

Photocatalytic Degradation of Air Emissions from Municipal Solid Waste Landfills

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ABSTRACT: This study examined the potential for photocatalytic oxidation to treat pollutants landfill gas (LFG). Three example LFG constituents were tested: methane, xylenes, and carbonyl sulfide. Methane, which comprises 40-60% of landfill emissions, is flammable and explosive at high concentrations, and is a greenhouse gas with global warming potential of 22 times that of carbon dioxide (100 year time horizon). Xylenes represent the second-highest concentration of hazardous air pollutants in LFG, and also contribute to ground-level ozone formation. Carbonyl sulfide was chosen as an example of a LFG constituent that is a hazardous air pollutant, as well as an odor-causing compound. Reaction rate constants are necessary for photocatalytic reactor design; accordingly, rate constants were determined for the compounds of interest over Degussa P-25 titanium dioxide (TiO₂) catalyst in a continuous mixed-batch reactor. Plots of compound concentration versus time indicated first-order decay for all compounds tested. Destruction rates were higher for the smaller molecules methane and carbonyl sulfide and lower for the more complex xylenes. The destruction rates for methane were found to depend on relative humidity. The research concludes that photocatalytic oxidation is a potentially promising method to treat emissions from landfills.

Keywords: Carbonyl Sulphide, Landfill Gas, Methane, Photocatalytic Oxidation, Xylene

ORIGINAL ARTICLE

INTRODUCTION

Refuse disposal is an issue that must be addressed by every community worldwide. Landfills can serve not only as waste repositories but also as significant sources of renewable energy. As microbes degrade the organic fraction of waste, methane (CH₄) is generated, along with carbon dioxide (CO₂), water, and other trace landfill gas (LFG) constituents. Comprising 40-60% of LFG by volume, methane is a potent greenhouse gas, with global warming potential 22 times that of CO₂ on a weight basis over a 100-year period (IPCC, 2004). Landfills are the 3rd largest human source of CH₄ emissions world-wide (12%). Capturing and converting a molecule of CH₄ to CO₂ reduces the molecule's ability to trap the Earth's outgoing radiation by a factor of 21/22, or 95%. In addition, methane control is necessary because methane can pose a danger to the operators of the plant and public residing near the landfill site: mixtures of methane with air are explosive within the range 5-15% by volume of methane (Comenius, 2007).

The trace LFG constituents include many volatile organic compounds (VOCs), which contribute to ground-level ozone formation, and many of which are air pollutants (HAPs). According to the U.S. Environmental Protection Agency's AP-42, nearly 30 compounds found in LFG are hazardous air pollutants; exposure to these pollutants can lead to adverse health effects (U.S. EPA, 2008). The trace constituents also include odor-causing compounds.

Potential pollutant removal techniques for the trace constituents in LFG include flaring, adsorption,

absorption, biofiltration and photocatalytic oxidation. EPA's New Source Performance Standards for landfills require a control device capable of reducing non-methane organic compounds (NMOCs) in the collected gas by 98% by weight (U.S. EPA, 2008). Flaring is a commonly-used technique, but studies have indicated that its efficiency in many cases is less than 98%; in addition, it requires a continuous fuel supply and can generate combustion by-products. Adsorption and absorption do not destroy contaminants, but transfer them to a solid or liquid media, respectively, which must then be cleaned; moreover, they are not effective in removing methane. Biofiltration uses microorganisms fixed to porous media to break down pollutants present in an air stream.

Photocatalytic oxidation is a promising technique for sources with small flow rates (Al-Ekabi et al., 1993; Zeltner et al., 1993; Lyons et al., 1995; Henschel, 1998; Stevens et al., 1998; Sattler and Liljestrand, 2003; Zhou and Yang, 2003). In cases where the methane concentration is too low for it to be burned as a source of fuel, PCO could be a useful method of reducing the global warming potential. Photocatalytic oxidation converts hydrocarbons to water and carbon dioxide in the presence of ultraviolet light (350 – 400 nm) and a catalyst such as titanium dioxide. Photocatalytic oxidation utilizes ultraviolet radiation to promote electrons from the valence band to the conduction band of the titanium dioxide semiconductor. As electrons are promoted to the conduction band, corresponding holes are created in the valence band. The electrons act as reducing species and

the holes act as oxidizing species. Although the exact mechanism is not completely understood, it is believed that in the presence of water vapor, the hole oxidizes OH- from adsorbed water vapor to form a hydroxyl radical (OH[•]). The hydroxyl radical, which is extremely reactive, acts as a nonselective oxidizer and repeatedly attacks most organics, converting them to carbon dioxide and water via free radical reactions. Although photocatalytic oxidation can occur via other mechanisms in the absence of water vapor, catalytic activity has been found to decrease dramatically after only a few minutes of irradiation and eventually to become negligible (Zeltner et al., 1993). Advantages of PCO over other available techniques include:

- High destruction efficiencies achieved at room temperature.
- Inexpensive, non-hazardous catalyst (titanium dioxide).
- Applicable to a large number of organics.
- Effective for low concentrations of pollutants.
- Applicable in humid conditions.
- No consumption of expensive oxidizing chemicals; the oxidant is atmospheric oxygen.
- No auxiliary fuel required.
- Complete oxidation of organics to carbon dioxide (CO₂) and water (H₂O) is possible.

The PCO technique has a wide range of applications in air as well as water. Some of the applications include (Stevens et al., 1993; Zhou and Yang, 2003; Gogate and Pandit, 2004; Lynntech, 2006):

- Portable indoor air cleaners for indoor gaseous pollutant removal.
- Preparation of high purity water for medical applications.
- Detoxification of drinking water.
- Preparation of high purity industrial water for electronics manufacture.
- Polishing wastewater effluent streams; PCO is effective in removal of BOD, COD, TOC, taste and odor components.
- TiO₂ applications on window panes, turning them into self cleaning panes.

Although numerous of studies have examined the effectiveness of PCO for treating landfill leachate (Bekbolet et al., 1996; Cho et al., 2002; Cho et al., 2004; Wiszniowski et al., 2004; de Moraes and Zamora, 2005; Wiszniowski et al., 2005; Zheng et al., 2009; Zhao et al., 2010; Jia et al., 2011; Poblete et al., 2011; Rocha et al., 2011; Vilar et al., 2011; Zhang et al., 2011; Jia et al., 2012; Meeroff et al., 2012; Poblete et al., 2012; Vilar et al., 2012a; Vilar et al., 2012b; Chemlal et al., 2013), none to our knowledge has examined the potential for using PCO to treat landfill gas. This study thus explored the potential of photocatalytic oxidation to treat landfill gas, by examining its effectiveness for several example constituents of landfill gas.

PCO reaction rate constants were determined for destruction of methane, o-xylene, m-xylene, p-xylene, and carbonyl sulfide. As mentioned previously, methane comprising 40-60% of LFG by volume and is a potent greenhouse gas. Xylenes together represent the second-highest concentration of hazardous air pollutants in LFG (9.23 ppm), according to the U.S. EPA's AP-42 (2008), for landfills with waste in place after 1992 (U.S. EPA,

2008). Xylenes also contribute to ground-level ozone formation, with an incremental reactivity of 0.5 ppm O₃/ppm C (Carter, 1991). Carbonyl sulfide (COS) was chosen as an example of a LFG constituent that is hazardous air pollutant, as well as an odor-causing compound.

A number of recent studies have examined PCO of methane in air (Wada et al., 1993; Dreyer, et al., 1997; Kleinschmidt and Hesse, 2002; Yoshida et al., 2003; Krishna et al., 2004; Bellobono et al., 2006a; Bellobono et al., 2006b; Imanaka et al., 2011; In Su-il et al., 2011; Costa et al., 2012; Suzuki et al., 2012) and xylene in air (Peral and Ollis, 1992; Blanco et al., 1995; dHennezel and Ollis, 1997; Ameen and Raupp, 1999; Ohkubo and Fukuzumi, 2000; Pichat et al., 2000; Chun et al., 2001; Jo et al., 2001; ; Ao et al., 2003; Ao and Lee, 2003; Kim et al., 2003; Lewandowski and Ollis, 2003; Negishi and Takeuchi, 2003; Disdier et al., 2005; Strini et al., 2005; Yu et al., 2006; Tsoukleris et al., 2007; Boularnanti et al., 2008; Jo and Kim, 2009; Jo and Yang, 2009; Park et al., 2009; Tseng et al., 2009; Liang et al., 2010; Phuong et al., 2011; Sumitsawan et al., 2011; Destailats et al., 2012; Jo and Kang, 2012a; Jo and Kang, 2012 b; Sangkhun et al., 2012; Tang and Yang, 2012; Ye, et al., 2012). However, these studies do not necessarily use concentrations representative of LFG, or use Degussa's P-25, a widely-used inexpensive TiO₂ photocatalyst. In particular, many of the studies examined xylene concentrations typical of indoor air (tens of ppbs), which is a factor of a hundred to a thousand lower than LFG. No previous PCO tests involving COS have been reported.

MATERIALS AND METHODS

Experimental setup

The photocatalytic oxidation system was a closed loop batch reactor comprised of a photocatalytic oxidation reactor, pump, DC supply double output system, injection/sampling port, and Teflon tubing. Figures 1 and 2 show the system layout.

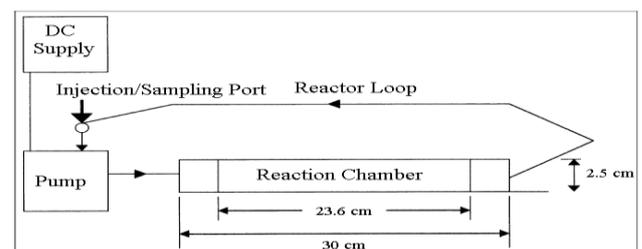


Figure 1. Photocatalytic reactor experimental setup - plan view

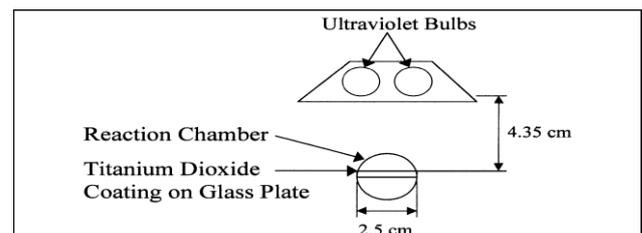


Figure 2. Photocatalytic reactor experimental setup - side view

A glass column, 30 cm in length and 3 cm in diameter, placed horizontally served as the photocatalytic

oxidation chamber, as shown in Figures 1 and 2. A 2.5x30 cm titanium dioxide-coated glass plate was placed in the column. However, only 23.6 cm of the length of the slide were directly exposed to the light due to the fact that the transparent portion of the chamber was only 23.6 cm. A lamp with two 15 watt cylindrical bulbs (NIS F15 T8BLB 15W black light blue), 2.6 cm in diameter set 2.6 cm apart, was set 4.35 cm above the glass slide. The bulbs provided illumination at a wavelength of 366 nm.

A diaphragm pump (Cole-Parmer Model No. L-79200-10) set at maximum pressure of 20 psi provided circulation through the closed loop for the purpose of mixing. A DC supply double output system from Shenzhen Mastech connected to the pump was set at 15 volts, which reduced the voltage reaching the pump from its normal value of 110 volts, and thus reduced the pump speed by a corresponding amount. The contaminated air stream circulated in the entire system via Teflon tubing. All the components of the system were made up of either glass or Teflon, neither of which react with organics.

Photocatalyst

Degussa's P-25 grade titanium dioxide (TiO₂), an effective and widely used photocatalyst, was chosen for this research. P-25 particles have an average surface area of 50 + 15 m²/g, an average diameter of 21 nm based on number count, and an average diameter of 32 nm based on surface area measurement (Nargiello and Herz, 1993). P-25 contains a mixture of 70-80% anatase and 20-30% rutile (Nargiello and Herz, 1993). The titanium dioxide was deposited onto the glass plate by immersing the plates in a suspension of titanium dioxide in distilled water and allowing the water to evaporate, leaving behind a titanium dioxide coating on the plate surface.

Compounds tested

The selected compounds were tested with their initial concentration equivalent to the concentrations at which they are emitted from landfills. Methane typically comprises 40-60% of landfill gas on a molar or volume basis (Tchobanoglous et al., 1993). In this research, due to experimental constraints, an initial methane concentration of 30% was tested.

U.S. EPA's AP-42 lists a default concentration of 9.23 ppm total xylenes for landfill gas from landfills with waste in place after 1992, and 12.1 ppm for landfills with waste in place prior to 1992 (U.S. EPA, 2008). For this research, due to detection limits associated with the gas chromatograph, higher initial xylene concentrations of 200-400 ppm were used.

U.S. EPA's AP-42 lists a default concentration of COS in municipal solid waste landfill gas of 0.122 for landfills with waste in place after 1992, and 0.49 ppm for landfills with waste in place prior to 1992 (U.S. EPA, 2008). Previous field data collected from wastewater treatment plants has shown COS concentrations of up to 2 ppm (Alan Plummer Associates, 2003a&b). Industrial processes can produce concentrations of up to 400-600 ppm. For this research, due to detection limits associated with the COS sensor and the COS cylinder regulator, an intermediate initial concentration of 30 ppm was chosen for testing. A compressed gas cylinder of 3% COS, with balance nitrogen, was obtained from Matheson Tri-Gas and diluted with air to 30 ppm.

During the experiments, the initial concentration varied slightly from the listed values since it was difficult to inject exactly the same concentration in the photocatalytic oxidation system for every experimental run.

Reactor operation and analysis methods for methane and xylene

The PCO system was left open to the atmosphere before starting the experiments to establish ambient conditions of temperature, pressure and humidity inside the system. Before starting each experimental run, the system was closed, the DC supply and pump were turned on, and the methane or xylene was slowly injected into the system through the injection/sampling port and allowed to mix inside the system for 6 minutes. During that time (with UV lights turned off), samples were collected at 2-minute intervals and analyzed by the gas chromatograph (GC) described below to ensure thorough mixing, no leakage and no destruction in the absence of UV light.

At the start of an experiment, a sample from the PCO system was collected and injected into the GC to determine the initial pollutant concentration. The UV light was then turned on to initiate PCO. During experiments, samples were collected at intervals of 2 minutes or more, depending on the destruction rate of the compound. Each experimental test was continued until at least 95% of the initial concentration was destroyed, or until the compound concentration was below the detection threshold of the GC.

The gas chromatograph used for measuring destruction of methane and the xylenes was an SRI Model 8610C, with flame ionization detector (FID). Methane destruction was detected by a Haysep D packed column, and xylene destruction was detected by a packed column from Restek, 2 m in length, which had the capability to detect BTEX compounds (benzene, toluene, ethyl benzene and xylene). Helium was used as the carrier gas. Windows based Peak Simple software regulated the carrier gas flow, temperature and other GC parameters. The software also displayed detector parameters and results.

Reactor operation and analysis methods for carbonyl sulfide

The carbonyl sulfide sensor was an International Sensor Technology model IQ-350 with a solid state sensor. It was configured to measure carbonyl sulfide concentrations within the range of 0 to 50 ppm. The sensor was incorporated into the photocatalytic system by connecting the input and output ends of the sensor to the photocatalytic system to form a closed loop batch reactor. This was possible since the sensor was non-destructive. During the COS experiments, the photocatalytic system DC supply double output unit and pump were turned off. The carbonyl sulfide sensor's pump aided the circulation of the contaminant laden air in the photocatalytic system.

Initially, the power supply to the sensor and the sensor pump were turned on. A sample of carbonyl sulfide was injected into the system via the injection/sampling port. The system was allowed to stabilize until a constant concentration value was displayed by the sensor's digital display, after which the UV bulbs were turned on. The carbonyl sulfide destruction rate was measured by observing the time

elapsed and concentration values at regular intervals. The experimental run was carried until the sensor read 0 ppm. After completion of the test, the system was opened to release the byproducts and ensure ambient conditions inside the system for the following run.

Determination of reaction rate constants

Previous studies (Sattler and Liljestrand, 2003; Wang and Chao, 2000) suggest that a first-order reaction is applicable to photocatalytic oxidation systems. In a first-order reaction, the reaction rate depends on the concentration of the reactants and the rate constant has units of 1/time. The general form of the reaction rate equation is:

$$\text{Rate of reaction} = -d[A]/dt = k[A] \quad (1)$$

Variable separation and integration results in:

$$[A] = [A]_0 \exp(-kt) \quad (2)$$

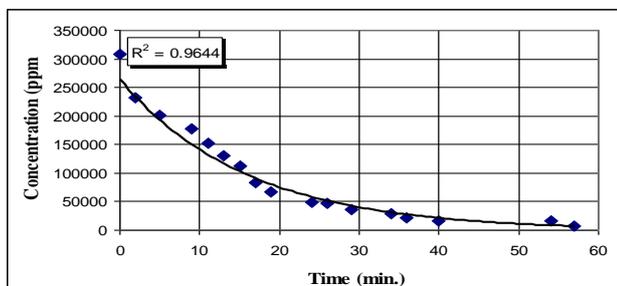
where $[A]$ = concentration of A, k = rate constant, $[A]_0$ = initial concentration of A.

A curve-fit of $[A]$ vs. time can be used to determine the value of the reaction rate constant.

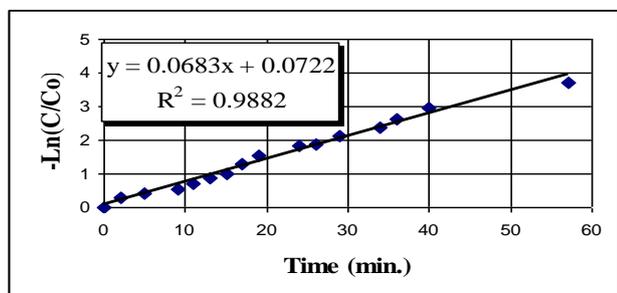
RESULTS AND DISCUSSION

Methane

Graph 1 shows the destruction of methane as an example. An exponential curve of the form $[A] = [A]_0 \exp(-kt)$ fits the data with an R^2 value of 0.96, indicating that a first-order rate expression fits the data well. Graph 2 shows the data from Graph 1 plotted in the form of $-\ln(C/Co)$ vs. time t , where the slope is equal to the first order rate constant k .



Graph 1. Example plot of methane concentration versus time.



Graph 2. Example plot of $-\ln(C/Co)$ vs. time for methane

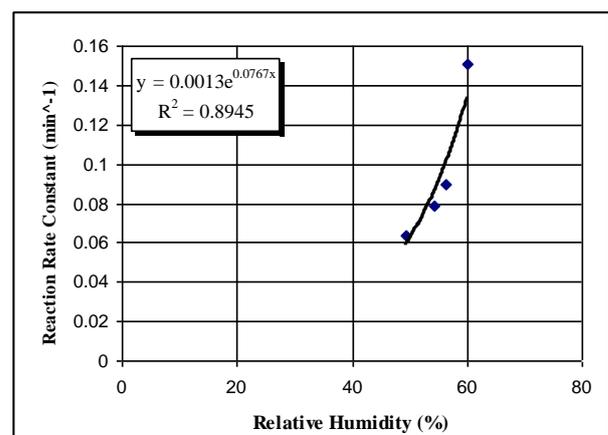
Table 1 presents results for methane. The overall average PCO rate constant for methane was 0.096 min^{-1} . There was a significant variation in the values of k for the 4 runs. Rate constants are known to depend on parameters

such as initial concentration, temperature, humidity, UV intensity, type of catalyst, reactor configuration and oxygen concentration. All tests were performed with the same experimental setup so the type of catalyst, reactor configuration and the UV light intensity remained same. Oxygen concentration can be assumed to be constant. Variations in initial concentration and temperature were small, and thus unlikely to significantly impact the rate constant. The only parameter that varied substantially and may have thus affected the rate constant is humidity. Due to its role in forming OH° radicals which attack organics, relative humidity would be expected to impact PCO destruction rate.

Table 1. Photocatalytic oxidation rate constants for methane

Run No.	Initial Conc. Co (ppm)	Temp. (°F)	Relative Humidity (%)	First -Order Rate Constant k (min^{-1})	R^2
1	277,827	72.1	60.1	0.151	0.81
2	307,390	72.4	49.3	0.064	0.99
3	319,872	70.5	54.3	0.079	0.84
4	302,980	72.0	56.4	0.090	0.89
AVG				0.096	

Graph 3 presents a graph of methane PCO destruction rate constant versus relative humidity. In the relative humidity range of 49.3% - 60.1%, the rate constant increases with the increase in the relative humidity. It was found that an exponential curve best describes the relationship. Previous studies have shown, however, that water vapor concentrations typically reach an optimum value; if humidity levels are too high, water vapor may decrease destruction rates by competing with contaminant molecules for available surface sites (Pichat et al., 1981; Obee and Brown, 1995; Wu et al., 2001). Further testing over a wider range of relative humidities is recommended.



Graph 3. Photocatalytic oxidation rate constant for methane as a function of relative humidity

Xylenes

The results for the tests carried out for o-, m-, and p-xylene are summarized in Table 2. The average reaction

rate constant values were 0.0275 min^{-1} , 0.025 min^{-1} , and 0.0125 min^{-1} for o-, m-, and p-xylene, respectively. These values are lower than the rate constant for methane, which would be anticipated due to the fact that the xylenes are larger molecules with more complex structures compared to methane.

Table 2. Photocatalytic oxidation rate constants for xylenes

Com-pound	Run No.	Initial Conc. Co (ppm)	Temp. (°F)	Relative Humidity (%)	First-order rate constant k (min^{-1})	R ²
o-xylene	1	207	71.5	44.5	0.028	0.89
	2	305	74.5	46.8	0.027	0.83
m-xylene	1	262	71.6	43.1	0.040	0.82
	2	211	72.3	47.5	0.010	0.71
p-xylene	1	401	72.1	55.0	0.012	0.74
	2	355	70.6	45.7	0.013	0.74

Carbonyl sulfide

Two runs with an initial concentration of 30 ppm were carried out to determine the rate constant for carbonyl sulfide. Results are presented in Table 3. The average first-order destruction rate constant for COS is 1.13 min^{-1} , which is substantially higher than that for methane. This may be due to the two double bonds in the COS structure, which contain high densities of electrons and are thus prone to hydroxyl radical attack. As mentioned previously, hydroxyl radical attack is likely a primary method of PCO compound destruction. Additionally, the humidity level was high (61.1 – 63.1%) during the COS experiments; increased water vapor concentrations lead to higher potential for hydroxyl radical production.

Table 3. Photocatalytic oxidation rate constants for carbonyl sulfide

Run No.	Initial Conc. Co (ppm)	Temp. (°F)	Relative Humidity (%)	First -Order Rate Constant k (min^{-1})	R ²
1	30	71.5	61.1	1.11	0.95
2	30	71.5	63.1	1.15	0.90
AVG				1.13	

Applicability of rate constants

The experiments were conducted at ambient temperature, pressure and humidity conditions. The rate constants developed during the experiments may not be directly applicable to another system, since they depend on various parameters like ultraviolet light intensity, reactor configuration, and catalyst characteristics, which are specific to any given system. However, since rate constants are functions of these parameters, they can be scaled and applied to another system (Sattler and Liljestrand, 2003).

CONCLUSIONS

This study determined first-order PCO rate constants for 3 constituents of landfill gas, methane, xylenes, and

carbonyl sulphide, over Degussa P-25 titanium dioxide (TiO_2). The average rate constant for COS destruction was substantially higher than that for methane, possibly due to the two double bonds in the COS structure, which contain high densities of electrons and are thus prone to hydroxyl radical attack. Methane destruction rates were found to depend on relative humidity, in an exponential relationship.

Reaction rate constants for methane and carbonyl sulfide were higher than those for the xylenes. A smaller and simpler molecule like methane or carbonyl sulfide would be anticipated to break down more quickly than a larger and more complex molecule like xylene. A reactor treating a mixture of compounds, such as those in landfill gas, would need to be designed large enough to provide sufficient residence time for the slowest-degrading compound.

Future research should test other landfill gas constituents, singly and in mixtures.

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