# Experimental study of the degradation of volatile organic compounds by photocatalytic oxidation using TiO<sub>2</sub> pellets

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## Abstract

A fixed bed photocatalytic reactor has been designed and built with a UV radiation source. TiO<sub>2</sub> pellets were placed on the three fixed beds within the reactor. Acetone was used as an indicator of volatile organic compounds (VOCs) during the experiment. Under the flow rate of 12.75 l/min, the oxidation efficiencies were obtained at four different concentrations of acetone laden gas streams ranged from 40ppm to 250ppm. It was found that the lower the acetone concentration of the untreated inlet gas, the higher the oxidation efficiency; the obtained oxidation efficiency was in the range of 40-70% for various concentrations of untreated gases. Two concentrations of toluene laden gas stream were also tested using the same reactor, similar trends of oxidation efficiencies were found as 50% for 120ppm toluene gas, and 45% for 300ppm toluene gas. It was found that the times for toluene to reach oxidization equilibrium were halved for the acetone gas stream. Other parameters such as flow rate and UV intensity were also altered to see their effects on the oxidation efficiency. A full spectrum scan was carried out using a Bio-rad Infrared spectrometer, it was found that the main components of the treated gas stream from the outlet of the reactor were  $CO_2$  and water along with small amounts of untreated acetone. The suspected intermediates of aliphatic hydrocarbons and CO are found in very minimal amounts or are non detectable. Keywords: degradation, air pollutants, VOCs, photocatalysis.

# 1 Introduction

Volatile organic compounds (VOCs) are a group of air pollutants that present both in ambient and indoor environments. Some of the more commonly known VOCs are benzene, toluene and formaldehyde which are toxic and potentially carcinogenic. The dominant sources of VOC emissions include burning of fossil fuels such as petrol, oil, wood, coal and natural. They are also found in industrial emissions including solvent, paints and glues. Short term exposure of high levels or long-term exposure to low levels of these compounds may cause health problems [1]. Methods currently used to treat VOCs include incineration, condensation, adsorption and absorption. Incineration and condensation are costeffective only for moderate to high VOC concentrations. Adsorption and absorption do not destroy VOCs but simply transfer them to another medium. Both methods are not cost-effective for gas streams with relatively low concentrations and large number of compounds, as the recovery and reuse of the compounds is not economically feasible. Using photocatalytic oxidation with UV irradiation on semiconductor TiO<sub>2</sub> to remove VOCs is a very promising process.

In the electronic band structure of a semiconductor such as  $TiO_2$ , the highest occupied band is the valence band, the lowest unoccupied energy band is the conductance band, and both bands are separated by a band gap, a region devoid of energy levels. Activation of the semiconductor photocatalyst is achieved through the absorption of a photon with ultra-band gap energy, which results in the promotion of an electron (e<sup>-</sup>) from the valence band. This causes aggressive oxidation of the surface adsorbed toxic organic pollutants and can lead to their complete degradation. The  $TiO_2$  material used is produced through high temperature flame hydrolysis of  $TiCl_4$  in the presence of hydrogen and oxygen, which is 99.5% pure  $TiO_2$  with 70% anatase and 30% rutile. It represents an environmental friendly and clean chemical technology and with potential applications to remove air pollutants from industrial sources and buildings.

Many researcher projects have been conducted using thin  $TiO_2$  thin film coated on a glass or metal surface by the sol-gel method [2-7], but the technical difficulty of coating affects the consistency and quality of the film, leading to variable degrading efficiencies and loss of catalyst during the reaction process. In This research, a non-film Titania media as pellets has been used, instead of thin film, in a multi-stage parallel plate photo-reactor. This format of Titania has the advantage of easy to handle during the industrial applications. Many other potential benefits of using non-film  $TiO_2$  have also been investigated. The degradation efficiencies of toluene and acetones, as indicators of VOCs, were obtained at various concentrations in feeding gas. Other parameters such as flow rate and UV intensity were also altered to see their effects on the oxidation efficiency. A full spectrum scan was carried out using Bio-rad Infrared spectrometer to confirm the final product and oxidation and see the possible intermediate by products.

# 2 Experimental methods

#### 2.1 Photocatalytic reaction system

A fixed bed photocatalytic reactor has been designed and built in the laboratory. It has three beds containing the  $TiO_2$  pellets as photocatalyst. The  $TiO_2$  pellets used is in cylindrical shape and has a dimension of 2.5mm in both diameter and height. It was made by extruding the P25 Titania powder. The UV black light lamps (8Wx12) were used in the experiment that can freely transmit the ultraviolet radiation with wavelength peaking at 356 nm. The primary design objective of a photocatalytic reactor is to ensure that maximum contacting of photons, catalyst and reactants occurs. Other desirable features include the ability to vary UV light intensities and reasonable low pressure drop.

The set up of the photocatalytic reaction system with the sampling and analysing is shown in figure 1. In addition to the photocatalytic reactor, the system contains a syringe pump, a vaporiser, two follow meters and a suction pump. The VOCs (toluene or acetone) liquid were injected by a syringe pump and passed through a vaporizer. Samples of the inlet and outlet gas stream were analysed by an on-line Infrared spectrum gas analyser (MIRAN IA) by switching the connecting valve.



Figure 1: Flow diagram of photocatalytic reaction system set up.

## 2.2 Experimental procedure

The concentrations of acetone and toluene in the feed gas were changed and passed through the reactor, by measuring the concentrations before and after the treatment, their photocatalytic conversion efficiencies can be obtained. Acetone laden gases were tested at four different initial concentrations, i.e. 40ppm, 90ppm, 130ppm and 250ppm. For toluene, only two initial concentrations were tested, i.e. 120ppm and 300ppm. Each experiment lasted from 100min up to 350min until the photocatalytic degradation reaching equilibrium.

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Several other parameters were varied to see their effects on the oxidation efficiency, include light intensity and flow rate. At the same initial concentration and flow rate of acetone laden gas, the conversion efficiencies were compared under three lighting conditions, the first was full UV radiation with all lamps on, where the measured average UV intensity is 47  $\mu$ W/cm<sup>2</sup>; the second was partial UV radiation with only some of the lamps on, where the measured average UV intensity was 14 $\mu$ W/cm<sup>2</sup> and the third was no UV lamps on, and UV radiation was zero. The flow rate of the system was varied at 8.51.min and 12.751/min, the effects of flow rate on the degradation efficiency were also studied.



Figure 2: The oxidation deficiencies of acetone gases with different acetone concentrations.

## 3 Results and discussions

#### 3.1 Destruction of VOCs at different initial concentrations

Toluene and acetone laden gas streams were prepared using syringe pump, vaporiser and mixing with zero gas to the appropriate concentration. The initial concentrations of untreated gas were measured by online infrared absorption gas analyser, and the final concentrations of treated gas were analysed again at the outlet of the reactor. Acetone was used as an indicator of VOCs during the experiment. Under the same flow rate, the oxidation efficiencies were obtained at four different concentrations of acetone laden gas stream ranged from 40 ppm to 250 ppm. It was found that the lower the acetone concentration, the higher the oxidation efficiencies were in the range of 40-70% for various concentrations. Figure 2 shows the results of oxidation efficiencies for acetone.

Two concentrations of toluene laden gas stream were also tested using the same reactor, the similar trend of oxidation efficiencies were found as 50% for

120 ppm toluene gas, and 45% for 300 ppm toluene gas. It was found that the times for toluene to reach oxidation equilibrium have been reduced than for acetone gas stream. Figure 3 shows the experimental results of oxidation toluene laden gas streams.



Figure 3: The oxidation efficiencies of toluene gases with different acetone concentrations.





#### 3.2 Destruction of VOCs under varying UV light intensities

In order to see the effects of UV light intensity on the oxidation efficiencies, experiments were run under three levels of UV intensities, i.e. all UV lights on

(47  $\mu$ W/cm<sup>2</sup>), partial UV lights on (14 $\mu$ W/cm<sup>2</sup>) and no UV lights on (zero UV radiation). It was found that the UV intensity impacted significantly on the oxidation efficiency of VOCs, i.e. the higher the UV intensity, the higher the oxidation efficiency. When UV intensity was 47  $\mu$ W/cm<sup>2</sup>, about 70% oxidation efficiency was achieved at equilibrium; when UV intensity was zero, the removal efficiency was reduced to 10%, where no photocatalytic oxidation occurred, only the physical adsorption contributed to the limited reduction of VOCs (Figure 4).



Figure 5: The oxidation efficiencies of acetone gases streams with different flow rates.

## 3.3 Oxidation efficiencies at different flow rates

Experiments were carried out at flow rates of 8.51/min and 12.75 l/min to see the effects of changing flow rate in the system on their oxidation efficiencies. It was found that very similar equilibrium conversion rates were achieved for two flow rates, but when the flow rate is higher, i.e. 12.751/min, the reaction reach equilibrium faster at about 150 min; in case of lower flow rate (8.51/min), it took longer time to reach the reaction equilibrium at about 200 min. In addition, the low flow rate helped better adsorption, and resulted in slightly higher conversion efficiency from the start of the reaction until reaching equilibrium (figure 5).

#### 3.4 Gas chemical composition analysis

A chemical composition analysis of the existing gas stream was conducted using a Bio-Rad Infrared spectrometer. This analysis aimed to determine the main components of the outlet gas from the reactor after the photocatalytic oxidation treatment, and also determine any intermediates formed from partial oxidation of acetone, in the form of aliphatic hydrocarbons such as acetaldehyde, acetic acid, and formaldehyde. From figure 6, CO<sub>2</sub> and H<sub>2</sub>O appeared to be the main gas component in the treated gas stream, with small amount untreated acetone The suspected intermediates of aliphatic hydrocarbons and CO are very minimal or non detectable.



Figure 6: Chemical composition of treated acetone gas stream.

The above experiments have proven that using  $TiO_2$  pellets can effectively treat the acetone and toluene as indicators of VOCs at quite high concentrations. In comparison to using thin TiO<sub>2</sub> film coated on media, TiO<sub>2</sub> pellets have a number of advantages. Firstly, a larger quantity of TiO<sub>2</sub> can be placed in the reactor compared to using thin film; the contoured shape of pellets provides larger surface areas to receive UV irradiation. When the air flow passing the packed titania pellets layer and better contact is achieved through increased mass transfer and the increased illuminated surface area. So that the number of TiO<sub>2</sub> molecules available for photocatalytic reaction has been significantly increased, and results in higher removal efficiency. Secondly, it is reported that the photocatalytic reactivity of the thin TiO<sub>2</sub> film is reduced by the chemical deposition process called sol-gel method whereas; the TiO<sub>2</sub> is in its pure form as the pellets and has higher reactivity. Thirdly, the TiO<sub>2</sub> pellets have much higher adsorption capacity than thin film: although some portion of the pellets does not participate in the photocatalytic reaction, it is still active in adsorbing the pollutant gas from the air stream onto the surface of the photocatalyst. This step is essential for consequent photodegradation, and helps to achieve the removal of air pollutants.

## 4 Conclusion

This study indicates that the  $TiO_2$  pellets can oxidize a sizeable percentage of VOC gases within a gas stream. It is a definite viable alternative of using  $TiO_2$  pellets as catalyst in the photocatalytic oxidation process. Under the flow rate of 12.75 l/min, the oxidation efficiencies were obtained at four different concentrations of acetone laden gas streams ranged from 40ppm to 250ppm. It

was found that the lower the acetone concentration of the untreated inlet gas, the higher the oxidation efficiency, the obtained oxidation efficiency were in the range of 40-70% for various concentrations of untreated gases. Two concentrations of toluene laden gas stream were also tested using the same reactor, the similar trend of oxidation efficiencies were found as 50% for 120ppm toluene gas, and 45% for 300ppm toluene gas. It was found that the times for toluene to reach oxidization equilibrium have been halved than for acetone gas stream. Other parameters such as flow rate and UV intensity were also altered to see their effects on the oxidation efficiency.

The chemical composition analysis by Infrared spectrometer confirmed that  $CO_2$  and water are the main oxidation products, the suspected intermediates due to partial oxidation of VOCs were found to be minimal and nearly non-detectable. It is recommended to conduct the further experiments to treat the VOCs at lower concentrations that representing indoor air quality, and based on the trend of conversion efficiency obtained from existing experiments, very high oxidation efficiency or 100% conversion are anticipated when treating the low concentration VOCs.

# Acknowledgement

The authors thank Mr Christopher Stepp for his involvement and contribution of the experimental work.

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