Transportation Research Part D 51 (2017) 53–61

Contents lists available at ScienceDirect

Transportation Research Part D

journal homepage: www.elsevier.com/locate/trd

Ammonia emissions from a light-duty vehicle

Vanderlei Borsari [a,b,*], João Vicente de Assunção [b]

[a] CETESB – Environmental Company of the State of São Paulo, Brazil
[b] USP – University of São Paulo, School of Public Health, Brazil

ARTICLE INFO

Article history:
Available online 10 January 2017

Keywords:
Ammonia
Vehicle emission
Dynamometer tests
Atmospheric pollutants

ABSTRACT

Ammonia (NH_3) is an air pollutant whose emission is partly caused by human activities. The objective of this study was to verify, in a vehicle with spark-ignition engine (Otto cycle), the values of ammonia emissions using the fuels gasohol 22 (gasoline plus 22% anhydrous ethanol), hydrous ethanol fuel (HEF) and compressed natural gas (CNG) with and without the presence of catalytic element (catalyst). The vehicle was tested on a chassis dynamometer following the method prescribed by the USEPA for measuring exhaust emissions and using the urban (FTP-75) driving cycle and highway cycle for measuring autonomy and the congestion (NYCC) and aggressive (US-06) driving cycles, which were also adopted by the US Environmental Protection Agency (USEPA). In addition to the methods of exhaust gas analysis prescribed in the standards, FTIR (Fourier transform infrared) spectroscopy was used for the measurement of NH_3.

1. Introduction

Ammonia is a chemical compound composed of one nitrogen atom (N) and three hydrogen atoms (H). These atoms are distributed in a tetrahedral molecular geometry, and the chemical formula of the compound is NH_3 (NIST, 2011). After N_2 and N_2O, NH_3 is the most abundant nitrogen compound in the atmosphere (Seinfeld and Pandis, 2006).

The atmospheric concentration of NH_3 is highly variable, depending on the proximity to the emission source. The typical continental concentration is from 0.1 to 10 ppb (Seinfeld and Pandis, 2006). The ammonium ion (NH_4^+) is an important component of continental tropospheric aerosol. Additionally, the reaction of NH_3 with nitric acid in the gaseous state generates ammonium nitrate, the main route for the formation of particulate nitrate, according to the following equation:

$$NH_3\ (g) + HNO_3\ (g) \rightarrow NH_4NO_3\ (s)$$

The reaction of ammonia with sulfuric acid in the gas phase also produces particulate matter:

$$2NH_3\ (g) + H_2SO_4\ (g) \rightarrow (NH_4)_2SO_4\ (s)$$

Reactive nitrogen compounds are important inducers of air pollution by particles and may even be dominant in some regions. The high reactivity makes these compounds participate in reactions, some of which lead to particle formation. For example, particles made up of ammonium nitrate constitute approximately 65% of all particulate matter (total suspended particulates) in Southern California, USA (Malm et al., 2014). Schiferl et al. (2014) estimate that about 40–60% of sur-

* Corresponding author at: CETESB – Environmental Company of the State of São Paulo, Av. Prof. Frederico Hermann Jr., 345, Sao Paulo 05459-900, Brazil.
E-mail address: vborsari@sp.gov.br (V. Borsari).
URL: http://www.cetesb.sp.gov.br (V. Borsari).

http://dx.doi.org/10.1016/j.trd.2016.12.008
1361-9209/

face inorganic PM 2.5 in California during the summer are attributable to anthropogenic sources of ammonia. Hasheminassab et al. (2014) affirmed that at eight distinct sampling locations in the state of California, including the Great Los Angeles area, secondary aerosols, including ammonium nitrate and sulfate, comprised the largest fraction of ambient PM 2.5, accounting for 26–63% of total, on an annual average basis.

Changes in the natural nitrogen cycle can significantly influence the air pollution in many ways. Studies have shown a positive correlation between the air pollution caused by fine particulate matter and cardiovascular and respiratory diseases, asthma, and a general increase in mortality (Pope et al., 2002).

Ammonium salt particles are capable of being respired and reach the alveoli, causing a number of respiratory disorders, such as asthma and bronchitis. This particulate form of ammonia is found in urban areas where gaseous ammonia reacts chemically with other compounds, leading to the formation of "smog".

2. Ammonia emissions from vehicles

Although the use of three-way catalysts has led to a considerable reduction in emissions, the activity of these components has been identified as being responsible for the higher ammonia emissions by vehicles (Gandhi and Shelef, 1991). The formation of ammonia is attributed to nitric oxide reacting with the hydrogen gas produced by the reaction of CO with water (Livingston et al., 2009):

$$CO + H_2O \rightarrow CO_2 + H_2$$
$$2NO + 2CO + 3H_2 \rightarrow 2NH_3 + 2CO_2$$

Durbin et al. (2002), Heeb et al. (2006), and Huai et al. (2003) reported an association between air/fuel ratio and ammonia emission. A low air/fuel ratio represents combustion of a rich mixture, which generally also leads to a higher CO emission. As vehicles generally tend to enrich the mixture during accelerations, a correlation between accelerations, CO emission and ammonia emission is expected.

One of the factors identified as influencing the emissions of ammonia is the sulfur content in fuel. Mejia-Centeno et al. (2007) reported that the removal of sulfur from gasoline increases the formation of NH_3 and decrease the formation of N_2O. A similar assertion can also be found in Durbin et al. (2004). Since NH_3 is primarily formed over the catalyst, these results suggest that sulfur could inhibit NH_3 formation on the catalyst by poisoning reaction sites for NH_3 formation (Gandhi and Shelef, 1991). Durbin et al. (2004) showed for tests on two vehicles that NH_3 emissions increased as the sulfur content in the fuel was decreased over the FTP and US06 cycles.

Recently, studies on ammonia emissions by vehicles have emerged in Brazil. Daemme et al. (2013) found a substantial increase in the ammonia emissions measured when testing a gasoline-fueled motorcycle with a 300 cm^3 engine. The emission before the catalyst was 0.732 mg km^{-1}, and after the catalyst was added, it was 87.441 mg km^{-1}. In the same test, the vehicle was equipped with an additional type of catalyst used in SCR (selective catalyst reduction) systems for NOx reduction in diesel-powered vehicles. After this second catalyst was added, the emission of ammonia was reduced to 48.996 mg km^{-1}, indicating a possible additional use for this type of technology.

Daemme et al. (2014) performed a study to find a correlation between the sulfur content of fuels and the emission of ammonia. Although they observed a tendency of an increase in the ammonia emission when the sulfur content was reduced (in tests on motorcycles and one automobile), they indicated the need for further research due to the small number of vehicles tested.

Although several papers have been published about the measurement of NH_3 emissions from vehicles, there is a gap with respect to the Brazilian reality. Brazil is a pioneer country in the use of ethanol produced from sugar cane as an automotive fuel. Since the 1970s, anhydrous ethanol has been added to gasoline. As a result, it was possible to completely eliminate the use of tetraethyl lead as an antiknock agent, an action that has undeniable environmental and health benefits. Since the 1980s, the country has developed a large fleet of cars that run on ethanol. In 2003, flexible fuel engine technology, capable of operating with any proportion of gasoline and ethanol mixture, was introduced. In practice, when the ethanol price presents an economic advantage for the user, flexible vehicles run almost only with hydrated ethanol. In 2012, the fleet of the country was a little more than 27 million cars, and approximately 40% of the Otto-cycle vehicle fleet consisted of gasohol-22 (a mixture containing 78% gasoline and 22% anhydrous ethanol) powered vehicles, 3% hydrated ethanol powered vehicles and 57% flexible fuel vehicles (FFV) (MMA, 2013). There were also approximately 1.7 million vehicles adapted to run on CNG (IBP, 2014). These figures show the importance of this study, which aimed to increase the knowledge of how some specific variables found in the Brazilian automobile fleet can affect NH_3 emissions.

The objective of this study was to verify, in a vehicle with a spark-ignition engine (Otto cycle), the values of ammonia emissions using the fuels gasohol 22, hydrous ethanol fuel (EHC) and compressed natural gas (CNG), with and without the presence of the catalytic component (catalyst). In addition, we attempted to verify the existence of a relationship between the emission of ammonia and driving the vehicle (driving cycle), as well as the existence of a relationship between two sulfur contents in gasohol 22 and the emission of ammonia in the sample tested.