

Energy efficiency of photocatalytic gas cleaning

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Abstract

The recovery of small amounts of organic compounds from gas streams is usually not a viable solution and so called “end-of-pipe” processes are preferred. For the destruction of volatile organic compounds (VOC) catalytic combustion is known as the most simple and reliable technology. It shall be compared with photocatalysis in terms of operating energy consumption. Photocatalysis uses light i.e. photons preferentially in the ultra-violet range as an energy source to reach the excited state of a semi-conducting material (TiO_2) which in turn creates radicals that can destroy the organic molecules. The chlorinated hydrocarbon trichloroethylene (TCE) is chosen as a model substance for the theoretical evaluation of the specific energy demand. The results show that energy efficiency of photocatalysis mainly depends on pollutant concentration, quantum yield and efficiency of the needed light source. It is energetically more favourable than catalytic combustion when the specific energy demand below $100\text{W}\cdot\text{h}\cdot\text{m}^{-3}$. This can be achieved for an inlet concentration below 1000-1500ppm, depended on the kind of organic.

Keywords: gas cleaning, energy efficiency, photocatalysis, VOC, TCE.

1 Introduction

Volatile organic compounds (VOC) like formaldehyde or chlorinated hydrocarbons (HVOC) are hazardous to human's health already at very low concentrations. Their recovery is usually energetically and economical unattractive and so called end-of-pipe processes are preferred. An abatement with state of the art technology is either technically complex or energetically expensive. The photocatalytic oxidation of organic pollutants represents a new and promising method for gas cleaning. Figure 1 gives an overview of various technologies and their range of application with respect to gas flow and HVOC concentration (adapted from Keller and Dyer). This work shows the energy demand of a photocatalytic reactor unit in comparison with the most commonly used catalytic combustion. Moreover the most promising range of operation of this technology is elaborated and it's result is already depicted in Fig. 1.

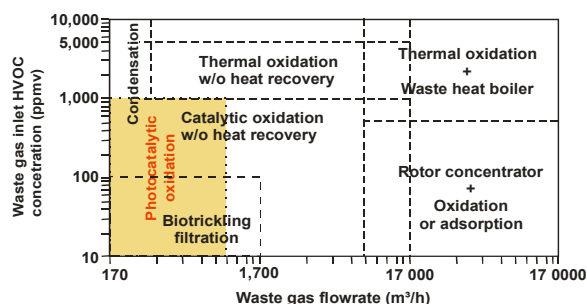


Figure 1: Fields of operation with lowest operation cost for different end-of-pipe treatment technologies (adapted from Keller & Dyer) extended with photocatalytic oxidation.

2 Background of photocatalytic gas cleaning

2.1 The physics behind

Photocatalysis is based on the photo-induced process of charge separation at the illuminated surface of a semi-conducting material (photo-catalyst). These charges can be transferred to adsorbed molecules like O_2 (Figure 2) or OH^- . Hence reactive radicals are formed that trigger oxidation with organic molecules. Equation 1 summarizes this global oxidation reaction. Inorganic species are transformed to mineral acids like HCl in the case of the complete mineralization of a chlorinated hydrocarbon. TiO_2 is regarded as the most common photo-catalyst which can be activated with light at a wavelength below 385nm (bandgap energy). Hence UV-light is needed to run a photocatalytic gas cleaning process.

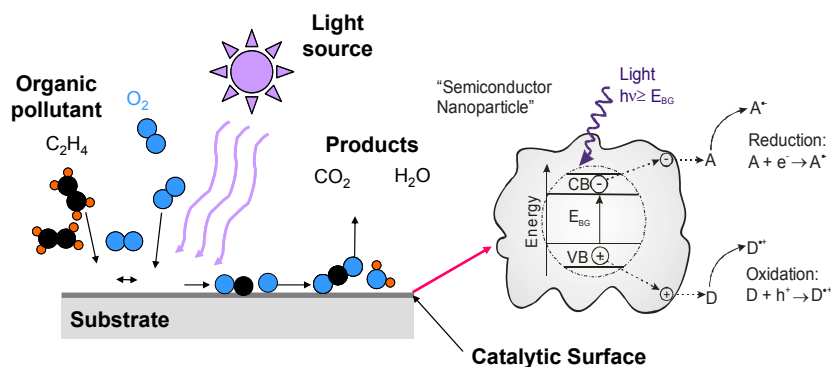
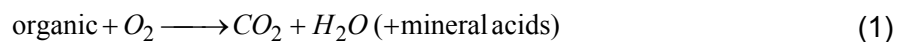


Figure 2: Principle scheme of the photocatalytic decomposition process on an illuminated catalyst surface: Adsorption (organics & oxygen) – Transfer of electrical charges - Radical-reactions – Desorption (products).



2.2 Energy conversion and quantum yield

The most simple and cost efficient way to illuminate a photocatalytic active layer with UV-A light is the use of commercial low pressure fluorescent blacklight tubes. They emit, depending on the composition of the fluorescent coating, light in the range of 320 – 400nm, which fits perfectly the absorption behaviour of TiO_2 . Modern T5-type tubes reach a conversion rate (electricity to photon flux) of up to 40% of the nominal lamp power. To maximize the efficiency of such a UV-A source, the use of an electronic instead of a magnetic ballast can reduce heat loss of the power supply down to 5% (Figure 3). The energy of the photon flux P_{ph} (Equ. 2) can be calculated based on the efficiency of ballast $\eta_{Ballast}$ and tube η_{Tube} respectively, which equates to the energy content E_{ph} of one generated photon at a certain wavelength λ (Equ. 3) multiplied with the photon flux N_{ph} (Equ. 4) and the Avogadro number N_A .

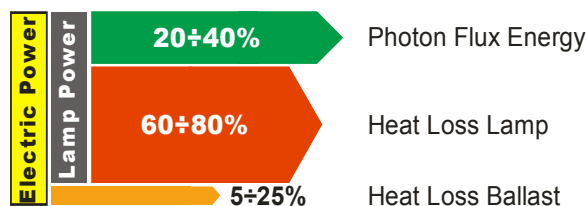


Figure 3: Sankey Diagram of a fluorescent light tube as a UV-A light source for creation of photons.

$$P_{ph} = P_{el} \cdot \eta_{Ballast} \cdot \eta_{Tube} = N_{ph} \cdot E_{ph} \cdot N_A \left(\frac{J}{\#} \cdot \frac{mol}{s} \cdot \frac{\#}{mol} = W \right) \quad (2)$$

$$E_{ph}(\lambda) = \frac{h \cdot c}{\lambda} \left(\frac{eV}{\#}, \frac{J}{\#} \right) \quad (3)$$

$$N_{ph}(\lambda) = \frac{I \cdot A \cdot \lambda}{h \cdot c \cdot N_A} \left(\frac{mol}{s} \right) \quad (4)$$

Not all generated photons are absorbed by the photocatalyst and not all absorbed photons generate a free charge couple that is transferred to adsorbed gas molecules on the surface. In fact, much more charge couples recombine again producing heat instead of being used to trigger the oxidation process of organic pollutants. This fact is expressed by the so called intrinsic quantum yield (QY). This key number for photocatalytic efficiency relates the number of changed (or destructed) pollutant molecules r_{PCO} (mol/s) by the number of photons N_{ph} (mol/s) emitted by the light source (Equ. 5).

$$QY = \frac{\text{rate of destructed pollutant}}{\text{flux of emitted photons}} = \frac{r_{PCO} \cdot A}{\sum N_{ph}(\lambda)} \left(\frac{mol/(m^2s) \cdot m^2}{mol/s} \right) \quad (5)$$

3 Case study on trichloroethylene abatement

3.1 Assumptions

The energy efficiency of a photocatalytic gas cleaning unit will be discussed and compared to catalytic oxidation by means of the abatement of a weakly loaded, cold gas stream (25°C). Trichloroethylene (TCE) is chosen as an exemplary pollutant for halogenated VOCs. HVOC are especially suited to be treated by a photocatalytic process because of a chlorine radical reaction. A minimum conversion of 90% of the inlet pollutant is demanded. A specific energy demand H_V is defined as a basis of comparison which is the ratio of the total energy demand divided by the waste gas flow rate.

3.2 Catalytic combustion

Catalytic combustion occurs on a metal based catalyst which lowers the required temperature to initiate and sustain a combustion process. Thus less energy is required to thermally decompose HVOC than for regular combustion. Since HCl is formed as a product, heat recovery is technically not feasible due to corrosion issues. Thus catalytic combustion without heat recovery is compared with the photocatalytic process. Miranda et al. investigated the oxidation of TCE over a chromium oxide catalyst in a lab scale facility. They found a total conversion of TCE (max. 2180ppm) at about 600K. The overall rate of reaction is nearly independent on the inlet concentration but a function of reactor temperature and residence time. Hence we assume a temperature of 600K as minimum requirement. Figure 4 shows the calculated specific energy demand H_V depending upon the inlet pollutant concentration at 600K combustion temperature. The specific energy demand H_V is determined for adiabatic combustion conditions. With increasing TCE concentration less additional fuel must be provided to reach the combustion temperature, until at around 2% TCE the combustion process is self-sustained.

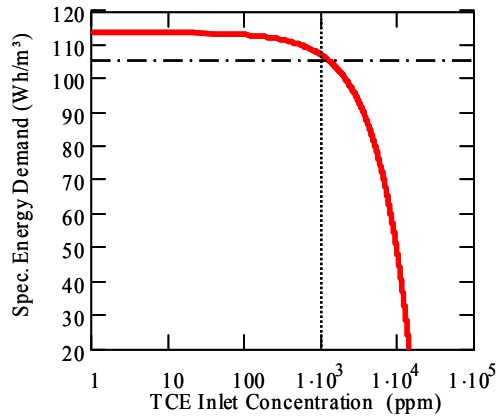


Figure 4: Specific energy demand for the catalytic combustion of TCE at 600K as a function of the inlet concentration.

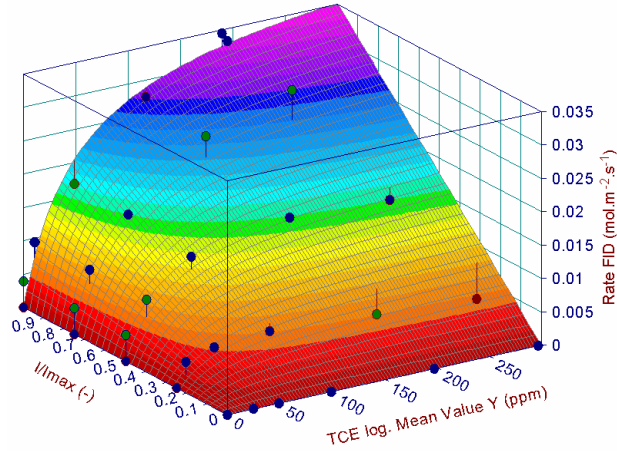


Figure 5: Experimental results (dots) and kinetic fit for the photocatalytic oxidation of TCE. The concentration of the pollutant is accounted as logarithmic mean value between inlet and outlet value.

3.3 Photocatalysis

Several kinetic studies are reported in literature (e.g. Anderson et al., Demeestere et al. Ducet et al.), but we found non providing sufficient information about the dependency of efficiency on reaction rate and light intensity. Thus an experimental kinetic study was performed in a plate reactor, using the most common photocatalyst, Degussa P25, immobilized on glass plates (76x52mm²). The gas feed (1 l/min s.t.p.) was supplied by gas cylinders over mass flow controllers. A flame ionization detector (FID) was used to measure the oxidation rate r_{PCO} (mol/m²·s) of TCE.

Doucet et al. used a Langmuir-Hinshelwood kinetic model for TCE decomposition which is also employed here. However the influence of the light intensity I on the reaction rate constant k_i is accounted for (Equ. 6). Thereby the light intensity I , measured for the UV-A (peak emission 360nm) with a Solartell Solarscope 2000, can be electrical dimmed from I_{max} (5mW/cm²). Figure 5 shows experimental results and the resulting model fitted with Equation 6.

$$r_{PCO}(Y, I) = \frac{k_I \cdot K_{Ad} \cdot Y}{1 + K_{Ad} \cdot Y} \cdot \left(1 - e^{-C \cdot \frac{I}{I_{max}}} \right) \quad \left(\frac{mol}{m^2 \cdot s} \right) \quad (6)$$

Based on Equations 2, 3, 4 and 6, the needed catalyst area A (Figure 6) and the specific energy demand (Figure 7) for 90% conversion of TCE can be calculated in dependence of TCE concentration Y and light intensity I . Thereby a medium electrical efficiency of ballast ($\eta_{Ballast}=0.90$) and UV-A tube ($\eta_{Tube}=0.25$) is set. A maximum QY of 0.25 is calculated (Equ. 5) for these experiments which is higher than one reported by Anderson et al. for TCE (0.17).

Figure 7 shows that the specific energy input needed to decompose a pollutant rises linear with increasing TCE concentration. The influence of the light intensity I is minor and lower light intensities lead to a reduced specific energy demand. But the size of the catalytic

surface is strongly dependent on the light intensity (Figure 6). Thus a trade-off between reactor size (catalyst area) and energy efficiency is asked for.

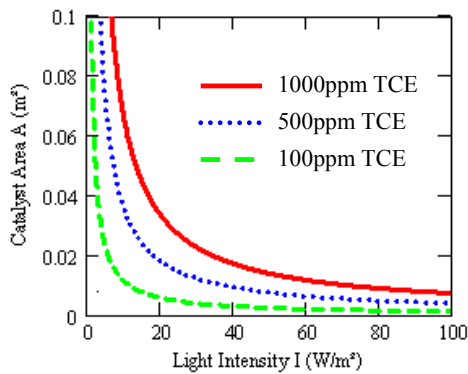


Figure 6: Calculated catalyst area for 90% photocatalytic destruction in dependence of light intensity and inlet TCE concentration (1 l/min s.t.p.).

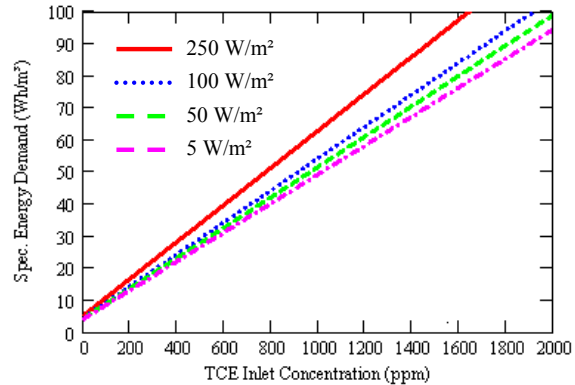


Figure 7: Specific energy demand for 90% photocatalytic destruction in dependence of inlet TCE concentration and light intensity.

Principally there is no technical limitation in the gas flow range of photocatalysis since it can be set up in a modular way. But when using a commercial UV-tubes, an economical and practical limit might be in the range of 15-30 kW electric (this corresponds already a number of 400-800 36W tubes). Hence gas flow should be below 1000m³/h for economical reasons.

3.4 Comparison between catalytic combustion and photocatalysis

A comparison between the specific energy demand of catalytic combustion and photocatalysis is shown in Figure 8. These results are computed for 90% conversion X_{VOC} with Equation 7, where R , p_0 and T_0 denote ideal gas constant, pressure and temperature at standard conditions, respectively. The chemical decomposition is now accounted for by the global QY. For TCE, photocatalysis is already energetically superior over catalytic combustion up to 2000ppm based on our lab facility conditions (Fig. 8 (c)). Already with today's commercially available light sources the conversion of electricity towards photon flux can be accomplished with an efficiency of 95% for the ballast and 40% for the tube. This situation is depicted in Figure 8 curve (d) indicating a substantial improvement of the specific energy demand.

The quantum yield QY is a measure for the utilization of photons. When each photon leads to the destruction of one pollutant molecule, the QY is one which can be regarded as the theoretical maximum. This situation is shown in Figure 8 curve (e) indicating the theoretical potential for further energy reduction. But the QY strongly depends on kind and concentration of pollutant, residence time and catalyst type. The conversion of TCE represents an optimum, other pollutants show lower maximum quantum yields. Haeger et al., for instance, report on a QY of about 0.1 for the photocatalytic destruction of gaseous propane. This situation is depicted in Figure 8 curve (b). Hence for gaseous photocatalysis a QY in the range of 5-25% can be seen as state of the art. Thus we conclude, that photocatalysis can be already energetically superior over catalytic combustion below a pollutant concentration of about 1000ppm, depending on QY and light efficiency.

$$H_V(Y, QY, \eta_{Ballast} \cdot \eta_{Tube}) = \frac{P_0}{R \cdot T_0} \cdot \frac{Y \cdot X_{VOC}}{QY} \cdot \frac{h \cdot c \cdot N_A}{\lambda \cdot \eta_{Ballast} \cdot \eta_{Tube}} \left(\frac{Ws}{m^3} = \frac{Wh}{3600 \cdot m^3} \right) \quad (7)$$

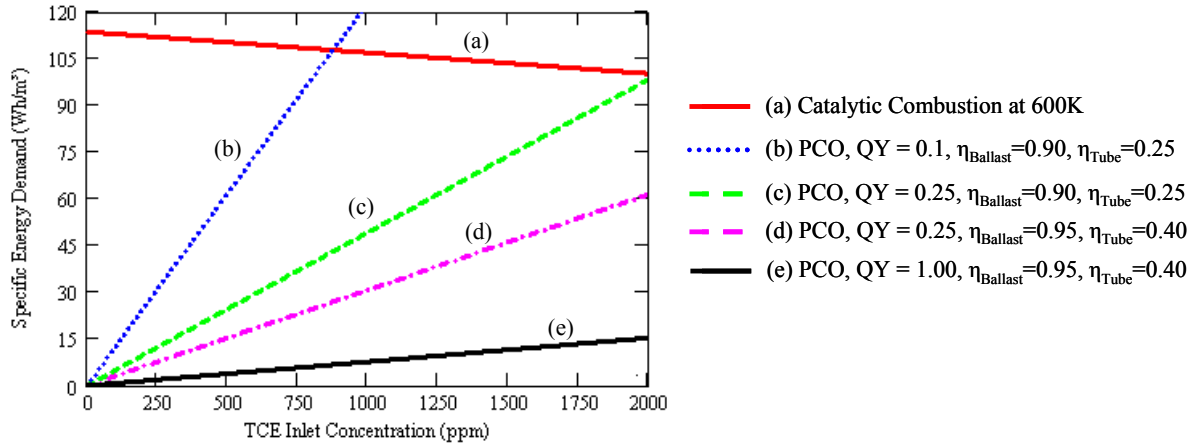


Figure 8: Comparison of the specific energy demand for catalytic combustion and photocatalysis for different quantum yields and different electrical efficiencies.

4 Conclusions

The specific energy demand for photocatalysis mainly depends on pollutant concentration, quantum yield and efficiency of the light source. The case study with the abatement of TCE shows an approximate specific energy demand of 100 Wh/m³ for catalytic combustion and only up to 50 Wh/m³ below 1000ppm TCE for photocatalysis. Improvements of the quantum yield and the electrical efficiency could lead to a substantially reduced energy requirement less than 10Wh/m³. Further studies are required to show the long term energy performance of the photocatalytic abatement system. Moreover a life cycle study will give further valuable information about the energy efficiencies beyond the mere immediate energy requirement for operation.

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