# Cleaning the Engine Exhaust without Precious Metal Catalysts

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## ABSTRACT

Internal combustion engine which serves as the main driver of modern transportation emits a number of pollutants which include carbon monoxide, nitrogen oxides, hydrocarbons and micrometer size particulates. Carbon dioxide ($CO_2$), which is not a regulated pollutant, is also included in the exhaust. About 20-30% of energy related CO2 emissions are attributed to the transportation sector and there is growing interest in reducing $CO_2$ from automotive vehicles. The exhaust system of a vehicle is equipped with a catalytic converter to reduce harmful emissions to levels permitted by the EPA. However the catalytic converter is not designed to treat $CO_2$. On the contrary, it neutralizes some of the pollutants by converting them into $CO_2$. What is proposed in this research is a method which does not use any precious or rare materials. The method utilizes positive electron affinity of exhaust gas molecules such as nitrogen dioxide. A charging unit provides electrons to those molecules to create stable negative ions. As the ions float through the exhaust gas, they interact with pollutants, water vapor and $CO_2$ and electrically attract them to form droplets. The droplets are removed before the exhaust gas is discharged into the atmosphere.

***Keywords***: Internal combustion engine, pollution control, carbon capture

## 1 PROBLEM

Internal combustion engine was invented in the late 19th century and commercialized in the early 20th century. Since then, it has become the de facto engine of modern transportation. In 2010 there were about 800 million cars on the road. This number is expected to increase to about 1.2 billion in 2030 primarily due to increasing demand in emerging economies in Asia [1]. Hybrid, plug-in hybrid and electric vehicles are attracting a lot of attention due to higher efficiency and reduced or zero usage of petroleum. Despite significant advances in the commercialization of these technologies, market penetration of such vehicles is expected to be limited to only about 15% by 2030 [1]. Currently more than 95% of the fuels used in transportation are petroleum based. In the future, share of alternatives such as biofuels, compressed natural gas or electricity is expected to increase. However, petroleum would still be the dominant fuel at nearly 90% market share in 2030 [2]. One can safely predict that transportation vehicles powered by the internal combustion engine which use primarily petroleum based fuels will be around for many years to come.

The internal combustion engine emits a number of pollutants which include particulate matter (PM), carbon monoxide (CO), nitrogen oxides (NOx), and hydrocarbons [3]. PM refers to micrometer size or smaller soot particles produced mainly by diesel engines. Carbon monoxide occurs as a result of incomplete oxidation of the carbons in the fuel. CO is poisonous to humans even in small concentrations like 100 ppm. Nitrogen oxides are generated when nitrogen and oxygen which are readily available in air react at high temperatures and pressures of a combustion chamber. NOx is both a pollutant by itself and can also generate secondary pollutants like ozone in combination with volatile organic compounds in air. Hydrocarbons are a group of organic compounds which can be either components of the fuel, for example benzene, passing through the engine unburned or are by-products of incomplete combustion, for example formaldehyde or acetaldehyde. Exhaust emissions of a typical car include 1 to 2% of CO, NOx and hydrocarbons combined. Other constituents of the exhaust are nitrogen gas ($N_2$) ~70%, water vapor ~10% and carbon dioxide ~15%. About 20-30% of energy related $CO_2$ emissions are attributed to the transportation sector. Although $CO_2$ is not a regulated pollutant, there is growing interest in reducing $CO_2$ from motor vehicles to limit global warming [4].

The exhaust system of a vehicle is equipped with a catalytic converter to reduce harmful emissions to levels permitted by the EPA. The device consists of a high surface area substrate coated with the rare earth material cerium and precious metal catalysts platinum (Pt), palladium (Pd), and rhodium (Rh). Functions of the catalysts include breaking NOx to nitrogen and oxygen, oxidizing carbon monoxide to $CO_2$ and neutralizing hydrocarbons to water and $CO_2$.

$$2\mathrm{NO}_x \rightarrow N_2 + xO_2 \quad (1)$$

$$2\mathrm{CO} + O_2 \rightarrow 2\mathrm{CO}_2 \quad (2)$$

$$C_x H_{2y} + \left(x + \frac{y}{2}\right) O_2 \rightarrow xCO_2 + yH_2O \quad (3)$$

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During the recent decade, there has been a significant increase in the prices of precious metals. For example the price of gold has increased from about \$300 in the 1990s to about \$1700 in 2012. Prices of platinum and other metals used in catalytic converters have been adversely impacted, as well. Therefore there is an ongoing effort to use less of or find alternatives to the mentioned precious metals [5]. As an additional issue, the catalytic converter is not designed to treat $CO_2$. As can be seen from the reactions in Equations 2 and 3, the catalytic converter neutralizes some of the pollutants by converting them into $CO_2$, which exacerbates the $CO_2$ problem.

## 2 PROPOSED SOLUTION

What is proposed in this research is a method which does not use any precious metals or rare materials. The cleaning process is illustrated in Fig. 1. Given an exhaust gas generated by an internal combustion engine, a charging device provides electrons to those exhaust gas molecules which have affinity to accept extra electrons. Molecules which acquire electrons and become ions are allowed to float through the exhaust gas without losing the charged state. They attract by electrical interaction other pollutants, water molecules and $CO_2$ to form droplets. Charged droplets are separated from the rest of the exhaust gas by manipulating them with electric and/or magnetic forces.

### 2.1 Electron Affinity of the Pollutants

Ability of a molecule to accept an extra electron can be quantified by calculating its electron affinity (Eea) which is defined as the energy required to detach an electron from its singly charged negative ion [6]. Eea can be calculated from the quantum mechanical energy of the molecule in the neutral state (En) and with an extra electron (Ei).

$$E_{ea} = E_n - E_i \tag{4}$$

Most of the molecules have their lowest energy in the neutral state, therefore Eea is generally negative. For example, energy of $CO_2$ minus ion is higher than that of neutral CO2 by about 0.9 eV. If $CO_2$ is bombarded with energetic electrons, an electron with more than 0.9 eV kinetic energy can get temporarily attached to the molecule. A small number of molecules exhibit positive electron affinity. For example energy of $O_2$ minus ion is about 0.6 eV lower than that of neutral $O_2$. Such a molecule accepts an extra electron readily and becomes a relatively stable negative ion. An investigation of the electron affinity of molecules typically encountered in the exhaust gas of the internal combustion engine indicates that pollutants like nitrogen dioxide and acrolein have Eea>0 {Table 1}. Hence these molecules have the potential to serve as ionic scavengers which can attract and capture other pollutants.

| Formula | Molecule | Eea (eV) |
|---|---|---|
| NO | Nitrogen monoxide | -0.9 |
| $NO_2$ | Nitrogen dioxide | 2.3 |
| $H_2C{=}CHCHO$ | Acrolein | 0.3 |
| $C_6H_6$ | Benzene | -1.8 |
| $CH_3CHO$ | Acetaldehyde | -0.8 |
| HCHO | Formaldehyde | -0.6 |
| $C_4H_6$ | 1,3-Butadiene | -0.6 |
| CO | Carbon monoxide | -1.1 |
| $CO_2$ | Carbon dioxide | -0.9 |

Table 1: Electron affinity (Eea) of the pollutants obtained by first principle quantum mechanical calculations [7].

### 2.2 Interaction Energy

Electron distribution of a molecule provides information about dipole, quadrupole or higher order electronic moments which are important to understand how ions and neutral molecules interact with each other. Exhaust gas molecules which have dipolar charge distributions include NO, $NO_2$, CO, acetaldehyde, formaldehyde, and $H_2O$. Those with quadrupolar charge distributions include $N_2$, $O_2$, 1,3-butadiene and benzene. Generally interaction of an ion with a dipole is stronger than that with a quadrupole. The strength of the interaction between an ion and other molecules in the flue gas can be quantified by calculating the interaction energy. Interaction between pairs of various molecules and ions has been investigated using first principle quantum mechanical calculations [7]. Results indicate that interaction energy ranges from 0.2 eV to 0.6 eV for dipolar molecules like NOx, acetaldehyde and $H_2O$ {Table 2}. These interaction energies are large enough for the ion to attract and capture dipolar pollutants and water molecules even at the relatively elevated temperature of the exhaust gas.

| Minus Ion | Molecule | IE (eV) |
|---|---|---|
| $NO_2$ | CO | 0.2 |
| $NO_2$ | NO | 0.3 |
| $NO_2$ | Formaldehyde | 0.5 |
| $NO_2$ | Acetaldehyde | 0.6 |
| $NO_2$ | $H_2O$ | 0.8 |

Table 2: Interaction energy (IE) between an ion and dipolar molecules as calculated by first principle methods.

The interaction energy between an ion and $N_2$ which is the most abundant gas in the exhaust is 0.07 eV which is comparable to the thermal energy of the flue gas. Another quadrupole of interest is $CO_2$ which has an electron distribution where carbon is slightly positive, 0.74Qe and oxygens are slightly negative, -0.37Qe (Qe: Unit charge). When $CO_2$ is in the vicinity of a negative ion, carbon gets attracted to the ion, whereas oxygens get repelled by the ion which bends the molecule from a linear to an angular shape (Fig. 2). The shape change creates a small dipole which yields an interaction energy of 0.4 eV. Although this energy is smaller than those of the other dipoles mentioned above, it is large enough to enhance the absorption of $CO_2$ into the droplets {Table 2}. Interaction energy between the ion and other quadrupolar molecules, such as benzene, is similar to $CO_2$,about 0.3 eV to 0.4 eV. The ions have the potential to scavenge not only dipolar pollutants, but also quadrupolar ones, as well.

| Minus Ion | Molecule | IE (eV) |
|---|---|---|
| $NO_2$ | $N_2$ | <0.1 |
| $NO_2$ | $CO_2$ | 0.4 |
| $NO_2$ | Benzene | 0.3 |
| $NO_2$ | 1,3-Butadiene | 0.4 |

Table 3: Interaction energy (IE) between an ion & quadrupolar molecules as calculated by first principle methods.

One can conclude from this analysis that the ions created within the flue gas would attract pollutants and water molecules to form droplets. $CO_2$ which exists in large quantities within the exhaust gas will be absorbed into these droplets to some extent, as well. Since the droplets are charged and they are in motion towards the exit, they can be manipulated with electric and/or magnetic forces to separate them from the rest of the exhaust gas. For example a wet electrostatic precipitator can be used to collect and condense the charged droplets.

### 2.3 Charging Method

Electrons which contribute to charging of pollutants can be created using a number of different approaches including electrical breakdown of a neutral molecule, thermionic emission from a metal, optical excitation of a photocathode, triboelectrical charging, and the like. In this application thermionic emission would be a simple and low cost method to implement. Basic principle of thermionic emission is the escape of electrons from a metal surface heated to a high enough temperature that energy of some of the electrons exceeds the work function of the metal. Emitted electrons do not have to be energetic, since pollutants which have positive electron affinity acquire them without effort. Thermionic emission is a mature technology widely used, for example, in cathode ray tubes or fluorescent lamps.

## 3 CONCLUSIONS

An exhaust gas treatment method for the internal combustion engine is proposed. This method involves:

1) Providing electrons to those pollutant molecules which can accept extra electrons by virtue of having a positive electron affinity,
2) Allowing the charged pollutants to float through the exhaust gas without losing the charged state,
3) The charged pollutants electrically attract other pollutants , water vapor and $CO_2$ in the exhaust gas to form droplets,
4) These droplets are separated from the rest of the exhaust gas by manipulating them with electric and/or magnetic forces.

Advantages of the proposed method can be listed as follows:

Removal of multiple pollutants with one ion: The proposed method is self amplifying where one ionized pollutant can attract and capture many other pollutants in the exhaust gas. Each pollutant does not have to have a positive electron affinity and does not have to be individually charged.

Absence of rare and expensive materials: The proposed method does not rely on the catalytic activity of precious metals or other rare materials, therefore it is potentially a low cost approach to cleaning the exhaust gas.

Reduction of $CO_2$: The proposed method is effective not only in scavenging regulated pollutants like $NO_x$ or hydrocarbons but also $CO_2$ which is a concern with regards to global warming. $CO_2$ which gets absorbed into the droplets is likely to react with the water molecules to form carbonic acid ($H_2CO_3$), which can be neutralized with a suitable base like $Ca(OH)_2$.

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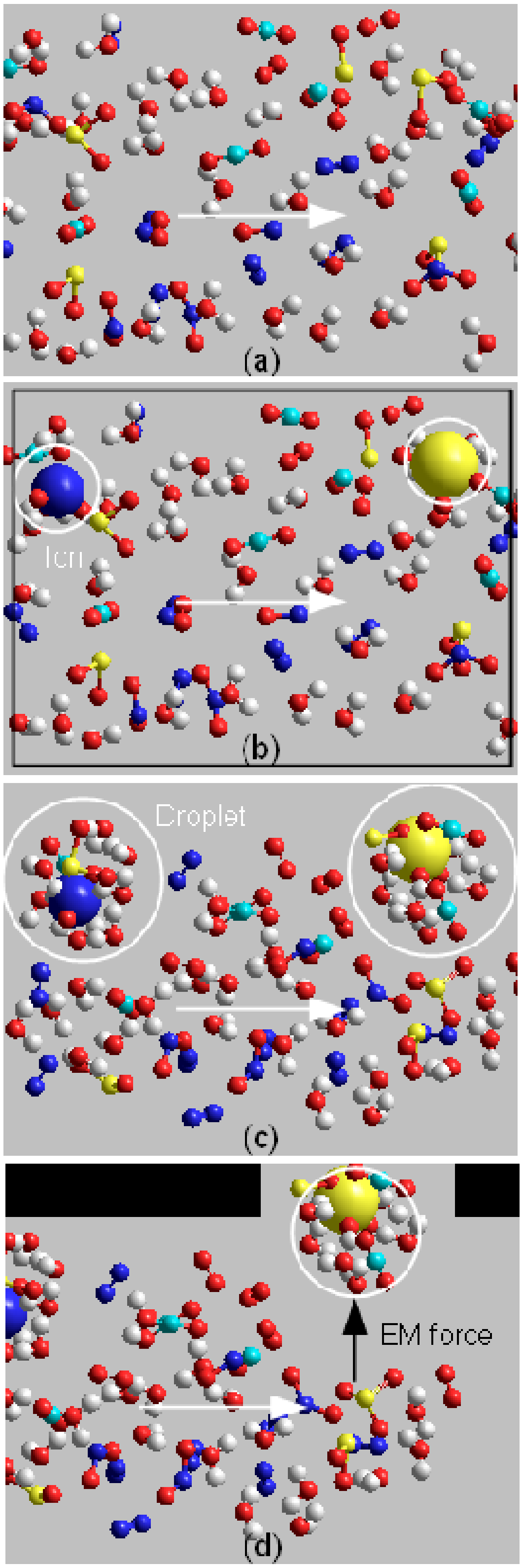


Figure 1: The proposed cleaning process: (a) Given an exhaust gas generated by an internal combustion engine, (b) provide electrons to molecules which have positive electron affinity; (c) allow the ions to attract other pollutants and water molecules to form droplets; (d) separate charged droplets with electric and/or magnetic forces.

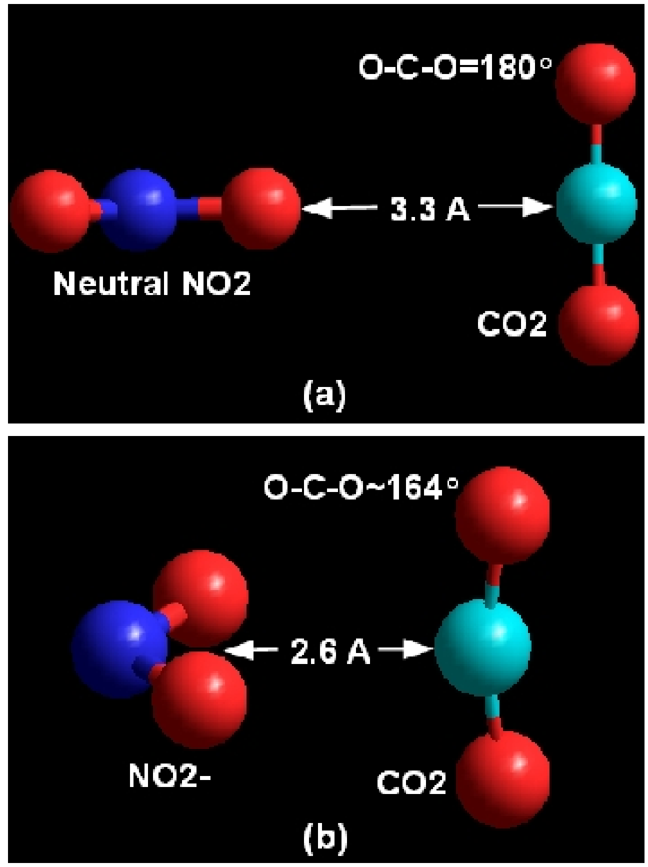


Figure 2: The interaction between (a) neutral $NO_2$ and $CO_2$, (b) $NO_2$ minus ion and $CO_2$; under the influence of the ion, $CO_2$ changes from a linear molecule to a slightly angular one creating a small dipole.


NSTI-Nanotech 2012, www.nsti.org, ISBN 978-1-4665-6276-9 Vol. 3, 2012