

A Comparison of Ammonia Emission Factors from Light-Duty Vehicles Operating on Gasoline, Liquefied Petroleum Gas (LPG) and Compressed Natural Gas (CNG)

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ABSTRACT

Vehicular ammonia emissions are currently unregulated, even though ammonia is harmful for a variety of reasons, and the gas is classed as toxic. Ammonia emissions represent a serious threat to air quality, particularly in urban settings; an ammonia emissions limit may be introduced in future legislation. Production of ammonia within the cylinder has long been known to be very limited. However, having reached its light-off temperature, a three-way catalyst can produce substantial quantities of ammonia through various reaction pathways. Production of ammonia is symptomatic of overly reducing conditions within the three-way catalyst (TWC), and depends somewhat upon the particular precious metals used. Emission is markedly higher during periods where demand for engine power is higher, when the engine will be operating under open-loop conditions. The air-to-fuel ratio, cylinder temperature and rate of availability of carbon monoxide and nitrogen monoxide all correlate to varying degrees with ammonia production. In addition to a literature review, this study presents ammonia emissions data from three European passenger cars, using three different fuels, with varying physicochemical characteristics and carbon:hydrogen ratios, namely gasoline, LPG and CNG. All vehicles were tested on BOSMAL's chassis dynamometer over the New European Driving Cycle, with undiluted ammonia quantified directly at tailpipe. Both cycle mean emission factors and second-by-second data are presented. The results indicate a degree of correlation between ammonia emission and demand for engine power, for example upon commencing acceleration and following gear shifts. Emission over the entire driving cycle was found to vary depending on the fuel used, and between the three vehicles used in this study. One vehicle emitted 93 % more ammonia when operating on gasoline than on CNG; the other vehicle emitted 2 % more ammonia when running on LPG than on gasoline. A simple numerical correction implied that the lower carbon:hydrogen ratio was at least partially responsible for the minimal ammonia emissions observed when running on this fuel.

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INTRODUCTION

AMMONIA AS A POLLUTANT IN AUTOMOTIVE EXHAUST GAS

Long recognized as an automotive exhaust gas component [1], (first studied in this context in 1967 [2]), ammonia (NH_3) is one of a group of exhaust gases that has received relatively little attention in comparison to CO , NO_x , and THC . Currently unregulated in the European and US markets, it belongs to a group of compounds which may feature in future regulations regarding exhaust emissions from light duty vehicles [3].

In the atmosphere, NH_3 plays a significant role in the formation of secondary particulate matter (PM) [4]. Ammonia can participate in multiple irreversible reactions at ambient temperatures. The main products of these reactions are various types of aerosols, the rate of formation of which is a strong function of the local concentrations of ammonia [4]. Ammonia has a relatively short atmospheric residence time and a limited range [1]. However, the secondary PM NH_3 produces can travel much further, and is widely recognized as being able to adversely affect human health, damage plants, corrode building materials and cause the acidification of rain and eutrophication of surface waters [3,4]. Ammonia is a toxic pollutant [3], with a distinctive, thoroughly disagreeable

Table 1. Simplified possible ammonia formation reactions [3]

Ammonia formation reactions	Eq. No.
$2\text{NO} + 5\text{CO} + 3\text{H}_2\text{O} \rightarrow 2\text{NH}_3 + 5\text{CO}_2$	(1)
$2\text{NO} + 5\text{H}_2 \rightarrow 2\text{NH}_3 + 2\text{H}_2\text{O}$	(2)
$2\text{NO} + 2\text{CO} + 3\text{H}_2 \rightarrow 2\text{NH}_3 + 2\text{CO}_2$	(3)
$4\text{H}_2 + \text{N}_2 + \text{O-R}' \rightarrow 2\text{NH}_3 + \text{H}_2\text{O}$	(4)
$\text{N} + \text{CO} \leftrightarrow \text{NCO}$	(5a)
$\text{NCO} + \text{H} \rightarrow \text{HNCO}$	(5b)
$\text{HNCO} + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{CO}_2$	(5c)

odor which is detectable by humans at relatively low concentrations.

A UNECE protocol [5] and an EU directive [6] set limits for total NH_3 emissions from EU member states, but have no specific quotas for the transport sector. Similarly, in the USA, the EPA's National Emissions Inventory (NEI) identifies ammonia as a criteria pollutant and monitors NH_3 concentrations, but the gas has yet to be regulated in the automotive arena.

Ammonia is a natural atmospheric trace gas, but certain anthropogenic sources are significant. While various agricultural and municipal activities are major anthropogenic sources [3], vehicles equipped with three-way catalysts (TWCs) also contribute [1,3,4,7,8, 9, 10, 11, 12, 13, 14, 15, 16]. At multiple locations, ambient levels of ammonia have increased, even when taking into account increases in traffic volumes [3]. Studies have found that even as emissions of regulated compounds have fallen, NH_3 emission from traffic appears to have risen [3]. Despite the fact that emission of ammonia is normally associated with agricultural activities, areas with heavy/regular traffic have on occasion been found to show higher concentrations of NH_3 than rural areas with only light/occasional traffic [3,12]. Field studies performed in tunnels and on large arterial roads may drastically underestimate rates of ammonia emission from SI vehicles, as the relatively static, low-acceleration driving observed is not conducive to ammonia formation [3,13].

Ammonia is one of a number of simple nitrogen compounds emitted by SI vehicles equipped with TWCs. Ammonia and NO_x are reactive compounds featuring a nitrogen atom, earning them the name *reactive nitrogen compounds* (RNCs) [3,8]. The vast majority of the gas influx into the cylinder is relatively inert nitrogen (N_2). Most of the nitrogen in the intake air simply passes through the powertrain; some reacts to produce various RNCs, both in the cylinder and in the TWC (Figure 1). The relative proportions of these gases are not means fixed [8], and concentrations of these species can vary by orders of magnitude from second to second, depending on the engine operating point. Higher proportions of NH_3 at tailpipe indicate a general overreduction of NO_x . An increase in the efficiency of NO_x

elimination may come at the expense of increased NH_3 emissions.



Figure 1. Schematic of a TWC's inputs and outputs of nitrogen atoms in various chemical forms

FORMATION OF AMMONIA IN A THREE-WAY CATALYST

The formation of NH_3 within the cylinders and non-catalytic exhaust systems has long been known to be very limited [2,3]. Post-catalyst (tailpipe) NH_3 levels are approximately two orders of magnitude greater than pre-catalyst (engine out) emissions, with little (if any) correlation between the two mass fluxes [3]. Thus, engine out emissions of NH_3 can effectively be negated. The detection of an NH_3 concentration above the atmospheric background level in automotive exhaust can be attributed to unintended side reactions occurring in the TWC. These side reactions include the *steam reforming* and *water-gas shift* reactions, both of which produce hydrogen, which can participate in further reactions to produce ammonia.

There are multiple known and proposed NH_3 formation pathways, both relatively direct (e.g. Eq. (1)) and indirect (involving many intermediates) (e.g. Eqs. (5a-5c) and these processes remain under investigation. Precious metal type/loading, gas temperature, exhaust gas lambda (λ) and fuel sulfur content all influence formation of NH_3 to varying degrees [3]. Some simplified ammonia formation reactions which have been suggested are as follows:

It is unlikely that any single reaction will be the only NH_3 formation route, and different reactions probably occur under different conditions, even for the same vehicle-TWC-fuel

combination. Multiple reactions may even occur simultaneously, thereby boosting the production rate. However, a certain temperature normally has to be reached before the TWC can catalyze the reactions, analogous to an NH_3 production light-off temperature [8].

In the literature, there is near-universal agreement that rich conditions favor NH_3 production [3], although emission of NH_3 has been observed under certain lean conditions [3]. However, one remote sensing study failed to find a significant correlation between λ and NH_3 emission [17]. Fuel-rich conditions mean the supply of reagents such as CO and HC is increased, and temperatures are higher. Lean operation also means hydrogen is not as chemically active [3]. Ideal conditions for the production of NH_3 appear to be rich, oxygen-poor, with high engine out temperatures - the conditions encountered at higher loads, particularly during periods of aggressive acceleration. Ammonia formation has been reported to correlate somewhat with engine out CO and NO mass fluxes, although correlations are often relatively weak [3]. The correlation between λ and the NH_3 emission factor for a particular vehicle has been reported as potentially significant but relatively weak [3]. Investigations into the effects of fuel chemistry on NH_3 emission have primarily focused on fuel sulfur content. In laboratory experiments, the injection of sulfur dioxide into a TWC has been shown to inhibit ammonia formation under certain conditions [3,15]. Despite concerns to the contrary, chassis dynamometer studies have revealed that for modern vehicles, low sulfur content fuel has a limited effect on ammonia emission [14], and may even reduce NH_3 emissions [3]. Regardless of this interest in the influence of gasoline chemistry on NH_3 emissions, very little has been published on NH_3 emissions from fuels other than gasoline. One of the main aims of this paper was to begin to address the paucity of data in the literature on NH_3 emissions from modern passenger cars fuelled with LPG and CNG.

METHODS

A series of emissions tests were performed on three vehicles, two bi fuel vehicles and one vehicle equipped with a standard gasoline engine. Selected key properties of the test vehicles are shown in Table 2. Tests were performed in BOSMAL's Euro 5/6/SULEV-compliant exhaust emissions laboratory; the test vehicles were tested on a chassis dynamometer located inside a climatic chamber (see [18] for a detailed description of this test facility). The New European Driving Cycle (NEDC) was used to test all vehicles (see appendix 1). All vehicles were subjected to a 12 hour soak period before commencing testing and were tested at an ambient temperature of 24 °C and 40-45% relative humidity. Three fuels were used: gasoline, LPG and CNG. These were all commercially-available European fuels; the gasoline fuel, whose key characteristics are shown in Table 3, contained 5 % v/v ethanol, in line with current European gasoline

specifications. Similarly, the LPG and CNG used represented typical mixtures as sold in the European Union. Their nominal carbon:hydrogen ratios were 1:2.525 and 1:4, respectively.

Table 2. Key characteristics of the test vehicles used in this study

Parameter	Vehicle 1	Vehicle 2	Vehicle 3
Engine type	SI	SI	SI
Fuel types supported	Gasoline, LPG	Gasoline, CNG	Gasoline
Approximate displacement [dm ³]	1.4	1.2	1.2
Number of valves	16	8	8
Emissions standard	Euro 5	Euro 4	Euro 3

Table 3. Key properties of the gasoline used in tests

Parameter	Value
Research Octane Number [-]	95.5
Density [kg/dm ³]	0.7535
Benzene content [%v/v]	< 1.0
Aromatics [%v/v]	< 35
Olefins [%v/v]	< 18
Ethanol content [%v/v]	5
Sulfur content [mg/kg]	5.6

In order to quantify ammonia emissions, ammonia concentrations were measured in the undiluted exhaust using a dedicated NH_3/NO_x analyzer. This automotive NH_3 analyzer utilized an infra-red detection method and featured heated sample tubing and measured NH_3 concentrations (0-1000 ppm) at a frequency of 1 Hz. Using this analyzer, background NH_3 levels (in the climatic chamber) were found to be low, but measurable. Following a correction for background levels, second-by-second NH_3 emissions factors were obtained by multiplying the measured concentration by the measured tailpipe mass flow rate and by the density of NH_3 . Quantification of engine out emissions of NH_3 was not performed (as previously mentioned, engine out NH_3 concentrations can be assumed to be no higher than background levels.) While the focus of the experiments was the emission of ammonia, emissions of HC, CO, NO_x and CO_2 were also measured. These criteria pollutants were measured second-by-second from the raw exhaust, sampled immediately downstream from the tailpipe. Additionally, diluted emissions were collected in sampling bags with the aid of a constant volume sampler, for high-accuracy analysis according to European emissions legislation. Data on these regulated pollutants and CO_2 emissions were used to ensure repeatability between tests, and also to analyze possible correlations between ammonia emissions and various other factors.