PROJECT FINAL REPORT

Innovative Biological Emissions Treatment Technology Deployment to Reduce Air Pollution for Petroleum and Petrochemical Operations

July 2016
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Project Title: Innovative Biological Emissions Treatment Technology Deployment to Reduce Air Pollution for Petroleum and Petrochemical Operations


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Executive Summary

A novel bio-oxidation system was demonstrated as a viable alternative to thermal oxidizers, chemical oxidation and carbon adsorption as an environmental friendly process in which only non-hazardous products such as water, carbon dioxide and biomass are produced as by-products. The two-stage bio-oxidation process consisted of a biotrickle (bacteria suspended growth) treatment unit and a biofilter (primarily bacteria attached growth) treatment unit. The biotrickling filter included cross flow media for increasing the interfacial area of air and liquid contact. The biofiltration portion of the system was filled with engineered media made from organic material and open plastic spheres for improved air flow.

A sequential bio-treatment system, defined as a combined treatment consisting of a bio-trickling filter and biofilter, was deployed at a BTX wastewater sump at the Citgo Corpus Christi Refinery to facilitate low-cost VOC removal. Vapor samples were collected from the wastewater sump for gas chromatography- mass spectrophotometry (GC-MS) analysis for vapor characterization to determine benzene amounts. Benzene constituted an estimated about 85% of the vapor stream with its primary concern being carcinogenic. The empty bed residence time (EBRT) established 90 seconds by controlling the vapor flow rate. The removal efficiency was 84% over a five-day period and the elimination capacity was in the range of 5.5 g m⁻³ hr⁻¹ 1600 g m⁻³ hr⁻¹ for a pollutant-loading rate of 6 g m⁻³ hr⁻¹ to 1750 g m⁻³ hr⁻¹.

The main focus of the second phase of the project was the design, construction and implementation of a field scale innovative sequential biotreatment system for control of oil and gas emissions from a remote oil and gas production facility. The field unit was fabricated by Diamond Fiberglass of Victoria, Texas, and successfully deployed at the Apache TAMU#2 storage tank battery in Snook, Texas, approximately 13 miles southwest of Bryan/College Station, Texas. The field unit consisted of a skid mounted two vessel system (150 cubic feet of total volume) made of fiberglass with corrosion resistant schedule 80 PVC piping.

The headspace VOC vapor concentrations were characterized using GC-MS analysis of vapor collected in Summa canisters and revealed the presence of Benzene, Toluene, Xylene and Hexane as Hazardous Air Pollutants (HAPs). The vapor phases collected from the TAMU #2 tank battery headspace were a mixture of different aromatic and aliphatic hydrocarbons. Benzene was identified as the HAP with the highest concentration at approximately 200 ppm. One water storage tank and two crude oil tank vents were connected to a common header at the well site, and the thief hatch on the water tank was propped open to allow oxygen to be pulled through the bio-oxidation system to help degrade the hydrocarbon compounds. The biofiltration unit operated for three months (May through July, 2016) at an average air flow of 25 cubic feet per minute which provided about 4 minutes of retention time in the system. VOC removal using PID measurements demonstrated an average of 50%-60% removal for total VOCs which was steadily increasing. This level of removal efficiency was due to preponderance of alkanes, and their relative high concentration of the total in the biofiltration unit. Alkanes in crude oil vapor are more difficult to biodegrade than aromatics in an aerobic environment. However, higher removal efficiencies for aromatics such as benzene and toluene were confirmed subsequent GC-FID analyses.
The bio-technology employed in this project has been demonstrated as a cost-effective treatment technique to mitigate VOCs emissions from oil and gas industries and could be considered as the Maximum Achievable Control Technology (MACT) to control HAPs. Subsequent phases of this project would be optimization of air flow, water flow and residence time for the most effective BTEX degradation for remote oil and gas facilities, and the deployment of more telemetry and modem communication, with a Programmable Logic Controller (PLC) to remotely monitor unit performance and operating conditions.
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Biofiltration technology pilot and field testing for oil and gas facilities

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</table>
Project Background

This project focused on the design and implementation of both a biotrickling filter and biofilter portions of a novel bio-oxidation system to provide optimum airflow, water recirculation and biofilm mass transfer relationships targeting energy savings for treating emissions for the petrochemical industry. A multi-stage bio-oxidation system can provide the petroleum refining and oil and gas industry an alternative to thermal oxidizers and flares, and their heavy natural gas usage and high cost of operation. This technology is ideal for the refining and oil and gas industry due to the reduced cost of supplemental fuels, the long-term sustainability of biological based systems, and broader interpretations of the EPA Maximum Achievable Control Technology (MACT) rules regarding control of Hazardous Air Pollutants (HAPs).

Petrochemical operations and refineries require significant amounts of water for desalting which must be treated prior to discharge and can be a significant source of HAPs (Hazardous Air Pollutants) and VOCs (Volatile Organic Compounds) emissions. Since VOC aromatics, such as benzene, are considered potential carcinogens, they have received considerable regulatory attention. The National Emission Standards for Hazardous Air Pollutants require that above a threshold of ten metric tons per year of a HAP (only 2.5 lbs/hr) stringent controls are required. VOC emissions are also regulated for their contribution as ozone-precursors in airsheds which are in non-attainment, such as Houston, or near non-attainment NAAQS status, such as Corpus Christi. Additional sources of emissions at refineries include amine sweetening operations, glycol dehydrators, and tank vents. When significant, these emissions must be collected and controlled. High temperature thermal oxidizers or flares are often the technology of choice to meet MACT emission control standards, yet supplemental fuel and power costs makes this control technology both expensive and energy intensive. Any new technology that could replace a single thermal oxidizer (100,000cfm size) could provide a savings of more than 4,166 MM BTUs of natural gas annually (based on 8,760 hrs of operation and 0.475 MM BTU per hour of usage). That represents enough natural gas to comfortably heat or cool approximately 120 homes annually for each thermal oxidizer or flare replaced.

Biological treatment of air emissions is a cost effective and sustainable control technology for petrochemical and oil and gas facilities facing increasingly stringent air emission standards. The technology offers an attractive alternative to costly conventional techniques such as thermal and catalytic oxidation. Biological waste air treatment achieves pollutant destruction at ambient temperatures and does not generate secondary pollutants such as nitrogen oxides or sulfur compounds, with significantly reduced CO2 emissions as compared to flaring operations. Contaminants are transformed to innocuous products through the action of microorganisms suspended in the aqueous phase or attached within a biofilm. Such bioreactors are generally classified into two categories – biofilters and biotrickling filters. Biotrickling filters are biological scrubbers where contaminated air is passed through a packed bed onto which a culture of microorganisms is immobilized. Water and nutrients are added continuously to the biotrickling filter unit. Biofilters on the other hand are simpler in construction with an organic substrate (often compost based) included in or on the packing media with only intermittent moisture application when necessary. Biotrickling filters tend to be more effective for higher concentrations since higher mass transfer rates can be achieved into the scrubbing liquid and
more concentrated biomass growth can be achieved, but biofilters provide more retention time for less water soluble VOC removal. This project proposal has integrated both biotrickling filter and biofilter technologies into an efficient sequential treatment system targeting control of refinery or other oil and gas industry emissions.

The general objective of this research was to prove the viability of biological air emission treatment for VOC control of certain petrochemical refinery and oil and gas emissions through focused work targeting the technological emission control challenges faced by the industry. Specific objectives were to (1) demonstrate the ability of bio-oxidation systems to treat variable loadings of VOC emissions as experienced in refineries and production facilities during routine operations, process turnarounds or upsets, and (2) begin work to optimize the process for the ability to efficiently degrade both aliphatic and aromatic compounds in the mixtures typically encountered in refinery and oil and gas facility emissions.

Previous investigations conducted at the Texas A&M University-Kingsville laboratories and at field applications for the forest products industry have determined the kinetics of both H₂S and VOC removal in biofilters using engineered media from Met-Pro Environmental Air Solutions (Met-Pro EAS). The research demonstrated the efficiency and capabilities of the odor removal process for waste gases with containing up to 100 ppmv H₂S (Jones et al, 2004). Additional studies successfully evaluated the sulfur removal capacity of bioreactors packed with the engineered media (Jones et al, 2005). The engineered media was demonstrated to be well suited for use in biological treatment units treating toxic emissions from wastewaters and has also been effective for removal of VOCs and air toxics in these emissions (Karre et al., 2012, Jones et al., 2011, Karre et al., 2011).

The primary application for this eco-technology was the collection and treatment of emissions in and around the wastewater treatment plant for the Corpus Christi Citgo Refinery and the Apache TAMU #2 well site tank battery vents. The project team worked closely with the Houston Advanced Research Center project manager and staff engineers from both Citgo and Apache to identify and employ the new bio-technology for two field applications.

This report is organized into summaries of the design work, data collection results and analysis for both projects – Phase I: the pilot test of the technology at the Citgo Corpus Christi wastewater sump and transfer station and Phase II: the field test of the technology at the Apache TAMU #2 well site tank battery vent system in Snook, Texas.
Phase I: Report on Field Pilot Test of Biological Emissions Control System at CITGO Corpus Christi Refinery – July 3-8, 2014

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Summary
The trailer mounted biological emissions treatment unit was deployed at the CITGO Refinery, Corpus Christi to potentially treat VOC vapors emitting from the wastewater BTX sump over the period of July 3 through July 8, 2014. During this period, some positive pressure encountered in the BTX sump apparently provided variable loadings of a small amount of VOC vapor to the pilot unit (Table 1). Even without an acclimation period for the biofilms, relatively high values of removal efficiency were measured almost immediately by PID meters placed at the unit inlet and outlet (Table 1). This positive result demonstrates the potential for even more effective refinery VOC removal efficiencies for more passive and remote applications such as tank vents and other collected fugitive emissions in buildings and work areas.

Summary of Pilot Test protocols and findings
The biological treatment unit was inoculated using several gallons of wastewater effluent from the CITGO treatment plant to introduce microbes into the treatment system. The nutrients required for microbial growth were provided with the addition of 500 mL of commercial fertilizer supplement.

The project team collected total VOC concentration data at the inlet and the outlet of the treatment unit using PID technology which demonstrated some high variations in inlet VOC concentration for each of the sampling days with VOC spikes as high as 15,000 (Table 1). The VOC inlet concentrations fluctuated significantly probably since the BTX sump receives wastewater discharges from over 60 process equipment drains throughout the refinery location; this fact could explain the high variability of emission strength and volume during the testing period (Table 1).

Preliminary evaluation of the test data has demonstrated the effectiveness of the sequential treatment system (> 68% Removal Efficiency {RE}) for total VOC emissions treatment in refining operation applications for such highly variable concentrations even without an extended
acclimation period. The unit performance would be expected to gradually improve with increased RE over time as the media and suspended biofilm growth become increasingly acclimated to the blend of VOCs. Removals as high as 96% were achieved for the mixture VOC levels in the range of 100 ppm.

Table 1. Removal Efficiency Data for the Pilot Scale Bio-Treatment System deployed at the BTX wastewater sump at the Citgo Corpus Christi Refinery July 3-8, 2014.

<table>
<thead>
<tr>
<th>Sampling Dates</th>
<th>July 3 - July 4</th>
<th>July 4 - July 5</th>
<th>July 5 - July 6</th>
<th>July 6 - July 7</th>
<th>July 7 - July 8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inlet</td>
<td>Outlet</td>
<td>Inlet</td>
<td>Outlet</td>
<td>Inlet</td>
</tr>
<tr>
<td>Peak (ppm)</td>
<td>15000</td>
<td>3725</td>
<td>1805</td>
<td>321</td>
<td>243</td>
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<tr>
<td>Minimum (ppm)</td>
<td>66</td>
<td>5</td>
<td>175</td>
<td>17</td>
<td>96</td>
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<tr>
<td>Average (ppm)</td>
<td>4600</td>
<td>1443</td>
<td>318</td>
<td>75</td>
<td>159</td>
</tr>
<tr>
<td>% Removal Efficiency (Based on Average)</td>
<td>69</td>
<td>76</td>
<td>88</td>
<td>91</td>
<td>96</td>
</tr>
</tbody>
</table>

% RE Average* 84

*Average removal efficiency (RE %) calculations based on grouping of 24 hours of data collected at BTX waste-water sump, CITGO Corpus Christi refinery, July 3rd-8th, 2014. Improved time series and trend analyses are ongoing for these data.

For more detail refer to the draft manuscript publication in Appendix A. This manuscript will be submitted to the Journal of Environmental Engineering Science.

Recommendations from Project Outcomes

- Complete a field scale unit with material upgrades to the BF unit including solvent resistant piping and leak testing of significant components
- Perform a complete evaluation and engineering analyses of the distribution of speciated hydrocarbons such as benzene from canister sampling before and during the next pilot or field testing of the technology
- A predictive model for design and scale up of the biofiltration equipment into field scale applications at the refinery will be developed
- Identify a new application site such as a hydrocarbon storage tank vent and develop baseline concentration data to aid in optimizing the treatment system
Phase II: The field scale biofiltration unit deployment to treat VOC vapors at the Apache TAMU#2 well tank battery headspace in Snook, Texas.

Project Background

Storage tanks are used in refineries and oil and gas operations to store various organic petroleum liquids such as crude oil and gasoline. During typical operations of these tank batteries such as venting, filling or dispensing, a significant amount of VOCs and HAPs may accumulate in the headspace and be vented periodically. These emissions not only depend on the specific design and structure of the storage tanks, but also the properties of the petroleum liquid. Atmospheric emissions of these substances, could have several adverse effects on the air quality due to its contribution to global environmental effects and also public health and welfare.

In order to meet the growing demand for having cleaner air, several control technologies such as adsorption, incineration and catalytic oxidation have been manipulated. Thermal oxidizers which are frequently used to treat VOCs do meet MACT (Maximum Achievable Control Technology) emission control standards but, due to their high operation cost of fuel and energy, they are not being considered as the most sustainable and energy efficient technology. On the other hand, bioprocesses have been developed as the Best Available Control Technology (BACT) for the treatment of waste gases. The replacement of conventional thermal oxidizers with biofilters will yield natural gas savings alone in the range of $82,500 to $231,000 per year per unit with significantly reduced CO2 emissions compared to flaring operations. They have numerous advantages comparing to other control technologies such as lack of production of secondary effluent and also low demand for addition of supplementary material to the system while in operation. The biological systems should be considered as a promising technology due to their lower cost and environmentally friendly aspect. In these systems, the bacteria and microorganisms use the pollutants as their carbon and energy source for their growth. Since the biological processes usually takes place under aerobic conditions, carbon dioxide, water, inorganic compounds and biomass will be formed at the end of process. Biofiltration and biotrickling filtration are two of the most promising technologies for removal of VOCs. In biofilters, a porous packed media such as compost, wood chips or any other bulking agent is used. The humidified polluted air is passed through this media and decomposed by the pollutant-degrading microorganisms/biofilm which is attached to the media. On the other hand, in the trickle filter processes, synthetic, inorganic or organic media is used and an aqueous phase is trickled over the media continuously to provide nutrients for microorganisms. Due to higher mass flow rates in biotrickling filters and also more concentrated biomass growth, they are more effective for higher concentrations. However, the biofilters could provide a higher retention time and hence a higher removal efficiency for less water soluble compounds.
The main goal of this project was demonstration the application of the sequential treatment technology- biotrickling filtration and biofiltration for removal of mixture of hazardous VOCs from a series of tanks at the Apache TAMU #2 well site production facility (Fig. 1).

![Photo of Apache TAMU #2 well site tank battery near Snook, Texas.](image)

Specific objectives are speciation of the VOCs emission from tank batteries using GC-MS/GC-FID and beginning to optimize the operational parameters of the process. Thus, this project presents an opportunity to optimize operating conditions, media and water recycle rates to apply the technology for steady application for the contaminated air mixtures encountered within the oil and gas industries.

**System Description**

The Apache TAMU #2 Well Site includes a gas compressor, two crude tanks, and a produced water tank (Figure 2). The crude petroleum tanks and produced water tanks are interconnected through ductwork and these were connected to the biofiltration system via a 3” diameter industrial hose. The TAMU #2 well produces a light oil condensate at a rate of about 14 barrels a day with an associated 10 barrels a day of water from a well completion in the Austin Chalk formation. The well is produced using gas lift technology to lighten the oil and water column in the wellbore to allow production to the surface. Production personnel estimated that the tanks are emptied approximately once or twice per week depending on the seasonal temperatures and flow conditions.
Figure 2. View of production tank battery (two crude oil and one water storage tanks) at the Apache TAMU #2 well site near Snook, Texas.

The biological sequential treatment system set up at the well site field location included a biotrickling filter (BTF) unit and one biofilter (BF) (each housed within a 4 ft. diameter and 7.5 ft. high fiberglass vessel. 4” Schedule 80 PVC pipes were used to connect both tanks and provide connections for inlet and outlet of the unit. Moreover, there was 2 alternative fresh air inlet valves at the inlets of the BTF and BF and 1 air inlet valve at the outlet of the BF unit to provide fresh air as needed. Several sampling ports was mounted at different locations of the unit to monitor the water and air parameters (Figure 3).

Figure 3. Side view of skid mounted sequential treatment system showing (left to right) polypropylene horizontal water storage makeup tank, vertical fiberglass BTF unit, and vertical fiberglass BF unit deployed at the Apache TAMU #2 well site.
System Startup

On May 10, 2016, the trailer mounted biotreatment unit was deployed at the Apache TAMU#2 well site. The system included a connection to an onboard water recirculation pump for the biotrickling filter and an induced-draft fan to pull vapor through the unit. The unit was mounted on a 17 foot trailer and the portable configuration was enabled at the remote location with the use of a 20kW diesel generator to provide power for the pump and the fan (Figure 4). The induced-draft fan provided the necessary driving force to pull the emissions through the system. This fan pulled in vapors from the tank battery through the bio-treatment system at negative pressure resulting in a minimum or no leaks. The air flow rate throughout the system could be changed by the volume dampening valve located before the induced fan.

The sumps of the two systems were connected together using 1.5” PVC piping. A 15 gpm water pump was used to send tap water or nutrients solution from the sumps to the filter bed. At the startup of the system, 10 gallons of oily water was collected from a water storage tank near the tank battery. This oily water was mixed with the compost and Miracle-Gro and acclimated for 2-4 days. At the end of the waiting period, the compost/particulate matter was removed and the leftover liquid inoculum were added to the sumps of the biofiltration system. Additionally, 25 gallons of oily water was mixed with the Miracle-Gro and added to the sump to reduce bacteria acclimation period. Water was recycled in the system and a 300 gallon storage tank was made available to replace used water when the water level is very low. A mixed culture water sample collected from the Citgo Corpus Christi Refinery sedimentation basin wastewater treatment plant on June 15, 2016, was used to further stimulate the bio-treatment system acclimation. Miracle-Gro powder was added to the water to provide required nutrients needed for microbial growth.

A sprinkler was installed at top of each of the BTF and BF tanks. The flowing water phase provided a continuous supply of nutrients for the BTF media. Furthermore, it provided humidification of the polluted air, enhanced diffusion of the hydrophilic compounds into the biofilm and also removed some by-products from the system. In order to support microbial growth for the BF media, an inline valve timer was used to spray water on the attached growth media for 2 minutes each day.

In order to prevent flooding or overflow in the bio-treatment unit, a float valve was mounted behind the inlet of the storage tank to the BTF sump. This float valve could close the storage tank flow in the overflow situations. Moreover, an overflow pipeline was installed on both the BF and BTF tanks to exit excess water during overflow periods. The water quality in terms of nutrients were being monitored during the operational period and the wastewater could be removed from the BTF sump through a drainage pipe.

The emissions from the 3 tanks entered the biotrickling filter column containing cross-flow plastic packing, from the bottom, passing out at the top and then into the bottom of the biofilter unit, consisting of the engineered media, flowing upward (countercurrent to the water flow from a sprinkler system).
**Field Scale Unit Performance Testing and Methods**

**Tank Headspace Vapor Characterization**

To characterize the potential influent vapor to the biotreatment unit, the vapor in the headspace in the production tanks was sampled for quantitative and qualitative analysis of VOCs. The tank hatch of one of the crude oil tanks was opened. A portable photoionization detector (PID – RAE Systems) and Summa gas sampling canisters were used to estimate the total VOC levels (PID) and speciated hydrocarbons using the canister samples for injection into the laboratory Gas Chromatograph-Mass Spectrometer (GC-MS) in the Texas A&M University Kingsville laboratories.
The vapor samples were collected in 6 L Summa canisters and transported to the laboratory. Before sampling, the canisters were evacuated in the laboratory using an Entech 3100A canister cleaning system using three cycles of evacuation and re-pressuring of the canister with UHP Nitrogen. Each canister was fitted in the inlet by a flow restrictor for 2 hr sampling and a pressure gauge to indicate the volume of the sample in the canister throughout the event. The vapor samples were analyzed by GC-MS using the U.S. EPA TO-15 method for VOC analysis.

The RAE Systems PID instruments measure VOCs which are common in oil and gas production areas in low concentrations from ppb up to 10000 ppm (1% by volume). The instrument was calibrated with isobutylene calibration gas and zero air as specified in the user’s guide. A handheld anemometer was used for monitoring the inlet gas flow rates, velocity and temperature at different sampling ports. The wind speed and temperature of the area were recorded for later analysis.

The canister samples which were filled with the headspace vapor were transported to the laboratory. After dilution of the canister (DF=10,000), the canister vapors were cold trapped and pre-concentrated using pre-concentrator (Entech 7100A) and then thermally desorbed into the GC-MS (Agilent-6890-5973) columns. To improve the data quality, an Internal Standard (IS) consisted of 3 components (bromochloromethane, chlorobenzene-d, and 1,4-difluorobenzene) at 100 ppbv each was added to the blank, calibration standards and samples. One working calibration standard with concentration of 100 ppbv containing 58 components was used to plot the calibration curve. Quantitative data for individual volatile substances were calculated based on the Relative Response Factor (RRF) of the internal and external standards. Using internal standards and a single point calibration standard, helped to determine the RRF. For an actual unknown sample, after addition of the internal standard, the amount of analyte in the sample is calculated by RRF and peak area of the actual sample. Each species of the sampled VOCs was identified qualitatively by comparing its mass spectrum with the corresponding one in the National Institute of Standards and Technology (NIST) mass spectra library. Based on the database of the GC-MS, the peaks for Benzene, Toluene, Xylene and Hexane were detected as the HAPs (Table 2). This Table also shows the retention time of each of the compounds in the canister samples. The GC-MS also detected other VOCs which are not considered as HAPs such as Butane, Pentane, Propane, Hexane, Heptane, Octane and Nonane. These data correlate well with Oyelakin et. Al (2004) data who quantified and analyzed the HAPs emissions from the an Eagle Ford Shale condensate storage facility in south Texas. In their study, the Benzene, Toluene, Xylene concentration in the condensate headspace was 138, 136 and 18 ppmv, respectively.
Table 2. Qualitative and quantitative analysis of VOCs using GC-MS (DF=10000)

<table>
<thead>
<tr>
<th>Peak #</th>
<th>Component</th>
<th>Retention Time</th>
<th>Conc. (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Butane</td>
<td>9.51</td>
<td>6709</td>
</tr>
<tr>
<td>2</td>
<td>Isobutane</td>
<td>9.21</td>
<td>5118</td>
</tr>
<tr>
<td>3</td>
<td>Pentane</td>
<td>10.88</td>
<td>4233</td>
</tr>
<tr>
<td>4</td>
<td>Butane, 2-methyl-</td>
<td>10.45</td>
<td>4189</td>
</tr>
<tr>
<td>5</td>
<td>Hexane</td>
<td>13.03</td>
<td>1553</td>
</tr>
<tr>
<td>6</td>
<td>Pentane, 2-methyl-</td>
<td>12.29</td>
<td>1497</td>
</tr>
<tr>
<td>7</td>
<td>Cyclohexane, methyl-</td>
<td>16.16</td>
<td>896</td>
</tr>
<tr>
<td>8</td>
<td>Heptane</td>
<td>15.50</td>
<td>649</td>
</tr>
<tr>
<td>9</td>
<td>Cyclopentane, methyl-</td>
<td>13.75</td>
<td>534</td>
</tr>
<tr>
<td>10</td>
<td>Toluene</td>
<td>16.93</td>
<td>282</td>
</tr>
<tr>
<td>11</td>
<td>Octane</td>
<td>17.83</td>
<td>218</td>
</tr>
<tr>
<td>12</td>
<td>Benzene</td>
<td>14.32</td>
<td>197</td>
</tr>
<tr>
<td>13</td>
<td>Nonane</td>
<td>19.90</td>
<td>110</td>
</tr>
<tr>
<td>14</td>
<td>p-Xylene</td>
<td>19.22</td>
<td>87</td>
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</table>

Additionally, the BTF sump water was characterized for the nutrients needed for bacterial growth using an Ion Chromatographic Method. This enabled monitoring of the nutrients present in the recycle water and the sump. Three pressure gauges were used to monitor the pressure drop throughout the system. In the month of July, the removal efficiency of specific VOCs (benzene) in the unit was estimated by collecting grab samples in 1L Tedlar bags and analyzing the sample using a field deployable gas chromatograph (GC) (8610C, SRI Instrument, CA,USA) equipped with a flame ionization detector (FID).

**Field Scale Test Results**

A principal objective was to determine the effectiveness of the biotreatment unit on the removal of total VOCs and specific HAPs in the tank headspace vapor (specifically benzene). The PID data were used to estimate the overall efficiency of the system in terms of total VOCs removal. Figure 5 illustrates some of the variation in VOC loading and removal efficiency for a week in June. The data do demonstrate that the biofiltration removal performance can be steady even with cyclic loadings of variable concentrations.

In Figure 6, the maximum removal efficiency of the total VOCs in the bio-treatment unit hovered around 50% during May and June 2016 probably due to acclimation of bacteria. The relatively low removal of VOCs can be explained due to preponderance of alkanes, and their relative high concentration of the total flowing into the biofiltration unit. Alkanes are difficult to biodegrade in an aerobic environment.
In Figure 6, the fluctuation in total VOCs concentration at the inlet and outlet of the bio-oxidation system is also demonstrated. These fluctuations could be explained from the filling and emptying of the oil tanks during the production cycles for the facility. These operations could affect the VOCs concentration at the headspace of the oil tanks. To the best of our knowledge these data are somewhat unique and potentially very valuable for emission control planning for remote facilities such as this.
Figure 6. PID measurements from the inlet and outlet of the bio-oxidation unit- 10 May 2016 to 29 June 2016- Apache TAMU #2 tank battery.

Table 3 depicts the statistical analysis of VOCs concentration using PID for the bio-oxidation system. The continuous improvement in removal efficiency since the start-up phase is typical of biotreatment systems reflecting the acclimation period of the bacteria. After this initial acclimation phase, the removal efficiency of the system improved and reached to a more optimum level of removal of nearly 50% during the month of July.

<table>
<thead>
<tr>
<th>Sampling period</th>
<th>05/14/2016-05/21/2016</th>
<th>05/21/2016-05/28/2016</th>
<th>05/28/2016-06/04/2016</th>
<th>06/04/2016-06/11/2016</th>
<th>06/11/2016-06/18/2016</th>
<th>06/18/2016-06/25/2016</th>
</tr>
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<tbody>
<tr>
<td>Location of the PID</td>
<td>Inlet</td>
<td>Outlet</td>
<td>Inlet</td>
<td>Outlet</td>
<td>Inlet</td>
<td>Outlet</td>
</tr>
<tr>
<td>Maximum conc. (ppm)</td>
<td>847</td>
<td>675</td>
<td>320</td>
<td>287</td>
<td>190</td>
<td>123</td>
</tr>
<tr>
<td>Minimum conc. (ppm)</td>
<td>27</td>
<td>30</td>
<td>27</td>
<td>18</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Average conc. (ppm)</td>
<td>313</td>
<td>282</td>
<td>128</td>
<td>104</td>
<td>54</td>
<td>38</td>
</tr>
<tr>
<td>SD of conc.</td>
<td>247</td>
<td>204</td>
<td>88</td>
<td>74</td>
<td>71</td>
<td>48</td>
</tr>
<tr>
<td>Average RE (%)</td>
<td>10</td>
<td>18</td>
<td>29</td>
<td>31</td>
<td>36</td>
<td>27</td>
</tr>
</tbody>
</table>

Table 3. Statistical analysis of PID data- 14 May 2016 to 25 June 2016- Apache TAMU #2 tank battery.
The local wind speeds may also slightly influence the influent VOC levels into the unit, since the tank hatch was open to allow oxygen to the unit. The wind speeds were monitored online using the ‘wunderground mobile app’ and a slight correlation between inlet VOC concentrations and wind speed seems to occur (Figure 7). It can be observed that the inlet VOC loadings has some fluctuations, varying from 700 to 10 ppm as isobutylene with an approximate average value of 200 ppm. Because of the open hatch on the water tank during the operation, the ambient air could dilute the VOCs that are pulled from the tank battery headspace. The water tank was continuously vented with ambient air to simulate the flow of air and oxygen needed for adequate retention and treatment in the biofilter. The project team measurements of local ambient air confirmed the average total VOC concentrations outside the tank battery’s immediate area were almost negligible in comparison with ambient air standards (i.e., far below 250 ppmv isobutylene equivalent).

![Figure 7. Example results for the effect of the wind speed on the inlet concentration of VOCs- 6-10 June 2016- Apache TAMU #2 tank battery headspace.](image)

Temperature data were collected using a hand held anemometer at 6 different sampling ports (Figure 8). Based on the trends, the average air temperature was 95 °F which suggested that the system is operating under mesophilic conditions for the bacteria. Moreover, by comparing the temperature and RE data, it seems evident that the temperature has no measurable effect on the removal efficiency of the system. It is noted that the temperature at the BTF outlet is less than the BTF inlet due to continuous spraying of the water on the polluted air. This effect could be
another advantage of the sequential bio-treatment system since this system operation should cool down thermal gases.

![Graph](image1.png)

Figure 8. Example results for the effect of the temperature on the removal efficiency - 6-10 June 2016 - Apache TAMU #2 tank battery.

The handheld anemometer was used for monitoring the air flow at 6 different sampling ports of the unit (Figure 9). The average air flow rate throughout the unit was 25 cubic feet per minute providing about 4 minutes of Empty Bed Retention Time (EBRT).

![Graph](image2.png)

Fig 9. Example results for the air flow rate and velocity throughout the system - 6-10 June 2016 - Apache TAMU #2 tank battery.
The BTF system sump water was collected weekly and the concentration of nutrients in the bio-treatment unit was monitored using Ion-Chromatography (IC). From the results of the IC, the peaks of chloride, nitrate and phosphate were estimated (Table 4). These nutrient levels are very sufficient for sustainable bacterial growth.

<table>
<thead>
<tr>
<th>Peak #</th>
<th>Component</th>
<th>Retention Time</th>
<th>Conc. (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chloride</td>
<td>6.84</td>
<td>61</td>
</tr>
<tr>
<td>2</td>
<td>Nitrate</td>
<td>13.10</td>
<td>2,138</td>
</tr>
<tr>
<td>3</td>
<td>Phosphate</td>
<td>18.41</td>
<td>3,732</td>
</tr>
</tbody>
</table>

Table 4. Example results of the nutrient analysis using IC.

Phase II References

5. Oyelakin, O., Ramirez, D. (2014) Quantification and analysis of hazardous air pollutant emissions from unconventional oil and gas exploration storage tanks. A&WMA’s 107th Annual Conference and Exhibition, June 24–27,
6. Long Beach, California.
Appendix A

Draft Manuscript entitled, “Pilot testing of a sequential biological air emissions treatment system for VOC emission control at a petrochemical refining operation,” for submission to the Journal of Environmental Engineering Science.
Pilot testing of a sequential biological air emissions treatment system for VOC emission control at a petrochemical refining operation

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Abstract
A sequential bio-treatment system, defined as a combined treatment consisting of a bio-trickling filter and biofilter, was deployed at a BTX wastewater sump at a coastal petrochemical refinery to facilitate low-cost VOC removal. Vapor samples were collected from the wastewater sump for gas chromatography-mass spectrophotometry (GC-MS) analysis for vapor characterization to determine benzene amounts. Benzene constituted an estimated about 85% of the vapor stream with its primary concern being carcinogenic. The empty bed residence time (EBRT) established 90 seconds by controlling the vapor flow rate. The removal efficiency was 84% over a five-day period and the elimination capacity was in the range of 5.5 g m⁻³ hr⁻¹ to 1750 g m⁻³ hr⁻¹ for a pollutant-loading rate of 6 g m⁻³ hr⁻¹ to 1750 g m⁻³ hr⁻¹.

Introduction
Biofiltration is an emerging technology that replaces other adsorption technology including carbon canisters to remove volatile organic compounds (VOCs) or inorganic toxic gases. Biofiltration units are operated by directing pollutants through microbial-composed engineered media. Bio-trickling filters and bio-filters have previously treated large volume of organic emissions (Santos et al. 2005; Singh et al. 2010; Garner 2002). The majority of biofiltration research has been completed in Europe; the United States until recently did not widely use biological treatment systems. Removal efficiencies of more than 90% have been achieved for many common air pollutants (Leson and Winer, 1991). However, few pilot studies have combined bio-trickling and bio-filter technologies in order to treat low volumes of pollutants (Boswell et al. 2008). Large quantities of water are needed by refineries and petrochemical industries for desalting, stripping, absorption, among other operations and is considered a significant source of HAPs and VOC emissions.
A major component within the wastewater sumps is benzene, a carcinogen, which is now a primary concern to several industries. Industries are readily needing to comply with the Benzene Waste Operation NESHAPs (BWON). Benzene is dangerous to human health and is typically adsorbed via carbon canisters. The carbon canisters must be regenerated each time they are saturated.
Thermal oxidizers do meet MACT (Maximum achievable control technology) emission control standards and are commonly used to burn VOC and other HAPs. Due to the operating costs of supplemental fuel and power, this technology is not the most sustainable and energy efficient. However, it is challenging for plant operators to select an efficient treatment technology with lower operational costs and low energy requirements (Deshusses et al. 1995). Biological treatment technology has been proven effective for VOC removal in paint and coating industries, forest products industries, and many others. In this project, the extension of this innovative biotechnology to control petrochemical emissions was proposed and evaluated.
Absorption, condensation, and adsorption are some of the typical conventional treatment technologies for VOC air emissions treatment. These techniques are physical methods which often leave saturated carbon which has to be disposed of or further treated as it is a hazardous waste (Zarook et al. 2005). Chemical methods to treat VOC emissions include thermal oxidation, chemical precipitation, and catalytic oxidation. High energy inputs and fuel are often required for some of these chemical methods which may not be sustainable for long term use. Some of these methods require the use of chemicals, which might result in the generation of toxic by-products that must be appropriately disposed of. A Condensation process for removal is economical only for compounds that have a higher boiling point and for gas streams that are concentrated (Altay et al. 1999). Adsorption processes are useful for treating gas streams with low pollutant concentration. The drawbacks of adsorption processes include regeneration of the adsorbent and safe disposal of saturated adsorbent.

There are some challenges and limitations of biological treatment systems. These treatment systems have proven to be less effective for high concentration of pollutants over a longer time. Large volumes of low concentration pollutants suit these systems. A larger footprint is one of the drawbacks of this treatment system. Extremely high inlet concentration loadings can destroy microbes over a long period affecting its removal efficiency. High empty bed residence time might be required for some applications. It is challenging, but necessary, to maintain a certain amount of moisture content and prevent the filter from clogging to reduce pressure drop. It is also challenging to maintain oxygen content in the filter needed for microbial growth. Variable loadings may prove to be harmful for the microbes.

This study aims to utilize sequential treatment system to treat VOC emissions consisting of BTEX from wastewater sump in a coastal petrochemical facility.

Materials and Methods

Sequential Bio-Treatment

The main components of the experimental set-up used for sequential biofiltration is shown in Figure 1. Operational conditions that affect microbial growth include recycled water quality, temperature, moisture content, and pH. The bio-trickling filter column and biofilter column were utilized for a two-step treatment of VOC emissions. The biofilter portion consisted of three vertical stages, each section was 0.45 m in height and made of plastic with a volume of 0.17 m³. Each biofilter vertical stage consisted of engineered 1 inch bio-balls composed of compost. The bio-balls were filled in each section until a height of 0.25 meters was reached. 3 inch PVC pipes were used to connect both columns and provide connections for the inlet and outlet of the unit.

The emissions from the BTX sump entered the treatment unit through a 3-way valve which also acts as an inlet for ambient air into the system for aerobic bacterial conditions. The bio-trickling unit and biofilter had 3 sampling ports along the height for measuring concentration of VOC vapors. Sampling ports are also located at the inlet and outlet.
The biotrickling filter is supplied with a continuous water sprinkling system to refine the inlet vapor stream before it enters the biofilter. The hydrophilic hydrocarbons are absorbed in water before it reaches the biofilter column. A digital flow meter kept before the inlet in the sprinkler system displays the water flow rate. The water flow rate can be controlled using a valve located before the digital meter and the biofilter column is provided with a sprinkler system having one sprinkler for each section. The continuous water flow was set on a timer to continuously flow for 2 minutes every 2 hours. A co-current flow is observed in the biofilter where vapors and water entered from the top and exit from the bottom. PG22

Figure 2: Sequential Biofiltration Schematic

Photo ionization detectors (PID) were used to measure the total VOC in a vapor stream in a range of 0 to 15000 ppm. The PID meters used in this study were capable of data logging for 6 months at an interval of 1 minute while data is collected each second with an average over 60 seconds is taken. Summa canisters were used to collect two 8 hour samples and one instantaneous sample to be tested in the gas chromatography-mass spectrometry (GC-MS) unit. A TSI Air Velocity meter was used to measure volumetric flow rate of vapor. The velocity range of this meter is 0 to 30 m/sec. It can also measure temperature up to 200°F. Oxygen in the system was measured using an oxygen gas sensor which had a range of 0-27% for oxygen content. PID meter was connected to ¼ inch connection on a pipe above the wastewater sump. Summa canister samples were taken in April to be analyzed via GC-MS to characterize the vapor concentration in terms of a ratio of benzene to toluene to xylene concentration. PID data was compared with GC-MS data to validate primary data as well as operating conditions.

Study Location
The coastal refinery wastewater sump had a minimum of 60 wastewater streams routed to the BTEX sump that vary in composition. The wastewater streams are routed to the sump during
equipment draining and cleaning unit outages; however, the BTX-7 and HYD-23 are continually flowing. Initial sampling at the BTX wastewater sump occurred in April and June using the MiniRAE 3000 PID meter to determine the total VOC concentrations in the sump and its variations over time. The PID meter was connected to a ¼ inch connection on a pipe above the wastewater sump.

The bio-treatment unit was mounted on a trailer and grounded for safety purposes. In order to establish an inoculated colony, wastewater from the facility and Miracle-Gro ® was applied to the media. Initial oxygen content in the system ranged between 17% to 19% with an initial flow rate of 13.6 m³/hour. The water flow rate into the trickling filter was 0.9 gallons per minute.

Results

The sequential biological filtration system was carried out for 4 days at various operating conditions. The initial readings demonstrated inlet benzene concentration of 1000 ppm and an outlet of 100 ppm, which suggests a 90% removal of benzene. The results gathered from the PID meters were in terms of ppm of isobutylene because of the calibration process using 100 ppm of isobutylene gas. To determine the ppm of benzene or any other individual compound in the total VOC concentration data and characterize the data, the PID data was compared to the GC-MS. Photoionization sensitivity of each compound had to be considered and using this, the GC-MS concentration data was used to determine individual compound concentration from the total VOC data in terms of ppm of isobutylene. The PID was calibrated using isobutylene gas, hence the correction factors of each compound are required to calculate actual ppm of each compound. 10.6 ev lamp was used, hence correction factors for the same have been used.

Table 2: GC-MS speciation analysis for the BTX wastewater sump VOC vapors on 4/17/2014

<table>
<thead>
<tr>
<th>Compound</th>
<th>RT (min)</th>
<th>Area</th>
<th>Amount</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butane, 2,2-dimethyl</td>
<td>2.669</td>
<td>637741</td>
<td>8.2</td>
<td>ppbv</td>
</tr>
<tr>
<td>Hexane</td>
<td>3.03</td>
<td>2317446</td>
<td>192.9</td>
<td>ppbv</td>
</tr>
<tr>
<td>Hexene</td>
<td>3.03</td>
<td>2348287</td>
<td>66.6</td>
<td>ppbv</td>
</tr>
<tr>
<td>Benzene</td>
<td>3.508</td>
<td>11948293</td>
<td>33.4</td>
<td>ppbv</td>
</tr>
<tr>
<td>Pentane, 2,2,4-trimethyl-</td>
<td>3.77</td>
<td>8352809</td>
<td>25.7</td>
<td>ppbv</td>
</tr>
<tr>
<td>Heptane</td>
<td>4.09</td>
<td>356562</td>
<td>10.1</td>
<td>ppbv</td>
</tr>
<tr>
<td>Toluene</td>
<td>5.825</td>
<td>1469140</td>
<td>5.7</td>
<td>ppbv</td>
</tr>
<tr>
<td>Heptane, 3-methyl-</td>
<td>5.825</td>
<td>1522981</td>
<td>1.6</td>
<td>ppbv</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>9.289</td>
<td>513140</td>
<td>2.9</td>
<td>ppbv</td>
</tr>
</tbody>
</table>

Sample #2: Date 4/18/2014 (5 hours sampling using Summa Canister)

Table 3: GC-MS speciation analysis for BTX wastewater sump VOC vapors on 4/18/2014

<table>
<thead>
<tr>
<th>Compound</th>
<th>RT (min)</th>
<th>Area</th>
<th>Amount</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butane, 2-methyl</td>
<td>2.137</td>
<td>222837</td>
<td>17.2</td>
<td>ppbv</td>
</tr>
<tr>
<td>Butane, 2,2-dimethyl</td>
<td>2.516</td>
<td>3219658</td>
<td>21.9</td>
<td>ppbv</td>
</tr>
<tr>
<td>Hexane</td>
<td>3.034</td>
<td>1517921</td>
<td>196.5</td>
<td>ppbv</td>
</tr>
<tr>
<td>Hexene</td>
<td>3.034</td>
<td>1609783</td>
<td>72.4</td>
<td>ppbv</td>
</tr>
<tr>
<td>Benzene</td>
<td>3.517</td>
<td>21102500</td>
<td>242.2</td>
<td>ppbv</td>
</tr>
</tbody>
</table>
Pentane, 2,2,4-trimethyl- 3.779 5639429 30.5 ppbv
Heptane 4.094 690529 12.0 ppbv
Cyclohexane, methyl- 4.565 411767 1.4 ppbv
Heptane, 3-methyl- 5.852 20138508 431.8 ppbv
Toluene 5.852 18570695 69.9 ppbv
p-xylene 9.200 9699214 21.7 ppbv
Nonane 9.986 5108690 32.8 ppbv
Decane 12.681 8254582 96.4 ppbv

Table 4: GC-MS speciation analysis for BTX wastewater sump VOC vapors on 4/29/2014

<table>
<thead>
<tr>
<th>Compound</th>
<th>RT (min)</th>
<th>Area</th>
<th>Amount</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>3.959</td>
<td>6.18E+08</td>
<td>1-1.5**</td>
<td>ppbv</td>
</tr>
<tr>
<td>Heptane</td>
<td>4.553</td>
<td>61656519</td>
<td>790.3</td>
<td>ppbv</td>
</tr>
<tr>
<td>Cyclohexane, methyl-</td>
<td>4.966</td>
<td>1933730</td>
<td>48.2</td>
<td>ppbv</td>
</tr>
<tr>
<td>Toluene</td>
<td>5.898</td>
<td>324213</td>
<td>6.4</td>
<td>ppbv</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>9.397</td>
<td>1241804</td>
<td>22.3</td>
<td>ppbv</td>
</tr>
<tr>
<td>p-xylene</td>
<td>9.397</td>
<td>592180</td>
<td>9.4</td>
<td>ppbv</td>
</tr>
<tr>
<td>Nonane</td>
<td>10.416</td>
<td>5.02E+08</td>
<td>355.7</td>
<td>ppbv</td>
</tr>
<tr>
<td>Decane</td>
<td>12.884</td>
<td>5.73E+08</td>
<td>928.5</td>
<td>ppbv</td>
</tr>
</tbody>
</table>

Figure 5: PID sampling data from BTX wastewater sump on 4/29/2014
The average concentration for the day was 2.32 ppm (measurement gas: Isobutylene). Data for PID and GC-MS are available for 4/29/2014 at 11:30 am. The PID recorded a concentration of 5.5 ppm in terms of isobutylene. The GC-MS data were converted into the form of ppm isobutylene to compare it with total VOC data available from PID.
Characterization of total VOC data:

**ppm of each compound (GC-MS data) = ppm in isobutylene (PID data) * correction factor**

Table 5: Comparing PID and GC-MS data

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Correction Factors</th>
<th>GC-MS data (ppm)</th>
<th>Calculated corresponding PID data (ppm)</th>
<th>Recorded PID data (ppm)</th>
</tr>
</thead>
</table>

27
In order to check accuracy of the PID data, the GC-MS speciation data collected on 4/29/2014 was compared with the PID data collected on the same date and time. The approach involved using correction factors for each compound available from the MiniRAE 3000 manual, assuming that the vapor stream contained only benzene as the sole compound. The concentration of benzene was 1.5 ppm as per the GC-MS analysis. If this vapor was sampled using a PID calibration for isobutylene gas, it would display a value of 3 ppm on the PID meter for 1.5 ppm of benzene. This is due to the fact that the PID meter is calibrated using isobutylene and the UV lamp responds accordingly. The PID meter would have read as 1.5 ppm if benzene was used for calibration. If a true concentration for benzene has to be determined from a PID calibrated with isobutylene, the value must be multiplied by its correction factor. In this application a reading on the PID of 1.5 ppm of benzene stream was routinely measured. A similar approach was opted for all compounds and their concentration in terms of ppm of isobutylene to compare with the available PID data.

Adding up the actual PID data of each compound in terms of ppm of isobutylene gives a total value of 4.63 ppm isobutylene which was very close to the value recorded by the PID i.e. 5.5 ppm. The difference can be attributed to the presence of few other compounds and mainly methane gas as the GC-MS is not able to characterize methane.

Vapor flow rate was initially set to 20 m³/hr; giving an EBRT of 1 minute. The vapor flow rate varied during days of operation and the average flow rate was found to be 13.6 m³/hr. The porosity of media was calculated to be 0.85.

Table 6: Removal Efficiency of treatment system during field test (Source: Aggarwal, 2014)

<table>
<thead>
<tr>
<th></th>
<th>July 3- July 4</th>
<th>July 4- July5</th>
<th>July 5- July 6</th>
<th>July 6- July7</th>
<th>July 7-July8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data-log</td>
<td>Inlet</td>
<td>Outlet</td>
<td>Inlet</td>
<td>Outlet</td>
<td>Inlet</td>
</tr>
<tr>
<td>Peak (ppm)</td>
<td>15000</td>
<td>3725</td>
<td>1805</td>
<td>321</td>
<td>243</td>
</tr>
<tr>
<td>Minimum (ppm)</td>
<td>66</td>
<td>5</td>
<td>175</td>
<td>17</td>
<td>96</td>
</tr>
<tr>
<td>Average (ppm)</td>
<td>4600</td>
<td>1443</td>
<td>318</td>
<td>75</td>
<td>159</td>
</tr>
</tbody>
</table>
Figure 6 illustrates the performance of the sequential biological treatment system for varying loading rates of benzene from 7/3/2014 to 7/7/2014. It is evident from the results that the treatment system showed a uniform and stable performance for a wide range of pollutant loading rates. Elimination capacity of 1600 g m\(^{-3}\) hr\(^{-1}\) was observed for a loading rate of 1750 g m\(^{-3}\) hr\(^{-1}\) for benzene on 7/3/2014. These results display the capability of the treatment system to treat high concentrations of pollutants at varying loadings.

Figures 6: Elimination capacity of treatment system at BTX sump for benzene loading from 7/3/2014 to 7/7/2014

The second day benzene concentrations were lower compared to day one. A maximum elimination capacity of 180 g m\(^{-3}\) hr\(^{-1}\) was observed for benzene loading rate of 190 g m\(^{-3}\) hr\(^{-1}\). A minor non linearity was observed for lower pollutant loading rate but more or less the system performance was stable. The performance of the biological treatment system on 7/5/2014 was stable. The benzene loading rates were in the range of 11 g m\(^{-3}\) hr\(^{-1}\) to 27.5 g m\(^{-3}\) hr\(^{-1}\). In spite of varying loadings, the treatment system showed stable performance. The elimination capacity ranged from 10 g m\(^{-3}\) hr\(^{-1}\) to 25 g m\(^{-3}\) hr\(^{-1}\) suggesting 91\% of benzene removal. The pollutant
loading rates remained more or less in a similar range on both days ranging from 6 g m$^{-3}$ hr$^{-1}$ to 20 g m$^{-3}$ hr$^{-1}$ on the last two test days. Different elimination capacity results were observed for similar loading rates on few occasions. Overall, the performance of the treatment system was stable and the elimination capacity ranged from 5.5 g m$^{-3}$ hr$^{-1}$ to 19 g m$^{-3}$ hr$^{-1}$. The elimination capacity calculated a 90% removal for benzene for a loading rate of 6 g m$^{-3}$ hr$^{-1}$. Individual trends for elimination capacity v/s benzene loading rates are present in the Appendix.

Table 8: Comparing Benzene loading rate with benzene biodegradation rate

<table>
<thead>
<tr>
<th>Date</th>
<th>Average biodegradation rate of benzene $r_j$ (g/m$^3$/hr)</th>
<th>Average benzene loading rate (g/m$^3$/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7/4/2014</td>
<td>20.90</td>
<td>36.19</td>
</tr>
<tr>
<td>7/5/2014</td>
<td>12.87</td>
<td>18.14</td>
</tr>
<tr>
<td>7/6/2014</td>
<td>8.56</td>
<td>13.04</td>
</tr>
<tr>
<td>7/7/2014</td>
<td>6.01</td>
<td>9.98</td>
</tr>
</tbody>
</table>

**Discussion**

The simulation results as shown in Figure 8 demonstrates that the experimental and model predicated elimination capacity v/s benzene loading rate plots for the sequential treatment system suggests that there is reasonable agreement between model data and experimental data. As the variations in concentration for each day were high, the modeled data and experimental data showed some differences. K$_m$ value of 6 g/m$^3$ gave a reasonable fit for the modeled values. It did under predict the outlet concentrations for low loading rates. While performing the mass balance for the treatment system, a steady state was assumed which was not the case during the field test. This model can be best used for applications that have lesser variations in flow rates and function close to steady state conditions. An acceptable value of K$_m$ can be estimated which predicts outlet concentrations and thus elimination capacity accurately for steady state conditions. This study was able to generate reasonable estimates for the volumetric biodegradation of benzene in the bio-treatment system ($r_j$).

Comparing the benzene loading rate with biodegradation rate it can be estimated that a significant amount of benzene was removed by the microbes in the biofilter. This conclusion is consistent with the fact that benzene is hydrophobic and it is difficult to remove benzene in the trickling filter. Table 8 shows average biodegradation rate of benzene v/s average loading rate of benzene for each day of field test.

**Conclusions**

A sequential trailer mounted biological treatment system was evaluated for treating VOC emissions from BTX wastewater sump situated at CITGO Corpus Christi Refinery. PID and GC-MS data was obtained for VOC vapors emitting from the sump. This was done to establish
baseline concentrations for the treatment system. PID and GC-MS data was compared for accuracy. VOC concentrations were measured at inlet and outlet of the treatment system using PID meter. Elimination capacity of the system was calculated and compared with the pollutant loading data. To elucidate benzene removal in the treatment system; a semi-empirical model based on mass balances along the bio-treatment unit was tested with input parameters obtained from literature and field test data. Volumetric biodegradation of benzene in the biofilter could be obtained by modeling.

The pressure drop across the unit, temperature, air flow rate, water recirculation rate and water level in the storage tank, pH, conductivity, inlet and outlet VOCs concentration are some of the most important parameters to be monitored through a PLC system.

**Acknowledgements**

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References


Publications/Presentations


