The Use of Photocatalysis and Titanium Dioxide on Diesel Exhaust Fumes for NO\textsubscript{X} Reduction

Beatrice A. Atzl \textsuperscript{†}, Maximilian Pupp \textsuperscript{†} and Marco Rupprich \textsuperscript{*},\textsuperscript{†}

Department of Environmental, Process and Energy Engineering, MCI—The Entrepreneurial School, Maximilianstrasse 2, 6020 Innsbruck, Austria; ba.atzl@mci4me.at (B.A.A.); maximilian.pupp@mci.edu (M.P.)

* Correspondence: marco.rupprich@mci.edu

† These authors contributed equally to this work.

Abstract: Nitrogen oxides are emitted in large quantities by vehicles, and solutions to the problem are sought after. Efforts towards abatement include Selective Catalytic Reduction, catalytic converters, and redesigning engines to make them more efficient. This article focuses on the photocatalytic oxidation, which involves the use of titanium dioxide and ultraviolet radiation to oxidise nitrogen oxides to nitrates. To test this, the interior of a serpentine reactor was coated with titanium dioxide and irradiated with various intensities of ultraviolet light, and the photocatalytic abatement was monitored for the exhaust fumes from a standalone 4-stroke test diesel engine. The conversion rates were calculated using the entering concentration and the concentration after a certain time increment. The rates varied between 13.7\% and 37.3\% and depended strongly on the relative humidity, as a higher relative humidity directly correlated with a better conversion. The irradiance was also varied, and a decline in the conversion rate occurred when the irradiance was increased.

Keywords: nitrogen oxides; photocatalysis; titanium dioxide; ultraviolet radiation; diesel; exhaust gas

1. Introduction

Nitrogen oxides—in this case referring to nitrogen oxide (NO), nitrogen dioxide (NO\textsubscript{2}), and nitrous oxide (N\textsubscript{2}O), collectively known as (NO\textsubscript{x})—are a much-observed group of air pollutants and contributors to global warming. With a combined Global Warming Potential comparable to that of methane [1], it is viewed as a critical issue to combat their presence. A primary emitter of NO\textsubscript{x} are vehicles that involve the use of combustion engines. Diesel engines, in particular, are regarded as a main source, despite their efficiency being higher than that of their petrol counterparts, due to their functioning under higher temperatures and pressures (compression ratios), which favours the production of thermal NO\textsubscript{x}. The European Union, in a legal effort to reduce NO\textsubscript{x} emissions, lower the limit of permissible levels with every stage (refer to Table 1), which gives manufacturers an incentive to design and build vehicles that comply with the most recent standard.
Table 1. EU norms for diesel passenger cars, Category M with Compression ignition, adapted from [2] (© European Union, https://eur-lex.europa.eu, 1998–2018).

| Stage   | Year | CO/(g/km) | HC/(g/km) | HC + NO\(_{x})/(g/km)$ | NO\(_{x})/(g/km)$ | PM/(g/km) |
|---------|------|-----------|-----------|--------------------------|-----------------|-----------|
| Euro 1  | 1992 | 3.16      | -         | 1.13                     | -               | 0.18      |
| Euro 2, IDI | 1996 | 1.0       | -         | 0.7                      | -               | 0.08      |
| Euro 2, DI | 1996 | 1.0       | -         | 0.9                      | -               | 0.10      |
| Euro 3  | 2000 | 0.64      | -         | 0.56                     | 0.50            | 0.05      |
| Euro 4  | 2005 | 0.50      | -         | 0.30                     | 0.25            | 0.025     |
| Euro 5a | 2009 | 0.50      | -         | 0.23                     | 0.18            | 0.005     |
| Euro 5b | 2011 | 0.50      | -         | 0.23                     | 0.18            | 0.005     |
| Euro 6  | 2014 | 0.50      | -         | 0.17                     | 0.08            | 0.005     |

The production of NO\(_{x}\) by diesel engines is explained by how a diesel engine functions. A petrol engine functions using an air-fuel mixture, which is then ignited, while a diesel engine injects fuel into the chamber filled with compressed air, which is then combusted. The air-fuel mixture in the petrol engine combusts at a lower temperature [3], while the instantaneous combustion of the fuel in the diesel engine, which has a higher compression ratio, creating higher temperatures, which favours the production of NO\(_{x}\). The residence time of air in the combustion chamber also affects the production of NO\(_{x}\), in that allowing the nitrogen to react with the available oxygen for longer, at high temperatures, produces more NO\(_{x}\) [4]. A successful effort to reduce NO\(_{x}\) emissions by diesel engines consisted of increasing the number of injector holes in the combustion chamber, i.e., increasing the number of injections per stroke, which resulted in better utilisation of the air, a smaller temperature range, and therefore less NO\(_{x}\) produced [5]. However, redesigning the engine presents many difficulties, of which the greatest is ensuring that the amount of air is sufficient for combustion without leading to a higher production of NO\(_{x}\), while the temperature must also be high enough for combustion but low enough to prevent additional thermal NO\(_{x}\). Other efforts, which involve the aftertreatment of emissions, include Selective Catalytic Reduction (SCR). The system involves the injection of a urea solution, which degrades to ammonia and carbon dioxide, or a 25% aqueous ammonia solution [6,7]. The ammonia reacts with the NO\(_{x}\) to produce nitrogen gas and water vapour. However, urea is an irritant and can damage the health of those involved in its use and transport, while ammonia is toxic. This represents an important disadvantage of SCR and SNCR (Selective Non-Catalytic Reduction). A further disadvantage of SCR is that the catalytic activity is only present at temperatures of 140 °C and above, which limits its ability to reduce emissions created during the cold start-up of an engine as it needs to be heated up. These difficulties sparked an interest in the photocatalytic ability of titanium dioxide, which does not require the addition of other chemicals and presents its activity at ambient temperatures. Two patents [8,9], filed by Volkswagen AG, Wolfsburg, Germany and Battelle Memorial Institute Inc., Columbus, Ohio, USA respectively, confirm and validate by using their own experimental results that titanium dioxide can be used in this manner for the reduction of emissions, especially for diesel and Otto engines. Titanium dioxide has also successfully been used to reduce the concentrations of unburnt hydrocarbons and carbon monoxide [10], which peak during cold start-ups. A larger scale study done [11], where an artificially closed-off area of an indoor car park was coated with paint containing titanium dioxide and filled with car exhaust fumes, showed that NO and NO\(_{2}\) concentrations were reduced by 19% and 20% respectively after a UV-activated period of 5 h.

Titanium dioxide is most extensively used as a pigment in white paints, toothpastes and cosmetic creams, due to its very high refractive index [12] that gives it its brilliant white appearance. Its photocatalytic properties were discovered by Japanese scientists Akira Fujishima and Kenichi Honda [13], which resulted in this particular quality being referred to as the Honda-Fujishima effect. Its initial use was the splitting of water molecules into hydrogen and oxygen, but it was later discovered to also aid air purification by degrading pollutants such as NO\(_{x}\) and volatile organic compounds.
(VOCs). Since then, titanium dioxide has seen success as an element in wall coatings, concretes and asphalts [14], and in air purification systems [15], particularly when combined with activated carbon.

Titanium dioxide, when irradiated, becomes activated and undergoes a relocation of electrons between its conduction and valence bands. This movement of electrons results in the formation of hydroxyl radicals, which stem from the water molecules present in the surrounding air in the form of humidity, as the hydroxide molecules are radicalised by the electron holes in the valence bands. The oxygen molecules in the surroundings are affected by the electrons that have relocated to the conduction bands, resulting in negatively charged oxygen molecules (active oxygen). Both the active oxygen and the hydroxyl radicals are utilised in the oxidation of NO\textsubscript{x} to NO\textsubscript{3}– [16]. The band gap energy of titanium dioxide is 3–3.2 eV, depending on its phase (anatase, rutile or brookite) [17], which correlates with a wavelength of 387–415 nm. This puts the photocatalytic activity of titanium dioxide in the UV spectrum, which allows for the use of titanium dioxide without external UV lights, as the photocatalysis is also triggered by sunlight. This makes titanium dioxide a very versatile tool in combating emissions.

However, the use of titanium dioxide faces obstacles, as many studies, such as those done by the American Association for Cancer Research and American Academy of Dermatology [18,19], suggest that titanium dioxide is carcinogenic and poses health risks, especially when in the form of nanoparticles and applied topically as a constituent of sunblock creams. A study done by Weir et al. [20] states that excessive amounts of titanium dioxide enter sewerage systems because of its widespread use of a pigment and colouring in food products. The effects of inhaling titanium dioxide nanoparticles were tested on mice [21], where it was shown that an exposure to titanium dioxide nanoparticles in the size range of 2–5 nm in a concentration of 8.88 mg/m\textsuperscript{3} resulted in significant lung inflammation. Another study done by the American Chemical Society [22] shows that, while Degussa P25 nanoparticles are not harmful to DNA when catalysed in the ultraviolet region of the electromagnetic radiation spectrum, they do cause lesions in DNA when exposed to light in the visible region.

The aim of this work was the removal of NO\textsubscript{x} present in the exhaust fumes of a diesel engine. This was done by allowing the exhaust fumes to flow through a meander-shaped chamber (also referred to as serpentine reactor) that had been coated with titanium dioxide and irradiated by 18 small UV-A light bulbs. Other focuses included external factors and their influence on the photocatalytic degradation, such as the relative humidity and the radiant dose. There is contradicting evidence pertaining to the effect of relative humidity on the photocatalytic properties of titanium dioxide: in [23] it is mentioned that an increase in relative humidity from 20% to 50% led to a decrease in photocatalytic activity in the removal of NO\textsubscript{x}. In [24], it is described that, while relative humidity is necessary for the hydrophilic properties of titanium dioxide, ergo a photocatalytic reaction, as the formation of hydroxyl radicals is crucial, an increase in relative humidity correlates with a decrease in the degradation of NO. This is further substantiated by [25], where it is described that performed tests provided the results that the reaction rate determined at 75% relative humidity was two thirds of the reaction rate determined at 25% relative humidity. In [26], the steady state uptake of nitrogen dioxide on the surface of irradiated titanium dioxide was found to be completely independent of relative humidity. Therefore, special attention was paid to the effect of relative humidity on the photocatalysis. The rate of the reaction is said to increase proportionally with the radiant dose [24,27]. The primary goal was to ascertain the function of the photocatalytic converter, whilst the secondary goal was to observe whether the outcome of the experiment correlated with precedent results.

2. Materials and Methods

2.1. Meander-Shaped Chamber (Serpentine Reactor)

The reactor used was a 120 × 120 mm (precise dimensions are represented in Figure 1) aluminium block with a meander-shaped cavity, consisting of 5 × 180° turns. The Reynolds number was
calculated for a flow range of 1–3 L/min and resulted in a laminar range. A ridge was hollowed out to allow for a silicone lining, which sealed the edges to prevent any gas losses when the reactor and the UV-A bulbs were screwed closed.

![Figure 1. The dimensions of the used serpentine reactor, measurements given in mm.](image)

2.2. Titanium Dioxide Coating

The titanium dioxide powder used was a standard anatase titanium (IV) dioxide powder (Merck, Darmstadt, Germany) with a specific surface area of 45–55 m² g and a particle diameter of \( d \geq 25 \) nm. The binding substance used was SILIKOPHEN® P40/W (Evonik, Essen, Germany) which is a methylethylpolysiloxane resin emulsified in isobutanol and xylene in a ratio of 1:3. It is resistant to high temperatures of up to 350 °C for stable pigments and consists of approximately 50% VOCs [28,29].

The reactor (see Figure 1) was coated as follows: 5 mL of SILIKOPHEN® P40/W was mixed with 35 mL of demineralised water, shaken vigorously and emptied into the reactor. The reactor was closed off and shaken to allow for an even coating. The remainders were disposed of, and the reactor was placed into an oven at 105 °C for five minutes, which resulted in a sticky surface. A titanium dioxide solution was prepared, consisting of 5 mL of titanium dioxide powder and 35 mL of demineralised water. This was also shaken and emptied into the reactor. The reactor was once again shaken until the entire inner surface was covered, and the remainders were poured out. The reactor was then placed into the same oven at 105 °C for 45 min until it was completely dry. The reactor was left to cool completely.

2.3. Irradiation

The radiation unit which consists of 18 UV-A LEDs. Each bulb measures 3.5 × 3.5 mm and transmits a wavelength of 365 ± 5 nm (see Figure 2a,b). The operating power per LED is approximately...
3.7 W, resulting in a maximum power of 67 W. The lights were controlled by use of an electronic control module, which allowed for variation of the radiant dose by varying the intensity. The intensity levels of 25%, 50%, 75% and 100% corresponds to an electrical input of 16.7, 33.3, 50.0 and 66.7 W, respectively.

![Diagram of the 18 UV-A LED bulbs from above](image1)

![Diagram of the circuit mounted on the reactor](image2)

**Figure 2.** (a) Photograph of the 18 UV-A LED bulbs from above; (b) an illustration of the circuit mounted on the reactor.

### 2.4. Gas Analysis

The gas analysis device used was an Ecom J2KN (ECOM America, Ltd., Gainsville, GA, USA), which is a measuring device designed specifically for determining the contents of exhaust gases. It consists of a probe attached to a computer, of which the probe has to be inserted into the exhaust of an engine or attached to a set-up that serves as a continuance of the engine. The machine sucked the exhaust fumes at a constant rate of 2.6 L min\(^{-1}\) and analysed them either continuously, or performed averaged measurements over a specified period of time. The probe was attached to the exit of the reactor using silicone piping.

The device used to measure the humidity and temperature of the gas in the system was a Testo 445 hygrometer (Testo SE & Co. KGaA, Lenzkirch, Germany). The probe was inserted into a three-headed Schlenk flask, which allowed the gas to enter, pass through a piece of filter tissue paper, be measured by the hygrometer, and exit the humidifier.

### 2.5. Engine

The engine used was an LDW 2004 by the manufacturer Lombardini (Reggio nell’Emilia, Italy). It was a four-stroke diesel engine with four cylinders and a total engine volume of 2199 cm\(^3\).

The engine was connected to a computer (see Figure 3) which automatically recorded data such as the operating pressure and temperature (measured with resistance temperature detectors (RTDs), as well as the rotational speed of the engine, which could be manually operated via a handle. The rotational speed was kept at 1000 ± 100 L/min to allow for better comparison of the results.
The experiments consisted of two parts. The first part was the minutely measurements, which were conducted according to the following procedure: the UV lights were switched off for 5 min, after which they were activated. This activation period lasted for another 5 min, during which a measurement (relative humidity, NO concentration, NO\(_2\) concentration) was taken every minute. The UV lights were switched off again for 5 min, subsequently reactivated for 5 min, deactivated for another 5 min, and reactivated for the final 5 min. This resulted in three activation periods and three deactivation periods. The aim was to first establish a baseline concentration, and to observe if the concentration would return to the baseline values. For the deactivation periods, a measurement was not taken every minute, but rather an averaged value was measured for the entire period. This was done for the intensity levels of 25%, 50%, 75% and 100%. Additionally, the gas was analysed after having been measured directly at the exhaust (no set-up) and with the set-up but for a deactivated UV light.

The second part consisted of ten-minute averaged values, in which the UV light was deactivated for 5 min and reactivated for 10 min. The gas analysis device was set to measure the values and determine a mean value automatically for these periods. After 5 min of deactivation, the intensity was increased, resulting in four deactivation periods and four activation periods.

2.6. Calculation Methods

The conversion rates were calculated using Equation (1):

\[
\text{NO}\_x\text{conversion} = \frac{\left[\text{NO}\_x\right]_0 - \left[\text{NO}\_x\right]_1}{\left[\text{NO}\_x\right]_0}.
\]  

(1)

The subscripts 0 and 1 refer to the initial concentration of the constituent, i.e., the concentration in the gas entering the testing system at \(t = 0\), and the concentration of the constituent after having been irradiated, respectively.

The reduction in emissions were calculated for a theoretical diesel consumption in kg/min to determine if the success of the titanium dioxide is applicable to EU standards, presented in Table 1.

As a first step, the volumetric flow rate of air required for the engine was calculated, using the volume of the engine and the rotational speed. This volumetric flow rate was converted to a mass rate, using the intake pressure and temperature and the specific gas constant of dry air. The mass flow rate of air was used, in combination with the mass flow rate of fuel, ambient pressure, molar mass of nitrogen oxides, the concentration in ppm, the ambient temperature, and the molar gas constant, in order to determine the emission rate in g \cdot s\(^{-1}\). This was converted to grams emissions per kg fuel by dividing by the fuel usage per time unit. This was further converted to grams emissions per l fuel by multiplying with the average density of diesel fuel of 0.83 kg/L, after which it was finally converted.
to grams emissions per kilometre travelled by using the average fuel consumption per kilometre for diesel cars of 0.065 L/km [30]:

\[
\dot{V}_{\text{air}} = \frac{V_{\text{engine}} \cdot n}{2},
\]

\[
\dot{m}_{\text{air}} = \frac{p_{\text{intake}} \cdot \dot{V}_{\text{air}}}{R_{\text{sp}} \cdot T_{\text{intake}}},
\]

\[
M_{\text{NO}} = M_{\text{NO}} \cdot \frac{[\text{NO}]}{[\text{NO}] + [\text{NO}_2]} + M_{\text{NO}_2} \cdot \frac{[\text{NO}_2]}{[\text{NO}] + [\text{NO}_2]},
\]

\[
\text{NO}_x \text{ emission rate} = \frac{(\dot{m}_{\text{air}} + \dot{m}_{\text{fuel}}) \cdot p_{\text{ambient}} \cdot M_{\text{NO}_x} \cdot \text{NO}_x \text{ ppm} \cdot 10^{-6}}{T_{\text{ambient}} \cdot R_u},
\]

\[
\text{NO}_x \text{ emissions per kg} = \frac{\text{NO}_x \text{ emission rate}}{\dot{m}_{\text{fuel}}},
\]

\[
\text{NO}_x \text{ emissions per litre} = \text{NO}_x \text{ emissions per kg} \cdot \rho_{\text{fuel}},
\]

\[
\text{NO}_x \text{ emissions per km} = \text{NO}_x \text{ emissions per litre} \cdot \text{fuel consumption in L per km},
\]

\[
R_{\text{sp}} = 287.1 \frac{\text{J}}{\text{kg} \cdot \text{K}},
\]

\[
R_u = 8.314.2 \frac{\text{J}}{\text{mol} \cdot \text{K}}.
\]

**3. Results**

3.1. Conversions

Table 2 list a summary of the results, in that the measured NO and NO\(_2\) concentrations (in ppm) have already been added to produce the NO\(_x\) concentrations. The conversion rate \(X\) was calculated after every time increment using Equation (1), and the progression shows a lower conversion rate for a lower relative humidity. This is true for every radiant dose intensity.

Figure 4 shows a distinct increase in both the average concentrations and the concentration minimum as the relative humidity decreases. The grey sections depict the periods during which the UV lights were activated, and an instant drop in concentration after activation is visible; however, this difference becomes visibly less as the relative humidity decreases. This implies a direct relationship between the relative humidity and photocatalytic properties of titanium dioxide which is in accordance to [24].
Table 2. Conversion rates for different UV intensities.

| Run | NOx | XNOx | RH | NOx | XNOx | RH | NOx | XNOx | RH | NOx | XNOx |
|-----|-----|------|----|-----|------|----|-----|------|----|-----|------|
| begin | 727 | 730 | 783 | 700 | | 83.1 | 822 | 85.0 | 776 | | 82.5 | 579 | 29.6 | 84.4 | 603 | 22.3 |
| # 1 | 0 | 83.2 | 786 | 77.0 | 780 | 83.1 | 822 | 85.0 | 776 | | 82.5 | 579 | 29.6 | 84.4 | 603 | 22.3 |
| | 1 | 82.4 | 493 | 37.3 | 572 | 26.7 | 82.5 | 579 | 29.6 | 84.4 | 603 | 22.3 |
| | 2 | 81.7 | 520 | 33.8 | 609 | 21.9 | 82.2 | 625 | 24.0 | 83.8 | 628 | 19.1 |
| | 3 | 81.0 | 571 | 27.4 | 754 | 19.5 | 81.7 | 648 | 21.2 | 83.1 | 646 | 16.8 |
| | 4 | 80.3 | 585 | 25.6 | 750 | 15.5 | 81.7 | 678 | 17.5 | 82.2 | 652 | 16.0 |
| | 5 | 79.4 | 606 | 22.9 | 74.6 | 14.1 | 81.3 | 701 | 14.7 | 81.5 | 676 | 13.7 |
| return | 779 | 829 | 670 | 768 | | 77.6 | 851 | 80.0 | 807 | | 77.4 | 633 | 25.6 | 80.1 | 600 | 25.7 |
| # 2 | 0 | 75.5 | 822 | 72.0 | 829 | 77.6 | 851 | 80.0 | 807 | | 77.4 | 633 | 25.6 | 80.1 | 600 | 25.7 |
| | 1 | 75.1 | 575 | 30.1 | 603 | 27.3 | 77.4 | 633 | 25.6 | 80.1 | 600 | 25.7 |
| | 2 | 74.7 | 608 | 26.6 | 633 | 23.6 | 77.0 | 662 | 22.2 | 80.5 | 640 | 20.7 |
| | 3 | 74.3 | 662 | 19.5 | 70.9 | 640 | 22.8 | 76.5 | 684 | 19.6 | 80.3 | 660 | 18.2 |
| | 4 | 74.0 | 671 | 18.4 | 70.6 | 655 | 21.0 | 76.4 | 674 | 20.8 | 80.0 | 654 | 19.0 |
| | 5 | 73.6 | 685 | 16.7 | 70.4 | 655 | 21.0 | 76.3 | 681 | 20.0 | 79.7 | 666 | 17.5 |
| return | 814 | 762 | 807 | 780 | | 77.6 | 851 | 80.0 | 807 | | 77.4 | 633 | 25.6 | 80.1 | 600 | 25.7 |

Figure 4. Exemplary graph depicting results of the abatement with a UV intensity of 25%.

Figure 5, which depicts the results listed in Table 3, does not represent the photocatalytic effect in relation to the relative humidity, but it addresses a point that Figure 4 does not, in that it shows
the conversion over a longer period. Figure 4 shows an increase in the concentration when the UV is activated, which leads to the concern that the concentration might return to normal after a certain period of time, erasing any effect the radiation might have had. This is addressed in Figure 5, in that a decrease is still visible over a longer period of time.

![Figure 5. Average values of ten-minute irradiation with 25%.](image)

**Table 3.** Ten-minute averaged measurements at various intensities for serpentine reactor and exhaust gas.

|                  | X_{NO}/% | X_{NO2}/% | X_{NO}/% |
|------------------|----------|-----------|----------|
| UV at 25%        | 18.31    | 16.47     | 17.68    |
| UV at 50%        | 19.82    | 19.93     | 19.86    |
| UV at 75%        | 13.59    | 14.76     | 14.06    |
| UV at 100%       | 14.05    | 18.44     | 15.93    |

3.2. Emissions per Kilometre Travelled

To calculate the emissions per kilometre travelled, the data measured for the engine listed in Table 4 and Equations (2)–(8) were used. A weighted molar mass for NO\textsubscript{x} was calculated for every intensity level, as seen in Table 5. This led to the various emission rates, based on time, gravimetric fuel consumption and volumetric fuel consumption, in order to result in the calculation of average emissions per kilometre travelled.

**Table 4.** Measurements used for calculations of each run.

| UV/%  | T\textsubscript{intake}/°C | T\textsubscript{ambient}/°C | P\textsubscript{intake}/Pa | P\textsubscript{ambient}/Pa | n/(l/min) |
|-------|--------------------------|--------------------------|--------------------------|--------------------------|-----------|
| No set-up | 25.93                    | 25.43                    | 100,199.61               | 99,328.88               | 1017.97   |
| 0     | 35.10                    | 27.16                    | 100,421.90               | 99,253.19               | 1073.12   |
| 25    | 22.68                    | 24.56                    | 99,739.83                | 99,794.90               | 1071.90   |
| 50    | 27.24                    | 25.11                    | 100,983.46               | 99,694.55               | 1082.30   |
| 75    | 27.67                    | 26.02                    | 99,890.31                | 99,509.30               | 958.07    |
| 100   | 28.93                    | 27.95                    | 100,927.43               | 9924.12                 | 1065.55   |
Table 5. Average emissions of theoretical mass flow rate of fuel, $\dot{m}_{\text{fuel}} = 0.01 \text{ kg/min}$.

| UV/% | $M_{\text{NO}_x}/(\text{g/mol})$ | $\text{mg \ NO}_x/\text{s}$ | $\text{g \ NO}_x/\text{kg \ Fuel}$ | $\text{g \ NO}_x/\text{L \ Fuel}$ | $\text{g \ NO}_x/\text{km}$ |
|------|------------------|-----------------|-----------------|-----------------|-----------------|
| No set-up | 36.24 | 0.308 ± 0.006 | 1.839 ± 0.038 | 1.526 ± 0.031 | 0.099 ± 0.002 |
| 0 | 35.99 | 0.282 ± 0.008 | 1.694 ± 0.046 | 1.406 ± 0.046 | 0.091 ± 0.003 |
| 25 | 36.09 | 0.214 ± 0.024 | 1.283 ± 0.145 | 1.064 ± 0.120 | 0.069 ± 0.008 |
| 50 | 36.44 | 0.210 ± 0.013 | 1.261 ± 0.078 | 1.047 ± 0.065 | 0.068 ± 0.004 |
| 75 | 36.06 | 0.196 ± 0.009 | 1.165 ± 0.054 | 0.967 ± 0.045 | 0.063 ± 0.003 |
| 100 | 36.14 | 0.211 ± 0.007 | 1.267 ± 0.043 | 1.052 ± 0.035 | 0.068 ± 0.002 |

Figure 6 shows a distinct difference in the NO$_x$ emissions when comparing the emissions without titanium dioxide and UV radiation present, and when the set-up is present and the light activated. The ranges do not differ greatly for the intensity levels; however, the best results can be seen for an intensity level of 75%. This represents potential for this topic, in that this experiment could be repeated so that a comparative calculation can be performed.

3.3. Prolonged Exposure

Figure 7 presents the results of a trial run with a lower volumetric flow rate of the analysis device ($2.4 \text{ L min}^{-1}$), where both the motor and the UV LEDs were left running for a longer period of time. The shaded region depicts the illumination period with a constant UV intensity of 50%. The initial decline in concentration, which was attained during the shorter trials, is seen directly after the light is activated. However, over time, the catalyst varies in efficacy, which is shown by the increase in NO$_2$. This can be due to the reaction of titanium dioxide to nitrates; nitrates negatively affect the photocatalytic abilities of titanium dioxide [31]. Nitrate ions adsorbed onto the surface of pure titanium dioxide can convert back into NO and NO$_2$ when irradiated by UV light [32]. However, this can be solved by using a VOC-free binding agent or a supplementary adsorber, such as zeolites, which traps
nitrates on the surface, or by choosing the retention time to be low enough for conversion but high enough to prevent the back reaction. An important aspect, however, is presented after the deactivation of the light. Titanium dioxide, when used as a photocatalyst, is capable of almost complete regeneration, which makes it a valuable catalyst. Precious metals used as catalysts for SCR are susceptible to catalyst poisoning, which leads to high costs over time when they are in need of replacing.

4. Discussion

The abatement of NO\textsubscript{x} depended greatly on the relative humidity, in that a direct decrease in a conversion rate could be seen when the relative humidity was lower, even if the radiant dose remained constant. This is explained by the reliance of the photocatalysis on the presence of water molecules in the surroundings in order to occur; more available water molecules result in a better conversion. A higher UV intensity did not result in a better conversion rate, as can be seen when comparing the run with the highest humidity at 25\% to that at 100\%. The best results were seen at the lowest radiant dose and the highest humidity. The results achieved are on par with those presented in [11], which records a reduction of 19–20\%. The conditions for these results were a steady-state reaction, in that an enclosed space (lined with titanium dioxide) was filled with exhaust fumes, illuminated by UV light and left for 5 h.

For the reduction in emissions according to EU standards, a theoretical mass flow rate of fuel was used, as measured mass flow rates varied too much, due to human/analytical device error, in order to allow for a good comparison. A decrease is, however, visible, and this is cause for more research into the topic of photocatalytic converters for NO\textsubscript{x} abatement. It must be added that the engine used did not have additional catalytic converters for carbon monoxide and unburned hydrocarbons, which is grounds for the statement that more practical results could be expected if this experiment were repeated with an engine that (a) had other converters, and (b) was tested under actual driving conditions with higher rotational speeds.
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Abbreviations

The following abbreviations are used in this manuscript:

- LED Light Emitting Diode
- NO$_2$ Nitrogen Dioxide
- NO Nitrogen Oxide
- NO$_x$ Nitrogen Oxides
- N$_2$O Nitrous Oxide
- RH Relative Humidity
- RTDa Resistance Temperature Detectors
- SCR Selective Catalytic Reduction
- UV Ultraviolet
- VOCs Volatile Organic Compounds

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