Experimental investigation of selective catalytic reduction system on CI engine for NO_x reduction using urea and animal urine as catalyst

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Abstract: Selective catalyst reduction systems are the popular and efficient post-combustion nitrogen oxides reduction techniques utilised in the automotive and power generating industries. They involve a chemical reaction in which vaporised ammonia is gathered from the mixture of urea and purified water. Conversion of nitrogen oxide to nitrogen and water is the main target. In this NO_x reduction system, costlier reductants have been utilised, which increases the operating cost of the vehicle. The methodologies adopted in this research work are the use of natural resources as a catalyst. Production of a modified selective catalyst reduction device was conducted in the first process. Secondly, the collection and preparation of diesel exhaust solution using various pure urea and urine (cow and sheep urines) with varying concentrations was carried out to inject the tailpipe via the selective catalyst reduction system's feed pump to assist in reducing the oxide of nitrogen. In a conclusion, there can be an important improvement in the oxide of nitrogen emissions using urea, cow, and sheep urines in the modified selective catalyst reduction. The urine-based solution shows a 2.3% reduction in NO_x emission as compared to the urea-based solution.

Keywords: CI engine; SCR; NO_x; catalyst; cow urine; sheep urine.

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1 Introduction

With high torque and thermal performance, diesel engines are commonly used in many industries, such as vehicles, locomotives, marine engines, steam generators, etc. While diesel engines deliver more advantages, these engines' pollutant emissions create more human discomfort.

Diesel engines' principal pollutants include particulate matter, hydro fuel, smoke, and nitrogen oxides (NO_x). NO_x is the most hazardous contaminant of these pollution discharges to human health, plants, and the atmosphere. NO_x emissions have been steadily increasing over the last 150 years over the world. The ecosystems of the earth and human welfare have been significantly impacted by their growing involvement in the atmosphere. The burning of fossil fuels and biomass is the main anthropogenic source of these emissions. The most common pollutants from engines are nitric oxide (NO), NO_2, and NO_2, with NO being the most significant of these (NO). Most of the NO_x reduction effort is concentrated on reducing NO produced during combustion since more than 90% of NO_x produced by combustion is in the shape of NO, which effectively transforms into NO_2 when reacting with ambient oxygen.

Mono NO_x, also known as NO and NO_2, are referred to as NO_x. They are created during combustion, especially at high temperatures, when nitrogen and oxygen gases mix. The quantity of NO_x released into the environment is crucial in metropolitan areas with heavy truck traffic. No matter where fuel combustion takes place, NO_x gases are created. Fossil fuel combustion and biomass production account for almost 90% of the world's energy production. Photochemical smog, acid rain, tropospheric ozone formation, and stratospheric ozone depletion are all primarily caused by elevated atmospheric NO_x (Praveen and Natrajan, 2014). Human activity, including combustion activities, accounts for approximately 66% of all NO_x emissions. Natural causes such as lightning, forest fires, and field fires account for roughly 16% of NO_x emissions, while microbiological activities account for approximately 18% of NO_x emissions. 50% of all combustion-related NO_x emissions come from stationary sources such as power plants with the remaining 40% coming from the transportation sector (Praveen and Natrajan, 2014).

Numerous studies have been conducted in the literature on reducing NO_x emissions. In some of these studies, NO_x emissions were reduced by using new and environmentally friendly fuel instead of conventional fuel. Below are some studies carried out with the use of new and environmentally friendly fuels. The palm methyl ester was employed as fuel and functions similarly to diesel, and reductions in NO_x emissions were seen, according to Hashimoto et al. (2008). When contrasted to clean diesel service with bio-fuel additive blends, Swaminathan and Sarangan (2012) found that employing diethylene glycol monomethyl ether and diethylene glycol as fuel resulted in a 10 to 30% reduction in NO_x. 2-ethylhexyl nitrate (EHN) was used as engine fuel by Ileri and Koçar (2014) who found that a 1,000 ppm concentration of EHN addition was effective for lowering NO_x levels. Roy et al. (2014) investigated the effect of biodiesel-diesel, biodiesel-diesel-additive, and kerosene-biodiesel on engine performance. They concluded that biodiesel-diesel additive had an impact on NO_x reduction. In their study of Jatropha biodiesel and N-diphenyl-1,4-phenylenediamine (DPPD) antioxidants on an engine, Palash et al. (2014) found that adding 0.15% DPPD additives to JB20 resulted in a maximum drop of 16.54%.

On the other hand, some researchers have improved the combustion process in their works. NO_x emissions were reduced by a maximum of 62% in high-load duty, according to research conducted on fuel at the top dead centre in Okude et al.'s (2004) work. Using homogeneous charge compression ignition (HCCI) technology, Kumar and Rehman (2016) discovered a 5 to 10% improvement in NO_x reduction. Abuelnuor et al. (2014) studied flameless combustion and they found that NO_x emissions were minimised using the flameless combustion technique. Singh et al. (2014) studied HCCI technology with biodiesel fuel and an important decrease in NO_x emission was observed. Ogunkoya et al. (2015) studied a stabiliser made from carboxymethylated wood lignin and they observed a dramatic reduction in NO_x emissions. Some researchers have carried out studies on after-treatment systems to control the amount of NO_x. Kumbhar et al. (2021, 2022) studied the RCCI combustion strategy for emission reduction by using the single cylinder engine. There was a reduction in NO_x emission but also an increase in HC emission in comparison with original engine performance. In Wang et al.'s (2007) work, SCR's experiments with ammonia N-agents resulted in a 60% reduction in NO_x and an 81.3% reduction in NO_x, respectively. NO_x emissions significantly decreased in Chi and DaCosta's (2005) study using SCR-urea. Schmieg and Lee (2005) examined the impacts of SCR on diesel engines between 150 and 550°C for the reduction of urea and NO_x. Thanks to SCR, Servati et al. (2005) were able to achieve that 70% average reduction in NO_x emissions. Working with the urea-SCR system, Acharya et al. (2006) significantly reduced NO_x emissions. Ishii et al.'s (2007) use of urea-SCR led to a major decrease in NO_x emissions. By Murata et al. (2008), employing a urea SCR device at 158°C for the inlet gas temperature could reduce NO_x emissions by 75%. After conducting experiments with biodiesel and the urea-SCR system, Mehregan and Moghiman (2020) concluded that the addition of nanoparticles significantly improved the system's ability to reduce pollutants. To evaluate the urea SCR systems for reducing NO_x emissions, Liu and Tan (2020) conducted experiments. They concluded that the NO_x emission having the urea SCR application was much greater than that of solid SCR. In Keskin et al.'s (2020) work, NO_x reduction tests were conducted using a variety of catalysts, including the HC-SCR system, tetraamin palladium (II) nitrate solution, TiO_2-based catalyst, and silver nitrate ($AgNO_3$)-based catalyst. When the engine was running at 4 kW with 100% 2-propanol spraying, the highest NO_x conversion rate that was 68.1%. Additionally, it was demonstrated that 2-propanol, as opposed to abBluereluctant, had a favourable impact on the NO_x conversion rate.

Numerous methods for reducing emissions have been examined by researchers including modifying the fuel, changing the way of the exhaust is currently treated, altering the engine's structure, and changing the fuel delivery system. These systems' complexity and expense are their main drawbacks. This study is novel since it examined the feasibility of using inexpensive, straightforward systems and aqueous solutions of different natural resources as catalysts. In this study, unlike many publications in the literature, the impact of sheep urine and cow urine on emissions in the modified SCR system was studied. Also, the conditions that do not use urea and SCR and the use of sheep urine and cow urine in the modified SCR system were compared. In this way, the effect of the green method of sheep urine and cow urine on NO_x emissions with the modified SCR system has been extensively investigated by engine experiments. Finally, this paper should be evaluated with authors previous publication (Tirpude et al., 2022) in the literature.

Table 1 Property of urea-water solution

Density (kg/m^3)	1,089
Thermal conductivity [W/mK]	0.57
Boiling point temperature (°C)	104
Surface tension [N/m]	0.0717
Specific heat (kJ/kg K]	3.4
Concentration (wt %)	32.5
Latent heat of vaporisation (kJ/kg]	2.258
Freezing point (°C)	–11
pH	8.8
Odour	Odourless
Colour	Colourless

Source: Arand et al. (1982)

2 Experimental study

Experimentation is done in two phases. In the first phase, the different aqueous solutions are prepared which are used to inject exhaust gas. In the second phase, performance and emission testing are measured. Many experiments involving the use of chemicals call for their use in solution form by mixing two or more substances in known proportion. Preparation of solutions accurately will improve the safety of the experimental investigation and lead to success. Basic three components are considered for the preparation of aqueous solutions, i.e., urea, cow urine, and sheep urine. In various quantities and arrangements, experiments are done, and the optimum solution is found. The properties are these components are given in Table 1. Urea is a chemical organic compound with the chemical formula $CO(NH_2)_2$. It is a compound of non-protein nitrogen used as an inexpensive nitrogen source in ruminant feeding. There is around 42–46% nitrogen in feed-grade urea, which corresponds to 260 to 288% crude protein equivalent. In Table 1, the detailed properties of the urea-water solution are given. Cow urine contains male, citric, tartaric, and calcium salts, as well as the vitamins A, B, C, D, and E, as well as minerals, lactose, enzymes, creatinine, hormones, nitrogen, sulphur, phosphate, sodium, manganese, iron, silicon, chlorine, and magnesium (Gulhane et al., 2017). Cow urine contains the same substances that make up human urine. Table 2 details the chemical makeup of the cow-urine solution. To better understand the reactions that urinary N experiences, the distribution of urinary nitrogen (N) was examined in five samples of sheep urine. The amount of nitrogen (N) in sheep urine ranged from 3.0 to 13^{-7} gm/litre, with urea making up 83% of that amount, creatine coming in at 53%, hippuric acid and allantoin coming in at 4.3%, and the other elements making up less than 1% of the total. Table 3 details the chemical composition of the sheep-urine.

Table 2 Chemical composition of cow urine

Ammonia nitrogen	1–1.7 ml/kg/day
Allantoin	20–60 ml/kg/day
Calcium	0.1–1.4 ml/kg/day
Chloride	0.1–1.1 mmol/kg/day
Creatinine	15–20 mg/kg/day
Magnesium	3.7 mg/kg/day
Potassium	0.08–0.15 mmol/kg/day
Sodium	0.2–1.1 mmol/kg/day
Sulphate	3–5 mg/kg/day
Uric acid	1.4 mg/kg/day
Leucocyte	<15 micro lt

Source: Gulhane et al. (2017)

Table 3 Chemical composition of sheep urine

Urea	15.29 gm/litre
Hippuric acid	5.24 gm/litre
Allantoin	1.08 gm/litre
Uric acid	0.06 gm/litre
Xanthine/hypoxanthine	0.19 gm/litre
Creatinine	0.12 gm/litre
Creatine	1.48 gm/litre
Free amino acids	0.06 gm/litre
Ammonia	0.01 gm/litre

Source: Bristow et al. (1992)

Table 4 Specification of measuring equipment

Digital fuel rate indicator		*Digital torque indicator*		*Digital speed indicator*		*Exhaust gas temperature indicator*	
Range	0–15,000 gms	Torque range	0–32 N-M	Speed range	30–3,000 rpm	Temperature range	0–800°C
Weighing resolution	1 gm	Torque resolution	0.1 N-M	Speed resolution	1 rpm	Resolution	1°C
Sensor load cell	20 kg	Load cell	35 kg	Speed sensor	Inductive proximity, N-type 18 mm dia	Type of sensor	K-type thermocouple

Diesel engine, eddy current dynamometer, fuel measuring system, speed measurement system, temperature measurement system, catalytic converter, AVL analyser, and denoxation injection system (Tirpude et al., 2022) are all used during tests. Also, the specification of measuring equipment is given in Table 4. All tests were performed on an air-cooled, four-stroke, direct injection engine. The tests were done in the variable speed diesel engine, for the speed of 800, 1,600, and 2,400 rpm for the 0 to 100% loading conditions in the increment of 20%. The tests are performed at room temperature and pressure while keeping the fuel injector and pump settings unchanged. The engine specification is given in Table 5. In this investigation, an eddy current dynamometer is evaluated as a loading device. The dynamometer can be operated in two different modes. They are fixed torque mode and constant speed mode. In this selection, the torque is kept fixed and hence the overall power output will be proportional to the speed of the engine. During this one, the speed remains fixed and, hence, the torque varies, the resultant power output also varies proportionally to the torque. A load cell is used to measure the force applied to the eddy current dynamometer. Torque value is indicated in digital indicator in nm. Initial adjustment and calibration are as follows:

a At no load condition, adjust the zero value of torque using the tare pot on the instrumental panel.

b After the initial adjustment of torque, torque can be measured directly from the metre.

c For calibration, initially, the load cell is kept load free by turning the loading arm to display zero reading.

d Keep the calibrated weight of known mass ranging from 10–40 kg. See the reading on the digital indicator, if it is correct, calibration is completed. Otherwise, the span trim pot is adjusted to show the correct reading.

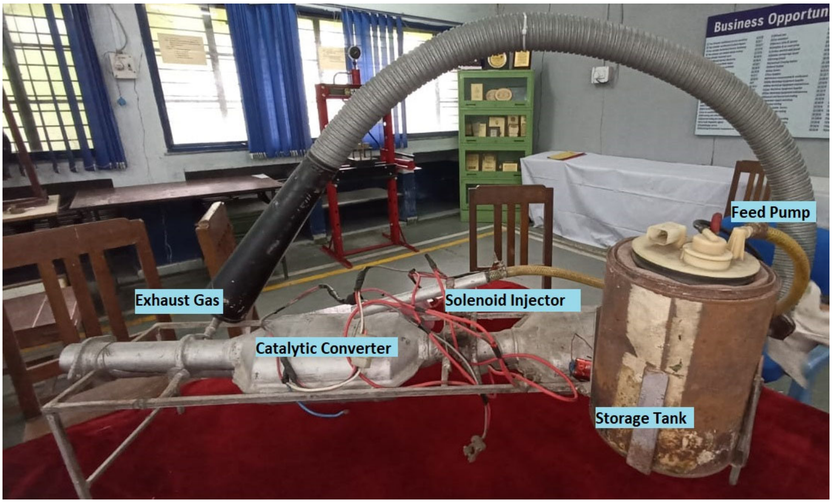
Table 5 Specification of engine

Type	*Air cooled, four stroke*
Bore, d (mm)	87.6
Stroke length, 1 mm	110
Compression ratio, r	17.5:1
Capacity, cc (cm^3)	661.5
Max. power (kw)	4.4
Fuel injection	Direct injection
Dynamometer types	Electrical dynamometer

Source: Tirpude et al. (2022)

For calibration of the thermocouples, a millivolt source output is applied to them as input. The trim pot is adjusted from the backside of the instrumental panel to adjust zero value for 0 mV as input of the thermocouple. Then 333.27 mV is applied as input to the thermocouple, which shows 800°C on display. Again, the input is adjusted to zero value, and the trim pot is adjusted to show ambient temperature. The proximity sensor is used to measure the speed. The proximity sensor calculates the speed as the inverse of the period. To confirm the accuracy of speed measurement, speed is also measured with a digital tachometer.

Figure 1 Photo of catalytic converter (storage tank, PWM controller, catalytic converter, exhaust gas, solenoid injector, and feed pump) (see online version for colours)



The fuel measurement system consists of a load cell to measure the weight loss for one minute. The stopwatch is used to measure the time in seconds. The fuel measurement system is separate from emulsion samples. For each sample, fuel containing vessel is clean to avoid measurement errors. The differential manometer is used to measure airflow. It can measure the flow rate up to 50 m^3/hr. The resolution is 0.1 m^3/hr.

The exhaust gas analyser measures the CO, HC, CO_2, and NO_x emissions. After, starting of exhaust analyser, it takes 14 minutes for sensor stabilisation. After sensor stabilisation, a leak check is done. If there is no leak, then readings are taken for various emissions by inserting a probe into the exhaust to sample. Various filters are mounted to remove moisture and other impurities. After stabilising, readings are noted. The specification and principle of measurement of the gas analyser and smoke metre are given in Tables 6 and 7, respectively. The calibration of the exhaust gas analyser is carried out as per the company.

Table 6 Specification of AVL DiGas exhausts gas analyser

Parameters	*Measurement principle*	*Measurement range*	*Resolution*
Carbon monoxide (CO)	Infrared	0–10% by vol.	0.01% by vol.
Hydrocarbon (HC)	Infrared	0–20,000 ppm vol.	1 ppm vol.
Carbon dioxide (CO_2)	Infrared	0–20% by vol.	0.1% by vol.
NO_x	Electrochemical	0–4,000 ppm vol.	1 ppm vol.

Source: Tirpude et al. (2022)

Table 7 AVL 437 C smoke metre

Parameters	*Measurement principle*	*Measurement range*	*Accuracy and reproducibility*
Smoke opacity	Extinction of light	0–99.99 opacity in %	+/– 1% full scale reading

Source: Khond et al. (2020)

Table 8 Experimental plan

Concentration of DES	*Engine speed 800 rpm*		
	Urea	*Cow urine*	*Sheep urine*
Without DES	√	√	√
250 ml/750ml water	√	√	√
500 ml/500ml water	√	√	√
750 ml/250 ml water	√	√	√

A smoke metre measures the smoke opacity in the exhaust gas. The details of the smoke metre are given in Table 7. The smoke metre is calibrated as per the AVL method. Initially, a heater is started to remove the moisture from the measurement system. After reaching the temperature above 700°C, the reading was noted down by inserting the probe into the exhaust pipe.

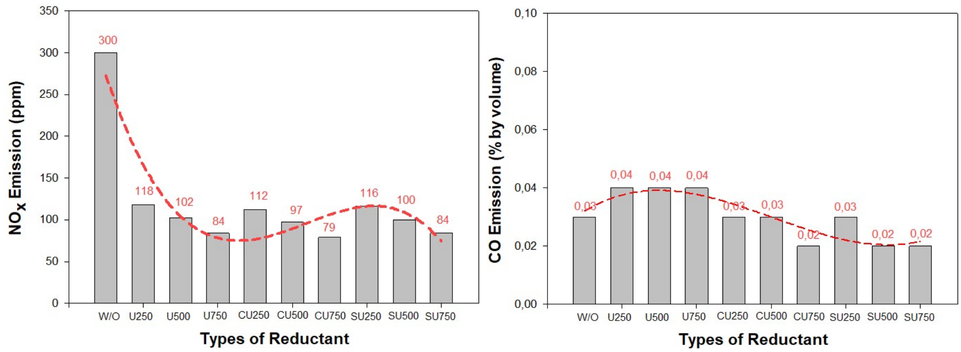
The aqueous solution storage tank, pump, and SCR are described in detail in Tirpude et al. (2022). Two catalytic converters one with a TiO_2 catalyst and the other with a vanadium-coated catalyst are part of the updated SCR system. These two catalysts are connected in the exhaust pipeline, as illustrated in Figure 1. Between these two catalysts, there is an injection system for injecting an aqueous solution of diesel exhaust. To automate the complete injection system, a PWM circuit is created and linked. The injection system is needed to supply the diesel exhaust system to the catalytic converter. The denoxation injection system is used in this experiment. It consists of a feed pump, connecting pipe, injector, and electrical circuit. The complete working of the system is electronically controlled. A detailed view of the system can be seen in the related figure.

The exhaust gas treatment system consists of an aqueous solution storage tank, a pump to maintain solution pressure and circulate the solution to the nozzle injector which is located closer to the engine in the exhaust pipe. To manage the flow of solution to the injector nozzle, a three-way flow control valve is fitted between the pump and the injector, as well as a piping line to return the surplus solution to the storage tank (Tirpude et al., 2022). After solution injection, the exhaust pipeline's two SCRs one with a TiO_2 catalyst and one with a vanadium-coated catalyst are linked together. The NH_3 mixture and NO_x effluent are then permitted to flow through two different series-connected catalysts after the solution injection. The modernised SCR system has two catalytic converters, one with a titanium dioxide catalyst and the other with a catalyst coated with vanadium. As seen in Figure 1(b), these two catalysts are connected via the exhaust pipeline. An injection system for injecting aqueous diesel exhaust solution is installed. PWM circuit is built and wired to automatically run the entire system.

3 Result and discussion

The results of experiments performed on a selective catalytic reduction diesel engine with distinct fluids made from animal urine (cow and sheep) have been reviewed. The results were compared with and without SCR for various pollutants. The test was performed at an engine speed of 800 rpm with three stages of varying diesel exhaust fluid concentrations (250, 500, and 750 ml). It also evaluated fuel economy and braking performance.

Figure 2 Effect of reluctant at 800 rpm on, (a) NO_x (b) CO emissions (see online version for colours)



(a) (b)

The NO_x was the main constituent of emission generated during combustion. In a diesel engine, Smoke and NO_x are major emissions and these emissions always have a trade-off between each other. The SCR technology has shown the ability to reduce NO_x without affecting other emissions (Tirpude et al., 2019). The experimentation was carried out using SCR and without SCR using various reluctant prepared from a natural waste fluid. Cow and sheep urine was used as a DES. Different concentrations of diesel exhaust fluid (250, 500, and 750 ml) at constant engine speed (800 rpm) were tested and the results were shown in Figure 2(a). It was depicted from related figures that; NO_x emission was reduced due to the rise in the concentration of all types of reductants. However, the maximum reduction of NO_x was observed in cow urine containing diesel exhaust solution. The NO_x emission formation relies on the combustion chamber temperature, availability of oxygen, and the time required completing the reaction. The urine-based diesel exhaust solution has lower NO_x emission than the urea-based solution due to more stable and catalytic activity due to other components in urine like magnesium, iron, etc., and ammonia. The maximum reduction at 800 rpm engine speed was 73.67% in the CU750 sample.

CO emission was the output of the unfinished combustion of the hydrocarbon. Figure 2(b) depicts the CO emission under 800 rpm speed for U, CU, and SU-based solution. It can be observed that CU and SU solutions showed similar trends, but the U solution showed higher at 800 rpm. Higher CO emission in U might be due to solid urea present with water causing some back pressure and resulting from low oxygen available for combustion. The unavailability of oxygen decreased the conversion rate of CO into CO_2. However, the other two solutions were naturally mixed, and no solid component was present. Therefore, concentration does not affect the CO emission as such.

Hydrocarbon emission was generated due to incomplete combustion. This emission was in a cylinder. Figure 3(a) shows the effect of variation of hydrocarbon emission for U, CU and SU-based solutions. The hydrocarbon emission was higher in the engine without SCR, but reduction of HC was obtained in SCR fitted engine with all solutions. The CU and SU have shown better performance in terms of HC emission. This may happen due to the presence of another oxidation promoter in CU and SU. Figure 3(b) shows the effect of SCR with various diesel exhaust solutions U, CU and SU with different concentrations ranging from 250 to 750 ml under 800 rpm constant engine speed. It was depicted that marginal reduction of CO_2 was obtained with SCR. However, SCR was not affecting the CO_2 significantly. The maximum value of CO_2 emission was 6.2% at 2,400 rpm without SCR and the minimum value was 4.1% in U750 and SU250.

Figure 3 Effect of reluctant at 800 rpm on, (a) HC (b) CO_2 emissions (see online version for colours)

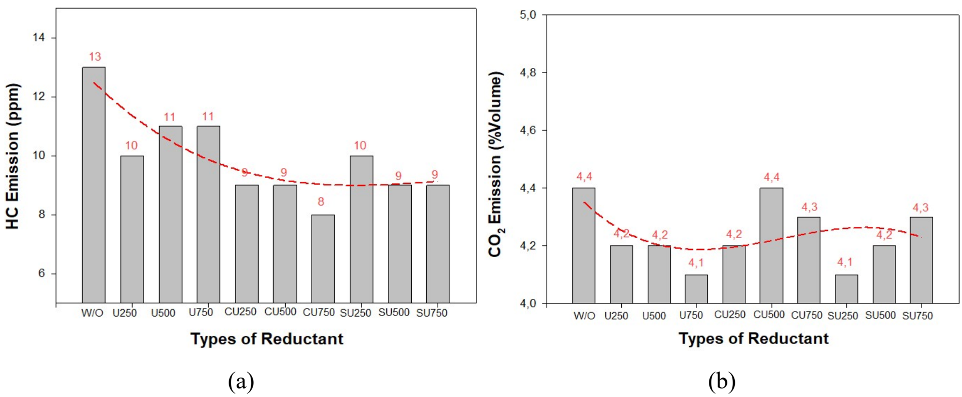
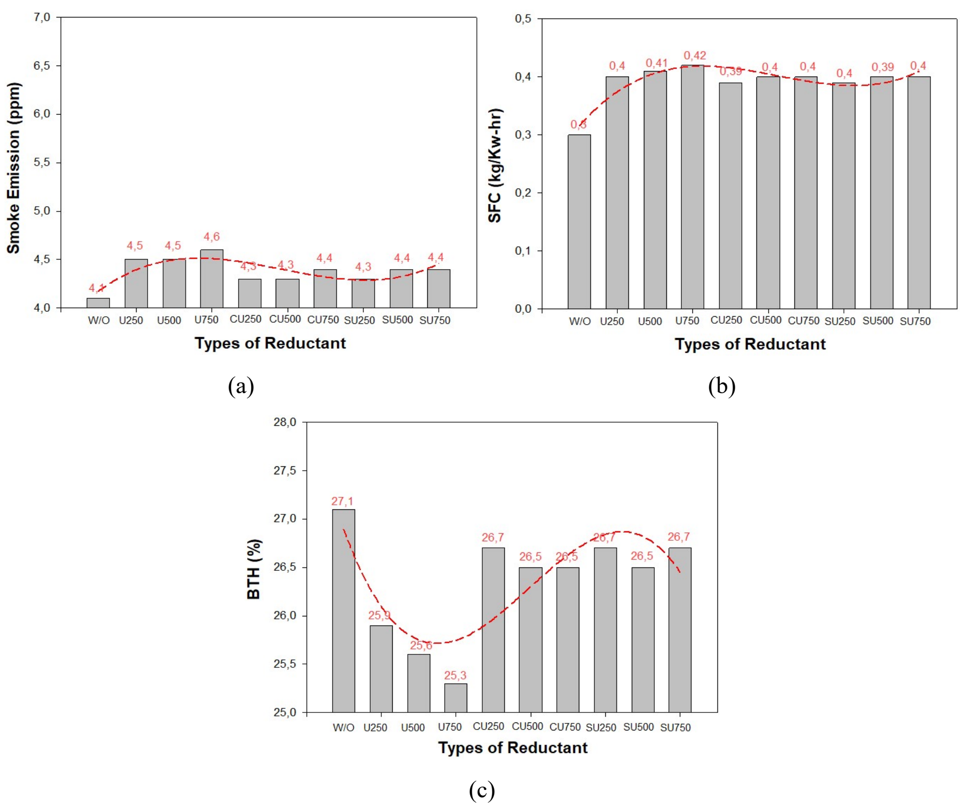


Figure 4 Effect of reluctant at 800 rpm on, (a) smoke (b) SFC (c) BTH (see online version for colours)



Smoke emission was a result of the low quantity of oxygen available for combustion of carbon and hydrogen in fuel as well as the quality of the charge since the premixed and mixing controlled strategies lead to generating the higher smoke emission resulting in the PM emission. The fuel injection application employed for this engine was a low-pressure fuel injection system which affected the homogeneity of the charge and resulted in smoke formation. It was seen from Figure 4 that smoke emission was lower without SCR in comparison with SCR. The Increase in smoke emission in SCR fitted conditions might be due to back pressure generated on a diesel engine. The maximum value of smoke was 4.6 ppm in U750 and the lower one was 4.1 ppm in W/O. It was inferred that urea-based solutions have more smoke emissions than urine-based ones. The SFC was described as the mass flow rate of fuel per unit of power developed by the engine. Figure 4(b) shows the variation of SFC for various DES with different concentrations ranging from 250 to 750 ml. It was obvious from the figures that SFC values were lower without SCR compared with SCR. The urea-based solution showed higher SFC due to slight high back pressure that might be developed due to solid urea. The BTH of the engine was described as brake power developed per unit of heat supplied. It is a measure of how much fuel energy is converted into power. Figure 4(c) indicates the variation of BTH for various DES for different concentrations at 800 rpm constant engine speed. The BTH was higher when SCR was not fitted on the engine. However, a slight decrease in SCR was observed with SCR that might be due to slight back pressure on the engine. The maximum efficiency (30%) was observed in CU500 and SU250, respectively. Even though, SCR decreased BTH slightly, urea-based solution showed a lower value of BTH than the urine-based solution. Hence, CU and SU could be used as DES for SCR.

4 Conclusions

In the current study, the impact of natural urine-based DES in an SCR unit was investigated. The conclusions from the practical results are as follows:

a The SCR was the most successful NO_x reduction method. On the other hand, there was less impact of SCR on the performance and emission.

b Research on diesel engines was carried out at the SCR experimental facility. It can be determined that urine-based solutions reduced NO_x more effectively than urea-based ones. NO_x levels were reduced by over 2.3% as compared to urea-based solutions. Among the two urine-based solutions, cow urine and sheep urine, the CU-based solution reduced NO_x the most.

c The greatest NO_x reduction was reported to be 73.67% for cow urine at 750 ml CU and 250 ml water evaluated at an 800 rpm speed.

d CO emissions were measured to be somewhat higher in SCR-equipped diesel engines. The urea-based solution produced more CO than the urine-based solution, which could be attributed to a minor growth in back pressure on the engine caused by urea settling into a solid. CU750 emitted the least amount of CO (0.01% by volume).

e All DES solutions demonstrated decreased HC emission when compared to those without SCR. Among all samples, the CU750 sample had the lowest HC emission.

f CO_2 emissions followed virtually identical patterns in urine-based and urea-based solutions.

g Smoke emission in urea-based DES was found to be greater than in urine-based DES.

h It was determined that SCR somewhat enhanced SFC owing to engine back pressure. However, SFC results were quite similar for all samples.

i Developments in BTH were quite similar to trends in SFC. In all DES samples, the BTH was slightly lower.

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Nomenclatures

AVL	AVL gas analyser
BSFC	Brake-specific fuel consumption
BTH	Brake thermal efficiency
CO	Carbon monoxide
CO_2	Carbon dioxide
CU	Cow urine
DES	Diesel exhaust solution
DPPD	N_0-diphenyl-1,4-phenylenediamine
EHN	2-ethylhexyl nitrate
H_2O	Water
HC	Hydrocarbon
HCCI	Homogeneous charge compression ignition
N	Urinary nitrogen
NO	Nitric oxide
NO_x	Oxide of nitrogen
N_2	Nitrogen
NH_3	Ammonia
PWM	Pulse width modulation
rpm	Revolution per minute
SCR	Selective catalyst reduction
SFC	Specific fuel consumption
SU	Sheep urine
TiO_2	Titanium dioxide
U	Urea