Evaluation of NH_3-Slip from Diesel Vehicles Equipped with Selective Catalytic Reduction Systems by Neural Networks Approach

Mona Lisa M. Oliveira, Nara A. Policarpo, Ana Luiza B. P. Barros, Carla A. Silva

Abstract**—**Selective catalytic reduction systems for nitrogen oxides reduction by ammonia has been the chosen technology by most of diesel vehicle (i.e. bus and truck) manufacturers in Brazil, as also in Europe. Furthermore, at some conditions, over-stoichiometric ammonia availability is also needed that increases the NH_3 slips even more. Ammonia (NH_3) by this vehicle exhaust aftertreatment system provides a maximum efficiency of NOx removal if a significant amount of NH_3 is stored on its catalyst surface. In the other words, the practice shows that slightly less than 100% of the NOx conversion is usually targeted, so that the aqueous urea solution hydrolyzes to NH_3 via other species formation, under relatively low temperatures. This paper presents a model based on neural networks integrated with a road vehicle simulator that allows to estimate NH_3-slip emission factors for different driving conditions and patterns. The proposed model generates high NH_3slips which are not also limited in Brazil, but more efforts needed to be made to elucidate the contribution of vehicle-emitted NH_3 to the urban atmosphere.

Keywords**—**Ammonia slip, neural-network, vehicles emissions, SCR-NOx.

I. Introduction

ROAD transportation has contributed to increase emissions of conventional air pollutants (i.e., NOx – nitrogen oxides, HC - hydrocarbons, PM – particulate matter, NH_3) and, consequently, to the increase of problems associated with the environment and human health [1], [2]. For example, the vehicle fleet in Ceará state, Brazil, has grown 180% over the last ten years. Fortaleza city is the capital of the state of Ceará, and has the seventh largest vehicle fleet in the country (387 vehicles per 1,000 inhabitants). At present, the vehicle fleet in Fortaleza Metropolitan Area (FMA) accounts more than 1 million vehicles. Totally, 8.4%of them are fueled with diesel (today with 8% v/v of biodiesel into mineral diesel) and 16% of these diesel vehicleshave been fitted with NOx aftertreatment systems since 2012 [3]-[5]. Although emission limits have become increasingly strict in the past years, road transport remains the most significant source of urban air pollution in Europe with respect to NOx, HC, and PM [22]. Furthermore, the presence of oxygen molecule in biodiesel might cause an increase in combustion gas temperature, which leads to an increase in NOx emissions, rising the flame temperature; this oxygen reacts with nitrogen and tends to form NOx [5], [20].

The Selective Catalytic Reduction (SCR) systems for NOx reduction by NH_3 has been the chosen technology by most of diesel-cycle bus and truck manufacturers in Brazil to meet the PROCONVE P7 [13] standards (EURO V equivalent). Significant NOx reduction is required, which demands higher amounts of NH_3, increasing its probability to slip to the environment. Thus, more complex aftertreatment systems have been needed to prevent the NH_3-slip. Two forms of NH_3 could be used in SCR systems: (i) pure anhydrous NH_3, and (ii) aqueous NH_3. Anhydrous NH_3 is toxic, hazardous, and requires thick-shell, pressurized storage tanks and piping due to its high vapor pressure. Aqueous NH_3 is less hazardous and easier to handle. Therefore, emission of NOx is reduced when introducing a reducing agent into the exhaust gases to convert NOx into harmless nitrogen and water, over an SCR catalyst. The commercialized SCR catalysts used in heavy-duty vehicles are monoliths catalyst based in V_2O_5-WO_3-TiO_2 (vanadium pentoxide-tungsten trioxide-titanium dioxide) [5], [6]. The SCR catalytic formulation is coated on a ceramic or metallic catalyst support encased in a stainless steel cylinder. Both precious metal and base metals can be used for an exhaust temperature range of 230 °C to 430 °C. Due to its toxicity, a vanadium-based SCR catalyst is expected to be removed from the heavy-duty diesel market within few years. Almost all major heavy-duty vehicles manufacturers have decided to use this technology to meet the new emission legislation on NOx emissions. This reaction usually requires a urea solution as a reducing agent (~32.5 % wt. urea), with brand names such as AdBlue® (in Europe) or Arla® (in Brazil).

The urea consumption can vary from 1 – 5% v/v relative to diesel fuel consumption (average consumption of aqueous NH_3 is about 0.1 liters per 100 kilometers). If the NH_3 /urea introduced into the system does not match the NOx to be converted, then there will be some NH_3 slip. In practice, slightly less than 100% of the NOx conversion is usually targeted [7], [8], so that the aqueous urea solution hydrolyses

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to NH_3, under relatively low temperatures (via formation of cyanic acid – HOCN), as shown in (1) and (2) [9]:

Thermolysis at 120 °C: $(NH_2)_2CO \rightarrow NH_3 + HOCN$ (1)

Hydrolysis at 160 °C: $(NH_2)_2CO + H_2O \rightarrow 2NH_3 + CO_2$ (2)

NH_3 -SCR provides a maximum efficiency of NOx removal if a significant amount of NH_3 is stored on its catalyst surface. This could produce NH_3 desorption during high temperature lapses since it affects the catalyst storage capacity. Furthermore, in some conditions, over-stoichiometric NH_3 availability is also needed, which increases the NH_3-slip even more. It should be noted that NH_3 is an aggressive gas to the eyes, skin, and respiratory trajectory. It has a maximum allowable concentration in air of 20 ppm. NH_3 can react with nitrate and sulphate in the exhaust gas and form respectively ammonium nitrate and sulphate that are emitted as secondary particles [10], [11].

The measurements also indicate that the NH_3 is a precursor of fine particles, or PM 2.5 μm, which deteriorates urban air quality, affects human health and impacts the global radiation budget since vehicles have been important sources of NH_3 in urban areas [2]. Experimental dynamometer NH_3 slippage has presented average values of 10 ppm and maximum values of 100 ppm, as reported in literature. The adoption of SCR system by the addition of urea or NH_3 to diesel exhaust to meet NOx emission standards could be also resulting in elevated NH_3 emissions from traffic. From this time, Carslaw and Rhys-Tyler [11] reported that NH_3 emissions in the United Kingdom are most important for older generation catalyst-equipped petrol vehicles and SCR-equipped buses [11]. More efforts are still needed to elucidate the contribution of vehicle-emitted NH_3 to the urban atmosphere. Thus, in this work, emission estimates were evaluated for mobile emissions of NH_3-slip from diesel vehicles when these are equipped with SCR-NOx. Neural networks have been used to model the system. A model based on neural networks integrated with a road vehicle simulator that allows to estimate NH_3-slip emission factors for different powertrain configurations along different driving conditions was proposed.

II. Methodologies

The evaluation of NH_3-split from heavy-duty vehicles with SCR-NOx systems using neural-networks was done according to a rigorous procedure well documented in literature [6], [9]. Accordingly, the evaluation of the NH_3 slip (in ppm or g/kWh) was carried out in a vehicle equipped with a SCR system under several traffic conditions, including one standard cycle as the Urban Dynamometer Driving Schedule - UDDS (Fig. 1) and real circuits measured both in Fortaleza-Brazil and Porto-Portugal cities (Fig. 2).

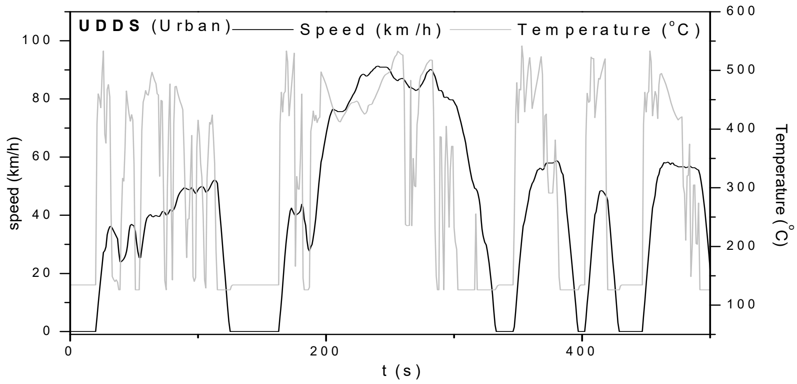

Fig. 1 Urban Dynamometer Driving Schedule (UDDS) driving cycle

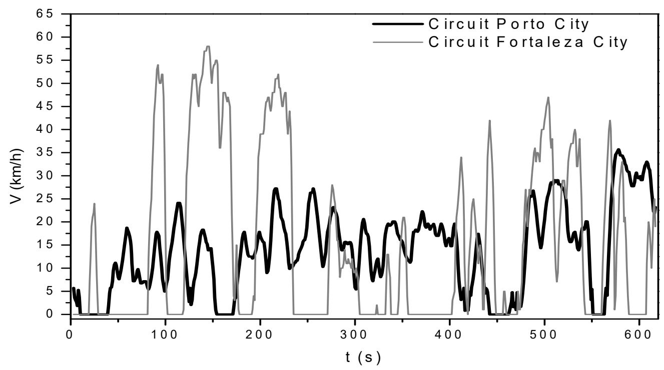

Fig. 2 Real driving cycle measured in Fortaleza and Porto cities

A. Emissions Regulations for Diesel Vehicles

In Brazil, Euro V standard was fully applied in January 2012, setting new upper bounds for heavy duty vehicles. Therefore, the SCR system for NOx reduction by nitrogen compounds, such as NH_3 or urea, commonly referred to as simply "SCR", has been developed for and well proven in industrial stationary applications. NOx maximum emissions are specially restricted, which leads to work under over-stoichiometric NH_3 conditions. It increases the chances for NH_3 to slip, requiring an assessment of NH_3-slip when it does not have an exact catalyst to mitigate this exhaust gas. Euro V engines have had 60% lower NOx emissions. At present, the actual European standard is the Euro VI. This fact has driven to new emission standards, forcing a reduction of 2 g/kWh in NOx emissions for heavy-Duty Diesel vehicles, as well as in Brazil [12]-[14].

B. Diesel Fleet Emissions: Fortaleza Metropolitan Area

In 2015, the total fleet of heavy-duty diesel trucks in FMA was more than 5,000 vehicles, 78% of which Fortaleza alone accounted. Only 16% of this fleet was fitted with SCR-NOx systems as of 2012 [4]. This fact might reflect directly on the reduction of NOx and PM emissions for this category, as shown in Fortaleza in Figs. 1 and 2 for NOx in 2010 and 2015, respectively. The emission decreases in recent years have been affected due to the introduction of aftertreatment systems into exhaust gases, as well as, the better quality of fuels [6], [15].

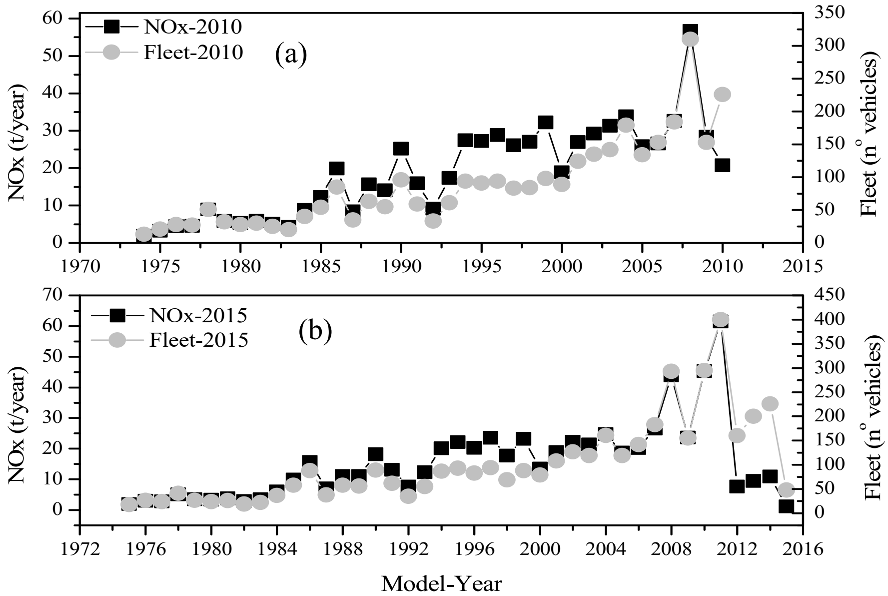

Fig. 3 NOx emissions and diesel vehicular fleet vs. model-year for the Fortaleza city/Brazil: (a) for year 2010 and (b) for year 2015

C. NH_3-slip by ANN Approach and ADVISOR Integration

The ANN was developed using the experimental dataset from typical exhaust gas characteristics of Diesel engines. The ANN was successfully trained accordingly to experimental data in SCR-NOx systems in order to predict transient changes in NOx emissions level in Diesel vehicle for operating conditions according to loads/engine speeds observed in driving cycles. NH_3 slippage heavy-duty vehicles along the standardized (UDDS) driving cycles and real measured driving cycle (in Fortaleza and Porto Cities), according to the model presented by Oliveira et al. [6]. Moreover, it was compared the performance of the other SCR catalysts investigated for UDDS and real driving cycle.

In this research, it was also used ADVISOR Version 2002, ran in the MATLAB® environment with Simulink, which is publicly available. ADVISOR does not cover any SCR-NOx model [6], [16], [17].

ADVISOR integration was available to ANN as an important simulation tool to evaluate the performance of vehicles equipped with SCR systems that use other catalysts, as well as possible to study the NH_3-slip in driving cycles for Diesel vehicles. The relevant seven inputs were considered for the NH_3-slip output: space velocity (SV, h^{-1}), exhaust gas temperature (T, ºC), oxygen concentration (O_2, v/v%), water concentration (H_2O, v/v%), sulphur dioxide concentration (SO_2, ppm), NOx concentration (ppm), NH_3 concentration initial (NH_3, ppm) (Fig. 4). The stochastic back propagation with the Levenberg-Marquardt algorithm (MATLAB®) was used to train the network [6], [9].

The SCR ANN was tested using 15% of data points measured by Oliveira et al. [6]. The other 85% of data (600 experimental points for each catalyst teste) were used to train and to validate several Network. The model is continuously updated with actual component test data from users and university validation efforts. It is flexible enough to model specific components and vehicle configurations for the needs of most users [21]. Taking all this into account, ADVISORs integration with the available ANN is an important simulation tool to evaluate the performance of the vehicles equipped with SCR system. Thus, it was possible to study the emissions NH_3-slip in driving cycles.

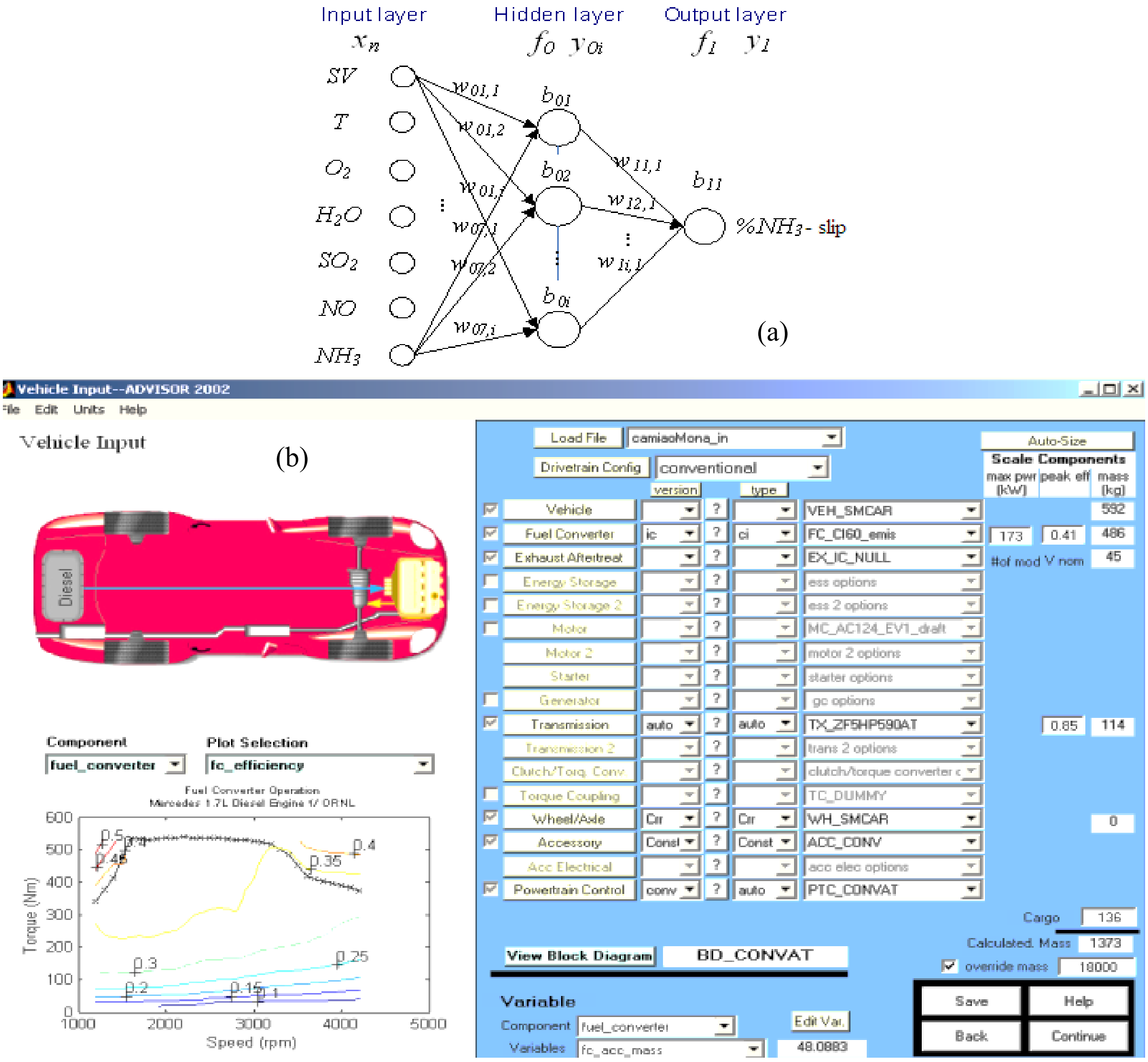

Fig. 4 (a) ANN architecture of the SCR model to NH_3-Slip and (b) ADVISOR integration tools

III. Results and Discussion

The correlation coefficients (R^2) between measured data and test, training and validation data are always higher than 0.70. This indicates that the developed ANN-based model can make good predictions of NH_3-slip on SCR systems for a Diesel vehicle. These R^2 values show a good adequacy of the developed mathematical correlations, for all studied catalysts (Table I), as reported by Oliveira et al. [6], [9] for % NOx conversion.

Simulated and measured data tests for NH_3 slippage, for all studied catalysts, are presented in Fig. 5. Generalization performance is reasonable, indicating confidence in the training results and produced fairly accurate forecasts.

TABLE I
R2 Value for the Test, Training and Validation Data

Correlation coefficients (R^2)	Catalyst	NH_3- Slip
	CATCO	0.80
Test	FeZSM5	0.72
	CuZSM5	0.80
	CATCO	0.82
Training	FeZSM5	0.76
	CuZSM5	0.90
	CATCO	0.80
Validation	FeZSM5	0.72
	CuZSM5	0.70

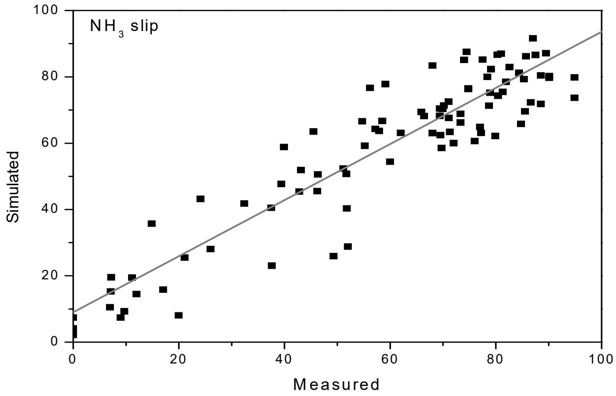

Fig. 5 Simulated and measured data for the test values of NH_3-slip for commercial catalyst (CATCO)

Emissions from diesel vehicles also can be expressed in grams of pollutant per unit of travelled distance (g/km) or ppm. Thus, NH_3-slip (ppm) data after the SCR system and the exhaust gas temperature are obtained for all the studied catalysts for UDDS driving cycle for heavy-duty vehicle. For all catalysts used in this study, a significant concentration of NH_3-slip during a sample (500 s) for real circuit measured is shown in the Figures below. The maximum NH_3 -slip concentration was estimated, approximately, 700 ppm for catalyst based in ZSM5 zeolite. Similar results were obtained for the remaining cycles and are summarized by Suarez-Bertoa et al. [2]. For all catalysts, a significant concentration of NH_3-slip during a sample of 500 s for real circuit is shown in Figs. 6 and 7.

The minimum NH_3 slip concentration was estimated, below 100 ppm for CATCO, while FeZSM5catalyst exhibited 250 ppm of NH_3 slippage. CuZSM5 catalyst showed maximum value up to 550 ppm. Similar results were obtained by Suarez-Bertoa et al. [2].

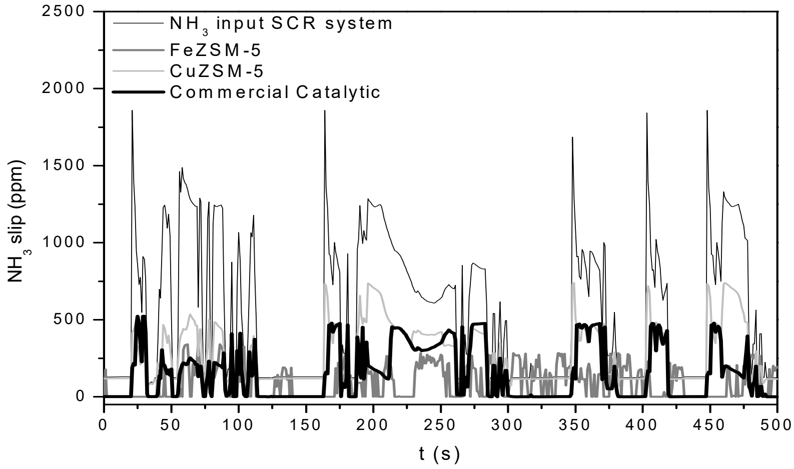

Fig. 6 Porto city real measured cycle when used in heavy-duty vehicle for NH_3-slip for metal-zeolite and commercial catalyst

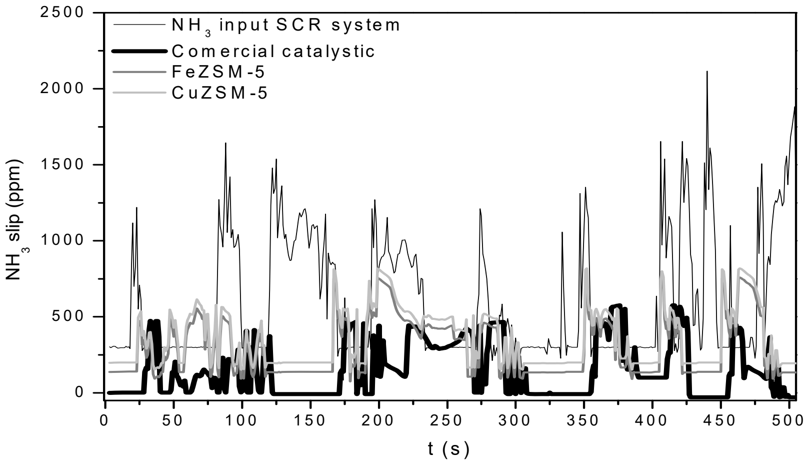

Fig. 7 Fortaleza city real measured cycle when used in heavy-duty vehicle for NH_3-slip for metal-zeolite and commercial catalyst

In the Porto cycle research, it was obtained a 100 ppm average and a maximum value of 500 ppm of NH_3 that passed through the SCR without reaction. It is noteworthy that the Fortaleza circuit shows slightly less than this value. At low exhaust temperatures, catalyst activity also falls sharply. This zeolite catalysts' behaviour could be explained not only by the support characteristics (i.e. acidity, framework structure, Si/Al ratio), but also by the metal ion-exchange. Consequently, this integration and simulation demonstrated to be a potential application tool in the development of emissions control strategies and emissions compliance or in the driving cycle test or real circuit validation of diesel vehicles. Fe-zeolites seem to be the best candidates for CATCO replacement. They reveal lower values of NH_3 slip tailpipe emissions.

In general, the results of the research show that the correlations obtained with ANN integrated with a road vehicle simulator, produce average NH_3 slippage results for commercial vanadium based catalyst consistent with experimental data and can be one more powerful tool for SCR simulation of diesel vehicles equipped with advanced after treatment systems, also studied by Faghihi and Shamekhi [18].

Emissions for diesel vehicles from NH_3-slipe are shown in Table II by grams of pollutant per unit of travelled distance. It is also assumed the average of % NO conversion for all catalysts studied to present UDDS standard and real circuit cycles.

TABLE II
PERFORMANCE OF THE SCR SYSTEM AND NH_3-SLIP FOR HEAVY-DUTY DIESEL VEHICLE

Catalyst	Cycles Driving	% NO Conversion Average	NH_3-slip (g/km) Average
CATCO (1)	UDDS	89.5	2.29
	Real Urban Circuit of Fortaleza city	87.3	2.62
	Real Urban Circuit of Porto city	83.7	2.97
FeZSM5(2)	UDDS	77.7	2.30
	Real Urban Circuit of Fortaleza city	72.5	3.03
	Real Urban Circuit of Porto city	70.1	4.12
CuZSM5(3)	UDDS	27.0	4.10
	Real Urban Circuit of Fortaleza city	25.6	5.07
	Real Urban Circuit of Porto city	23.0	6.40

(1) Commercial catalyst, (2) iron zeolite catalyst and (3) copper zeolite catalyst

These driving cycles were used in the present work because contrasting with the remaining cycles, they are very demanding in terms of accelerations rates, low average speed, aggressive topography and ambient temperature [19]. Complementing, these results show the performance of the SCR systems concerning the NH_3-slip (g/km) for the remaining (non-homologation) driving cycle simulated. Moreover, the remaining catalysts exhibited high NH_3-slip. Some authors have attributed this difference of behavior to characteristics of catalysts in function of temperature or probably to the reach of the maximum absorption limit of NH_3 and characteristic of the real circuit presented, as shown in both Fortaleza circuit (2.62-5.07 g/km) and Porto circuit (2.97-6.40 g/km) tested. The performance of SCR systems can be improved with thermal management to increase exhaust temperatures [20]. Start-stop systems are also effective at keeping the SCR system warm by avoiding the cooler exhaust temperature of idling conditions [7], [9], [16].

IV. CONCLUSION

The Euro V standard fixes the maximum levels of NOx released by heavy duty vehicles and it was being fully applied in Europe since January 2012, while the Brazilian equivalent regulation was stablished only in January 2014. NOx emission is especially further restricted, which needs more severe urea injection in order to let the NH_3 -SCR storing significant amount of NH_3 for NOx reduction. In general, the results of the research show that the correlations obtained with ANN integrated with a road vehicle simulator produce average NH_3 slippage results for commercial vanadium based catalyst consistent with experimental data and can be one more powerful tool for SCR simulation of diesel vehicles equipped with advanced after treatment systems. The minimum NH_3 slip concentration was estimated; below 100 ppm for commercial catalytic and FeZSM5 zeolite catalytic exhibited 250 ppm NH_3-slip, while CuZSM5 showed maximum value up to 550 ppm. Similar results were obtained for the remaining tests.

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