

INFLUENCE OF VOC EMISSIONS ON GLOBAL WARMING. MITIGATION OF THEIR IMPACT USING CERAMIC MONOLITHS SUPPORTED Pt, Mn AND Ce CATALYSTS AT PILOT SCALE

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Abstract - The removal of a mixture of volatile organic compounds (CHCl₃, methyl ethyl ketone, toluene and xylenes), was evaluated by adapting a commercial exhaust fan with a catalytic system applicable to small and medium enterprises. The catalysts used were Pt, Mn, Ce, Pt/Mn and Ce/Mn supported on ceramic monoliths. It was observed that all catalysts tested were able to reduce emissions of volatile organic compounds into the atmosphere. The CO₂ equivalent emission of VOCs into the atmosphere (with and without treatment) was determined taking into account the power consumption of the exhaust system + catalyst, being observed for all catalysts tested a reduction in CO₂ equivalent emissions. When a heat exchanger is attached to the exhaust system + catalyst to reduce power consumption, the emission of CO₂ equivalent decreases appreciably in the order of 24.8%–45.3% compared to untreated emissions.

Keywords— Monoliths, Manganese, VOCs, CO₂, Global Warming.

I. INTRODUCTION

Volatile Organic Compounds (VOCs) comprise a major group of air pollutants, which include alkanes, aromatic hydrocarbons, chlorinated hydrocarbons and oxygenated hydrocarbons. Exposure to VOCs is associated with negative effects on respiration and allergies. Also the role of VOCs as a major source of tropospheric ozone, a known respiratory irritant, has recently been acknowledged (Adgate *et al.*, 2004; Who, 2009).

VOCs contribute to the most serious air pollution problems; first, they have proved active in the formation of smog and ground level ozone production. Second, there are several VOCs that can be classified as carcinogenic. Benzene has been classified as a known human carcinogen by the International Agency for Research on Cancer (IARC) based on evidence from epidemiologic studies and animal data (IARC, 1987; IARC, 2012), and styrene and tetrachlorethylene are classified as possible or probable carcinogens for human beings (IARC, 1995; IARC, 2002).

From the point of view of climate change, VOCs

contribute in two ways (Murrells and Derwent, 2007), a major contribution derived from a direct effect if the VOC is a halogenated hydrocarbon, due to its atmospheric life-time and its properties of absorption of infrared radiation in the value of "GWP" (Global Warming Potentials) or indirectly if the VOC is a hydrocarbon due to its atmospheric chemistry. A secondary contribution from CO₂ results from the degradation of each VOC determined by the number of carbon atoms present in the VOC.

The most important VOC treatment techniques are incineration, catalytic oxidation, adsorption, and condensation, among others, depending on the VOC concentration. Different authors have proposed a catalytic oxidation technology to remove volatile organic compounds from indoor air (Ho and Park, 2004; Mo *et al.*, 2009). Metal oxides or supported noble metals can be used in catalytic oxidation of VOCs. Manganese and cerium materials are widely used in VOC oxidation due to their low cost and high activity, which is attributed to the labile lattice oxygen and their capacity of storing oxygen in the crystalline structure (Craciun, 2003; Tang *et al.*, 2008).

The catalytic oxidation of individual VOCs has been widely studied; however, there are few articles about the removal of VOCs from mixtures. In practical applications, such as treatment of contaminated air from solvent evaporation processes (quick drying systems, printing, paint shops, etc.), the gas stream contains mixtures of volatile organic compounds that are generally of variable composition. In general it is observed that the removal of a single VOC differs from the removal of a mixture of compounds, the effect being attributed to the interaction of the various organic species with the catalyst (Li *et al.*, 2009; Diehl *et al.*, 2010).

The aim of this study is to report on the development and optimization of commercial air extractor coupled to a pilot scale catalytic system for use in small and medium enterprises, and the impact of its implementation on the reduction of VOCs emissions into the atmosphere and consequently, the impact on global warming, by estimating the emission of VOCs as CO₂ equivalent, on

treated and untreated effluent.

II. METHODS

A. Catalysts Preparation

Ceramic monoliths and Pt, Mn and Pt/Mn supported catalyst preparation are explained in detail in a previous paper (Colman-Lerner *et al.*, 2013). Briefly, ceramic monoliths made of natural clays and gibbsite (denoted B), were impregnated with platinum (using 0.02 M $H_2PtCl_6 \cdot H_2O$ aqueous solution) or manganese (using 1M $Mn(NO_3)_2$ and 0.66M $KMnO_4$ aqueous solutions) named Pt/B and Mn/B respectively. Platinum/ manganese (Pt/Mn/B) monoliths were prepared impregnated Mn/B monoliths with 0.02 M $H_2PtCl_6 \cdot H_2O$ aqueous solution). The preparation of Ce supported catalysts was carried out as follows:

Ce/B: ceramic monoliths were immersed in an aqueous solution of $Ce(NO_3)_3$ 0.02M, inside a closed vessel and put through to mechanical orbital agitation for 60 min., the monoliths were washed with deionized water.

Ce/Mn/B: Mn/B monoliths, after having been calcined at 500 ° C, were impregnated with $Ce(NO_3)_3$ 0.02M in the same way as the Ce/B monoliths.

All the monoliths were dried overnight at 100°C and calcined at 500°C for 2 h.

B. Characterization

The catalysts were characterized by X-ray photoelectron spectroscopy (XPS) and the Manganese, cerium and platinum content were measured by atomic absorption spectroscopy in Varian AA 240 equipment after dissolving previously crushed and milling monoliths with $HF-HNO_3-HCl$ mixture. Catalyst characterization of Mn/B, Pt/B and Pt/Mn/B is explained in detail elsewhere (Colman-Lerner *et al.*, 2013). A summary of the catalyst characterization results is presented in Table 1. X-ray photoelectron spectra (XPS) of the compounds in powder form (previously ground monolith) were obtained using a multitechnique system, with a Mg X-ray source and a hemispherical PHOIBOS 150 analyzer operating in the fixed analyzer transmission mode. Binding energies (BE: ± 0.1 eV) were calculated using adventitious hydrocarbon (C 1s = 284.6 eV) as the internal reference. Curve fitting was performed with the CasaXPS software.

C. Catalytic Activity

For the measure of the catalytic activity a commercial air extractor was coupled to a catalytic system (Colman

et al., 2015). The catalyst system was heated by electrical resistances in an exhaust outlet duct and operating at a flow rate of $1.3 \text{ m}^3 \text{ min}^{-1}$. The catalytic system was composed of eight monoliths, of length 25mm, diameter 17mm, wall thickness 2.04 mm, number of channels 7, perimeter channel 13.4mm and opening channel 8.0 mm^2 , placed in an aluminum cylindrical support of 100 mm of diameter. As in previous studies (Colman-Lerner *et al.*, 2012) a VOC mixture from different indoor environments in small and medium enterprises was selected to be tested in the catalytic system ($CHCl_3$, methyl ethyl ketone, toluene and xylenes). The concentration in the liquid phase was 41.5, 26.0 and 32.5% of H, Cl and C, respectively, which represents a concentration of $38 \text{ mg H N}^{-1} \text{ m}^{-3}$, $24 \text{ mg Cl N}^{-1} \text{ m}^{-3}$ and $30 \text{ mg C N}^{-1} \text{ m}^{-3}$. The VOC gas stream is generated from the evaporation of a liquid mixture of VOCs at constant temperature ($28 \pm 1^\circ\text{C}$), in order to reproduce the observed mean temperature inside the enterprises. The catalytic activity is described in detail by Colman-Lerner *et al.* (2015).

The conversion of VOCs (%C) was calculated as

$$\%C = \left(\frac{(mgm^{-3})_{IN} - (mgm^{-3})_{OUT}}{(mgm^{-3})_{IN}} \right) \times 100 \quad (1)$$

where the suffix *IN* indicates the VOC concentration at the inlet of the catalyst support and the suffix *OUT*, the VOC concentration at the outlet of the catalyst support. The VOC will contribute to climate change in two ways:

A) A primary contribution arising from the direct effect if the VOC is a halocarbon, due to the atmospheric lifetime and infrared absorption properties of the VOC and reflected by its direct GWP (Global Warming Potentials) or the indirect effect if the VOC is a hydrocarbon, due to its chemical effect on the atmosphere.

B) A secondary contribution from the CO_2 eventually arising from the atmospheric degradation of the VOC determined by the amount of carbon present in the VOC (Murrells and Derwent, 2007).

The CO_2 equivalent emissions arising from (A) are simply given by the GWP and the mass of the VOC released

$$CO_{2\text{primary}} = GWP_{\text{VOC}} m_{\text{VOC}}, \quad (2)$$

where GWP_{VOC} is the direct or indirect GWP for the VOC species (14 for $CHCl_3$ and 10 for the other VOCs) and m_{VOC} is the number of tonnes of the VOC emitted and $CO_{2\text{primary}}$ is in tonnes CO_2 equivalent. The secondary CO_2 equivalent emissions arising from (B) depend on the number of carbon atoms in the VOC, its molecular weight and the mass of the VOC released

$$CO_{2\text{secondary}} = \frac{44 n_{\text{VOC}} m_{\text{VOC}}}{MW_{\text{VOC}}}, \quad (3)$$

where n_{VOC} is the number of carbon atoms in a molecule of the VOC, MW_{VOC} is its molecular weight in g mol^{-1} and $CO_{2\text{secondary}}$ is in tonnes CO_2 (44 refers to the molecular weight of CO_2). The total CO_2 equivalent emissions (in tonnes) arising from the direct release of the VOC are

Table 1. Summary of the catalyst characterization

	SBET (m^2/g)	% w/w of cata- lyst	Mn 3s (eV)	Mn 2p _{3/2} (eV)	Pt 4d _{5/2} (eV)	Ce 3d _{5/2-3/2} (eV)	O 1s (eV)
Pt/B	35.5	0.23	----	----	315.4 318.4	----	528.9 530.8
Mn/B	56.9	2.00	84.9 89.6	641.1 643.1	----	----	529.5 530.9
Pt/Mn/B	58.2	1.90	----	643.9	317.1	----	530.1 532.1
Ce/B	56.4	0.30	----	----	----	882.9 888.5	529.8 531.2
Ce/Mn/B	54.3	0.20	84.6 89.1	642.0 643.5	----	----	528.6 530.2

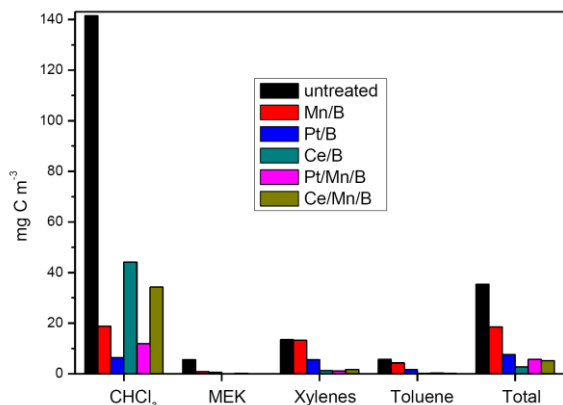


Figure 1. Values of VOCs emitted in mg C m^{-3} (STP) untreated and treated with the catalyst system.

$$\text{CO}_{2\text{equiv}} = \text{CO}_{2\text{primary}} + \text{CO}_{2\text{secondary}} \quad (4)$$

For a complete analysis, it is necessary to consider the equivalent CO_2 generated ($\text{CO}_{2(\text{E})}$) by power consumption of the system, and this is given by

$$\text{CO}_{2(\text{E})} = F \times E \quad (5)$$

where F (tonnes per MWh) is a conversion factor that relates electricity consumption (in MWh) in CO_2 (tonnes) (Murrells and Derwent, 2007) and E is the energy consumed by the electrical system.

D. Results and Discussion

The performance of the supported Pt, MnO_x , Ce, Pt/ MnO_x and Ce/ MnO_x ceramics monoliths in the destruction of a mixture of chloroform, MEK, toluene and xylenes is shown in Fig. 1.

No partial oxidation products were detected in the aromatic VOCs examined. Only traces of acetaldehyde were detected in MEK oxidation at low levels of conversion. In the combustion of chloroform, the reaction products detected were HCl, CO_2 and H_2O . Comparing the catalysts in the combustion of CHCl_3 , the conversion decreases in the order: Pt/B \approx Pt/ MnO_x /B > MnO_x /B > Ce/ MnO_x /B > Ce/B. Nevertheless, in all cases the conversion at 295°C is over 75%, being more than 90% for the most active catalyst. In contrast, the conversion order in the combustion of MEK, toluene and xylenes decrease in the order: Ce/ MnO_x /B \approx Ce/B > Pt/ MnO_x /B > Pt/B > MnO_x /B. For the most active catalysts, the conversion of MEK, toluene and xylenes at 295°C reaches about the 100, 85 and 95%, respectively. These results demonstrated that the prepared monoliths were promising catalysts for the reduction of emission of mixture of VOCs.

To assess the impact of VOCs on global warming we calculated the equivalence of VOCs in the catalytic system studied (chloroform, toluene, methylethylketone and xylenes) assuming that the system emits into the atmosphere at a flow rate of $1.3 \text{ m}^3 \text{ min}^{-1}$ (work flow of the exhaust system) for 12 hours daily over the course of 1 year. Then we calculated the concentration of VOCs emitted with the same system but catalytically treated, and added the amount of CO_2 generated in the combustion reaction (complete combustion). Figure 1

shows the levels of concentration of VOCs emitted untreated and treated with the catalyst system (individually and expressed as carbon in mg m^{-3}) and Fig. 2 shows emission levels calculated as CO_2 equivalent (kg per year) with and without catalytic treatment. The VOCs emissions values for all catalysts evaluated are below the EPA VOC emission limit values in waste gases (U.S. EPA, 2002), which for activities such as heatset web offset printing, surface cleaning and manufacturing of pharmaceutical products are 20 mg C m^{-3} (STP).

Considering that the oxidation reactions are highly exothermic, the possibility of harnessing the energy released by the reactions through a heat exchanger constitutes an attractive way to save energy.

By analyzing the characteristics of the streams and the energy fraction to be recuperated, compact plate-fin heat exchangers are a suitable alternative to be considered (Campesi *et al.*, 2007). This type of compact heat exchanger consists of a stack of alternate flat plates called parting sheets and corrugated fins brazed together as a block. Cold and hot streams flow along the passages made by the fins between the parting sheets in a crossflow mode (Hewitt *et al.*, 1994; Picón Nuñez *et al.*, 1999).

The material selected for this kind of heat exchanger is particularly important for thermal evaluation, because the heat transfer through the corrugated fins is determinant for the design. Aluminum is remarkable due to its low density and high conductivity; however, it has a limitation in temperature. On the other hand, carbon steel, although denser, allows working at temperatures up to 800°C (Hewitt *et al.*, 1994).

For the heat exchanger design it was decided to employ only one type of fins, conforming rectangular channels, with the dimensions defined in Fig. 3. To carry out the design of the heat exchanger, a numerical program was developed employing the ϵ -NTU method (Campesi, 2012).

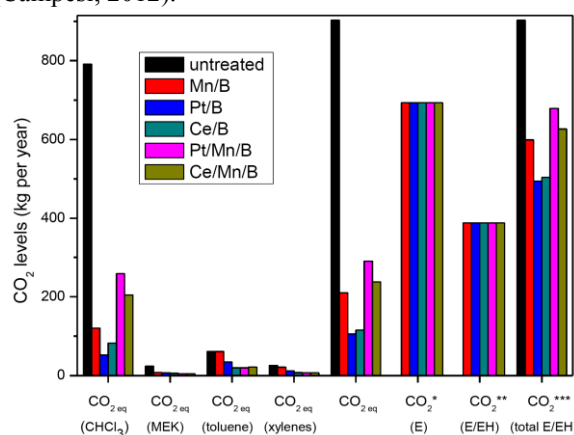


Figure 2. CO_2 levels (kg per year) emitted into the atmosphere with and without catalytic treatment. * $\text{CO}_{2(\text{E})}$: CO_2 equivalent power consumption associated with the catalytic system. ** $\text{CO}_{2(\text{E/EH})}$: CO_2 equivalent power consumption associated with the catalytic system and the heat exchanger. *** $\text{CO}_{2(\text{total E/EH})}$: CO_2 equivalent power consumption associated with the catalytic system plus the heat exchanger and the associated CO_2 equivalent emissions of VOCs treated catalytically.

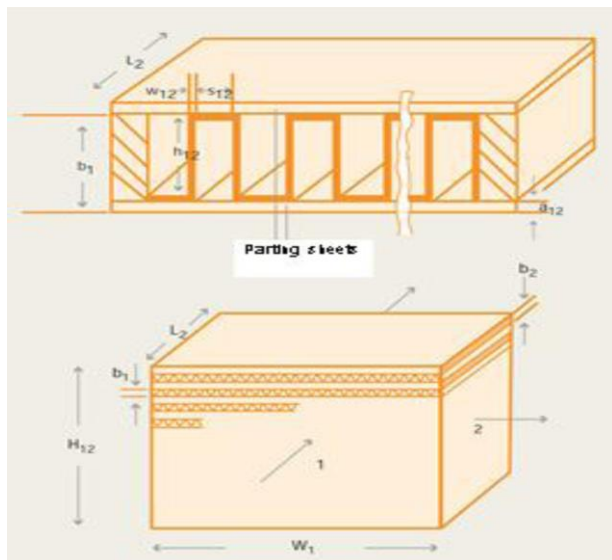


Figure 3. Geometric characteristics of the plate-fin heat exchanger

The gas temperature at the exit of the reactor (hot stream) can be modified by using electrical resistances. Two levels were fixed (A: 300° C, B: 250° C) in order to design the heat exchanger. The operating conditions are displayed in Table 2. Table 3 presents the geometric characteristics and pressure drop for both situations studied.

The results of implementing the system heat exchanger, demonstrated that with the inclusion of the heat exchange (Fig. 4) it is possible to reduce the power consumption of the system as well as the emission of CO₂.

In this way, the inlet stream temperature can be raised up to 150°C, instead of 28°C, when no preheating is employed and an energy saving of about 45% is achieved

$$CO_{2(E/HE)} = CO_{2(E)} \times j, \tag{6}$$

where *j*, is the correction factor for energetic saving using the heat exchange system, and its value equal to 0.55 and CO_{2(E/HE)} is CO₂ equivalent power consumption associated with the catalytic system and the heat exchanger.

When evaluating the content of CO₂ equivalent, with and without catalytic treatment, there is a decrease in all the catalysts tested, the best case obtained being with the system Pt/B, 88% reduction in CO₂ equivalent emissions. When electric consumption is considered, with the heat exchanger system, (7) there is a positive balance in the amount of CO₂ emitted into the atmosphere, achieving a clear reduction in the emission of CO₂ equivalent between 24.8%–45.3% (Fig. 2).

$$CO_{2(totalE/EH)} = CO_{2(E/EH)} + CO_{2equiv} \tag{7}$$

where CO_{2(totalE/EH)} is the CO₂ equivalent power consumption associated with the catalytic system plus the heat exchanger and the associated CO₂ equivalent emissions of VOCs treated catalytically.

By taking into account the power consumption using the heat exchanger, a positive balance in CO₂ equivalent

Table 2. Operating conditions of the streams

	T = 300° C	T = 250° C
Flow rate of the hot stream [kg/s]	2.53 10 ⁻²	2.53 10 ⁻²
Flow rate of the cold stream [kg/s]	2.53 10 ⁻²	2.53 10 ⁻²
Inlet temperature of the hot stream [°C]	300	250
Outlet temperature of the hot stream [°C]	228.96	178.72
Inlet temperature of the cold stream [°C]	28	28
Outlet temperature of the cold stream [°C]	150	150

Table 3. Characteristics of the heat exchangers

	T = 300° C	T = 250° C
Global Dimensions		
Height (H ₁₂) [m]	0.12	0.12
Width (W ₁) [m]	0.09	0.126
Depth (L ₂) [m]	0.128	0.16
Channels Dimensions		
Height (h ₁₂) [mm]	5.55	5.55
Width (s ₁₂) [mm]	1.85	1.85
Thickness of the flat plate (a ₁₂) [mm]	0.3	0.3
Thickness of the corrugated fins (w ₁₂) [mm]	0.15	0.15
Material volume (V) [m ³]	2.03 10 ⁻⁴	3.60 10 ⁻⁴
Pressure drop (ΔP) [atm]	0.0016	0.0013

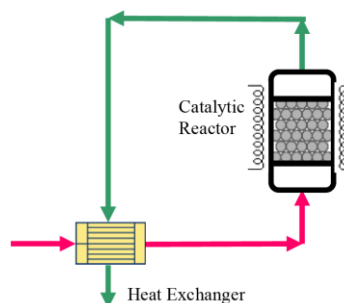


Figure 4. Flowsheet of heat exchanger-Catalytic Reactor.

emissions can be maintained. That is, the emission of CO₂ equivalent using the reactor system + heat exchanger is less than the emission of untreated gases (if VOCs were released directly into the atmosphere).

III. CONCLUSIONS

From simple modifications of a commercial air pump, placing the vent stack of the catalytic device, the destruction of a solvent mixture consisting of MEK, chloroform, toluene and xylenes was analyzed. There is a great potential of using catalytic systems to control the emission of VOCs into the atmosphere by small businesses. With all the catalysts tested it was possible to reduce the emission of the volatile organic compounds studied below the limit value set by U.S. EPA. Taking into account the emission of VOCs as CO₂ equivalent, it was observed that emissions decrease compared to the untreated gaseous effluent. By coupling the exhaust system + catalyst to a heat exchange system, it was possible to reduce power consumption, achieving a clear reduction in the emission of CO₂ equivalent between 24.8% and 45.3% compared to the emission of catalytically untreated VOCs into the atmosphere

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