

Evaluation of Environmental Emissions for Combustion of Landfill Gas  
in a Texas Petrochemical Plant

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## Executive Summary

This report deals with the technical feasibility of using mixed fuels such as natural gas and landfill gas (LFG) in steam generation. The focus of this report is on the environmental aspects of substituting LFG for natural gas in combustion. Due to the rising cost of natural gas, there is an economic incentive to use LFG if certain technical and environmental issues can be resolved.

- (1) Landfill gas has a beneficial effect on nitrogen oxides emission compared to natural gas, causing a significant (50%) reduction in ppm levels if the gases are co-fired or if LFG is used separately. Low NO<sub>x</sub> burners and flue gas recirculation can further reduce NO<sub>x</sub> levels in the flue gas to the 30 ppm level. In the future computational fluid dynamics (CFD) software may be improved sufficiently to make accurate emissions predictions for a given control strategy but currently only semi-quantitative predictions are possible with CFD at this time.
- (2) Added constituents (oxygen; carbon dioxide, hydrogen sulfide) in LFG (vs. natural gas) do influence combustion and emission properties of the fuel. A small amount of oxygen (<2%) does not raise safety concerns for pipelining and only slightly changes the necessary air/fuel ratio in a furnace. Carbon dioxide volume fraction in LFG usually ranges from 40 to 50%, which lowers the heating value but also the flame temperature, which are beneficial for reducing NO<sub>x</sub> emissions significantly. In fact in some cases blending of LFG with natural gas may obviate the need for low NO<sub>x</sub> burners and for flue gas recirculation. Finally the presence of hydrogen sulfide could be problematic if it is too high because it might require sulfur oxide control technology. However, for the application considered here, the H<sub>2</sub>S concentration was low enough that projected sulfur oxide emissions did not exceed currently permitted levels. An analysis of HAP (hazardous air pollutant) components for LFG combustion was also performed and found two HAP's that may be of concern.

- (3) Segregation of LFG from natural gas might be desirable to ensure that current combustion equipment for natural gas can be fully utilized, but it will add significantly to the cost. Current technology for co-firing LFG and natural gas seems to be adequate for handling both gases without requiring major design changes or added capital cost. In the plant considered in this study, co-firing modifications are being made by a combustion vendor.
- (4) When burner modifications are made, there can be a question as to whether the existing guarantee on the burners will be valid. However, the current application demonstrates that burner modifications for LFG are now routinely made and that there is a high level of confidence that satisfactory performance of the co-fired system in terms of combustion efficiency and reduced emissions will be realized. Improved process controls of the air/fuel ratio can be installed to ensure that performance of the new system can be maximized.
- (5) The permitting of the existing combustion equipment for NO<sub>x</sub> and CO emissions does not appear to be an obstacle for implementation of this LFG project. The permitted values were already below current NSPS standards, due to the fact that the plant is located in the Houston-Galveston-Brazoria (HGB) non-attainment area. Implementation will result in reduction of NO<sub>x</sub> emissions from the current 120 ppm to around 30 ppm, which is desirable because of HRVOC (highly reactive volatile organic compounds) issues in the HGB.
- (6) The cycling of landfill gas production to deal with variable steam demand was analyzed and found not to be a desirable alternative for this application. This is because the plant requires a larger amount of energy than can be provided by LFG alone. The variable nature of energy demand can be satisfied by adjusting the flow rates of natural gas, since that will provide 85% of the total energy once the LFG pipeline is operating (currently natural gas provides 100% of the fuel requirements). The petrochemical plant is located 31 miles from the landfill.

## 1.0 Introduction

The goal of this project was to conduct a feasibility analysis of the use of landfill gas in a refinery mixed-fuel system. Refineries and petrochemical plants are large natural gas consumers, accounting for 14% of the natural gas used as fuel by industry in the U.S. Landfill gas has been used in boiler applications where it has replaced natural gas. However, these plants typically have boilers, co-generation units, and heaters that burn natural gas or are multi-fuel, able to burn natural gas and/or waste fuel gas such as refinery gas. The introduction of landfill gas into this system poses a number of questions that have not been sufficiently addressed in the technical literature.

This project examines the feasibility of burning landfill gas in refinery boilers, turbines, and fuel gas systems. The potential impact of adoption of this practice is estimated for Texas and Louisiana alone to total 21.75 trillion Btu/yr. This is based on the refinery capacities in these states, the amount of natural gas consumed as a fuel by refineries in these states, and an assumption that 5% of this natural gas fuel could be substituted. Implementation of this practice would depend on resolving certain technical issues and the economics of transporting the landfill gas to refineries. Adoption nationwide could yield far larger savings.

The original plan for this project was to work with the Valero Houston Refinery, a 130,000 barrel per day facility that is located in the Houston ozone non-attainment area. Boilers in that refinery are low-NO<sub>x</sub> and have selective catalytic reduction (SCR) controls in order to meet strict limits on NO<sub>x</sub> emissions. However, for business reasons Valero did not pursue purchase of LFG. Instead a petrochemical plant 30 miles away entered into a contract to purchase the gas if a dedicated pipeline could be built to deliver the gas. Therefore this report focuses on the petrochemical application of LFG.

The questions originally to be answered by the project include:

1. How are nitrogen oxide emissions affected by burning landfill gas, versus natural gas or waste fuel gas? Is the mechanism for achieving lower NO<sub>x</sub> levels understood?
2. Are the effects of the added oxygen, carbon dioxide, and hydrogen sulfide fully understood when landfill gas is used in a mixed combustion gas system?
3. If segregation of fuels is required, what would need to be done by a plant to ensure safe operation and maintain the segregation of the landfill gas from the fuel gas? What procedures, policies, and on-line testing would be required to ensure compatibility in the boiler and/or heater fuel system?
4. How would the guarantee on the burners be affected by burning landfill gas? What would need to be done to address this so that guarantees would cover this situation?
5. What would be the impact on re-permitting of combustion units, since current permits specify natural gas and waste fuel gas?
6. How can the landfill gas be cycled so that it can be used during peak power periods? Can the gas be produced during parts of each day at higher production levels (and shut off during the remainder of each day)?

Some of these questions, namely nos. 3 and 6, are not examined in depth because they were formulated in the context of the Valero refinery application but they are discussed in Section 5.0. The principal investigator (T.F. Edgar) entered into a non-disclosure agreement (NDA) with the petrochemical company in order to obtain specific information about the planned use of the LFG, so that the results of this study could be tailored to be of value to that company. However, this report may be of general interest to companies at other sites who are considering the use of LFG.

The report has four main sections covering the general use of LFG for steam production, the particular application at the Texas petrochemical plant, the impact of substituting LFG for natural gas on air emissions, and other implementation issues that might be relevant at other sites.

## **2.0 Overview of Landfill Gas Utilization and Technology**

Utilization of landfill gas (LFG) in place of a conventional fuel such as natural gas, fuel oil, or coal in boilers is an established practice with more than 25 years of application. There are more than 70 boilers operating with LFG in the U.S., either alone or co-fired with other fuels (EPA [1]). LFG is comprised about 50 percent by volume of non-combustible gas, mostly carbon dioxide (CO<sub>2</sub>). LFG is classified as a “medium Btu gas” with a heating value of about 500 Btu/per standard cubic foot (SCF), about half the heating value of natural gas. Therefore, when LFG is substituted for natural gas, the volume of LFG that must be handled by the fuel train and burner is twice that of natural gas, which means that modifications to the fuel train and burner are usually required to accommodate the higher overall gas flowrate for the same heat duty. The increased gas flow, however, does not have an appreciable effect on the design and operation of boiler components downstream of the burner. Some installations have retained the original burners but modified them for LFG (e.g., by installing separate LFG fuel train and gas spuds), while maintaining the existing natural gas fuel train and gas ring to permit LFG/natural gas co-firing. Other installations have replaced the entire burner, controls, and fuel train with a dual-fuel burner and dual-fuel trains specifically designed to handle medium Btu gas. Because LFG is typically a wet gas often containing trace corrosive compounds, the fuel train and possibly some burner “internals” should be replaced with corrosion-resistant materials. Stainless steel has typically been the material selected. However, if the gas is dewatered before transport in a pipeline, then the corrosion problem becomes less severe.

The controls associated with fuel flow and combustion air flow need to be engineered to cope with the variable heat content of LFG. The complexity of the burner management

system will depend upon whether the boiler is to be co-fired with natural gas. Modern controls, fast-responding oxygen analyzers, and responsive flame sensors make it possible to fire LFG with the same level of safety that is characteristic of current natural gas systems. A family of organo-silicon compounds (known as siloxanes) is usually found in the solid waste stream and can pass into LFG. Their quantity in LFG is small and varies with the age of the landfilled material. When LFG is burned, the siloxanes are oxidized to silicon oxide, resulting in deposits of white powder on the boiler tubes and the boiler floor. Operator experience to date indicates that annual cleaning is sufficient to avoid operational problems related to silicon oxide accumulation. Because LFG is generally saturated with moisture, gas treatment is needed before entering the boiler to avoid condensation and corrosion. The level of LFG clean-up required for boiler use is minimal, with only large particle and moisture removal needed. Carbon dioxide could also be removed but may not be economically justified if the burners can be modified as discussed above. Burner manufacturers (e.g., Todd, North American, and Coen) have provided specially designed LFG burners or have experience modifying standard natural gas burners for LFG service.

Two examples of a successful boiler LFG energy projects are illustrative of many LFG projects undertaken recently [1]. In early 2003, NASA's Goddard Space Flight Center in Greenbelt, Maryland, began firing LFG in two water tube boilers, each capable of producing 50,000 pounds per hour of steam. The gas is piped approximately five miles from the Sandy Hill Landfill to the boiler house at Goddard. NASA modified the burners and controls to co-fire LFG, natural gas, and oil; however, LFG provides the total firing requirement for approximately nine months of the year. At the Cone Mills White Oak textile manufacturing plant in Greensboro, North Carolina, LFG is utilized in a brick set boiler with two multi-fuel burners supplied by Coen Company, Inc. Full operation began in early 1997, with a steaming capacity of 30,000 pounds per hour from the LFG fuel. Additional steam is provided as needed by co-firing with natural gas or fuel oil.

### **3.0 Landfill Gas Utilization at Houston, TX Petrochemical Plant**

In December, 2007, we discovered that Valero was apparently not actively pursuing the use of LFG because Landfill Gas Solutions of Houston, TX had entered into a contract to deliver landfill gas to a petrochemical plant south of Houston that requires construction of a new dedicated pipeline. The plant's fuel demand exceeds by a factor of eight the amount of LFG available (7500 ft<sup>3</sup>/min). The gas composition is approximately 51-55% CH<sub>4</sub>, 38-42% CO<sub>2</sub>, 2% O<sub>2</sub>, 4% N<sub>2</sub>, 2% other (such as H<sub>2</sub>S). After gas dewatering, the LFG is transported by pipeline over 31 miles, which would make this pipeline the longest LFG pipeline in the U.S. A private study on economic feasibility and evaluation of the Babcock & Wilcox (B&W) boilers has been performed by CPL Systems of Lafayette, LA. According to engineer David Mauney from CPL Systems, very little modification of the boiler burners will need to be done for this specific LFG.

According to Mr. Mauney, there will be capital costs for right-of-way pipeline construction and operating costs for the pipeline, mostly due to power costs. The annualized capital costs of LFG cleanup and pipelining can be benchmarked relative to other energy costs. Based on estimated costs of compression, dewatering and installation of a new pipeline (total of \$15 million), annualized capital costs at an interest rate of 8% amortized over 30 years would be \$1.25 million per year. Based on 7500 ft<sup>3</sup>/min, the total heating value delivered would be  $2 \times 10^{12}$  Btu/yr. Ratioed to a basis of 10<sup>6</sup> Btu, the cost would be about \$.67/10<sup>6</sup> Btu for the capital facilities, which can be contrasted with current methane prices of \$7.00/10<sup>6</sup> Btu. Although these figures are estimates developed for this report, it is clear that the economics of using LFG are quite attractive from a capital cost point of view. The main operating cost for such a pipeline would be the cost of compression, with the goal of delivering the gas to the boilers at close to atmospheric pressure. For a 14 inch pipeline and a distance of 30 miles, the pressure drop can be calculated for a compressible gas using a mechanical energy balance. Using the flow rate above, the pressure drop would be about 30 psi, which means only one compressor would be required at the LFG generation site. The costs of operating this compressor would be approximately \$0.30/10<sup>6</sup> Btu, again fairly low compared to the benchmark cost for methane. The overall capital and operating costs would total \$1.55/year, which is quite attractive. Added to this cost would be modifications to the combustion system, which

are discussed below. The petrochemical plant contracted for a delivered price, which is not public information.

#### **4.0 Impact on Air Emissions by Substitution of Landfill Gas for Natural Gas**

##### **4.1 Heating value and flame temperature effects**

One of the technological limitations of LFG is that its heating value is approximately one-half that of methane (due to presence of CO<sub>2</sub>), the fuel it typically replaces. However, this does not necessarily mean that the LFG burning temperature is significantly lower than that of methane. One relevant indicator is the adiabatic flame temperature (AFT), which can be computed using an energy balance under the assumption of no heat loss during combustion. During the course of this study, we developed a software package to calculate the AFT for typical LFG compositions. For methane the AFT is computed to be 2300K, while for a typical LFG the AFT is computed to be 2100K, only 200K less. A 50/50 mixture of LFG and natural gas would have AFT = 2200K. The reason for this relatively small difference is that the AFT calculation is based on stoichiometric combustion with air. In both cases the nitrogen in air must be heated to the flame temperature, which has a significant effect on the energy balance because more nitrogen than oxygen is involved in combustion with air. For LFG about half as many moles of air are required compared to methane, although the CO<sub>2</sub> in LFG is inert and must be heated up as well. If flue gas recirculation (FGR) is used as a control measure for nitrogen oxides (NO<sub>x</sub>), flame temperatures will be lower [3].

Although the AFT does not appear to be a problem for combustion of LFG, other issues such as flame stability must be addressed. A recent research study has evaluated other combustion properties of LFG such as flame stability and burning velocity (Lee and Hwang [2]). For strong swirl (mixing) conditions in the combustor, LFG fuels were shown to exhibit stable burning conditions over a similar range of operating conditions (and fuel stream velocities) that would be stable for methane combustion. These authors concluded that LFG is a suitable alternative replacement fuel for methane (or as a blend

with methane), except that the turndown ratio was narrower (change in boiler heat rate). They found that the stable zone of combustion for LFG is smaller than that for methane, which means air to fuel ratios will need to be monitored more carefully. This also suggests that precautions will need to be taken for LFG to ensure that the heating value is monitored frequently using an online sensor to avoid loss of efficiency. If the LFG heating value proves to be too highly variable, it would need to be mixed with methane. For the petrochemical plant application, this is not a problem because their current natural gas requirements are eight times what can be supplied by the LFG site in Pearland, TX.

## **4.2 Combustion characteristics**

Minor modifications are needed to adapt the boiler to the greater gas flow, higher corrosivity, and lower flame temperature associated with LFG. The average lower heating value of LFG due to its lower concentration of methane, together with fluctuations in its heating value, can affect boiler flame stability. This issue can be addressed by the application of redundant ultraviolet (UV) sensors and dual fuel capability. UV sensors are standard safety features that monitor the boiler flame and verify that the flame has not been extinguished. Since the flame from LFG is more difficult to detect due to its lower temperature, redundant UV sensors should be employed and equipped with voltage indicators. The boiler in this study has dual fuel burners that can accommodate natural gas as a co-fired fuel, which is another method of ensuring fuel consistency and flame stability. Dual fuel burners are fed by separate gas lines that connect at an intake flow regulator valve. The valve regulates the proportional flow of the two fuels to maintain a constant air to fuel ratio of the gas entering the burner.

Corrosion potentially resulting from LFG use alone with no blending with methane can be circumvented with equipment modifications. Air pre-heaters and stacks are susceptible to corrosion from chlorine compounds in the exhaust gas of boilers that use LFG. Sulfur trioxide (SO<sub>3</sub>) formed from the sulfur content in LFG raises the dew point in boiler exhaust gas to approximately 280°F. If the temperature of the exhaust gas falls below the dew point, the chlorine in the gas will corrode even stainless steel components.

Using steam coils to pre-heat the combustion air helps keep the temperature high enough. Stack corrosion can be prevented by insulating the stack to prevent the exhaust gas temperature from lowering to the dew point. In addition, the stack should be made of carbon steel coated with corrosion-resistant materials such as inorganic zinc. Fuel control valves and associated piping should use stainless steel to protect against corrosion. Proper water circulation needs to be ensured after the conversion to LFG. The lower flame temperature of LFG can affect the circulation in water wall boilers and cause steam blanketing against the walls of the steam tubes. On some boilers with low circulation velocity, the lower energy of the steam can result in water condensing out of the steam onto the water wall tube risers where corrosive impurities may be deposited. The circulation pattern of the boiler should be checked independently to alleviate these concerns. Deposits of silica, iron, sulfur, and chlorine are known to accumulate on air pre-heaters and flue gas ductwork. The deposits can be removed by soot blowing and manual cleaning during routine maintenance. Because LFG/natural gas will be used in a 30/70 mixture, these corrosion concerns detailed above should not be a major issue.

Burners at the petrochemical plant have to be retrofitted to burn landfill gas. Because landfill gas has almost half of the heat content as natural gas, consequently a larger flow of gas must be allowed to supply an equivalent amount of energy. From a practical standpoint, this means that valve openings need to be made larger for fuel control, which reduces pressure loss. Burner modification design to co-fire LFG, natural gas, and waste fuel gas is continuing by CPL Systems for the petrochemical plant, and the final design is not decided at this time. Also the specific burner features for low-NO<sub>x</sub> operation are not known, although CPL has done many such installations in the past.

### **4.3 Reduction of nitrogen oxides emissions with landfill gas**

Two driving forces for the project are to lower energy costs as well as to reduce the nitrogen oxide emissions from the plant complex, since the area where the plant is located is in the Houston-Galveston-Brazoria non-attainment region, which has problems with excessive ozone formation which is driven by chemical reactions with nitrogen

oxides, as discussed below. There is a general belief that the use of LFG will reduce the NO<sub>x</sub> emissions for steam generation, but the amount has not been quantified at this point. Also the LFG contains a number of trace species that are not present in methane/natural gas. By performing literature review and analysis of industry data that are publicly available, we investigated the expected reduction in NO<sub>x</sub> emissions when LFG is blended with methane. The effects of using low NO<sub>x</sub> burners and flue gas recirculation have been factored into this analysis.

Since 2002, concentrations of ozone in the Houston-Galveston-Brazoria (HGB) area have frequently exceeded levels specified in the Environmental Protection Agency's ambient air quality standards at 1-hour and 8-hour averaging times, despite implementation of measures designed to reduce emissions of the two major contaminants responsible for formation of elevated ozone: volatile organic compounds (VOCs) and nitrogen oxides (NO<sub>x</sub>). Field study results have shown that short-term releases of highly reactive VOCs (HRVOCs) can explain occurrences of ozone formation that have been observed in the HGB. HRVOCs represent a specific group of VOC species that are particularly efficient at producing ozone when mixed with NO<sub>x</sub> in sunlight. HRVOCs are released from petroleum refining and chemical manufacturing sources in the HGB.

Recent research results suggest that control of HRVOC releases is likely to be an important part of an ozone attainment strategy for the HGB, as opposed to focusing only on nitrogen oxides. Air quality managers in the HGB area have considered a combination of NO<sub>x</sub> and VOC reductions as the most efficient means of reducing peak ozone concentrations. Achieving the proper balance of VOC and NO<sub>x</sub> controls is difficult and conclusions regarding the optimal approach are subject to change over time for the region. The Texas Commission on Environmental Quality (TCEQ) has concluded that it will be most cost-effective to substitute HRVOC control measures for some of the more expensive NO<sub>x</sub> control measures included in earlier version of the HGB ozone State Implementation Plan. TCEQ's analyses show that limiting emissions of HRVOCs in conjunction with an 80 percent reduction in NO<sub>x</sub> is estimated to have the same benefit as a 90% reduction in NO<sub>x</sub> alone.

Several species of HRVOC have been identified as contributing disproportionately to the formation of ozone in HGB. Due to the high reactivity of these species, ethylene, propylene, isomers of butane and 1,3-butadiene have been designated as HRVOCs and targeted for reduction. The most important sources of these HRVOCs are petroleum refineries and chemical plants. The Texas petrochemical plant considered in this study manufactures olefins, so its principal products are HRVOC's. Fugitive and flare emissions are the principal sources of uncontrolled HRVOC emissions for this plant, and these emissions are minimized in order to maximize production of desired products. However, the environmental issues are more appropriately considered in a regional context due to pollutant transport in the airshed.

The petrochemical plant studied here has a typical  $\text{NO}_x$  emission of 120 ppm using natural gas (NG). The goal is to reduce the  $\text{NO}_x$  emission to about 30 ppm by blending LFG with NG, installing low  $\text{NO}_x$  burners, and using flue gas recirculation (FGR). The expected reductions from each of the three design changes are not predictable, although experience with similar facilities may be indicative. Table 1 shows six different installations that were originally fired with NG, although none shows greater than 100 ppm  $\text{NO}_x$  in the original facility. This information was provided by the environmental vendor used for the LFG project, CPL Systems of Lafayette, LA. Incremental improvements due to adding LFG and low  $\text{NO}_x$  burners can be estimated from the data in the table, but there is too much variability in the data to make reliable projections. Facility 6 also includes some data for flue gas recirculation, but the changes are too small to be used with much confidence. Because of the lack of sufficient data, we reviewed additional experimental data plus the technical literature on mathematical modeling of combustion of NG and LFG to make better projections.

There are three different types of  $\text{NO}_x$ : thermal  $\text{NO}_x$ , prompt  $\text{NO}_x$ , and fuel-bound  $\text{NO}_x$ . The Appendix in Section 8.0 contains a review of the various formation mechanisms for nitrogen oxides during combustion. Thermal  $\text{NO}_x$  is  $\text{NO}_x$  that forms at high temperatures when the radicals of oxygen or nitrogen are present. When these radicals are present,

diatomic nitrogen will react with an oxygen radical or diatomic oxygen will react with a nitrogen radical producing thermal  $\text{NO}_x$ . Prompt  $\text{NO}_x$  is formed through nitrogen in the atmosphere reacting with intermediate hydrocarbon species. Fuel-bound  $\text{NO}_x$  is emitted from fuels such as coal that contain nitrogen, but neither natural gas or landfill gas contain organically-bound nitrogen compounds. By controlling the temperature of combustion,  $\text{NO}_x$  production can be reduced by 90-95% in many cases (the component that is attributed to thermal  $\text{NO}_x$ ). It is relatively easy to control thermal  $\text{NO}_x$  because lowering the temperature reduces  $\text{NO}_x$  formation.

Since landfill gas may have a larger amount of nitrogen in the fuel than natural gas, there should be more prompt  $\text{NO}_x$  production than associated with natural gas. The  $\text{NO}_x$  is not fuel bound since it is not part of the fuel chemical formula, but rather a component in the fuel. Commonly, prompt  $\text{NO}_x$  is controlled by combustion staging. However, prompt  $\text{NO}_x$  usually does not occur unless the mixture is very fuel rich, so keeping stoichiometric proportions of air and fuel should prevent most prompt  $\text{NO}_x$  from forming. Also, since there are diluents such as carbon dioxide and nitrogen in landfill gas, the combustion temperature should be lower since the inert species will absorb some of the reaction heat. Thus, thermal  $\text{NO}_x$  is expected to decrease when landfill gas is substituted for natural gas.

#### **4.4 Additional control technologies for $\text{NO}_x$ reduction**

There are two types of primary control techniques for nitrogen oxide emissions: (1) combustion modification to suppress the formation of nitrogen oxides, and (2) add-on controls to reduce nitrogen oxides to molecular nitrogen. In the petrochemical plant application, only the first type is being considered, hence that is the focus of this section.

**Table 1**  
**Nitrogen Oxides Emissions from LFG Combustion**  
**(Source: CPL Systems, 2006)**

<u>Facility</u>	<u>Fuel</u>	<u>NO<sub>x</sub> (ppm)</u>	<u>Comments</u>
1	100% NG	67	44 MM Btu/hr
1	81% LFG, 19% NG	31	
2	100% NG	83	52 MM Btu/hr
2	100% NG	43	low NO <sub>x</sub> burner
2	50% LFG, 50% NG	19	low NO <sub>x</sub> burner
2	100% LFG	11	low NO <sub>x</sub> burner
3	100% NG	96	45 MM Btu/hr
3	100% NG	82	low NO <sub>x</sub> burner
3	40% LFG, 60% NG	45	48 MM Btu/hr
3	100% LFG	36	19 MM Btu/hr
4	100% NG	60	low NO <sub>x</sub> burner
4	50% LFG, 50% NG	39	low NO <sub>x</sub> burner
4	100% LFG	31	low NO <sub>x</sub> burner
5	100% NG	86	220 MM Btu/hr
5	100% NG	81	low NO <sub>x</sub> burner
5	50% LFG, 50% NG	55	low burner
5	100% LFG	36	low NO <sub>x</sub> burner
6	100% NG	42	90 MM Btu/hr, 15% FGR
6	100% NG	39	low NO <sub>x</sub> burner, 7% FGR
6	50% LFG, 50% NG	34	low NO <sub>x</sub> burner, 15% FGR
6	100% LFG	20	low NO <sub>x</sub> burner, 15% FGR

LFG = landfill gas, NG = natural gas, FGR = flue gas recirculation

The purpose of combustion modification is to change design and operating conditions to minimize the formation of both thermal and fuel NO<sub>x</sub>. Most of these techniques involve reduction in the peak gas temperatures, reduction in the oxygen concentrations in the high temperature areas of the burner flame, and/or reduction in the residence time of combustion products in the high temperature areas of the burner flame. Combustion modifications that were considered in this report to reduce NO<sub>x</sub> formation include low excess air operation, off-stoichiometric combustion, flue gas recirculation, and low NO<sub>x</sub> burners [3]. Low excess air operation involves a reduction in the total quantity of air used in the combustion process. All combustion systems use slightly more air than theoretically needed to ensure complete combustion of the fuel. By reducing the excess air levels down to the lowest possible level, the oxygen concentrations in the high temperature zone of the combustion process can be minimized, thereby reducing NO<sub>x</sub> formation. This is being done in the boiler application by upgrading the control system so that the air to fuel ratio can be precisely controlled.

Off-stoichiometric combustion involves the mixing of the fuel and air in a way that reduces the peak gas temperatures and peak oxygen concentrations. Usually a portion of the combustion flame is operated with very low oxygen levels (fuel rich) to allow a major portion of the fuel oxidation to occur under conditions where NO<sub>x</sub> formation is suppressed (see Section 8.0, Appendix). Combustion is completed in the remaining portion of the flame and/or combustion chamber by providing the remainder of the oxygen needed for complete fuel oxidation. There are a variety of different approaches for achieving off-stoichiometric firing conditions. The primary alternative considered here is low NO<sub>x</sub> burners. Low NO<sub>x</sub> burners control the mixing of fuel and air in a pattern that keeps the flame temperature low and dissipates the heat quickly. In the planned co-firing of natural gas and landfill gas, CPL Systems will customize the burner configuration to give the desired mixing and temperature profiles.

Flue gas recirculation (FGR) involves the return of combustion gases to the burner area of the boiler. The slightly cooled combustion gas from the boiler exit is recycled and

mixed in the burner flame to reduce the peak flame temperatures and lower oxygen concentration, thereby suppressing  $\text{NO}_x$  formation. This approach requires a separate recirculation fan and duct system along with a modified windbox. This is planned in a later phase of the petrochemical plant project (although it is possible that it may not be required if the other steps are successful in achieving the desired reduction in  $\text{NO}_x$  emissions from 120 ppm to 30 ppm).

FGR typically costs less than low  $\text{NO}_x$  burners and generally satisfies state  $\text{NO}_x$  Reasonably Available Control Technology (RACT) regulations. Disadvantages of FGR include additional space requirements for recirculation ducts, fans, and additional air ports if FGR is retrofitted onto an existing boiler. Added costs are due to the auxiliary equipment and also the additional energy to run the recirculation fans. According to Schnelle and Brown [3], an FGR recirculation rate of 20% can yield  $\text{NO}_x$  reductions approaching 80%. A 6% FGR rate can reduce  $\text{NO}_x$  ppm by 40%, and at this rate the inert gas entering the boiler is equivalent to the added volume of non-combustible (inert) gas in LFG [1], based on the molar ratio of fuel gas to inerts. Baltasar [4] in a study of FGR in a laboratory scale furnace showed that  $\text{NO}_x$  emission was very sensitive to excess air ranging from 1% to 14%, with  $\text{NO}_x$  reductions of about two-thirds for the lower excess air. They concluded that prompt  $\text{NO}_x$  formation (see Section 8.0) is effectively suppressed by FGR.

Low- $\text{NO}_x$  burners are designed to stage either the air or the fuel within the burner tip. With staged-air burners, the primary flame is burned fuel rich and the low oxygen concentration minimizes  $\text{NO}_x$  formation. Additional air is introduced outside of the primary flame where the temperature is lower, thereby keeping the thermodynamic equilibrium  $\text{NO}_x$  concentration low, but hot enough to complete combustion. Staged-fuel burners introduce fuel in two locations. A portion of the fuel is mixed with all of the combustion air in the first zone, forming a hot primary flame with abundant excess air.  $\text{NO}_x$  formation is high in this zone. Then additional fuel is introduced outside of the primary flame zone, forming a low-oxygen zone that is still hot enough for kinetics to bring the  $\text{NO}_x$  concentration to equilibrium in a short period of time. In this zone,  $\text{NO}_x$

formed in the primary flame zone reverts back to nitrogen and oxygen. Low NO<sub>x</sub> burners can reduce NO<sub>x</sub> emissions by 40 to 65% from emissions produced by conventional burners [3].

Because low-NO<sub>x</sub> burners stage either the air or the fuel, the flame zone is lengthened. The typical flame length of low-NO<sub>x</sub> burners is about 50 to 100% longer than that of standard burners. This can cause a problem in some retrofit applications if the longer flame impinges on the walls of the combustion chamber. Flame impingement can cause the chamber walls to erode and fail.

Advanced combustion controls are also critical to reducing NO<sub>x</sub> emissions as well as to ensure complete combustion (to minimize CO emissions). The petrochemical plant currently has PEMS (predictive emissions monitoring system), which is a neural-net based model that measures boiler variables and predicts NO<sub>x</sub> emissions (approved by TCEQ). The PEMS can be used in a feedback loop to adjust oxygen in the boiler (by manipulating excess air). According to CPL Systems, there will also be CEMS (continuous emission monitoring system) sensor hardware installed in the future, and improved control valve and stepper hardware will be added to improve process control performance.

In summary, in order for the NO<sub>x</sub> emissions to be reduced from 130 ppm to 30 ppm, it seems likely that the following four steps will all contribute significantly:

- (1) blending of LFG (30/70 mixture) to replace part of natural gas, which will lower combustion temperature.
- (2) better control of excess air to minimize nitrogen content during combustion
- (3) low NO<sub>x</sub> burners
- (4) flue gas recirculation

Based on current technology, it will be very difficult to reduce NO<sub>x</sub> emissions below 30 ppm.

The combustion modifications described above are capable of reducing nitrogen oxides well below the levels that would exist in less sophisticated combustion system designs for natural gas. The use of mixed landfill gas would allow an additional reduction in the NO<sub>x</sub> emissions. However, there are several practical limits to the combustion modifications. If the combustion conditions are altered too much, some partially oxidized organic compounds and carbon monoxide can form due to impaired oxidation conditions, which could violate the permitted CO levels. Flame instability can occur from minimizing oxygen and temperature levels. Also, by operating at fuel-rich conditions, the combustion processes can become vulnerable to operating problems.

#### **4.5 Impact of other air emissions (VOC, HAP)**

We also investigated the potential trace species and their fate during combustion of LFG and whether there are possible negative environmental impacts from the combustion step. The landfill gas composition analysis of the main gas components provided by the petrochemical company is as follows (assumed to be typical):

51%	CH <sub>4</sub>	1.6%	O <sub>2</sub>
40%	CO <sub>2</sub>	0.075%	H <sub>2</sub>
7.4%	N <sub>2</sub>	0.015%	C <sub>6+</sub>

This would give an approximate higher heating value of about 520 Btu/SCF, which is consistent with other reported compositions for LFG in the U.S. Over 50 trace components including a number of HAP's (hazardous air pollutants) were reported, but the only ones of significance (> 8 ppm) are:

Hydrogen sulfide	25 ppm
Ethanol	65 ppm
Toluene	16 ppm (HAP)
Methyl ethyl ketone	14 ppm (HAP)
2 propanol	11 ppm
Acetone	9 ppm
Xylenes	8 ppm (HAP)

Table 2 gives a much more detailed list of trace organic compounds in LFG. Of the HAP's, only one (toluene) has an emission factor reported by EPA, hence not much data are available for these compounds that would allow a post-combustion emission to be estimated. It is expected that 99+% of these organic species will be consumed during the combustion process.

Hydrogen sulfide would be converted to sulfur dioxide during combustion, but the resulting uncontrolled sulfur oxide emissions would not be significant (lower than sulfur oxides emitted from coal-fired power plants with stack gas scrubbing) and would be covered under the current air permit for the petrochemical plant. The appropriate environmental regulation for this case appears to be 0.5 lb SO<sub>2</sub>/10<sup>6</sup> Btu. Calculating the SO<sub>2</sub> for landfill gas combustion gives 0.009 lb SO<sub>2</sub>/10<sup>6</sup> Btu, which is well below the regulatory standard.

### Health Effects

The criteria for the health effects analysis was taken from two different sources:

- EPA. List of Health Effects Fact Sheets  
<http://www.epa.gov/ttn/atw/hlthef/hapindex.html>
- ATSDR ToxFAQs™  
[http://www.ehso.com/ehshome/chemical\\_factsheets2.htm](http://www.ehso.com/ehshome/chemical_factsheets2.htm)

**Table 2**  
**Summary of Detected Trace Compounds (Landfill Gas)**

<b>Compound</b>	<b>Amount (ppbv)</b>	<b>HAP</b>
Hydrogen Sulfide	25000	
Methyl Mercaptan	1400	
Dimethyl Sulfide	940	
Isopropyl Mercaptan	160	
Freon 12	1000	
Vinyl Chloride	610	√
Ethanol	65000	
Acetone	8800	
2-Propanol	11000	
Hexane	450	√
2-Butanone (Methyl Ethyl Ketone)	14000	√
Cis-1,2-Dichloroethene	1300	√
Tetrahydrofuran	2400	
Cyclohexane	600	
Benzene	560	√
Heptane	1100	
Trichloroethene	440	√
4-Methyl-2-pentanone	710	√
Toluene	16000	√
Tetrachloroethene	770	√
Ethyl Benzene	3400	√
m,p-Xylene	6800	√
o-Xylene	1600	√
Cumene	340	√
4-Ethyltoluene	610	√
1,2,4-Trimethylbenzene	470	√

List of HAP's at [www.epa.gov/ttn/atw/orig189.html](http://www.epa.gov/ttn/atw/orig189.html)

For consideration of individual HAPs, health effects were considered to establish a priority list as done in other environmental studies. Table 3 lists Health Effects Screening Levels (ESL) used by the Texas Commission for Environmental Quality (TCEQ) to evaluate the public health threat from ambient concentrations of various HAPs. The lower the ESL, the

lower is the exposure level for which adverse health impacts occur. The list of priority HAPs used for this study was: benzene, toluene, xylenes (all isomers), ethylbenzene, n-hexane, 1,2,4-trimethylbenzene, 2,2,4-trimethylpentane, and methyl ethyl ketone. Examples of health effects for these HAPs are also shown in Table 3. The right-hand column assumes 99% combustion of the component in landfill gas shown in Table 2 (thus 1% by volume is emitted). Note that benzene and methyl ethyl ketone both exceed the screening level for health affects, so this may need to be further evaluated. In many cases the possible health affects are not adequately supported by human studies (vs. animal studies), so this assessment may be more qualitative than quantitative.

## **5.0 Other Implementation Issues**

Several questions were posed in the introduction (Section 1.0) that are discussed here:

- (3) *If segregation of fuels is required, what would need to be done by a plant to assure safe operation and maintain the segregation of the landfill gas from the fuel gas?*

In order to maintain segregation of the natural gas and the landfill gas, changes would have to be made in the plant. First, a separate set of boilers, co-generation units, and heaters would have to be installed to burn the landfill gas. This would then allow the original units to burn natural gas while the separate units would be specific to landfill gas. These separate units would have complete internal combustion hardware, which would allow landfill gas to be burned in an ecologically safe manner, although at greater expense. In addition to the installation of new capital equipment, it would be necessary to install a separate piping system to transport the landfill gas so that it can be kept separate from the natural gas.

**Table 3**  
**Examples of Specific Health Effects for Some Priority HAPs**

<b>Substance</b>	<b>Basis for Concern</b>	<b>Effects Screening Level (long-term, ppbv)</b>	<b>Possible Adverse Health Effects (Incomplete Human Studies)</b>	<b>Post-combustion emission ppbv based on 99% combustion</b>
Benzene	High emissions, Carcinogen, Reactivity	1.4	Eye, skin and respiratory tract irritation. Blood disorders. Reproductive effects. Carcinogen.	5.6
Ethylbenzene	High emissions	46	Neurological and respiratory effects, chronic effects on the blood.	34
n-Hexane	High emissions	57	Central nervous system effects. Polyneuropathy in humans, with numbness in the extremities, muscular weakness, blurred vision, headache, and fatigue	4.5
Toluene	High emissions	330	Central nervous system dysfunction. Eyes, skin respiratory tract irritation. Developmental and reproductive effects.	160
1,2,4-Trimethylbenzene	High emissions, Reactivity	25	Nervous system dysfunction. Reproductive system and developing fetus effects. Photochemical smog contributor in combination with other VOCs.	4.7
Xylene (Mixed Isomers of Dimethyl Benzene)	High emissions, Carcinogen, Reactivity	100	Eye, nose, throat irritation. Gastrointestinal, neurological, cardiovascular, respiratory, kidney and central nervous system effects.	84
Methyl Ethyl Ketone	High emissions	130	Eye, nose, throat irritation. neurological, liver and kidney effects.	140

Sources:

EPA List of Health Effects Fact Sheets, <http://www.epa.gov/ttn/atw/hlthef/hapindex.html>

ATSDR ToxFAQs™, [http://www.ehso.com/ehshome/chemical\\_factsheets2.htm](http://www.ehso.com/ehshome/chemical_factsheets2.htm)

It would be necessary for the plant to set up a second set of protocols and best known methods for controlling the process while landfill gas is being burned. These new protocols would inform operators and engineers what the optimum process variables are for maximizing the economic efficiency of the process while also keeping the NO<sub>x</sub> emissions within environmental regulation limits. Ultimately one must determine whether the cost advantage of landfill gas would justify the capital expenses of gas segregation.

Clearly the petrochemical plant in this study determined that it is technically feasible to mix natural gas and landfill gas in the boiler, thus obviating the duplication of equipment.

(6) *How can the landfill gas be cycled so that it can be used during peak power periods? Can the gas be produced during parts of each day at higher production levels (and shut off during the remainder of each day)?*

Landfill gas is ideal for baseload operation. It cannot economically be stored, so it is better to have a power plant using landfill gas running at all times since the gas is constantly produced and has an over 90% availability factor. However, if use is needed only during peak periods, it could be used similarly to natural gas, but something has to be done with the gas when the landfill gas power plant is not running. There are several ways of cycling landfill gas for use during peak periods. The first is a control system that increases landfill gas use with demand. Gas would have to be stored in a pressurized tank. A second method could be to burn landfill gas during peak demand and then flare it during non peak usage. This would not require a storage tank. Both of these methods assume a constant production of landfill gas. If the landfill is heated by sunlight, then the production of landfill gas would increase with temperature during the day, thus producing the most gas during peak electrical usage times. This could be used to supplement the electrical demand except the landfill gas production cannot be easily controlled. As mentioned earlier, the petrochemical plant does not plan to cycle LFG because it is co-firing LFG with natural gas.

## 6.0 Conclusions and Recommendations

The major conclusions from the project are:

- (1) Landfill gas has a beneficial effect on nitrogen oxides emission compared to natural gas, causing a significant (50%) reduction in ppm levels if the gases are co-fired or if LFG is used separately. Low NO<sub>x</sub> burners and flue gas recirculation can further reduce NO<sub>x</sub> levels in the flue gas to the 30 ppm level. In the future computational fluid dynamics (CFD) software may be improved sufficiently to make accurate emissions predictions for a given control strategy but currently only semi-quantitative predictions are possible with CFD at this time.
- (2) Added constituents (oxygen; carbon dioxide, hydrogen sulfide) in LFG (vs. natural gas) do influence combustion and emission properties of the fuel. A small amount of oxygen (<2%) does not raise safety concerns for pipelining and only slightly changes the necessary air/fuel ratio in a furnace. Carbon dioxide volume fraction in LFG usually ranges from 40 to 50%, which lowers the heating value but also the flame temperature, which are beneficial for reducing NO<sub>x</sub> emissions significantly. In fact in some cases blending of LFG with natural gas may obviate the need for low NO<sub>x</sub> burners and for flue gas recirculation. Finally the presence of hydrogen sulfide could be problematic if it is too high because it might require sulfur oxide control technology. However, for the application considered here, the H<sub>2</sub>S concentration was low enough that projected sulfur oxide emissions did not exceed currently permitted levels. An analysis of HAP (hazardous air pollutant) components for LFG combustion was also performed and found two HAP's that may be of concern.
- (3) Segregation of LFG from natural gas might be desirable to ensure that current combustion equipment for natural gas can be fully utilized, but it will add significantly to the cost. Current technology for co-firing LFG and natural gas seems to be adequate for handling both gases without requiring major design

changes or added capital cost. In the plant considered in this study, co-firing modifications are being made by a combustion vendor.

- (4) When burner modifications are made, there can be a question as to whether the existing guarantee on the burners will be valid. However, the current application demonstrates that burner modifications for LFG are now routinely made and that there is a high level of confidence that satisfactory performance of the co-fired system in terms of combustion efficiency and reduced emissions will be realized. Improved process controls of the air/fuel ratio can be installed to ensure that performance of the new system can be maximized.
- (5) The permitting of the existing combustion equipment for NO<sub>x</sub> and CO emissions does not appear to be an obstacle for implementation of this LFG project. The permitted values were already below current NSPS standards, due to the fact that the plant is located in the Houston-Galveston-Brazoria (HGB) non-attainment area. Implementation will result in reduction of NO<sub>x</sub> emissions from the current 120 ppm to around 30 ppm, which is desirable because of HRVOC (highly reactive volatile organic compounds) issues in the HGB.
- (6) The cycling of landfill gas production to deal with variable steam demand was analyzed and found not to be a desirable alternative for this application. This is because the plant requires a larger amount of energy than can be provided by LFG alone. The variable nature of energy demand can be satisfied by adjusting the flow rates of natural gas, since that will provide 70% of the total energy once the LFG pipeline is operating (currently natural gas provides 100% of the fuel requirements). The petrochemical plant is located 31 miles from the landfill.

## 7.0 References

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## 8.0 Appendix: Modeling of Nitrogen Oxides Formation in Combustion

NO<sub>x</sub> is an important atmospheric pollutant since it is one of the main ingredients in the formation of photochemical smog and contributes to acid rain. In fact, oxides of nitrogen in the atmosphere, when exposed to sunlight, react chemically with other gaseous compounds in the atmosphere such as "volatile organic compounds" (VOCs) through photosynthesis to form ground-level ozone, which can trigger serious respiratory problems. NO<sub>x</sub> emissions can also form acids in the atmosphere that fall to earth as rain, fog, snow or dry particles. This acid precipitation (known as "acid rain") is often carried hundreds of miles by the wind. Acid rain damages forests and causes lakes and streams to become acidic, killing the fish. NO<sub>x</sub> also contributes to the formation of atmospheric particles, which cause visibility impairment most noticeable in national parks. NO<sub>x</sub> also contributes to global warming.

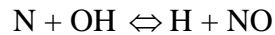
There are four general accepted mechanisms for NO<sub>x</sub> production discussed below: thermal NO<sub>x</sub>, prompt NO<sub>x</sub>, fuel NO<sub>x</sub> and N<sub>2</sub>O-path NO<sub>x</sub>.

### Thermal NO<sub>x</sub>

Thermal NO<sub>x</sub> is produced by the oxidation at high temperature of nitrogen contained in the combustion air. The formation of thermal NO<sub>x</sub> is determined by a set of highly temperature-dependent chemical reactions known as the extended Zeldovich mechanism [5]. The principal reactions governing the formation of thermal NO<sub>x</sub> from molecular nitrogen are as follows:



A third reaction has been shown to contribute to the formation of thermal NO<sub>x</sub>, particularly at near-stoichiometric conditions and in fuel-rich mixtures:



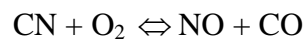
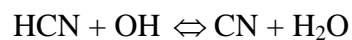
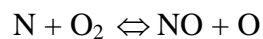
Thermal  $\text{NO}_x$  increases exponentially with temperature. At about 2000 °F (1100 °C) it is generally the predominant mechanism, so it is likely to be the most important mechanism for  $\text{NO}_x$  formation in industrial flares.

### Prompt $\text{NO}_x$

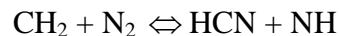
Prompt  $\text{NO}_x$  is formed by the relatively fast reaction between nitrogen, oxygen, and hydrocarbon radicals. These reactions occur at the flame front. Prompt  $\text{NO}_x$  is an important mechanism in lower temperature combustion processes, fuel-rich conditions and where residence times are short. However, at high temperatures, its contribution to total  $\text{NO}_x$  formation is small compared to the thermal  $\text{NO}_x$ .

This mechanism for prompt  $\text{NO}_x$  formation was first identified by Fenimore [6]. The actual formation involves a complex series of reactions and many possible intermediate species.

The route now accepted is as follows:



A number of species resulting from fuel fragmentation have been suggested as the source of prompt  $\text{NO}_x$  in hydrocarbon flames (e.g., CH,  $\text{CH}_2$ , C,  $\text{C}_2\text{H}$ ), but the major contribution is from CH and  $\text{CH}_2$  via



The products of these reactions could lead to formation of amines and cyano compounds that subsequently react to form NO by reactions similar to those occurring in oxidation of fuel nitrogen.

### Fuel NO<sub>x</sub>

Fuel NO<sub>x</sub> is formed by direct oxidation of organo-nitrogen compounds contained in the fuel gas. Fuel NO<sub>x</sub> is not a concern for high-quality gaseous fuel like natural gas or propane, which normally have no organically bound nitrogen. However, fuel NO<sub>x</sub> may be important when the fuel gas contains significant amounts of organically bound nitrogen.

The chemical mechanism for fuel NO<sub>x</sub> formation has been subject to several detailed investigations [7]. The extent of conversion of fuel nitrogen to NO<sub>x</sub> is dependent on the local combustion characteristics and the initial concentration of nitrogen-bound compounds.

### N<sub>2</sub>O-path NO<sub>x</sub>

At elevated pressures and oxygen-rich conditions, NO<sub>x</sub> may also be formed from molecular nitrogen (N<sub>2</sub>) via N<sub>2</sub>O. Melte and Pratt [8] proposed the first mechanism for this type of NO<sub>x</sub> formation. Under favorable conditions, which are elevated pressures and oxygen-rich conditions, this intermediate mechanism can contribute as much as 90% of the NO<sub>x</sub> formed during combustion.

For the particular case of combustion to produce steam, thermal NO<sub>x</sub> is the predominant mechanism since high temperatures are inherently present in the flame. Prompt NO<sub>x</sub>, which becomes more relevant at low temperatures, may be important to model flames at near-extinction conditions. On the other hand, fuel NO<sub>x</sub> should only be considered when organo-nitrogen compounds are present in the fuel. N<sub>2</sub>O-path NO<sub>x</sub> is not a large concern since these systems do not operate at high pressures or oxygen-rich conditions.

$\text{NO}_x$  concentrations generated in combustion systems are generally low. Thus  $\text{NO}_x$  chemistry has negligible influence on the predicted flow field, temperature, and major combustion product concentrations.