

Article

A Novel Application of Photocatalysis: A UV-LED Photocatalytic Device for Controlling Diurnal Evaporative Fuel Vapor Emissions from Automobiles

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Abstract: A novel application of photocatalysis was investigated to reduce diurnal evaporative fuel vapor emissions from automobiles. A light-weight annulus photocatalytic device was designed, fabricated, and characterized for its performance for the oxidation of diurnal evaporative fuel vapor emissions. The prototype photocatalytic device was made with PVC pipe and ultraviolet ($\lambda = 365$ nm) light emitting diodes (UV LEDs) as light sources. Commercially available Evonik P25 TiO_2 was used as the photocatalyst. The study results demonstrate that the UV LED photocatalytic device is capable of reducing diurnal evaporative fuel vapor emissions from automobiles by 60 wt%. However, the presence of high concentrations of light alkanes and aromatic fuel vapors in the diurnal emissions may limit the longevity of the device due to photocatalyst deactivation. Further development of the idea to enhance the longevity of its performance is recommended.

Keywords: UV LED; photocatalysis; fuel vapors; VOCs



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1. Introduction

In this study, an ultraviolet light-emitting diode (UV LED) photocatalytic device was fabricated to demonstrate the feasibility of using photocatalysis to reduce diurnal evaporative fuel vapor emissions from automobiles. Evaporative fuel vapor emissions are a significant source of volatile organic carbon (VOC) emissions from automobiles, and they may amount to as much as 2.8 g/vehicle/day [1]. Therefore, the motivation of this study was to reduce VOC emissions from automobiles by developing a device to control diurnal evaporative fuel vapor emissions.

1.1. ORVR and Diurnal Evaporative Fuel Vapor Emissions

For over two decades, automobiles in the United States (US) have been equipped with onboard refueling vapor recovery (ORVR) systems to reduce the evaporative fuel vapor emissions [2]. The ORVR system works by directing fuel vapors from the gas tank to a canister filled with activated carbon. The activated carbon adsorbs fuel vapors from the gasoline tank when the car is parked and when the car is being refueled. However, when the car is in operation, ambient air is drawn into the engine through the carbon canister. The fuel vapors that desorb from the activated carbon during operation, then, are burned in the engine of the automobile [2].

Activated carbon has an adsorption capacity for fuel vapors that is dependent upon many factors, including temperature, fuel type, and humidity. When the temperature of the activated carbon increases, fuel vapors desorb from the activated carbon. Ambient temperature fluctuations throughout a day cause the temperature in the carbon canister of parked automobiles to fluctuate. The fuel vapor emissions resulting from these temperature swings, while the car is not in operation, are called diurnal evaporative fuel vapor emissions [3].

The activated carbon in the ORVR can become saturated with fuel vapors if the automobile is parked for an extended period of time or if the gasoline engine operates only intermittently, as with hybrid electric vehicles. Once the activated carbon is saturated with fuel vapors, emissions from the fuel tank are emitted directly to the environment. Evaporative fuel vapor emissions standards have been set on all light-duty vehicles and trucks from 2004 to the present, and more stringent regulations are to be implemented worldwide, especially within the US [3,4]. Therefore, an alternative emission control technology may be needed in order to reduce fuel vapor emissions from gasoline and hybrid-electric automobiles [4].

Gasoline is a mixture of hundreds of hydrocarbons, predominantly those with 4 to 12 carbon atoms in their structures. The compositions of fuels can vary widely, depending upon the specific grades, regions, and environmental regulations [5]. The approximate composition is 55% alkanes and iso-alkanes, 10% cycloalkanes, 10% alkenes, and 25% aromatics [5]. The headspace of a fuel tank, however, would be concentrated with the more volatile hydrocarbons. Chin and Batterman (2012) investigated the headspaces of gasoline and E85 and found the headspace to contain predominantly benzene, cyclohexane, methylcyclohexane, and n-heptane [6]. However, lighter hydrocarbons were not analyzed in their study. Doskey et al. (1992) measured refueling vapor emissions and found that approximately 70 wt% of the emissions were butanes and pentanes, while aromatic compounds contributed approximately 3 wt% of the emissions [7]. More recently (2010), the US EPA measured the headspace of gasoline with and without ethanol [8]. For E0 (no ethanol) and E10 (10 vol% ethanol) gasoline formulations, butanes and pentanes contributed greater than 30 wt% of the headspace hydrocarbons, whereas the aromatics contributed approximately 5 wt% of the headspace hydrocarbons [8,9]. Ethanol vapors contributed up to 12 wt%, depending upon the formulation of the gasoline [8].

1.2. Photocatalysis

Photocatalysis is an advanced oxidation process that has been studied extensively for the oxidation of volatile organic carbons (VOCs) in air [10–14]. It is a process in which light, as opposed to heat, activates a catalyst. Therefore, photocatalysis can be used to oxidize VOCs at room temperature. The mechanism for photocatalysis [10–14] is described pictorially in Figure 1 and briefly below in Equations (1)–(7).

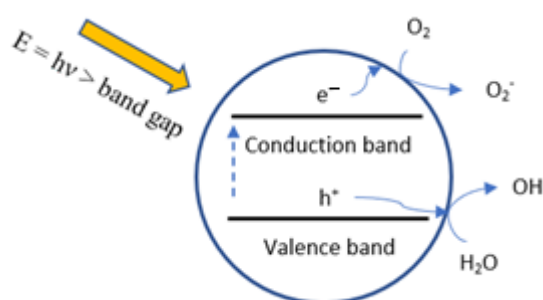
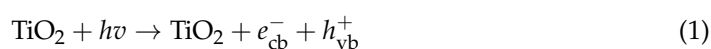


Figure 1. Schematic of the photocatalytic process to form hydroxyl radicals.

The absorption of light, at sufficient energy to overcome the band-gap of the photocatalyst (e.g., TiO_2), will generate an electron-hole pair (Equation (1)).



The electron, e_{cb}^- , jumps to the conduction band (cb), whereas the hole, h_{vb}^+ , is left in the valence band (vb) of the electronic structure of the photocatalyst. These charges migrate to the surface of the photocatalyst where they undergo redox reactions.

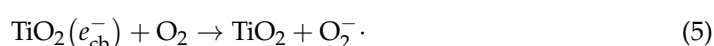
The hole (h_{vb}^+) will oxidize adsorbed water or a hydroxyl group at the surface, forming a hydroxyl radical, as shown in Equations (2) and (3).



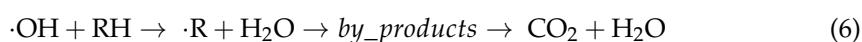
The hole (h_{vb}^+) can also react with adsorbed organic compounds (RH), forming an organic radical, as shown in Equation (4).



The electron (e_{cb}^-) will reduce an adsorbed oxygen molecule or other electron scavenger at the surface of the photocatalyst to produce a superoxide anion, as shown in Equation (5).



The hydroxyl radicals subsequently react with the organic compound (RH) as shown in Equation (6).



The recombination of generated electrons and holes is depicted in Equation (7) and accounts for the inefficiency in the photocatalysis process.



The photocatalysts used by researchers for investigating the photocatalytic oxidation of VOCs are predominantly semiconductor materials, such as titanium dioxide (TiO_2) [15–24], zinc oxide (ZnO) [20,24–29], and tungsten oxide (WO_3) [29–33], among many others [17,20,24,34]. TiO_2 -based photocatalysts, however, have been the most widely studied and reported in the published literature [15–24], because they have low toxicity, high photocatalytic activity, good chemical stability, and low cost [15,18].

Although TiO_2 -based photocatalysts have many attractive qualities, they also have some shortcomings [15,17,18,22]. For example, without modifications, TiO_2 is photoactive upon absorption of UV light [15,16,18]. In addition, TiO_2 has a low quantum yield [15,18] due to the recombination of electron-hole pairs. Many researchers have investigated methods to overcome these shortcomings. For example, researchers have modified TiO_2 to increase its activity in visible light [16,17,21] and to reduce the rate of electron-hole recombination [17] by doping it with other metals [17,18,21] or by combining it with other semiconductors to form composite materials [17,18,21].

Evonik P25 TiO_2 , a commercially available photocatalyst, was used in this study, because it is one of the most photoactive commercially available materials [19,23]. Developing a novel photocatalyst was outside the scope of this study.

1.3. Ultraviolet Light Emitting Diodes (UV LEDs)

UV LEDs are small and rugged solid-state light sources. UV LEDs require low direct current (DC) power, which could be provided by the battery already contained within the automobile. In addition, they can be turned on and off instantaneously (i.e., no warm-up time). UV LEDs have very long lifetimes, upwards of 10,000 h [35]. In addition, UV LEDs contain no hazardous materials [35]. UV LEDs are ideal for niche mobile photocatalytic applications, such as in photocatalytic processes within automobiles.

In this project, the performance of a UV LED photocatalytic device was assessed with selected VOCs that are representative of fuel vapors, including ethanol, n-butane, n-hexane, cyclohexane, and benzene. In addition, the device was tested in a standard

ORVR test system [36,37] at an automobile parts manufacturing company to demonstrate its effectiveness as a method to control diurnal evaporative fuel vapor emissions.

2. Results

Selected VOCs (ethanol, n-butane, n-hexane, cyclohexane, and benzene) were used as representative fuel vapors to assess the performance of our UV LED photocatalytic device. Ethanol was used as a vapor challenge, since fuel can be blended with ethanol at ethanol concentrations from 10 vol% to 85 vol% [8,38]. N-butane was selected because lighter hydrocarbons (butanes and pentanes) contribute greater than 30 wt% of the total hydrocarbons in the headspace of a fuel tank [8,9]. In an effort to assess the effects of chemical structure on the performance of the device, the VOC challenges to our system included n-hexane, cyclohexane, and benzene, all of which have six carbon atoms in their structure.

Figure 2A,B show the results of our laboratory studies using these compounds. Figure 2A compares the photocatalytic oxidation rates as functions of VOC type and concentration. Figure 2B shows the rate at which carbon is oxidized per area of illuminated surface as a function of the rate at which carbon enters the device per area. By presenting the data in this manner, the limits at which carbon is oxidized in our UV LED photocatalytic device are shown, and it could facilitate the scaling of the device to various applications.

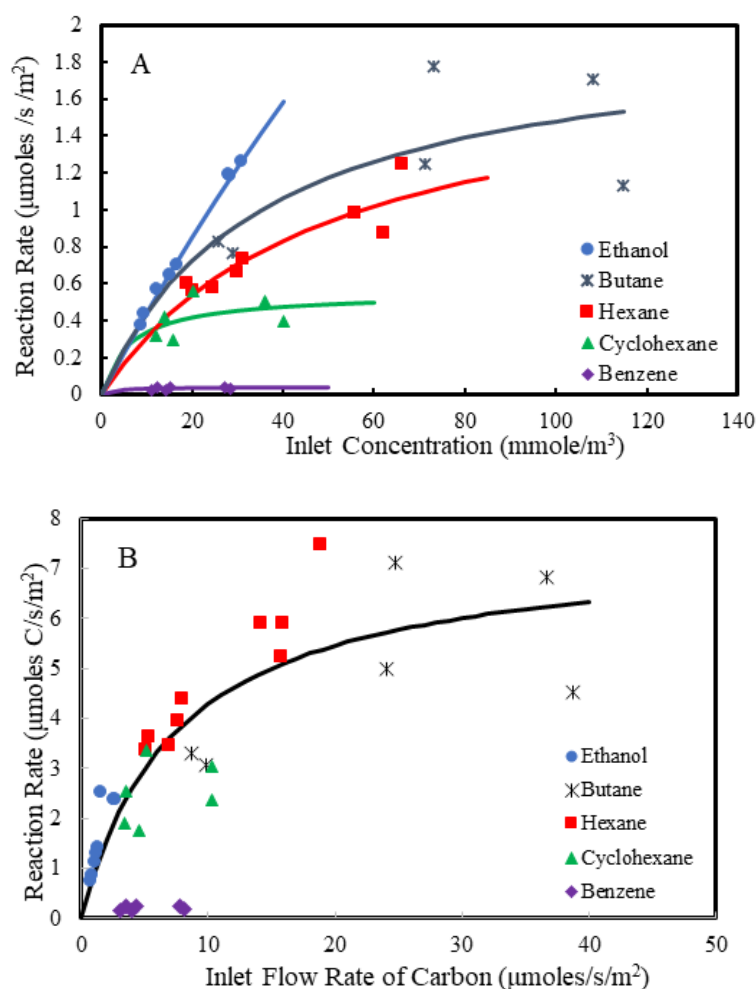


Figure 2. Summary of photocatalytic oxidation rates observed for selected representative fuel vapors. The reactor temperature for all trials was approximately 32 °C. (A) reaction rate ($\mu\text{moles/s/m}^2$) vs. concentration (mmoles/m^3). (B) reaction rate ($\mu\text{moles carbon/s/m}^2$) vs. flow rate of carbon into the reactor ($\mu\text{moles/s/m}^2$). The reaction rates were normalized to illuminated surface area. mmoles = millimoles. μmoles = micromoles.

The Langmuir-Hinshelwood model was applied to the rate of reaction as a function of the VOC concentration (Figure 2A) and as a function of the rate at which carbon entered the reactor (moles of carbon/s/m²) (Figure 2B). The solid lines in Figure 2A,B represent the results of the modeling effort. The application of Langmuir-Hinshelwood kinetic models to the photocatalytic oxidation of VOCs is supported by the published literature [10,12–14,39,40]. The model used is shown in Equation (8):

$$-r_A = \frac{kKC_A}{1 + KC_A} \quad (8)$$

where $-r_A$ is the rate of reaction in moles/s/m², C_A is the concentration of the VOC (moles/m³), k is the maximum rate constant per illuminated surface area (moles/s/m²), and K (m³/mole) is an adsorption equilibrium parameter.

The values of the model parameters (k , K , and the coefficient of determination, R^2) are summarized in Table 1. A comparison of the values of the model parameters, k and K , show that their values are affected by molecular size and structure. Considering only n-hexane, cyclohexane, and benzene, the parameter k decreases while the parameter K increases with molecular structure from linear alkane to cyclical alkane to aromatic structure. This is due to the differences in the adsorption of the hydrocarbon to the surface of the photocatalyst as well as the relative rates of desorption of the by-products from the photocatalyst.

Table 1. Summary of model parameters used to fit the Langmuir-Hinshelwood model to experimental data.

	k (10 ⁵ moles/s/m ²) ¹	K (m ³ /mole)	R^2
Ethanol	11	4.23	0.997
N-butane	2.0	28.3	0.553
Hexane	1.9	20.4	0.836
Cyclohexane	0.55	157	0.232
Benzene	0.04	347	0.087
Figure 2B			0.77

¹ values for k in Table 1 were multiplied by 10⁵.

In comparing n-butane and n-hexane, both straight-chained alkanes, the parameters k and K are relatively similar. It was expected that the reaction rate of n-hexane would be greater than that of n-butane based upon a discussion by Hays et al. (2015) [41], who state that under the same reaction conditions, higher rates of removal by photocatalysis would be observed for the larger molecules due to the greater binding energies between the photocatalyst and the larger molecules. This is supported by the experimental data in this study shown in Figure 2B, where the photocatalytic oxidation rate of n-hexane trends slightly higher than that of n-butane when similar influent molar flow rates of carbon is used as the basis for comparison. However, Hays et al. (2015) also state that larger molecules will require additional steps to mineralize the larger molecule, which acts conversely to the effects of binding energies [41]. In Figure 2A, the observed rate of reaction of n-butane was slightly higher than that of n-hexane when similar influent molecular molar flow rates were used as the basis for comparison. One possible reason for the relative trends for n-butane and n-hexane in Figure 2A is the difference in time-on-stream. The results for n-hexane were taken 24 h after the reaction was initiated, whereas in the tests with n-butane, the results were acquired 1 h after initiation of the tests. Therefore, the relative amounts of by-products built up on the photocatalyst may have contributed to the observed higher rates of n-butane oxidation compared to those for n-hexane.

The R^2 values for benzene and cyclohexane are very low due to the fact that the data acquired do not change appreciably with the inlet concentrations used in this study. In addition, the relative data scatter is greater at low conversions.

The results for each hydrocarbon are further discussed below.

Ethanol.

In this study, ethanol vapors were degraded by greater than 99% in all experimental trials. At the higher concentrations (near 30 mmol/m³), acetaldehyde was observed in the effluent, with a selectivity of approximately 10%. In some trials, trace amounts of acetic acid were observed but not quantified in the effluent. Carbon dioxide was the predominant by-product in all trials.

Ethanol photocatalytic oxidation has been studied by many researchers [42–49]. The reported mechanisms of ethanol photocatalytic oxidation on TiO₂ [44–48] indicate that acetaldehyde is the first partial oxidation product formed. Adsorbed acetaldehyde is further oxidized to acetic acid, which may further oxidize to formic acid and formaldehyde, and ultimately to carbon dioxide [44–48]. In a previous study, the photocatalytic oxidation of ethanol was maintained at greater than 98% for 30 days at ethanol concentrations of 300 ppm [42]. However, during that time, the presence of acetaldehyde increased from a selectivity of <2% to approximately 10%. This suggests that the deactivation of the photocatalyst will occur over time. Piera et al. (2002) investigated the deactivation of TiO₂ during the gas-phase photocatalytic oxidation of ethanol, and the authors found that dark adsorption of ethanol on TiO₂ decreased by 48% when comparing fresh TiO₂ with re-used TiO₂ [49]. In addition, the rate of ethanol photocatalytic oxidation decreased in subsequent trials in which the photocatalyst was re-used. The accumulation of carbonaceous deposits was blamed for the catalyst deactivation [49].

n-Butane.

The photocatalytic oxidation of n-butane was investigated in this study at relatively high concentrations (~2900 ppm or ~120 mmol/m³), because butanes and pentanes, being the more volatile constituents of gasoline, contribute most to evaporative fuel vapor emissions [7–9]. At these high concentrations of n-butane, the conversion in the UV LED photocatalytic device was less than 30%. No partial oxidation by-products were observed in the gas-phase. These results are supported by Brigden et al. (2001), who also reported low conversions of n-butane in a flow reactor at high (>600 ppm) inlet concentrations [50]. Brigden et al. (2001) reported that n-butane caused the photocatalyst to change color from white to brown, and significant photocatalyst deactivation was observed [50]. Twesme et al. (2006), however, reported complete n-butane conversion at an inlet flow rate of 1000 ppm and at a reaction temperature of 70 °C [51]. Twesme et al. (2006) also reported that the extent of mineralization of n-butane increases with reaction temperature up to 70 °C [51]. Štengl et al. (2014) investigated the photocatalytic oxidation of n-butane in a batch reactor, and similarly to this study, they did not observe gas-phase organic by-products [52].

n-Hexane.

The photocatalytic oxidation of n-hexane was investigated at molar concentrations ranging from approximately 20 mmol/m³ (~500 ppm) to 70 mmol/m³ (~1700 ppm). Over this range, the conversion of n-hexane ranged from approximately 30% at the higher concentrations to 70% at the lower concentrations. Partial oxidation products were not observed in this study.

The photocatalytic oxidation of n-hexane vapor was studied by several researchers [42,53–56]. Saucedo-Lucero and Arriaga [53] reported hexanol and hexanone as partial oxidation products. These partial oxidation products, however, are much less volatile than n-hexane, and so they would tend to stay on the catalyst surface. This is supported by other researchers [54,55] who reported that partial oxidation products of n-hexane were not detectable in the gas phase. It is likely that the partial oxidation products of n-hexane adhere to the surface of the photocatalyst until deeply oxidized to carbon dioxide [42]. Bridgen et al. (2001), also investigated the photocatalytic oxidation of n-hexane and found that hexane fouls the photocatalyst, turning its color from white to brown [50].

Cyclohexane.

In this study, the observed reaction rate of cyclohexane was significantly slower than that of n-hexane under similar reaction conditions. Partial oxidation products were not observed in the gas phase. It is likely that partial oxidation products of cyclohexane remained on the surface of the photocatalyst until they were mineralized to carbon dioxide and water.

The photocatalytic oxidation of cyclohexane was investigated and reported in the published literature [56–59]. In a study by Fujimoto et al. (2017), approximately 60% of 120 ppmv cyclohexane was degraded over TiO₂ in a flow reactor with a 35 s residence time [56]. Interestingly, using the reported dimensions of the reactor and gas flow rates through the reactor, the resulting catalytic oxidation rate of cyclohexane was approximately 30 $\mu\text{moles}/\text{min}/\text{m}^2$ illuminated surface area, which is similar to the photocatalytic oxidation rate of cyclohexane observed in this study. Almeida et al. (2011) investigated the mechanism of cyclohexane photocatalytic oxidation to cyclohexanone [59]. The authors found evidence that the reaction occurs via a Mars-van Krevelen mechanism. In this mechanism, the reactive oxygen species on the catalyst surface reacts with adsorbed cyclohexane to form cyclohexanone, and the oxygen is regenerated by oxygen from the fluid phase.

Benzene.

In this study, the benzene photocatalytic oxidation rate was very low with conversions less than 20% in all experimental trials. It was clear that the photocatalyst had become deactivated in our prototype device. Our results are supported by other published studies in which the gas-phase photocatalytic oxidation of benzene was investigated [60–67]. The rate of photocatalytic oxidation of benzene is dependent upon many factors, including the inlet benzene concentration and humidity [60–63,65,67]. In a study by Long et al. (2012), the benzene conversion (300 ppm inlet concentration) was < 10% over several hours, and benzene conversion decreased with time [66]. Similar results were published by Einaga et al. (2004) [61].

Benzene deactivated the TiO₂ photocatalyst in this study, as indicated by the low benzene conversion and the change in color of the photocatalyst from white to tan. Our data is supported by several published works [61–63,65] in which deactivation of the photocatalyst by benzene was investigated. According to the published literature, the photocatalytic oxidation of benzene can occur by two routes: (1) benzene reaction with a hole (h_{vb}^+), which forms a benzene radical, and (2) benzene reaction with a hydroxyl radical ($\cdot\text{OH}$), which forms an oxygenated by-product (e.g., phenol) [63,65]. Benzene radicals are apt to cause polymerization of organic compounds on the surface of the photocatalyst, thus causing deactivation [61–63,65]. The addition of water vapor to the reactant stream may inhibit the formation of these carbonaceous deposits [60,61,63,65].

Following the trials with benzene, the photocatalytic film was scraped from the inside of the UV LED photocatalytic device and was analyzed using FTIR. The FTIR analyses on used and unused photocatalyst samples are shown in Figure 3. A comparison of the FTIR analyses show several regions that support the presence of partial oxidation products on the used photocatalyst sample. The absorption bands in the region of 2700 cm^{-1} to 3000 cm^{-1} are attributed to the stretching of C-H bonds. The absorption bands in the region of 1250 cm^{-1} to 1500 cm^{-1} can be assigned to the vibrations and stretching of C-H, C-O, and C-C bonds. The absorption bands in the 1500 cm^{-1} to 1800 cm^{-1} region can be attributed to the bending of C-H bonds [68].

Standard ORVR Tests with Gasoline

Figure 4 shows the results of the standard evaporative fuel vapor emission test data conducted at an automobile parts manufacturing facility. The tests were conducted in sealed housings for evaporative fuel vapor emissions determinations (SHEDs). The mass of hydrocarbons and the temperature within three SHEDs were tracked with time for just over 12 h. Each SHED contained a fuel tank and a carbon canister prepared according to standard methods [36,37]. In one SHED, the UV LED device was in line between the

SHED and the carbon canister with UV LEDs on. One SHED contained the same apparatus, except the UV LED device had the LEDs off. The third SHED did not have a UV LED device. As shown in Figure 4, the mass of hydrocarbons emitted with time and temperature followed similar trends in the SHEDs containing the UV LED device with the LEDs off and that containing no UV LED device. This supports that the fuel vapors were not adsorbed to a measurable extent in the device itself. In contrast, in the SHED with the device with the UV LEDs powered on, there was >60 wt% decrease in the mass emissions of fuel vapors compared with the measured emissions in the other two SHEDs. The results show that the photocatalytic activity within the UV LED device was responsible for the reduction in diurnal evaporative fuel vapor emissions.

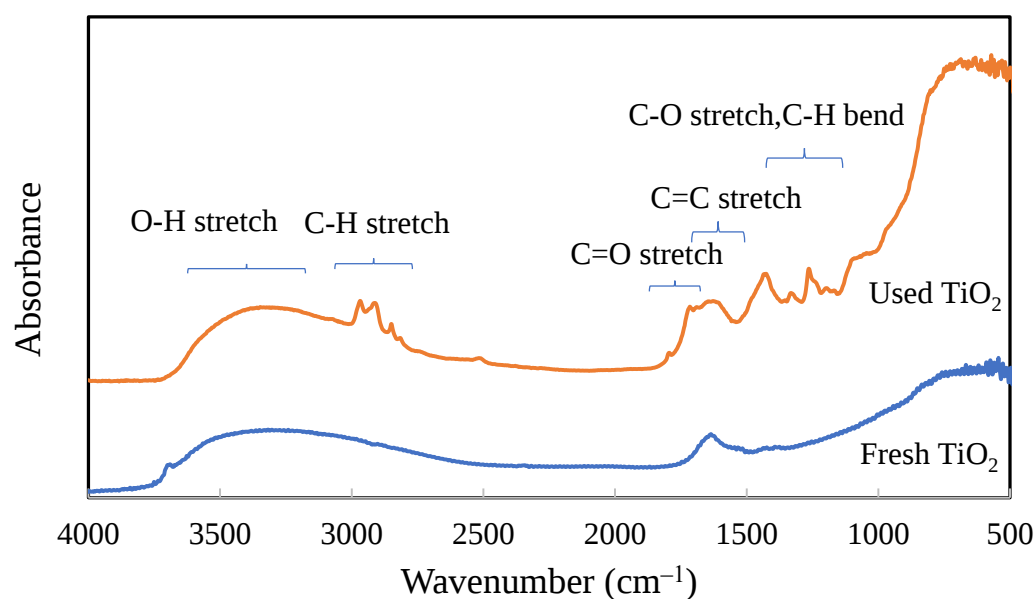


Figure 3. FTIR analyses of new (fresh) and used P25 TiO₂. The used photocatalyst was taken from the UV LED device following experimental trials with benzene.

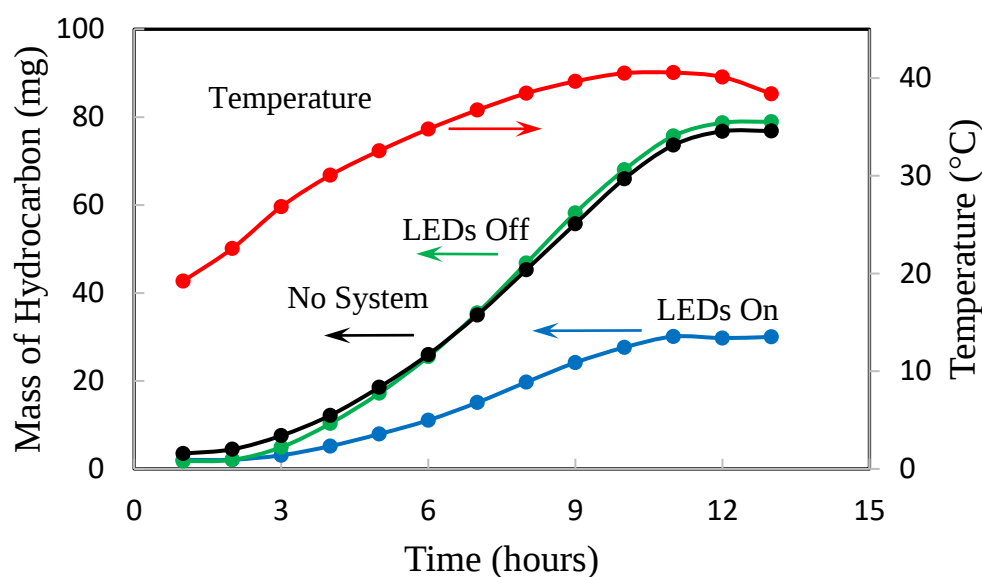


Figure 4. Results from standard evaporative fuel vapor emissions tests.

3. Discussion

The US EPA Tier 3 regulations for evaporative fuel vapor emissions are designed to eliminate fuel vapor evaporative emissions [69,70]. Considering all types of evaporative fuel vapor emissions from a light-duty automobile, the Tier 3 standards require less than 0.300 g/test over a 2-day and 3-day evaporative emission test [70]. The Tier 3 standard for just the diurnal evaporative fuel vapor emissions from the fuel tank and carbon canister of a light-duty vehicle is <0.02 g/test [70]. Regrettably, the data in Figure 4 shows that the device did not meet the Tier 3 standard diurnal evaporative fuel vapor emissions, as approximately 30 mg or 0.03 g of fuel vapors were emitted to the SHED in only 12 h of the emissions test.

A challenging dilemma to overcome with gas-phase photocatalysis is catalyst deactivation. In this study, the high concentrations of fuel vapors in the headspace of a fuel tank and the presence of aromatic hydrocarbons leads to rapid photocatalyst deactivation. Methods to regenerate the photocatalyst and modifications to the photocatalyst to prevent deactivation must be further developed to open up more new and innovative applications of gas-phase photocatalysis.

Constraints on size, weight, cost, and power were placed on the device from the automobile manufacturing industry. At the advice of the automobile parts manufacturer, the device was to be relatively small and lightweight, and the power required was to be as low as possible. As a result, our device was made of lightweight materials (polyvinyl chloride (PVC) pipe) that were readily available. While it is recognized that PVC may photocatalytically degrade over time [71], this was not investigated in this study. The size and mass of the device are provided in Table 2.

Table 2. Dimensions of UV LED photocatalytic devices.

Dimension	Value
Inner diameter of the outer tube	3.8 cm
Outer diameter of the inner tube	2 cm
Length	19 cm
Illuminated surface area	200 cm ²
Open volume	160 cm ³
Mass of system	300 g

The materials cost of the device is approximately USD 35. This cost is reasonable, considering that vehicle technology changes to meet Tier 3 evaporative fuel vapor emissions is projected to cost USD 130 per vehicle [72]. Considering the results in Figure 4, however, the cost of using the UV LED photocatalytic device for reducing evaporative fuel vapor emissions by 60% is nearly USD 900/g of fuel vapor emissions mitigated.

The power to the device must also be considered. A typical car battery is rated at approximately 50 amp-hours (Ah) [73], and it can provide the required 12 V for the UV LEDs in our device. The UV LED photocatalytic device uses approximately 0.5 A (12 V, 6 W), and so the standard car battery could power the UV LED device for ~100 h (or approximately 4 days) before the battery would need to be re-charged.

Other aspects must be considered regarding the use of a UV LED photocatalytic device for diurnal evaporative fuel vapor emissions control in an automobile. These include longevity of the photocatalyst, regeneration of the deactivated catalyst, and ease of maintenance and installation of the device. In addition, all safety aspects and controls for the device must be considered when incorporated into an automobile. The operational controls must also be considered to determine when the device should be powered on and off.

4. Materials and Methods

4.1. Materials

Ethanol, n-hexane, cyclohexane, and benzene were purchased from laboratory chemical suppliers as liquids and were used as received. N-butane was purchased from Airgas as a compressed gas at a concentration of 0.9 mole% in air. Regular unleaded gasoline was purchased from southwest Ohio and was used in the standard test system as received. Titanium dioxide (TiO₂) P25 was purchased from Evonik and was used as received.

4.2. Design and Construction of the Photocatalytic Device

Four photocatalytic devices were made using polyvinyl chloride (PVC) schedule 40 pipe. The devices were annulus reactors, with dimensions and details provided in Table 2. A photograph of a prototype device is shown in Figure 5.



Figure 5. Photograph of one of four UV LED photocatalytic devices used in this study.

The light sources were strip UV LEDs from Waveform Lighting. The strips were adhered vertically to the outside surface of the inside tube so that they were facing outward. The emission spectrum of the UV LEDs center at a wavelength near 365 nm [74]. The light intensity from the strip LEDs was characterized as a function of distance away from the strip using an Omega light meter (HHUV254SD Model) with a UVA sensor, and the resulting data are shown graphically in Figure 6. In the photocatalytic device, the distance between the UV LEDs and the photocatalytic film was approximately 1.8 cm, so the power intensity at the photocatalyst was approximately 2 mW/cm². The direct current (DC) power required for the UV LEDs in each device was approximately 6 W (12 V, 0.5 Amps).

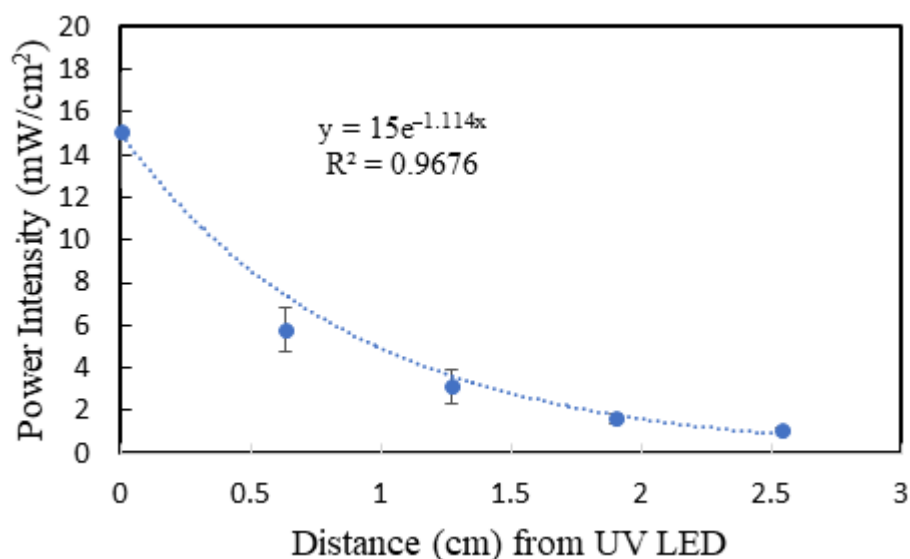


Figure 6. UVA (365 nm) light intensity as a function of distance away from the UV LEDs.

4.3. Photocatalytic Films

Evonik P25 TiO₂ has been characterized in previously published works [42,43,75–80]. P25 TiO₂ has a crystal structure that contains both anatase and rutile in a ratio of approximately 4 to 1 [42,43,74–78]. P25 TiO₂ has a surface area of approximately 50 m²/g [42,77–80], a band gap of approximately 3 eV [42,43,80], and a crystal size of approximately 25 nm [42,76–80].

The photocatalytic film was formed on the inside of the outer tube using a dip coating method. A concentrated slurry of P25 TiO₂ in ethanol (800 g/L) was warmed to temperatures near 40 °C. The slurry was then introduced to the inside of the outer shell of the device and manually agitated. The slurry was then poured out of PVC pipe, and the PVC pipe was continuously rotated manually until the solvent evaporated. By inspection, the coating of TiO₂ on the inside of the PVC pipe appeared relatively uniform. The device was placed in an oven at 100 °C for 1 h to evaporate the ethanol from the photocatalyst film. The mass of the photocatalytic film was approximately 0.5 mg/cm² of illuminated surface area.

Efforts were made to assess the possible reasons for photocatalyst deactivation in this study. Fourier transform infrared analyses (FTIR analyses, Nicolet 670 FTIR, Thermo Electron Corporation (now Thermo Fisher Scientific, Waltham Massachusetts, USA)) were conducted on the TiO₂ photocatalytic powders before and after use in the device, specifically following the experimental trials with benzene. The FTIR analyses were used to characterize organic functional groups remaining on the photocatalyst in the UV LED photocatalytic devices.

4.4. Test Systems

4.4.1. Laboratory Test System

The test apparatus used for this study included mass flow controllers to control air flow rates through the test systems, a power supply for the UV LEDs, and a cylindrical photocatalytic device. All tests were conducted with two identical test systems to assess reproducibility.

With the exceptions of those with n-butane, all tests were conducted at 50 cm³/min. Lab-made diffusion cells were used to generate the VOC vapor challenges to the reactors. A wide range of VOC concentrations was achieved by varying the diffusion path length and diameter. Samples of the reactor influent and effluent were collected 24 h after the flow rates and vapor challenges were initiated to the reactor. Initial photocatalyst effectiveness was not measured in this study; rather, photocatalyst effectiveness after 24 h of operation was assessed.

The tests conducted with n-butane were modified because a limited supply of n-butane was available for the tests. Small canisters containing 0.9 mole% n-butane in air were purchased for this study. Therefore, tests could not be run for 24 h. For n-butane, the respective flow rates of air and n-butane were varied to vary the n-butane concentration, while keeping the total flow constant at 100 cm³/min. Samples were taken before and after the reactor 1 h after the flow was initiated to the device.

For all hydrocarbons, gas samples were taken from the flow lines before and after the photocatalytic device using a 250 µL gas tight syringe, and the samples were analyzed using a Hewlett Packard (HP) 5890 gas chromatograph with a flame ionization detector (GC/FID). The GC/FID was used to quantify the VOCs by comparing the respective peak areas to those of gas-phase calibration standards. CO₂ was measured in selected studies using a calibrated Amprobe CO₂ meter.

4.4.2. Standard ORVR Test System

A standard test system at an automobile parts manufacturing facility was used to assess the performance of our device against diurnal evaporative fuel vapor emissions. The test methods are specified in 40 Code of Federal Regulations (CFR) 86.133–90 [36,37]. For our purposes, three tests were conducted simultaneously: (1) a test system with no UV LED device; (2) a test system with a UV LED device with LEDs off; and (3) a test system with a UV LED device with LEDs on. Each test system was contained in a sealed housing for evaporative emissions determination (SHED). Each test system consisted of a fuel tank, a carbon canister, and a variable volume device that accounted for the expansion and contraction of gases with temperature changes to maintain a constant pressure inside the SHED. The SHED was heated from 18.1 °C to 43.5 °C in a 12 h period of time, according to a standard test temperature profile. Fuel vapors were sampled from the SHED every hour for 12 h, and the samples were analyzed using gas chromatography with flame ionization detection (GC/FID). Our tests were terminated after 12 h, when the peak temperature (43.5 °C) was reached. A photograph of one of the test systems is shown in Figure 7.

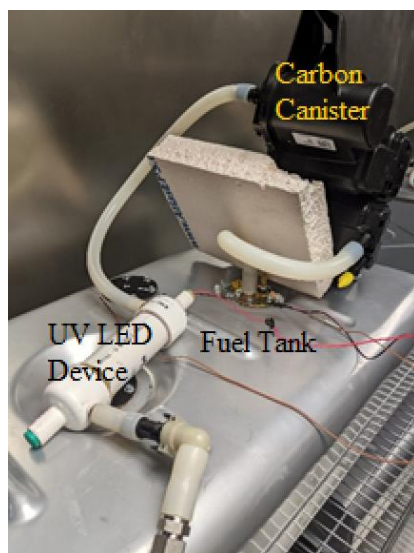


Figure 7. Photograph of test apparatus within a SHED during standard testing for evaporative fuel vapor emission control.

5. Conclusions

UV-LED photocatalytic devices were designed, fabricated, and demonstrated as tools to degrade evaporative fuel vapor emissions. Our results indicate that the type and concentration of VOCs impact the effectiveness of the UV LED photocatalytic device in its intended application.

The results of this study demonstrated a novel and innovative application for photocatalysis. A 60 wt% reduction in diurnal evaporative fuel vapor emissions were observed when our device was in service between the carbon canister of the ORVR and the environment. However, the extent of evaporative fuel vapor emission degradation with the UV LED device was not sufficient to meet future evaporative fuel vapor emissions regulations for automobiles. In addition, the deactivation of the photocatalyst must be addressed, since both high concentrations of fuel vapors and aromatic compounds are known to deactivate photocatalyst films.

Despite the limitations observed in this study, the authors believe that UV LED photocatalytic devices can lead to new and innovative ways to apply photocatalysis to niche mobile applications.

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