Final Report

DOE Phase I - SBIR

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Recipient:
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Title:
**“Raman Scattering Sensor for Control of the Acid Alkylation
Process in Gasoline Production”**

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3. Executive Summary

Gasoline refineries utilize a process called acid alkylation to increase the octane rating of blended gasoline, and this is the single most expensive process in the refinery. For process efficiency and safety reasons, the sulfuric acid can only be used while it is in the concentration range of 98 to 86 %. The conventional technique to monitor the acid concentration is time consuming and is typically conducted only a few times per day. This results in running higher acid concentrations than they would like to ensure that the process proceeds uninterrupted. Maintaining an excessively high acid concentration costs the refineries millions of dollars each year. Using SBIR funding, Process Instruments Inc. has developed an inline sensor for real time monitoring of acid concentrations in gasoline refinery alkylation units. Real time data was then collected over time from the instrument and its responses were matched up with the laboratory analysis. A model was then developed to correlate the laboratory acid values to the Raman signal that is transmitted back to the instrument from the process stream. The instrument was then used to demonstrate that it could create real-time predictions of the acid concentrations. The results from this test showed that the instrument could accurately predict the acid concentrations to within ~0.15% acid strength, and this level of prediction proved to be similar or better than the laboratory analysis. By utilizing a sensor for process monitoring the most economic acid concentrations can be maintained. A single smaller refinery (50,000 barrels/day) estimates that they should save over \$120,000/year, with larger refineries saving considerably more.

4. Comparison of the Actual Accomplishments with the Goals and Objectives of the Project

- A. **Goals:** Because of the reactivity of concentrated sulfuric acid in the alkylation process, samples cannot be taken from the process and measured via Raman scattering at a later time. The samples must be measured on-line, in the process where the acid is under pressure and in a cooled environment. The first goal of this project was to install a Raman probe in a flow cell in the recycled acid (spent acid) circuit of the alkylation acid process, and initially excite the acid with a standard, 785 nm laser and attempt to collect Raman spectra. Should there be too much fluorescence we will move to a longer wavelength; i.e., 830 nm and repeat the measurements to determine the optimum excitation to maximize the Raman signal while minimizing fluorescence and increasing Raman signal-to-noise ratios.

Accomplishments: Initially we used our standard 785 nm laser and immersion probe to collect Raman spectra from the acid alkylation stream. The dominate 913 cm^{-1} acid peak was located directly on top of a larger fluorescence background signal that had a maximum around 845 nm. To try to minimize the amount of background fluorescence, we then shifted our laser excitation further to the red with an 830 nm laser and probe. When using the 830 nm laser the Raman peaks were located further out on the tail of the fluorescence background. By not having the Raman peaks on a curved fluorescence background it becomes easier to conduct a background correction to remove the fluorescence background from the spectrum. Chemometric

models were then created with both excitation wavelengths, and the model from the 830 nm excitation was able to better predict the acid concentrations compared to the 785 nm excitation model. The improvement with the longer wavelength excitation was mainly from the ability to perform a better fluorescence background correction compared to the shorter wavelength excitation. In Phase II we plan on testing even longer wavelengths.

- B. **Goals:** We will determine the optimum location for the Raman probe within the alkylation process so we can obtain samples of acid strength covering the full range of interest, from fresh acid at ~98 Wt%, to the fully spent acid of ~ 85 Wt%. We will begin the project looking at the depleted acid circuit since there should be less hydrocarbon contamination in this portion of the process, compared to the two phase acid reactor or settler stages of the alkylation unit. However, it may turn out that there are better locations for measuring the acid strength that would provide more informative system performance and process control measurements.

Accomplishments: In Phase I we worked with the Tesoro refinery in Salt Lake City UT on collecting Raman spectra from an alkylation unit with an *in-situ* coupled optical fiber Raman probe to demonstrate the feasibility of monitoring the acid strength in a industrial alkylation process. The optimum location of the probe was chosen so that it would only be a few feet away from the sample port that was used to collect laboratory grab samples. The closeness between the retain sample port and our on-line probe was desired to ensure that there were no chemical changes in the samples stream between the two different locations.

- C. **Goals:** Once we have determined the best excitation wavelength and the best location to monitor the acid, we will begin collecting on-line acid Raman spectra to correlate with lab samples drawn on-line and run in their laboratory by refinery personnel using conventional titration techniques. Chemometric models will be developed utilizing the Raman spectra that were collected at the same time solutions are drawn for *ex-situ* acid concentration determinations. Using the known acid concentrations and its associated Raman spectrum as our model, a partial least squares (PLS) technique will be used to build quantitative calibrations for discriminate analysis. The accuracy of the model to determine the acid concentration will then be tested against future *ex-situ* titrated samples. Development of the model will also be conducted to determine the number of independent samples with known acid concentrations, along with the range of sample concentrations that are initially needed to be acquired so that the model works correctly.

Accomplishments: During Phase I we collected Raman spectra from an actual alkylation process with a remotely located (~ 115 ft) industrial 830 nm Raman probe to demonstrate the feasibility of monitoring the acid strength in the alkylation process. Initially spectra were collected every five minutes over a three week time

period. To generate a chemometric model that can be used to predict the acid on-line strength, we correlated the Raman spectral responses to the laboratory values. This was accomplished by matching up the collected spectra to the times that a grab sample was collected for a laboratory analysis. Using the known acid concentrations and their associated Raman spectra as our testing set, a partial least squares (PLS) technique was used to build a quantitative calibration for discriminate analysis. The model was set up so that it only analyzed the 825 - 1250 cm^{-1} region of the spectrum. This region was chosen since it only contains spectral features associated with the acid, and does not have any spectral overlap with any of the other components in the acid alkylation stream. Using the narrower spectral region for analysis, the PLS model only required three independent factors. The three factors correspond to the three different acid peaks. The two Raman peaks located at 913 cm^{-1} and 1162 cm^{-1} both decrease when the acid is diluted while the Raman peak at 1043 cm^{-1} increases substantially. The fact that some of the peaks decrease and another increases with decreasing acid concentration allows PLS to model all of the spectral variations and correlate them to acid concentrations. To test the accuracy and robustness of the model, alternate Raman spectral predictions were compared to the laboratory titrations. Using three PLS factors, the predicted acid concentrations obtained with the PLS model as a function of the nominal acid concentrations obtained from the lab had a correlation coefficient $R=0.94$. The predicted values had a standard deviation of 0.11 Wt% when compared to the laboratory values. This standard deviation from the model was similar or slightly better than the laboratory standard deviation of 0.2 Wt% for acid concentration determinations.

5. Summary of Project Activities for the Entire Period of Funding

Introduction: The Problem of Monitoring Acid Concentrations in Alkylation Units

Most automobiles require a minimum octane number in gasoline for optimum performance, and the measurement or control of the octane number is an important quality parameter in gasoline production. Over the past several decades refineries have been utilizing alkylates as a key component to help increase the octane rating and at the same time lower the vapor pressure of the blended gasoline. The manufacturing of the alkylates is the single most expensive process in the refinery. The most popular alkylate gasoline blend component is isooctane because it can both raise gasoline octane and at the same time lower the vapor pressure of the blended gasoline, and by definition isooctane (2, 2, 4-trimethylpentane) has an octane rating of 100.⁽¹⁾ Recent changes in the reformulated gasoline legislation⁽²⁾ have called for maximizing the efficiencies of the alkylation process in refineries while maintaining the increasing throughput rates to keep up with the rising demand for gasoline. This demand on the alkylation process is creating a need for *in-situ* monitoring to provide instantaneous feedback on changes in the process which can then lead to real time process control to enable uniform product quality and minimum waste.

The alkylation process used to manufacture isooctane was developed in the early 1940s.⁽³⁾ It became very popular during World War II to provide high octane aviation fuel. The alkylation

process is quite complex, but basically it converts simple, relatively inexpensive, straight-chain hydrocarbons including olefins (isobutene, propylene, etc.) and alkanes (isobutane) into highly branched, low vapor pressure alkylates that provide much higher octane. A typical commercial alkylation process requires mixing the simple olefin and isobutane with concentrated sulfuric (H_2SO_4) or hydrofluoric (HF) acid in a two phase emulsion (acid phase and hydrocarbon phase) under pressure and in a cooled reactor. Hydrofluoric acid is considered a more dangerous reaction. Thus, many refineries continue to use the sulfuric acid process for safety considerations. To optimize the process, acid concentration measurements must be available at all times.

The sulfuric acid used in the alkylation process acts like a catalyst to convert the straight-chain components into the higher octane, branched hydrocarbons.⁽¹⁾ Since the acid is a catalyst, it should not be consumed, but in reality certain feed impurities and olefins that generate acid soluble compounds such as red oils (organic contaminants) and water will dilute the acid concentration. For process efficiency and safety reasons, the sulfuric acid can only be used while it is in the concentration range of 98 to 86 Wt%.⁽¹⁾ If the acid concentration falls below ~86 Wt%, the alkylation process could runaway, resulting in reaction conditions that do not favor the alkylation reaction between isobutane and olefins. When this occurs, the olefins preferentially react with each other to produce highly unsaturated polymers that are soluble in the acid which reduces the acid strength. The decrease in sulfuric acid concentration promotes an increase in the polymer production, and the undesirable reaction accelerates quickly. To ensure that the overall acid strength of the alkylation process does not fall below a safe level ~86 Wt%, fresh sulfuric acid ~98 Wt% is continually added to the process and likewise spent acid ~85 Wt% is constantly being removed. Another important consideration is if the acid strength reaches a value greater than 99.5 Wt% then there is a greater chance for sulfur trioxide to be present, and this compound is both toxic and corrosive. Both the fresh and spent acid strength need to be continuously monitored to eliminate the possibility of acid runaway and to maximize the process efficiency of the alkylate production for the various straight chain hydrocarbon feed streams.

Current methods monitor the acid strength via traditional wet chemistry titration techniques. Refinery personnel typically conduct this titration only once or twice per shift for a total of 3 to 6 times per day.⁽⁴⁾ Even though the acid strength is critical, the current measurement techniques are very time consuming requiring an hour or two for the result to be called in from the laboratory. If a unit operator obtains a titration determination that falls below the predefined acid strength concentration limits, they will increase the fresh acid flow to reduce the chance of acid runaway before the results from an immediate resample can be analyzed. Often the alkylation process is run using more fresh sulfuric acid than necessary just to be on the safe side and not to risk having the system run away, causing terrible consequences.

A need exists for a reliable, *in-situ* method to continually monitor sulfuric acid concentration in the alkylation process (see Figure 1). Ideally, a non-contact sensor would be inserted into the acid process in an appropriate location and allowed to communicate with a base instrument located remotely in the safe environment of a control room. In Phase I we started developing fiber-coupled, Raman scattering instrumentation for this application (discussed below). We have also developed

SULFURIC ACID ALKYLATION ACID PROCESS

Figure 1. Illustration of a typical sulfuric acid alkylation unit. The hydrocarbons are mixed with the concentrated sulfuric acid and allowed to react in a cooled reactor. This two phase system is then allowed to settle with the light hydrocarbon (alkylate) removed from the top of the settling tank and the acid recirculated. The acid concentration cannot be allowed to fall below $\sim 86\%$ or the system will catastrophically fail.

similar technology for the monitoring of polymers and various industrial processes including gasoline blending.⁽⁵⁾ We were first exposed to the problems with measuring the sulfuric acid concentration in the alkylation process because of our experience with developing Raman instrumentation to monitor gasoline blending. Preliminary results from Phase I indicate that Raman scattering is particularly well suited for this acid monitoring application because it can be used with two phase systems such as the acid phase mixed with the hydrocarbon phase, and unique Raman peaks associated with both components (acid and hydrocarbon) can be detected.

The Raman system includes a long-life, frequency-stabilized diode laser for optical excitation; an industrial fiber-optic probe with appropriate optical filtering for guiding the excitation light to the sample and directing the Raman scattered light back to a remotely located spectrograph; and a TE-cooled CCD camera for full-spectrum detection.⁽⁵⁾ Fiber optic switching technology combined with low loss optical-fibers would allow one Raman instrument to be used to monitor the acid concentration of several reactors as well as the hydrocarbon (alkylate) product at various locations throughout the alkylation process unit.

The Raman technique is often assumed to be similar to near-infrared and mid-infrared methods in the sense that both approaches rely on measuring molecular vibrational frequencies for chemical analysis and the strength of optical interactions for determining molecular concentrations.⁽⁶⁾ However, since infrared is based on optical absorption whereas Raman is based on light scattering, there are some key differences between the two different methods. A significant advantage of Raman scattering is that it can be used to characterize systems containing water whereas infrared absorption normally cannot because the strong infrared absorption of water dominates the absorption by other compounds. Since there is no sample preparation required for the Raman measurement, this technique has some very important advantages for use with chemical monitoring of the complex chemical interactions associated with sulfuric acid inside an alkylation unit.⁽⁷⁻⁹⁾

Often, one can collect on-line samples and run them on a Raman instrument in the laboratory to determine the feasibility of using Raman scattering technology for product monitoring. However, the sulfuric acid inside an alkylation unit offers some unique challenges. The sulfuric acid that is under pressure and cooled in the reactor will quickly react with oxygen in the air and oxidize, turning black when it is removed from the reactor. Raman spectra cannot be obtained from these black samples because these dark solutions exhibit a strong fluorescence background which dominates the Raman signal strength. Sulfuric acid is a rather unique acid, in that when highly concentrated, it acts as a weak acid and a poor electrolyte because very little of the acid is dissociated into ions at room temperature. When cold, it does not react readily with common metals such as iron, however when hot, it is quite reactive.⁽¹⁾ This is why the refineries refrigerate the alkylation process so that the acid will not deteriorate their plant, and why we must make our Raman measurements on-line maintaining the sample under stable conditions (pressurized, cooled, and free of oxygen). For this reason arrangements were made with Tesoro Petroleum in Salt Lake City, UT, to obtain access to their acid alkylation process reactor so that we could obtain real-time, on-line Raman spectra from the process while at the same time having access to their wet chemistry titrated acid measurements.

Many other techniques have been tried for measuring the acid concentration in order to better control the overall reaction.⁽¹⁰⁾ These methods include attempting to measure the change in acid density with concentration using speed of sound through the sample, the change in the mass of the acid (coriolis meter), and others. Since the acid is part of a two phase system, these techniques do not work well because they rely on the acid being completely isolated from the hydrocarbon phase which is very difficult to do on-line, in a continuous fashion. A NMR technique has also been used but this instrumentation is expensive and maintenance intensive. Again, Raman scattering does not require that we completely separate the two phases, has no moving parts offering excellent reliability, and via fiber-optic coupling can be used remotely. Another advantage with our Raman instrument is the ability to monitor the acid concentration of several reactors as well as the hydrocarbon (alkylate) product in various locations throughout the plant with a single instrument. To obtain that Raman scattering signal from multiple probes with a single laser and spectrograph, we will utilize a multiplexing system (discussed below) recently developed in our laboratories for this type of application.

Figure 2 illustrates the Raman spectra obtained from sulfuric acid solutions made up in the laboratory using clean, fresh acid. To dilute the acid, fixed amounts of acid were added to calculated amounts of water. Large changes in the Raman spectra are observed when comparing a 95.8% acid with a more dilute sample at 87%. The Raman peaks located at 913 cm^{-1} and 1162 cm^{-1} both decrease when the acid is diluted while the Raman peak at 1043 cm^{-1} increases substantially. The fact that some peaks decrease with decreasing acid concentration and others increase allows chemometric techniques such as Partial Least Squares (PLS) to model all of the spectral variations and correlate them to acid concentrations.⁽¹¹⁾ In Phase I, we collected Raman spectra from an actual alkylation process with a remotely located industrial Raman probe to demonstrate the feasibility of monitoring the acid strength in the real alkylation process (discussed below). In Phase II, we will install Raman fiber-optic probes into alternate alkylation unit reactors that have a wider acid concentration range to develop a more robust model. Development of a more robust immersion Raman probe will continue, as the corrosive environment of the alkylation stream will cause a common stainless steel probe to dissolve over time. We will also work with the Tesoro refinery to determine additional parameters that can be measured with the Raman scattering technology including the concentrations of acid soluble oils, the ratio of hydrocarbon to acid, and saturate / olefin ratios. Raman probes will then be located in the alkylate product stream to monitor the octane number and Reid vapor pressure (RVP). Currently we have demonstrated that our Raman instrumentation is able to monitor these parameters in gasoline blending.⁽¹²⁾

Phase I Technical Results

A. Raman Spectroscopy Determination of Acid Concentration

We have utilized our PI-200 fiber-coupled Raman instrument incorporating a solid-state laser operating in an external-cavity configuration at 785 nm together with our proprietary, optically fast, grating spectrograph, and TE-cooled CCD array to record the Raman spectra of laboratory prepared sulfuric acid samples. We prepared a series (~18 samples) of acid dilutions from ~96% to 70% acid mixed with water. Using our standard, 785 nm excitation, we integrated the Raman signal for ~120 seconds to obtain sufficient signal strength. Figure 3 illustrates how the Raman spectra change with

Figure 2. Raman spectra of fresh, laboratory prepared sulfuric acid solutions. The fact that some peaks decrease with decreasing acid concentration and others increase suggests that a simple peak height ratio might make a good indicator of acid concentration. However, we will explore the use of more sophisticated chemometric techniques such as Partial Least Squares (PLS) to model all of the spectral variations and correlate them to acid concentration.

Figure 3 We prepared a series (~18 samples) of acid dilutions from ~96% to 70% acid mixed with water. Using our standard, 785 nm excitation, we integrated the Raman signal for ~120 seconds to obtain sufficient signal strength. Notice the rather large decrease in the Raman peaks at 913 and 1162 cm^{-1} and the increase in the Raman peak at 1043 cm^{-1} with the decrease in acid concentrations.

acid concentration. Note again, as shown in Figure 2, the rather large increase in the Raman peaks at 913 and 1162 cm^{-1} and the decrease in the Raman peak at 1043 cm^{-1} with the increase in acid concentrations.

After making the Raman measurements on these known samples, we entered the data into a commercial chemometric software package, GRAMS/AIv7.0/PLSplus/IQ from Thermo. The PLS algorithm was chosen to correlate the measured sample spectra with their nominal acid concentrations. The Raman spectra were mean-centered, normalized to be of unit area, and background corrected by subtracting a linear baseline spectrum. The ability to develop a model using normalized spectra has the advantage that the model is quite robust and insensitive to small changes in laser power or variations in system throughput as a function of time. Figure 4 compares the predicted acid concentrations obtained with the PLS model as a function of the nominal acid concentrations. Using four PLS factors, the correlation coefficient $R = 0.996$.

Our Raman instrumentation data acquisition software (PROspect™) is designed to operate with the GRAMS predictor package. Once we install the appropriate model (calibration file) into our software, the Raman instrument can be used for real-time chemometric predictions; i.e., it directly provides acid concentration predictions and not just Raman spectra.

B. On-Line Probe Development

In Phase I we worked with the Tesoro refinery in Salt Lake City UT on collecting Raman spectra from an alkylation unit with an *in-situ* coupled optical fiber Raman probe to demonstrate the feasibility of monitoring the acid strength in a industrial alkylation process. Figure 5 illustrates how the Raman probe was directly inserted into the spent acid return stream that runs from the alkylation unit's settler stage. The location of the probe was chosen so that it would only be a few feet away from the sample port that was used to collect laboratory grab samples. The closeness between the retain sample port and our on-line probe was desired to insure that there were no chemical changes in the samples stream between the two different locations. The outer section of the Raman probe isolates the internal optical components in the probe from the sulfuric acid stream with a 2 mm thick sapphire window. The main advantage with this design is that it allows us to easily change the internal optics of the Raman probes and/or excitation wavelengths without having to remove the outer probe and interfere with the acid stream.

All of the pipes and tanks used in Tesoro's alkylation unit are manufactured from carbon steel. This type of material is desired since it forms a robust outer oxide coating that will resist corrosion from the harsh acid environment. During the start of the Phase I project we did not have an in-line probe with an outer sleeve that was manufactured from carbon steel. Therefore, during our first rounds of testing we utilized a probe that had an outer sleeve that was manufactured from 316 stainless steel. The probe was inserted into the acid line, and no Raman signal degradation was observed over the first month of operation. After that time period, the observed Raman signal from the acid content dropped rapidly over a 24 hour time period. The decrease in observed signal intensity indicated that the caustic environment had started to corrode the outer sleeve of the probe, and that acid had started to leak into interior probes optical components. When the entire probe was

Figure 4. Comparison of the predicted acid concentrations obtained with the PLS model (normalized) as a function of the nominal acid concentrations. Using four PLS factors, the correlation coefficient $R = 0.996$. The ability to develop a model using normalized spectra has the advantage that the model is quite robust and insensitive to small changes in laser power or variations in system throughput as a function of time.

ON-LINE RAMAN PROBE

Figure 5 Schematic of the on-line Raman probe inserted into an alkylolation unit acid line.

removed from the acid line, one could detect that the acid stream had corroded part of the probe. Figure 6 displays some photographs of the probe after it had been removed from the stream. The harsh sulfuric acid chemical environment inside an alkylation unit requires that all of the material used to be resistant to any form of corrosion or degradation of the material. Because of this requirement most of the pipes and tanks used in an alkylation unit are manufactured out of carbon steel. This type of material forms a robust outer oxide coating over time that will resist corrosion from the sulfuric acid environment.⁽¹³⁾ Currently we are conducting some longer term corrosion-proof tests with a probe that has an outer sheath manufactured out of carbon steel. The results from this experiment will aid in the development of a more robust probe sheath that could be used in a Phase II project.

C. Excitation Laser Wavelength Determination

The on-line acid stream is a darker red color that produces a fluorescence background, and tests were conducted to determine the optimum excitation wavelength. Process Instruments, Inc. is uniquely qualified for this project since we are the developers of high-power, frequency-stabilized, narrow linewidth diode lasers. We have the ability to tune and build lasers at almost any excitation wavelength. This allows us to readily investigate different excitation wavelengths for this particular application.

Initially we used our standard 785 nm laser and probe to collect Raman spectra from the acid alkylation stream. Figure 7A displays the observed Raman spectrum with the 785 nm excitation. The dominate 913 cm^{-1} acid peak can be seen sitting directly on top of a larger fluorescence background signal that has a maximum around 845 nm. To try to minimize the amount of background fluorescence, we then shifted our laser excitation further to the red with an 830 nm laser and probe. Figure 7B shows the observed Raman spectrum using an excitation wavelength of 830 nm. Comparing the two different figures one can notice that with the 830 nm laser the Raman peaks are located further out on the tail of the fluorescence background. By not having the Raman peaks on a curved fluorescence background it becomes easier to conduct a background correction to remove the fluorescence background from the spectrum. The background correction that was subtracted from each spectrum to remove the fluorescence background is indicated with a black dashed line in Figure 7. Chemometric models were then created with both excitation wavelengths, and the model from the 830 nm excitation was able to better predict the acid concentrations compared to the 785 nm excitation model. The improvement with the longer wavelength excitation was mainly from the ability to preform a better fluorescence background correction compared to the shorter wavelength excitation. Because of the improved results obtained with the 830 nm excitation, all of the alkylation spectra collected after this test were conducted with the longer wavelength excitation. In Phase II we plan on testing even longer wavelengths.

D. Compare On-Line Acid Spectrum to Pristine Laboratory Samples

The pristine acid laboratory sample spectra displayed in Figures 2 and 3 did not have the larger fluorescence background that was observed with the on-line alkylation acid spectra. To demonstrate that we can easily remove the background from the on-line response, a spectral comparison between the on-line and laboratory results is displayed in Figure 8. The top spectrum

Outer Sleeve (316-SS) On-Line Probe After Removed From Alkylation Unit

A

B

C

Figure 6 Photographs of the Raman probe's outer sleeve after it had remained in the spent acid for over a month. The sleeve was manufactured from 316-SS, and currently we are conducting corrosion tests with probes made out of alternate material. Red arrows indicate the direction of flow when the probe was located in the alkylation process stream.

Figure 7 Raman spectra obtained with excitation at 785 [A] and 830 nm [B]. The black dashed lines are the background corrections that are subtracted from the Raman data to remove the fluorescent background. The wavelength range for each spectrum is 805-931 nm with the 785 nm excitation and 852-995 nm for the 830 nm excitation.

Figure 8 In-situ spectral response from an alkylation unit's spent acid stream containing 90 Wt% sulfuric acid (top). Freshly prepared 95 Wt% sulfuric acid sample (bottom). Similarities in the Raman bands between the two different spectra indicate ability to obtain real time spectral identification from a Raman probe located in the spent acid stream of an alkylation unit.

in Figure 8 is the in-situ spectral response from the spent acid stream that contained a 90 Wt% sulfuric acid solution. The bottom spectrum in Figure 8 represents a freshly prepared sample. The spectral features from this on-site measurement were consistent with our freshly prepared samples. Similarities in the Raman bands between 850 to 1200 cm^{-1} demonstrate the ability to obtain real time *in-situ* Raman spectrum from the spent acid stream that could be used to monitor the real time acid concentrations within an alkylation unit.

E. Chemometric Predictions of the On-Line Acid Concentrations

During Phase I we collected Raman spectra from an actual alkylation process with a remotely located industrial 830 nm Raman probe to demonstrate the feasibility of monitoring the acid strength in the alkylation process. Initially spectra were collected every five minutes over a three week time period. To generate a chemometric model that can be used to predict the acid on-line strength, we correlated the Raman spectral responses to the laboratory values. This was accomplished by matching up the collected spectra to the times that a grab sample was collected for a laboratory analysis. Using the known acid concentrations and their associated Raman spectra as our testing set, a partial least squares (PLS) technique was used to build a quantitative calibration for discriminate analysis. The PLS algorithm used was from a commercial chemometric software package, GRAMS/AIv7.0/PLSplus/IQ from Thermo. The software was designed so that it would first conduct a baseline correction to the data, normalize the spectra to be of a unit area, and mean center the data. The normalization and mean centering were used to develop a model that would be quite robust and insensitive to small changes in laser power or variations in system throughput as a function of time. A simple peak height ratio and other modeling preprocessing procedures like gap derivatives were also tested, but these alternate techniques had higher prediction errors when compared to the original model.

The model was also set up so that it only analyzed the 825 - 1250 cm^{-1} region of the spectrum. This region was chosen since it only contains spectral features associated with the acid (displayed in Figure 8), and does not have any spectral overlap with any of the other components in the acid alkylation stream. Using the narrower spectral region for analysis, the PLS model only required three independent factors. The three factors correspond to the three different acid peaks. The two Raman peaks located at 913 cm^{-1} and 1162 cm^{-1} both decrease when the acid is diluted while the Raman peak at 1043 cm^{-1} increases substantially (See Figure 3). The fact that some of the peaks decrease and another increases with decreasing acid concentration allows PLS to model all of the spectral variations and correlate them to acid concentrations. To test the accuracy and robustness of the model, alternate Raman spectral predictions were compared to the laboratory titrations. Figure 9 shows the predicted acid concentrations obtained with the PLS model as a function of the nominal acid concentrations obtained from the lab. Using three PLS factors, the correlation coefficient $R=0.94$. The predicted values had a standard deviation of 0.11 Wt% when compared to the laboratory values. This standard deviation from the model was similar or slightly better than the laboratory standard deviation of 0.2 Wt% for acid concentration determinations.

The data for this experiment was conducted on a single alkylation unit at Tesoro Petroleum in Salt Lake City, UT and the spent acid stream from that settler contained the lowest acid

Figure 9 Comparisons of the predicted acid concentrations with the PLS model (normalized) as a function of the nominal acid concentration. Using three PLS factors the correlation coefficient $R=0.94$ and the standard deviation was 0.11 Wt%. The ability to develop a model using normalized spectra has the advantage that the model is quite robust and insensitive to small changes in laser power or variations in system throughput as a function of time.

concentrations (89-91.5 Wt%). A PLS model has the best predictive ability when the observed acid concentrations fall within the central 75% range of the model. Generally models are built with additional samples that are slightly outside the concentration range of interest to help build a more robust model. However, the acid alkylation samples can only be measured on-line since they start to immediately oxidize when exposed to air. To generate a more robust model we plan in Phase II to obtain spectra from alternate alkylation units that would provide the model with a bigger acid concentration range.

Our initial Phase I results indicate that Raman scattering can be used to quickly and accurately identify and measure the acid concentrations in an industrial alkylation processes. The objective of this project was to develop a fiber optic Raman instrument that could conduct real time *in-situ* monitoring of sulfuric acid concentration in refinery alkylation units. For this reason arrangements were made with a local refinery to obtain access to their acid alkylation process reactor so that we can obtain real-time, on-line Raman spectra from the process while at the same time having access to their *ex-situ* process measurements. In a Phase II project we would initially start testing alternate in-line Raman probes made out of carbon steel or hastelloy to determine which material will not degrade over time in the harsh acid environment. The Raman probes would then be placed in various alkylation units spent acid streams to obtain a larger range of acid concentrations that can be used with the model. We would also set up Raman probes in alternate locations (not the spent acid stream) to determine additional parameters that can be measured so that refiners can optimize the monitoring process in an alkylation unit. Spectral variations over time from these multiple locations would be utilized to establish the ability of Raman scattering technology to monitor the chemical reactions that occur within an alkylation unit. We would also identify and define the instrumentation features that will be needed for an on-line Raman system designed for long term commercial applications.

Anticipated Public Benefits:

A better way is required to closely monitor the alkylation acid concentration and improve the alkylation process performance to reduce the overall cost of higher octane gasoline. Currently, refineries monitor the acid strength via titration techniques once or twice per shift, which results in running higher acid concentrations than they would like to ensure that the process proceeds uninterrupted. Maintaining an excessively high acid concentration costs millions of dollars annually for each refinery.

A second advantage is that continuous *in-situ* measurements of acid concentrations can prevent any panic between titration measurements, so that operators would be less concerned about having an acid runaway occur between the individual discrete titration measurements. This technology could easily be applied to many other industries that use sulfuric acid and have difficulty controlling or monitoring its concentration. An *in-situ* Raman sensor can also be used to provide instantaneous feedback on changes in the process which can then lead to real time process control to enable uniform product quality and minimum waste. By also monitoring additional parameters in the alkylation unit like saturate / olefin ratios or octane rating and RVP of the finalized alkylate product, it would allow refiners to gain a better understanding of the operating trends and unit

performance that would provide them with the additional information required to reduce their alkylation unit production costs.

6. Products Developed Under the Award

A. Publications: None

B. Web Sites:

<http://www.process-instruments-inc.com/pages/acid.html>

C. Network or Collaborations Fostered:

Tesoro Petroleum
474 West 900 North
Salt Lake City, UT 84103

British Petroleum
2831 Indianapolis Blvd.
Whiting, IN 46394

D. Technologies/Techniques:

Develop an on-line acid analyzer for measuring the concentrations of sulfuric acid in a refinery alkylation unit.

E. Inventions/Patent Applications: None

F. Other Products: None

7. Projects Involving Computer Modeling

None

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