantages and

![Figure 3: Regenerator Flue Gas Treatment: General Layout [6]](image)
remains a common practice to this day. Partial combustion regeneration has the advantage of offering a higher range of coke yields, translating into greater FCC feed flexibility and product yield [4]. The level of combustion achieved, and consequently the amount of CO present in the regenerator flue gas, is usually controlled by adjusting the flow of supply air. Regenerator flue gas containing CO can be routed to a CO furnace or CO boiler, where the CO is combusted to near completion with excess O$_2$ present. Heat energy in the CO furnace (COF) flue gas is usually captured via steam generation. Finally, before being released to the atmosphere, the COF flue gas is sent through either an electrostatic precipitator (ESP) and/or a wet gas scrubber (WGS) in order to remove catalyst fines and various environmental pollutants.

The treatment of flue gas in FCC units is a process designed to eliminate or significantly limit the release of harmful compounds to the atmosphere. The three types of compounds of chief concern are carbon monoxide, sulfur oxides, and nitrogen oxides. Strict environmental regulations surround the release of these compounds, as CO is a toxic gas, and sulfur oxides (SO$_x$) and nitrogen oxides (NO$_x$) are known contributors to ozone/smog and acid rain [1]. Carbon monoxide release from FCC units is almost completely eliminated by combustion in the CO furnace or CO boiler. SO$_x$ release is abated in various ways, including the utilization of scrubbers and the use of additives with the catalyst in the regenerator [4]. The abatement of nitrogen oxides, however, tends to be more complex and is most relevant to this paper, thus warranting further discussion.

NO$_x$ produced by FCC units includes almost exclusively NO and NO$_2$, about 90% of which is NO [4]. NO$_x$ compounds are produced by the FCC regenerator from two
sources: nitrogen in combustion air and deposits on spent catalyst from nitrogen in the feed. As combustion takes place in the regenerator, nitrogen reacts with oxygen to form primarily NO in the following manner:

\[ \text{N}_2 + \text{O}_2 \rightarrow 2\text{NO} \]

While the concept of NO\textsubscript{x} formation during combustion is quite simple, methods of reducing NO\textsubscript{x} emissions get more complicated. Now, various process variables surrounding the FCC regenerator can be manipulated in order to mitigate NO\textsubscript{x} formation, such as reducing excess O\textsubscript{2} or reducing dense bed temperature. However, these methods are marginal and are not usually sufficient to meet the required NO\textsubscript{x} abatement [4].

To date, one of the most effective methods, both chemically and economically, of controlling NO\textsubscript{x} in flue gas was pioneered by Exxon Research & Engineering Co. in the late 1970s. This method involves injecting vaporized ammonia in a process usually referred to as Selective Non-Catalytic Reduction (SNCR) or Thermal DeNO\textsubscript{x}. This process is only effective up to around a 70% reduction in NO\textsubscript{x} [3], but this is typically adequate for FCC applications [4].

Thermal DeNO\textsubscript{x} involves the selective reduction of NO by vaporized ammonia (NH\textsubscript{3}) in the presence of excess O\textsubscript{2} [3]. Thermal DeNO\textsubscript{x} involves a complex chain of free-radical reactions, the kinetics of which are highly temperature dependent; however, the net overall effect of the process, given the correct temperature range is shown by the following reaction:

\[ \text{NH}_2 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O} \]
The fact that Thermal DeNOₓ requires a specific temperature window in order to be effective can make its application challenging. There is not a known method to increase the upper temperature limit; however, it is known that the addition of H₂ can make the method effective at lower temperatures (down to ~1300°F). According to the generally accepted mechanism [3], the oxidation of H₂ assists in creating more NH₂ radicals at lower temperatures through the following series of reactions:

\[ \text{H}_2 + \text{OH} \rightarrow \text{H} + \text{H}_2\text{O} \]
\[ \text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O} \]
\[ \text{O} + \text{NH}_3 \rightarrow \text{OH} + \text{NH}_2 \]
\[ \text{OH} + \text{NH}_3 \rightarrow \text{H}_2\text{O} + \text{NH}_2 \]

The net temperature effect of adding more H₂ per mole of NH₃ is illustrated in Figure 4, taken from US Patent 4115515-A (assigned to Exxon Research & Engineering Co.). The figure shows the measured outlet NOₓ concentration (vppm) for a Thermal DeNOₓ process versus temperature in °F (increasing from right to left). The different curves pictured show that the temperature window for Thermal DeNOₓ varies as the H₂/NH₃ molar ratio is adjusted. Adjusting the amount of H₂ present makes the process effective over a wider temperature range versus the use of NH₃ alone, making Thermal DeNOₓ a more widely applicable method of NOₓ abatement. Several other variables affect the Thermal DeNOₓ process, including, but not limited to, temperature distribution in the furnace/boiler, carrier medium used for the ammonia, residence time, injection method, efficiency of distribution, flue gas velocity, and the molar ratio between NH₃ and NO. Increasing this ratio will increase the effectiveness of the process up to a certain
point, beyond which unreacted ammonia is likely to “slip” past the furnace to the stack, which can also be an environmental concern [4]. The effect and significance of each one of these factors should be examined when examining the feasibility of a specific Thermal DeNO$_x$ application.

Fig. 4: *Temperature Effect of H$_2$ on Thermal DeNO$_x$* [5]
Case Study: FCC Thermal DeNO\textsubscript{x} Optimization

Background

Having discussed Thermal DeNO\textsubscript{x} and FCC units in general, it is now possible to discuss project work for a specific application on PCLA-2 and PCLA-3 (“Powdered Catalyst Louisiana” FCC units) at ExxonMobil’s Baton Rouge Refinery. Interestingly enough, this is the same site where the world’s first FCC unit, PCLA-1, was started up in 1942, which initially had a capacity of 12,000 barrels/day (bpd). After many additions and improvements over the years, these two units are now capable of producing over ten times that amount, 120,000 bpd each! This capacity equates to the production of approximately 10 million gal/day of gasoline by these units alone.

The area of focus for this project is the flue gas section for both PCLA units, specifically the CO furnace (COF) and Thermal DeNO\textsubscript{x} systems (see Figure 5). PCLA-2 and PCLA-3 operate in parallel, being nearly identical with few exceptions. Each unit has its own CO furnace, but both share the same wet gas scrubber (WGS). A Thermal DeNO\textsubscript{x} system is installed on each COF, where vaporized ammonia is injected through a

![Fig. 5: PCLA CO Furnace Process Flow [courtesy of ExxonMobil]](image-url)
series of nozzles using pressurized steam as a carrier. The combination of these systems is designed to reduce NO\(_x\) effluent concentration at the WGS to <50 vppm, in accordance with environmental regulations.

About 18 months prior to the start of this project, waste heat boilers (WHB) were removed from the PCLA-3 flue gas system as part of a turnaround, or a period designated for equipment maintenance and replacement. An orifice chamber was installed in its place in order to meet the necessary pressure drop for the process. As a result of this change, the average operating temperature of the PCLA-3 COF increased from \(~1600^\circ F\) to \(~1750^\circ F\), varying within a temperature window of approximately 100\(^\circ F\). Consequently, fuel gas feed to the furnace could be reduced, a cost savings for the refinery. However, it was observed that the usage of ammonia, which had to be purchased from an external vendor, by the PCLA-3 DeNO\(_x\) system significantly increased at this time. Following technical guidance, hydrogen feed to the DeNO\(_x\) system was reduced to a minimum. Ammonia usage decreased as a result but was still greater than before WHB removal. Therefore, a project was initiated to scope the possibility of optimizing the Thermal DeNO\(_x\) system for each unit, specifically concerning efficiency related to temperature shifts, with the goal of realizing OPEX savings by reducing ammonia usage.

**Methods**

After consulting technical resources and learning how FCC process variables affect Thermal DeNO\(_x\) efficiency, the next logical step was to conduct experiments in
order to quantify the effect of these process variables and optimize unit controls accordingly. Of course, the concentrations of NO\(_x\) entering and exiting the COF are the key variables for this system, with furnace temperature, ammonia, and hydrogen flowrates also being of importance. The ability to measure or take into account each of these process variables was not a trivial matter.

Fortunately, COF temperature was one process variable which could be measured with relative ease. Because of the importance of COF temperature to the efficiency of CO combustion in flue gas, it is a closely monitored variable. Parallel thermocouples are installed on the CO furnace for each unit. Obviously, the high temperature (~1700°F) makes the reliability of this instrumentation a challenge, and these thermocouples often have to be replaced. However, that was not an issue for this specific test. It was assumed that temperature distribution within the furnace was approximately even and considered constant.

Ammonia flowrate was another variable where instrumentation was readily available. The NH\(_3\) supply for this system, a ~30 wt. % aqueous solution, comes from a large on-site tank with a capacity of several hundred tons. Flowmeters are installed on the liquid supply to each DeNO\(_x\) unit before the ammonia is vaporized by heat exchangers. Therefore, the flowrate to each unit in lb/hr was a reliably measured process variable. The distribution of ammonia within the furnace was assumed to be constant for the purpose of this test. Carrier steam rate was monitored to ensure no major upsets to this condition.

Hydrogen flowrate was a more difficult variable to accurately monitor. Historically, the flowrate of H\(_2\) to each DeNO\(_x\) unit was not a closely monitored variable,
having usually been controlled by providing a constant set point as input and leaving it in place. Additionally, with the PCLA-3 DeNO\textsubscript{x} system now operating at a higher temperature and requiring less hydrogen, the control valve is not appropriately sized for the application, making flowrate precision a possible issue. It was also discovered that this specific flowmeter did not have an accurate zero reading, requiring calibration by instrumentation technicians before proceeding further with any testing.

Accounting for the inlet concentration of NO\textsubscript{x} was challenging. Unfortunately, there are no analyzers on the gas feed to the COF to be relied upon. Fortunately, the experimental design used required a constant inlet NO\textsubscript{x} concentration throughout the testing period, so that an accurate NO\textsubscript{x} measurement was not essential. Unit process variables such as feed composition and rate, regenerator combustion air rate, and regenerator efficiency (i.e. CO percent in flue gas) were monitored and held as constant as possible during the test, as each of these variables was known to impact regenerator flue gas NO\textsubscript{x}. Therefore, the COF inlet NO\textsubscript{x} concentration could be assumed constant.

Measuring outlet NO\textsubscript{x} concentration was another challenge. The only NO\textsubscript{x} analyzer available is installed at the wet gas scrubber, downstream of both CO furnaces (PCLA-2 and PCLA-3 share the same WGS). Therefore, it is not possible to isolate the outlet NO\textsubscript{x} concentration for either DeNO\textsubscript{x} unit. Therefore, it had to be assumed that PCLA-2 NO\textsubscript{x} emissions to the WGS were constant throughout testing. The same parameters that were monitored for PCLA-3 (feed rate and composition, regenerator combustion air rate, and flue gas CO percent) were similarly monitored for PCLA-2.

Having identified the process variables involved and how to monitor each, it was possible to consider how experimentation on the unit would be conducted. These
experiments were intended to measure the efficiency of the DeNO$_x$ system over a range of furnace temperatures. The furnace temperature would be adjusted between the limits of normal operation by changing fuel gas and combustion air rates. DeNO$_x$ efficiency was measured by determining the flowrate of ammonia required to maintain the WGS NO$_x$ concentration at a set point of 45 vppm (the usual target). This test would be conducted for two distinct regenerator operating conditions: 6% CO and 7% CO, in order to determine if this change in flue gas CO, a normal variation, would significantly impact DeNO$_x$ efficiency. Most importantly, these experiments were to be run with zero H$_2$ in the system, so that the effect of having H$_2$ present could be isolated in further testing.

Conducting these first two experimental test runs involved a great deal of preparation, most importantly regarding safety and environmental concerns surrounding the adjustment of COF temperature. Conducting this test involved writing a procedure for the unit controller to follow, along with establishing limits on certain process conditions that, if exceeded, would require a stoppage of the test and a further review of the test plan before attempting to repeat. Fortunately, each run conducted under this test plan was successful on its first attempt, each requiring approximately four hours to complete. Each test run was conducted on a separate day with the requirement that unit conditions be approximately the same on each day.

The first test run was conducted at 6% CO in the flue gas entering the CO furnace. To begin, H$_2$ flow to the DeNO$_x$ system was shut off with a manual block valve. The furnace was cooled by reducing fuel gas flow and increasing quench air flow, while closely monitoring fuel/air ratio to avoid possible upset. Holding steady at around
1680°F, minute-average data values for temperature, NH₃ flowrate, and WGS NOₓ concentration were recorded for 30 minutes. The temperature was increased step-wise by approximately 30°F, 30 minutes at each step, to ~1800°F. The second run of this test was similarly conducted at 7% CO in the regenerator flue gas.

Following this initial testing, it was possible to conduct additional testing in order to identify the effect of hydrogen on the system. Essentially, the same experimental design was used with one exception – the addition of H₂. Since it is known that DeNOₓ chemistry is dependent on the ratio between H₂ and NH₃ and not an absolute amount, this test required the creation and implementation of a ratio control on the unit. This control was designed to adjust the H₂ flowrate NH₃ flowrate changes, according to a set mol:mol ratio. Because the anticipated effect of adding H₂ was to shift the efficiency curve to lower temperatures, 6% CO was chosen as a target for the regenerator flue gas, as a lower CO percent makes it possible to reach lower furnace temperatures. After the successful run of this test, it was possible to examine the data and determine if optimization of unit controls was economically feasible.

**Results and Discussion**

The data from the initial test runs at 6% and 7% CO is plotted along with a curve fit in Figure 6. From this data, it was found that the efficiency of the Thermal DeNOₓ unit varied greatly with temperature, finding maximum efficiency at approximately 1770°F. The maximum efficiency for this system is the point at which ammonia injection
Fig. 6: Effect of Regenerator CO Percent on Thermal DeNOx Efficiency: Ammonia Injection Rate at Constant Outlet NOx vs. COF Temperature for zero H2

Fig. 7: Effect of Hydrogen Injection on Thermal DeNOx Efficiency: Ammonia Injection Rate at Constant Outlet NOx vs. COF Temperature

[Graph showing the effect of CO and hydrogen injection on thermal DeNOx efficiency]
rate is at a minimum for a given amount of NO\textsubscript{x} reduction, i.e. NO\textsubscript{x} concentration at the WGS. As for the effect of regenerator CO\%, it was found that this variable did not significantly affect the efficiency of the DeNO\textsubscript{x} system either absolutely or relatively with temperature.

The data from the second round of testing with the addition of H\textsubscript{2} was plotted and curve fit in a similar manner as previous tests. In Figure 7, this data is shown compared to baseline data at 6\% CO and zero H\textsubscript{2} injection. The value of the H\textsubscript{2}:NH\textsubscript{3} ratio used is proprietary information to ExxonMobil and thus not published in this report. The data gathered from this test supports the theory that increasing H\textsubscript{2} relative to NH\textsubscript{3} shifts the DeNO\textsubscript{x} efficiency curve to a lower temperature range. The minimum of the curve, being the point of maximum efficiency for the system, lies around 1720\textdegree F, a shift of approximately 50\textdegree F from the baseline condition. This temperature shift is, again, within the normal operating temperature variation for the CO furnace, which is driven by CO percent in the flue gas. CO percent is an important variable for the unit driven by several economic factors having to do with feed composition and, to a lesser extent, COF steam production rates, but those factors are not detailed here. The objective of this project was to optimize the Thermal DeNO\textsubscript{x} systems within the confines of these existing economic parameters.

Having determined experimentally the per-mole temperature effect of additional hydrogen on the DeNO\textsubscript{x} system, it became possible to design an optimal control scheme. Knowing that, for optimal DeNO\textsubscript{x} efficiency, the H\textsubscript{2}:NH\textsubscript{3} molar ratio needed to be zero at 1770\textdegree F and greater, and X mol:mol at 1720\textdegree F, it was possible to build off the simple ratio control built for testing in order to adjust this ratio linearly with temperature. It was
suggested by available technical resources that this temperature effect increases linearly with the H₂:NH₃ molar ratio and so determined that further testing was not necessary.

As a result of these experimental findings and modified unit controls, a 27% reduction in ammonia usage was projected. The associated OPEX savings with this improvement on PCLA-3, and following the implementation of this control scheme on PCLA-2 following turnaround in 2017, are anticipated to be approximately $250,000 per year. With these returns anticipated for the foreseeable future, this annual savings of $250,000 can be expressed as having a present value of $2.5 million dollars, assuming a conservative annual interest rate of 10 percent. Although this is not a tremendous amount of money considering the scope of other projects at a petroleum refinery, it is important to consider the market here. In a commodity market, as is the market for petroleum fuels, any cost savings effort has a direct impact on profitability. The costs associated with this project were quite minimal. Essentially the only cost was the time spent by the members of the team - including unit controllers and supervisors, controls engineers, process engineers, and an engineering intern - in the undertaking of unit testing over the course of a few days and the design of a simple control program.

Beyond the tangible outcomes from this project, there are several other takeaways to consider. First and foremost, it became quite obvious safety is priority number one when it comes to any sort of activity in a manufacturing environment. This importance cannot be overstated. At times, this can offer quite a challenge with planning and moving forward with a process unit change, considering the propagating effect any sort of change can have. Because of this, a number of reviews, modifications, and approvals are usually required before taking action. For this particular application, the most important safety
consideration had to do with the manipulation of furnace controls. It was determined that a risk of “tripping” or “flooding” the furnace, meaning the loss of combustion, existed while conducting the unit tests. A furnace trip such as this could result in a CO release near the unit, a significant environmental concern, as well as a safety concern for personnel having to re-ignite the furnace. This risk was mitigated by placing limits on furnace fuel gas and air feed, as well as ensuring controls were not adjusted too quickly by operations. Especially at a refinery, steady-state operation is not usually upset by quick manual control changes.

Along the lines of process controls, another challenging aspect of this project had to do with instrumentation. Because it was not possible to have reliable and accurate instrumentation for every variable considered, it was necessary to get creative with the experimental design. This came into play in this project where gas analyzers were lacking around the CO furnace. The experiment had to be designed so that the inlet NO\textsubscript{x} concentration could confidently be held constant without being able to monitor it directly. This meant many other upstream variables had to be monitored to confirm that the NO\textsubscript{x} concentration variation was acceptable. The process control manipulation required for the unit tests conducted here involved adjusting the steady state temperature of the CO furnace, and again, these units are not designed for quick manual upsets of steady state, which is an economically determined operating condition for the unit.

It also became apparent that the challenges associated with conducting an experiment in an industrial manufacturing setting are quite different from those associated with conducting an experiment in a laboratory or similar setting. This is especially true in an environment as fast-paced as a petroleum refinery, where there can
be essentially an unlimited number of variables to consider. Practically must govern one’s thought process here. The priority is not to achieve perfect experimental results, but simply to achieve results that provide enough information and confidence to move forward with a decision. Although ideas behind good experimental design, i.e. identifying and controlling for important variables, can be universal between the two settings, that is about where the similarities stop.

Some of the differences associated with conducting an experiment in industry are evident in the data collected during this project as well. For the purposes of laboratory research, these experimental results would likely not be adequate to draw reliable conclusions. In the third test run, for example (Figure 7), the data was not as precise as previous runs. However, the data was good enough to confirm predictions about the effect of adding H₂ to the process. Therefore, it was worthwhile to move forward in creating a simple unit control rather than repeat the test for better data! Although repeatability is required in science, in industry, if something suggests there is a good chance of making money though a minor unit change, there is no reason to wait to implement the idea (after the safety risk has been considered of course). This is especially true for such a minor change as the one made from these experimental results. Having considered the associated cost and risk (minimal) and the substantial potential benefit, the decision to move forward was made with confidence.

Another point of discussion concerns the experimental methods used regarding the measure of DeNOₓ efficiency. The best experimental method, perhaps, in a fully controlled setting such as a lab, would be to measure the change in outlet NOₓ concentration with temperature at a constant ammonia injection rate. However, this
method was not used for the tests conducted on existing units because of practical considerations. Conducting the experiments with the chosen method allowed made it possible to calculate not only the most efficient unit operating conditions for COF Thermal DeNO\(_x\), but an estimate of the allowed reduction in ammonia injection rate at the optimized unit operating conditions as well. Therefore, fewer experimental runs were required to obtain the same information.

When working on a project in industry, difficulties can arise from prioritization and scheduling. As stated before, there can be an overwhelming number of moving parts in any given industrial environment, especially at a refinery. For this particular project, priority was quite low, all things considered. This project did not involve a safety critical unit change, and it was not one of the most pressing issues on the unit as far as economics were concerned. With that being said, scheduling did cause concern at times. With an upcoming multi-hundred million dollar turnaround for one of the FCC units, the operations personnel required for conducting these unit tests were usually quite busy! Once the experimental phase of this project was completed, it was important to move quickly in order to translate the data into actionable results.

Another crucially important consideration for this project, and for engineering projects in the general sense, is that of clear and concise communication. For any given project, there will be numerous stakeholders to consider. It is crucially important to effectively communicate the objective of the project as effectively as possible to everyone involved so that all are on the same page. More specifically, in regards to a written plan or procedure, communication must not only be detailed and accurate, but concise and easy to understand. If communication is inadequate from any individual, the
whole team can be affected. The result of inadequate communication can have not only significant safety ramifications, but can often result in an economic loss or waste of available resources.

When it comes to leading an engineering project in an industrial manufacturing setting, and specifically attempting a controlled experiment on a process unit, there are many considerations that must be taken into account. In the unique case discussed here, while several challenges were presented, all were addressed and mitigated so that the project could be completed successfully. This methodology enabled the successful undertaking of unit tests and implementation of unit control changes, with a projected economic return of $250,000 per year for the foreseeable future.
Conclusion

My project work with the FCC Thermal DeNO\textsubscript{x} systems at the ExxonMobil Baton Rouge Refinery involved overcoming many of the challenges that can be associated with process engineering. This specific project required effectively designing a series of controlled experiments and conducting them successfully on the unit. After gathering data from these experimental runs, it was possible to draw conclusions on the effects on various process variables on the FCC Thermal DeNO\textsubscript{x} system and adjust unit controls accordingly, resulting in a projected economic return of $250,000 per year for the refinery. With the assistance of my colleagues at ExxonMobil, I was able to overcome both the technical challenges of unit testing and the interpersonal challenges associated with leading an engineering project.
Bibliography


