

The effect of biodiesel on activity of diesel oxidation catalyst and selective catalytic reduction catalysts in diesel engine

Ibrahim Aslan Resitoglu

Department of Automotive Technology, Mersin University, Technical Sciences Vocational School, TR-33343, Mersin, Turkey

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ABSTRACT

NO_x emission is one of the most important pollutants and held responsible for damages on human health and environment worldwide. Undoubtedly, diesel engines, which are widely used in many fields, are the most important sources of NO_x emissions. Currently, SCR technology is the most effective method used to eliminate NO_x emissions from diesel engines. Thanks to SCR technology, NO_x emissions can be eliminated at very high rates by using a reductant and a catalyst. The NO_x conversion efficiency of SCR system can be significantly improved using a DOC before the SCR system.

This study focused on the effect of biodiesel, which is the primary fuel that can be an alternative to diesel fuel, on DOC and SCR efficiency. In the study, besides the traditional SCR catalyst (V₂O₅-WO₃/TiO₂), Ag/Al₂O₃ catalyst was also tested. The effect of using biodiesel and Ag/Al₂O₃ catalyst on NO_x conversion performance especially at lean conditions is investigated in detail. In addition, the conversion performance of the DOC used in the tests was also examined in this experimental study. The results showed that biodiesel promoted the activity of DOC. The use of biodiesel increased the DOC conversion up to 14.66% compared to diesel while caused no significant change in NO_x conversion of SCR catalyst. Maximum conversion rates of Va/SCR and Ag/SCR catalysts were obtained as 70.25% and 70.48% respectively with diesel.

1. Introduction

Air pollution is a problem faced by many countries that causes severe damages to human health and the environment. It is reported by many organizations that millions of casualties are caused by air pollution every year [1,2]. Internal combustion engines have become an indispensable element for humanity since they were invented. Internal combustion engines that provide great convenience in daily activities of people, especially transportation, are among the leading sources of air pollution. Diesel engines, which are widely used in many different fields (energy providers, vehicles, agriculture, industry, etc.) due to their low fuel consumption, high durability and high efficiency, cause unrecoverable damages on human health and environment due to their pollutant emissions (PM, CO, HC, SO₂ and especially NO_x). NO_x (NO and NO₂) emissions from diesel engines give rise to various symptoms (irritation in the eyes and throat, headache, weakness, shortness of breath, asthma, lung cancer, etc.) [3]. On the other hand, NO_x emissions released to the environment contribute to global warming effectively in the formation of undesired ground level ozone. Also the interaction of NO₂ emissions and vapour in air creates nitrous acid (HNO₂) and nitric acid (HNO₃)

that lead to acid rains, which are very harmful especially for plants. These negative effects caused by NO_x emissions have made necessary the elimination of NO_x emissions from diesel engines. For this purpose, standards such as Euro, Tier etc. have been developed and put into effect by various organizations and these standards have been made more stringent day by day. In order to meet the responsibilities required by the standards, many studies have been carried out and many technologies have been developed by both automotive manufacturers and scientists. Although many scientific and R&D studies have been focused on issues such as improving fuel properties, use of alternative fuels and fuel additives, exhaust gas recirculation, electronically controlled fuel injection systems and engine modifications, these technologies have not been sufficient in meeting the requirements of current standards. The current standards can only be achieved through aftertreatment emission control technologies. Selective Catalytic Reduction (SCR) system is one of the aftertreatment control technologies used as the most effective method to eliminate NO_x emissions. Thanks to the SCR system, NO_x emissions can be reduced by almost 100% and the requirement of current standards can be ensured. In addition, SCR allows the engine to be fully optimized without the restraint of NO_x formation since having great NO_x conversion efficiency. With the optimizations such as in EGR

E-mail address: aslanresitoglu@mersin.edu.tr.

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Nomenclature			
Al ₂ O ₃	Aluminium Oxide	HNO ₃	Nitric Acid
B20	%20 Biodiesel + %80 Diesel	(NH ₂) ₂ CO	Urea
B40	%40 Biodiesel + %60 Diesel	NH ₃	Ammonia
B60	%60 Biodiesel + %40 Diesel	NO	Nitrogen Oxide
BET	Brunauer-Emmett-Teller	NO ₂	Nitrogen Dioxide
CO(NH ₂) ₂	Urea Solution	NO _x	Nitrogen Oxides
CO	Carbon Monoxide	Ppm	Part per million
Cpsi	Cell per square inch	PM	Particulate Matter
D	Diesel	Pt	Platinum
DOC	Diesel Oxidation Catalyst	SCR	Selective Catalytic Reduction
HC	Hydrocarbon	SO ₂	Sulphur Dioxide
HNO ₂	Nitrous Acid	TiO ₂	Titanium Dioxide
		V ₂ O ₅	Vanadium Pentoxide
		WO ₃	Tungsten Trioxide

rate, compression ratio, injection advance etc., performance of diesel engine can be improved and fuel consumption can be reduced by 5% [4].

NO_x emissions are eliminated in the SCR system with a reductant and catalyst. The most commonly used reductant in SCR system is ammonia [5]. To prevent the self ignition of ammonia because of high exhaust temperature, it cannot be forwarded directly to exhaust gas and the urea solution (CO(NH₂)₂) is used in applications. The main reactions taking place in the SCR system are presented in equations below.



Among these equations, the most efficient conversion is achieved in the realization of the reaction in Equation (1). This reaction occurs when a suitable DOC catalyst is used before the SCR catalyst. The DOC converts the NO emissions to NO₂ form. The aim of this conversion is to equalize the NO and NO₂ content in the exhaust gas content. Thus, the SCR system provides maximum NO_x conversion efficiency.

V₂O₅-WO₃/TiO₂ and Fe-zeolites are the most commonly used catalyst types in SCR applications [6]. In addition to these catalysts, Cu-ZSM5 and Ag/Al₂O₃ catalysts can also be preferred. In particular, Ag/Al₂O₃ catalysts can exhibit high performance for HC-SCR systems which HCs used as reductant. Although V₂O₅-WO₃/TiO₂ catalyst has a common use in applications and high NO_x conversion rates at high exhaust gas temperatures, the toxic effects, high activity in SO₂ oxidation and mediocre activity at low exhaust gas temperatures constitutes its negative aspects [7]. Compared to V₂O₅-WO₃/TiO₂ catalyst, Ag/Al₂O₃ catalyst promotes relatively better resistance against SO₂ and preferable catalytic activity at low temperatures besides being non-toxic [8].

Many studies on different types of catalysts and reductants in SCR systems have been performed in the literature. These studies focused on the characterization of catalyst and/or reductants and NO_x conversion performance in general [9–15].

In these days that the environmental and economic concerns are increasing day by day, researches on alternative fuels for diesel are of great importance. Undoubtedly, biodiesel produced from renewable sources is the most widely used alternative fuel for diesel. Biodiesel is nontoxic and biodegradable fuel and contains no sulphur and no aromatic hydrocarbons. With the use of biodiesel in diesel engine, emission characteristic of diesel engine in terms of CO, HC and PM can be improved in general without significant change in engine performance. On the other hand, it is an accepted opinion that biodiesel causes some increase in NO_x emissions because of oxygen content, lower compressibility, lower soot formation and higher adiabatic flame temperature

compared to diesel [14,15]. The oxygen content of biodiesel increases the reaction of O₂ with N₂ to produce NO_x. The lower compressibility of biodiesel compared to diesel increases pressure more quickly in mechanical direct injection system. The rise of pressure impels ejecting the fuel into the cylinder earlier. Thus, biodiesel has a longer residence time which allows fuel and air mix more thoroughly leading more intense combustion, heat release and hence higher NO_x emissions. The lower soot formation prevents the radiative heat release which decrease combustion end temperature in cylinder. Further, unsaturated compounds of biodiesel cause increase in adiabatic flame temperature.

Many studies have been carried out to prevent the NO_x formation caused by biodiesel. The use of fuel additives such as alcohols, metal nanoparticles, carbon nanotubes etc. with biodiesel to decrease NO_x have been tried in many researches [15–19] and a sum of decreases in NO_x emissions were obtained. On the other hand, the use of SCR system on engine exhaust pipe line provides exact solution to this problem. Xiaoyan and et al. [20] tested biodiesel-ethanol-diesel blends in a diesel engine equipped with HC-SCR systems. Also, they adapted DOCs to control HC emissions after HC-SCR catalyst which include ethanol as reductant and Ag/Al₂O₃ as catalyst. With this combination they obtained significant results to control NO_x and PM emission without Diesel Particulate Filter (DPF). Vallinayagam et al. [21] studied on emission characteristics of a diesel engine fuelled by pine oil biofuel using SCR and catalytic converter. The use of SCR and catalytic converter increase the NO_x conversion rates as 15.2% and 32.4% for diesel and B50, respectively. Zhang et al. [22] studied on the durability of biodiesel-powered engine equipped with a DOC and SCR system. They focused on durability, power and fuel economy performance of biodiesel-powered engine in this experimental study. Like the study performed by Zhang et al. [22], Iojoiu et al. [23] and Williams et al. [24] investigated the biofuels impact on the durability of the catalytic exhaust system. Fayad et al. [25] examined the effect of DOC and alternative fuels on PM characteristics of a diesel engine. Brookshear et al. [26] carried out an experimental study on Sodium (Na) exposure of emission control technologies. 20% bio- and petrol-diesel fuel with elevated levels of Na was used for running the engine in the tests. The effect of trace elements in fatty acid methyl ester biodiesel on DOC activity was worked by Granstrand et al. [27]. They found that Phosphorus (P) had poison effect on DOC which decrease its activity significantly. In other comprehensive study, DOC, DPF and SCR was exposed Na, Potassium (K) and P impurities. Catalytic results showed Na has adverse impact on oxidation of CO. On the other hand, P improved C₃H₆ conversion. Also, NO oxidation was deteriorated with all elements [23]. Also, the effects of impurities on aftertreatment systems were studied by Anguita and similar results were obtained [28].

The effect of biodiesel impurities on aftertreatment systems and the combination of biodiesel-aftertreatment systems are well-established subjects in literature. However, the variation in activity of DOC and

Table 1
Specifications of fuels used in tests.

Fuel Code/Specifications	D	B	B20	B40	B60	EN14214	EN590
Density at 15 °C (kg/m ³)	841.62	886.71	850.43	859.54	868.42	860–900	820–845
Calorific value (MJ/kg)	45.41	40.65	44.42	43.51	42.48	–	–
Cetane number	52.170	47.939	51.275	50.364	49.618	≥51	≥51
Viscosity kinematic at 40 °C (mm ² /s)	2.679	4.432	3.029	3.376	3.732	3.5–5.0	2.0–4.5
Flash Point (°C)	61	104	70	78	89	≥120	≥55
Pour Point (°C)	–14	–5	–12	–10	–8	–	–

SCR systems depending on use of biodiesel keeps up date. Also the comparison of V and Ag based catalysts to control NO_x emissions in a diesel engine fuelled by biodiesel-diesel blends is an enigma.

This experimental study is aimed to investigate the effects of biodiesel on the conversion efficiency of DOC and SCR system. To understand the impact of biodiesel blends on the performance of DOC and SCR catalysts, three different ratios of biodiesel (20%, 40%, 60%) were used in the tests. Conventional V₂O₅-WO₃/TiO₂ catalyst and Ag/Al₂O₃ catalyst with urea reductant were used in tests to catalytic reduction of NO_x emissions while Pt/Al₂O₃ catalyst was used for oxidation the CO and HCs. Especially, the conversion performance of catalysts in lean conditions with the use of biodiesel was scrutinized. The conversion performance of the V₂O₅-WO₃/TiO₂ and Ag/Al₂O₃ catalyst used in SCR systems was also compared in the study.

2. Material and methods

2.1. Preparation and characterization of test fuels

The biodiesel used in the study was supplied commercially. It was derived from sunflower oil contained 63% linoleic acid, 27% oleic acid, 6% palmitic acid and 4% stearic acid. The production of biodiesel was carried out in condition of 6/1 methanol/oil molar ratio, 1 wt% sodium hydroxide catalyst, 60 °C reaction temperature and 2 h reaction time. It was blended with diesel in 20%, 40% and 60% ratios. While the blends was named B20, B40 and B60 according to the biodiesel ratio in the fuels, Diesel was named as “D”. Each blend was mixed in a magnetic stirrer for 15 min to prevent phase formation between fuels.

Table 1 shows the fuel properties of diesel, biodiesel and blends. Density, calorific value, Cetane number, kinematic viscosity and flash point values of each test fuel were determined. KYOTO DA-130 Portable Digital Density Tester (Kyoto Electronics Manufacturing Co., Ltd., Shanghai, China), K 40091 Kinematic Viscosity Meter (Expotech, Houston, TX), IKA WERKE Bomb Calorimeter (IKA-Werke GmbH & Co. KG, Staufen im Breisgau, Germany), ZX-440 Analyzer (ZELTEX, Maryland, USA), TANAKA Flash Point Tester and Tanaka MPC-102 (Tanaka Sci.Lim., Tokyo, Japan) were used respectively in the determination of density, viscosity, calorific value, Cetane number, flash point and pour

point values of test fuels. The Cetane number was measured by near infrared (NIR) transmission spectroscopy using ZX-440 Analyzer while flash point was determined as the lowest temperature at which the application of an ignition source causes the vapour of a sample to ignite using Tanaka Flash Point Tester. Each fuel specification was measured three times and the measured values were averaged.

The use of biodiesel with diesel fuel caused an increase in density, viscosity and flash point values, while it caused decrease in calorific value and Cetane number. Compared to diesel, the maximum increase rates achieved with B60 fuel were 3.18% for density, 39.3% for viscosity and 45.9% for flash point. The high rate of increase in viscosity is likely to create problems on the fuel system in the long run. This situation limits the rate of biodiesel use. On the other hand, the increase in flash point provides important advantages in safe use and storage of fuel. The maximum decreases in calorific value and Cetane number were obtained with B60 fuel at 6.45% and 4.97%, respectively. Decreases in the calorific value and Cetane cause reduction in combustion end temperature and pressure and hence reduction in the exhaust gas temperature. The specifications of test fuel conformed to EN14214 and EN590 standards in general.

2.2. Catalysts used in tests

In the study, 3 different catalysts were used: one DOC catalyst (Pt/Al₂O₃) and two SCR catalysts (V₂O₅-WO₃/TiO₂ and Ag/Al₂O₃). V₂O₅-WO₃/TiO₂ catalyst was coded as Va/SCR and Ag/Al₂O₃ catalyst was coded as Ag/SCR. All of the catalysts have 400 cpsi porosity and are supplied commercially. Thanks to the Pt-containing DOC catalyst, which was placed next to the engine exhaust outlet and used in all tests, CO emissions in the exhaust content were eliminated, NO emissions were converted to NO₂ form and thus the efficiency of SCR catalyst was increased. While the Pt amount in DOC catalyst is 50 g/ft³, Ag loading amount in Ag/SCR catalyst is 90 g/ft³. BET surface area of catalyst was determined by TriStar II Micrometrics Surface Area and Porosity Device. The BET Surface Area of DOC, Va/SCR and Ag/SCR catalyst were obtained as 30.3267 m²/g, 26.2497 m²/g and 95.4729 m²/g respectively. After the characterization of catalysts, they were inserted in specially designed exhaust systems.

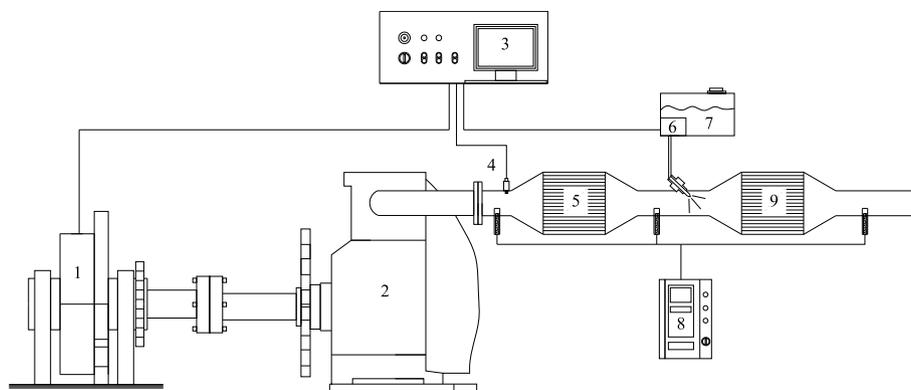


Fig. 1. Schematic Display of Experimental Setup [1.Dynamometer, 2.Engine, 3.Control Board, 4.Temperature sensor, 5.DOC, 6.Pump 7.Blue tank, 8. Emission analyzer, 9.SCR catalyst].

Table 2
Specifications of Testo 350-S gas analyzer.

Measurement	Unit	Measuring range	Resolution
CO	ppm	0-10,000	1
NO _x	ppm	0-3000	1
O ₂	% (vol)	0-25	0.01
NO	Ppm	0-3000	1

Table 3
Uncertainties of the measurements.

Parameters	Percent uncertainty (%)
CO	1.52
O ₂	0.76
NO	1.34
NO _x	1.86
Exhaust gas temperatures	1.08
Engine speed	0.14
Engine torque	0.26

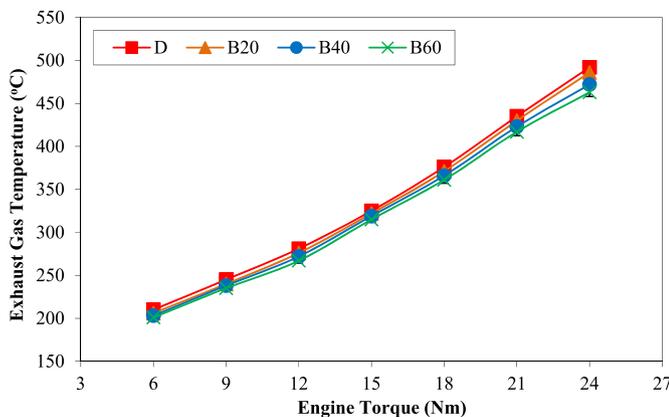


Fig. 2. The effect of biodiesel on exhaust gas temperature.

2.3. Experimental setup

The graphical drawing of the experimental setup is presented in Fig. 1. A single cylinder, water-cooled, 4-stroke, direct injection diesel engine with 661 cc stroke volume, 18/1 compression ratio, 1500 rpm maximum speed, 270 bar injection pressure at full load and 5 kW

maximum power was used in tests. Loading of engine was carried out by an electrical dynamometer connected to the engine output.

Depending on the NO_x content in the exhaust gas, spraying of the reductant was carried out via an electronically controlled pump and injector in the SCR system. 9682 KJRSE Logging Temperature Meter capable of measuring between 0 and 800 °C was used to measure the exhaust gas temperature. Control of the elements in the system and the recording of the data are provided through the control board in the experimental setup. The exhaust emissions were measured with the Testo 350-S gas analyzer (Table 2).

In the study, before the tests were carried out, the engine was heated for 15 min to reach the operating temperature. Testing of blends and diesel with different types of catalysts was performed 3 times at each torque value in the range of 6–24 Nm at 3 Nm intervals. The averages of the values obtained as a result of these tests were determined the exhaust gas temperature, O₂, CO, NO and NO_x values of the diesel engine. Uncertainty details of the measured parameters in tests are presented in Table 3.

3. Results and discussion

3.1. Variation in exhaust gas temperature

Fig. 2 shows the change in exhaust gas temperature with the use of biodiesel. Thermal efficiency and calorific value of fuels have a high effect on the exhaust gas temperature and the exhaust gas temperature is an indication of the effective heat energy of a fuel [29]. Lower conversion rates of fuel heat energy to useful work generate high exhaust temperatures. Increases in thermal efficiency with biodiesel reduce the exhaust gas temperature as a result of lower calorific value of biodiesel [30]. Lower exhaust gas temperatures signify an effective combustion and undoubtedly the superior properties of biodiesel such as having oxygen content and no aromatic hydrocarbons contributes an effective combustion. Besides, lower volatility of biodiesel due to high viscosity influences fuel atomization in the combustion chamber causing to slower combustion and low exhaust gas temperatures [31]. Compared to diesel fuel, some decreases in exhaust gas temperature was obtained with the fuels containing biodiesel (Fig. 2). The decrease in the exhaust gas temperature tended to increase as the biodiesel ratio in the mixture fuel content increased. Compared with diesel fuel, the maximum reduction in exhaust gas temperature was 5.89% with B60 fuel at 24 Nm engine torque. Considering all engine loads, the average drop rates in exhaust gas temperature were 1.48%, 2.96%, and 4.35% for B20, B40 and B60 fuels, respectively. The decreases in exhaust gas temperatures using

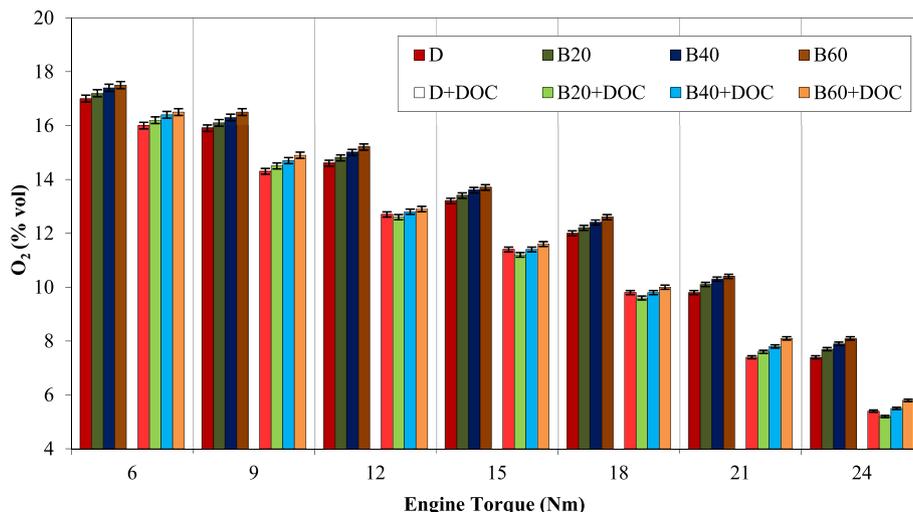


Fig. 3. Variation of O₂ content in exhaust gas with the effect of biodiesel and DOC.

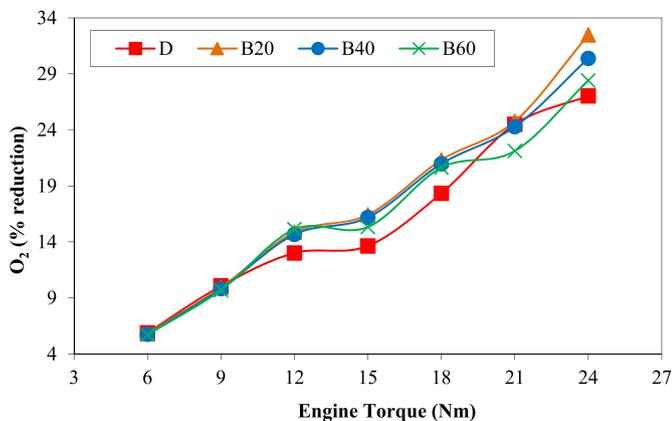


Fig. 4. O₂ reduction rates in DOC catalyst.

biodiesel were obtained by many researchers [29,31–33].

3.2. Variation in O₂ value of exhaust gas

Fig. 3 shows the change of oxygen content in exhaust gas before and after DOC with the use of biodiesel. Due to the fact that the biodiesel fuels contain oxygen and has lower stoichiometric air/fuel ratio compared to diesel, increases in the amount of O₂ in the exhaust gas have been observed with the use of biodiesel. Compared with diesel, the maximum increase in the O₂ ratio in the exhaust gas content was achieved with B60 fuel at a rate of 9.46% at 24 Nm.

Considering the O₂ reduction rates in the DOC presented in Fig. 4, It was observed that the O₂ reduction rates in low engine loads are similar for all test fuels, the O₂ reduction rates of biodiesel blends in medium engine loads are higher compared to diesel and the O₂ reduction of diesel is higher in high engine loads. O₂ reduction rate of DOC increased linearly with the increase in engine load. The reduction in O₂ content is due to using this content in oxidation of CO, HCs or PMs in exhaust gas. Strong catalytic activity in DOC at high engine loads (high temperatures) supports the reduction of O₂ content in exhaust line.

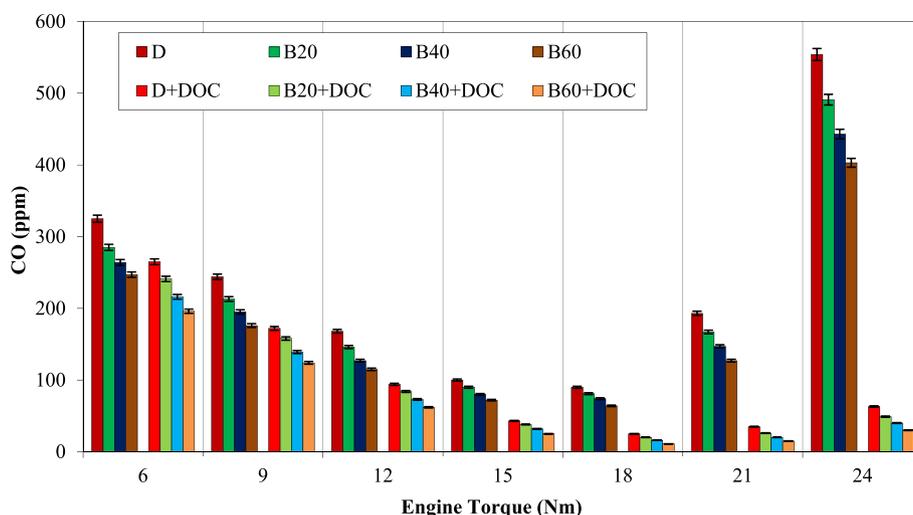


Fig. 5. Variation of CO emissions in exhaust gas with the effect of biodiesel and DOC.

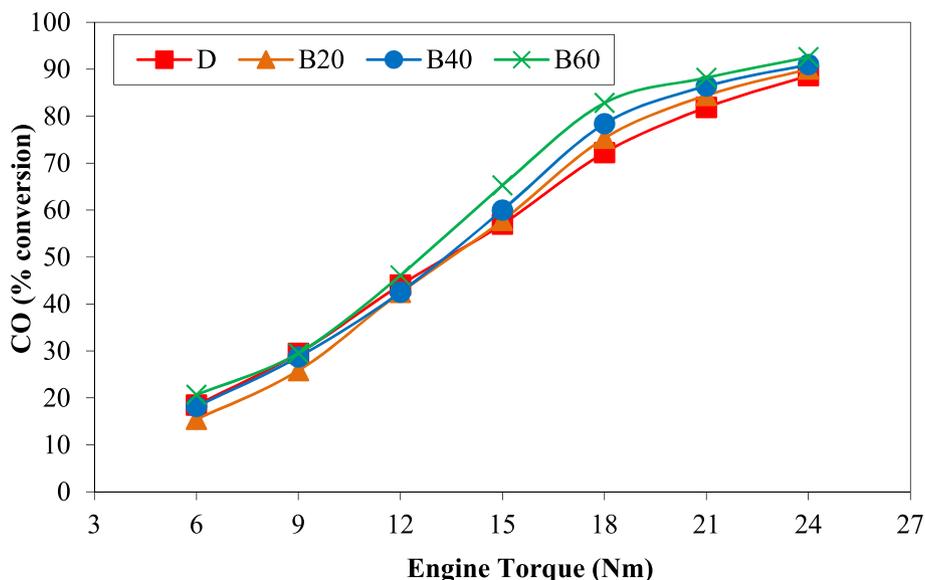


Fig. 6. CO conversion rates in DOC.

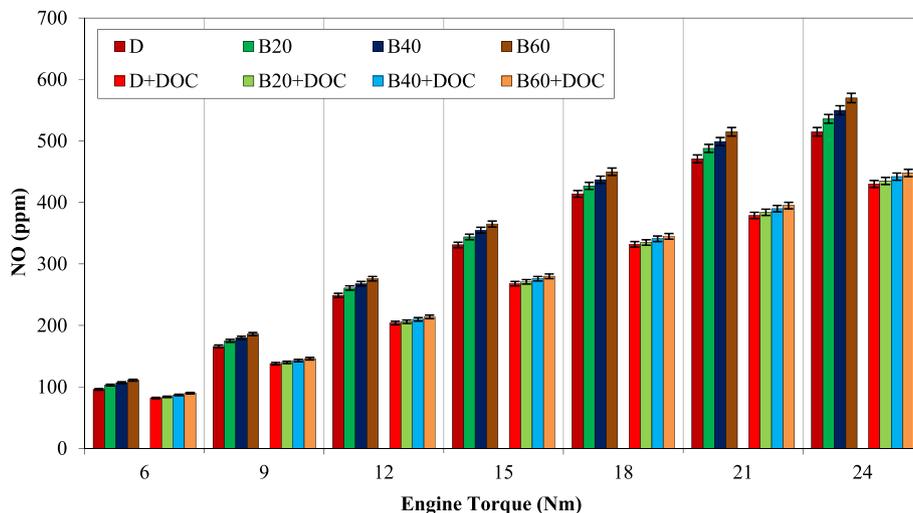


Fig. 7. Variation of NO emissions in exhaust gas with the effect of biodiesel and DOC.

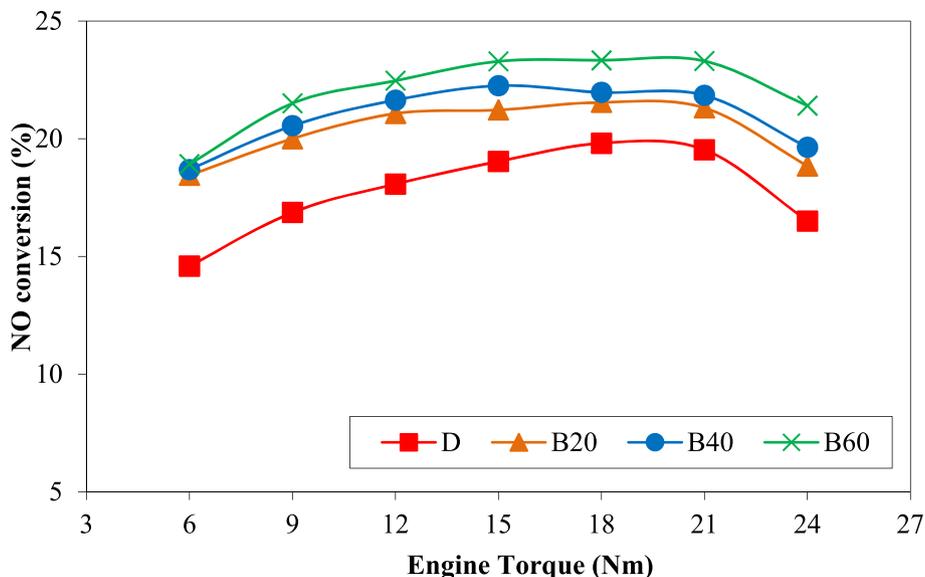


Fig. 8. NO conversion rates in DOC catalyst.

3.3. Variations in CO emission

CO emissions decreased with the use of biodiesel, compared to diesel fuel (Fig. 5). The maximum reduction in CO emissions was achieved at 34.2% with B60 fuel at 21 Nm. Considering all engine loads, average reduction values in CO emissions were measured as 11.85%, 20.70% and 28.82% for B20, B40 and B60 fuels, respectively. Compared to diesel, the fact, that biodiesel does not contain sulphur and aromatics, in other words, it is less toxic and also contains oxygen, improves diesel engine combustion efficiency and reduce pollutant emissions, especially CO emissions [34]. Also, the fact, that the carbon/hydrogen ratio in biodiesel is lower than diesel, triggers the decrease in CO emissions [35].

The use of biodiesel had a positive effect on CO conversion efficiency of DOC (Fig. 6). Increases in CO conversion efficiency of DOC have been observed with the use of biodiesel. Compared to diesel, the maximum increase in CO conversion efficiency was determined as 14.66% with B60 fuel at 18 Nm engine load. The maximum CO conversion value achieved with DOC was achieved with B60 fuel as 92.56% at 24 Nm engine load. The use of biodiesel has been observed to have a positive effect on CO emission conversion efficiency, especially in the engine load range of 15–21 Nm. Maximum CO conversion efficiency for all

tested fuels was achieved at maximum engine load (24 Nm). Exhaust gas temperature value is very important for DOC. The increase in exhaust gas temperature due to the increase in engine load has an effect that increases DOC performance.

The increases in DOC conversion activity with use of biodiesel could be explained the lower CO emissions of biodiesel compared to diesel. The high level of CO emissions restrains the CO adsorption onto the catalyst. Thus, higher CO concentration of diesel compared to biodiesel causes degradation in CO conversion of DOC.

3.4. Variations in NO emission

NO_x (NO + NO₂) emissions, which are the biggest obstacle in the use of diesel engines, are the primary pollutants that cause significant damage to human health and the environment. A high rate (80–85%) of NO_x emissions generated by combustion in diesel engines is in NO form. Fig. 7 and Fig. 8 demonstrate the effect of biodiesel on the amount of NO in the exhaust gas and the NO conversion in the DOC catalyst, respectively. Use of biodiesel caused an increase in NO emissions in the exhaust outlet while had a positive effect on NO conversion efficiency of DOC. The maximum NO value at the exhaust outlet was measured as

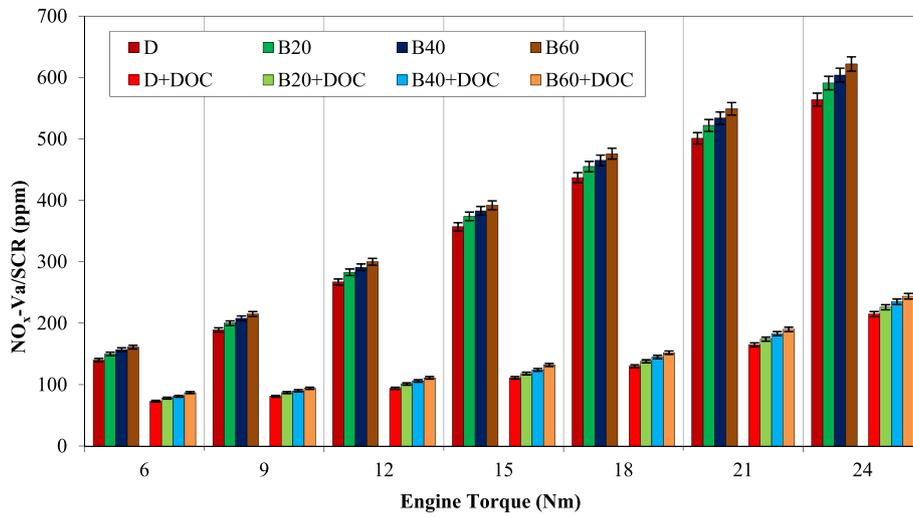


Fig. 9. Variation of NO_x emissions in exhaust gas with the effect of biodiesel and Va/SCR.

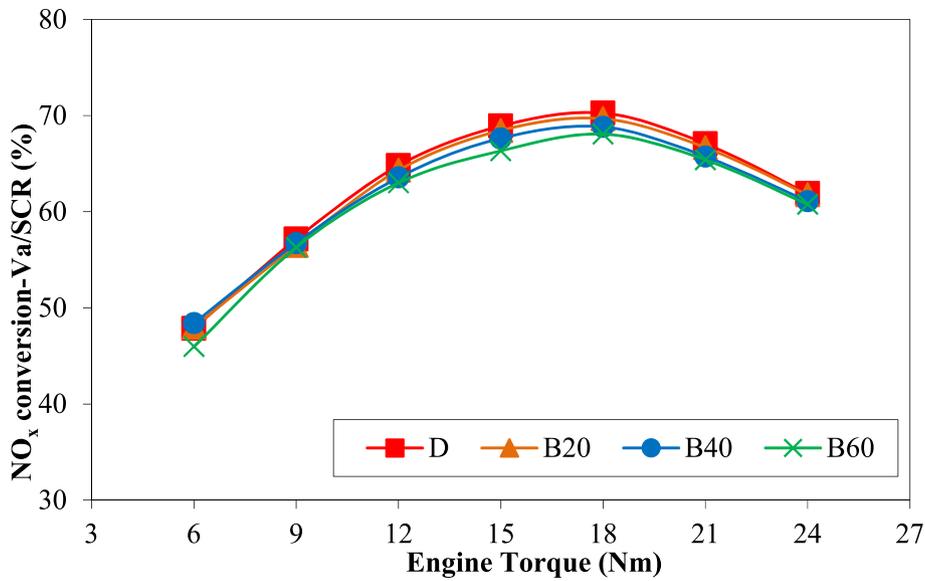


Fig. 10. NO_x conversion rates in Va/SCR catalyst.

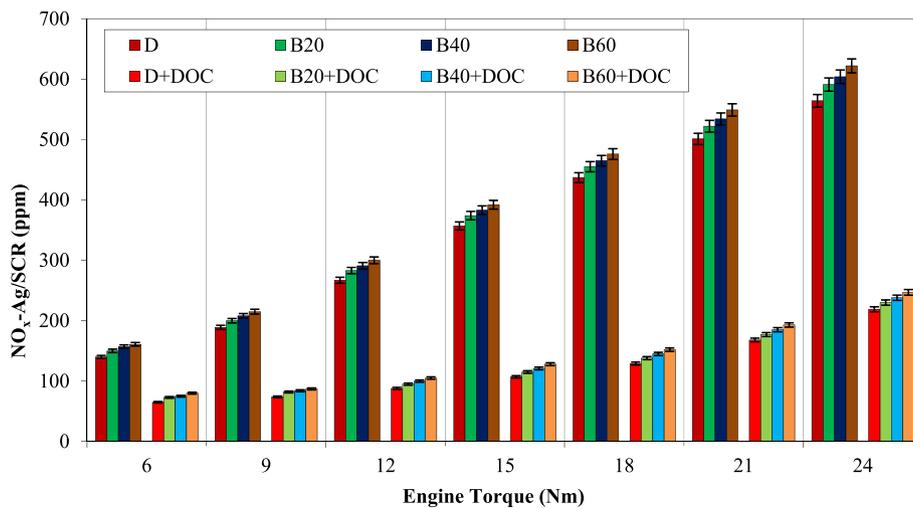


Fig. 11. Variation of NO_x emissions in exhaust gas with the effect of biodiesel and Ag/SCR.

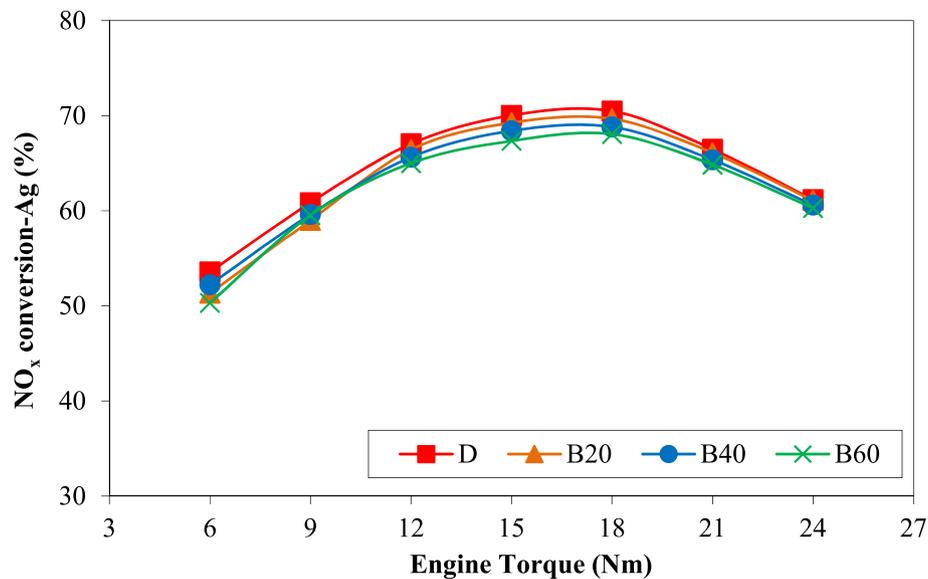


Fig. 12. NO_x conversion rates in Ag/SCR catalyst.

570 ppm at 24 Nm engine load with B60 fuel. This value is 10.68% higher than that of diesel. The maximum NO conversion rate in the DOC catalyst was achieved with B60 fuel as 23.33% at 18 Nm. Although the use of biodiesel creates an effect to increase the amount of NO in the exhaust content, the positive effect of NO conversion efficiency in DOC eliminates this disadvantage.

3.5. Variations in NO_x emission

Fig. 9 and Fig. 11 present the variation of NO_x emissions for Va/SCR and Ag/SCR respectively. NO_x emissions vary depending on the O₂ content and hydrocarbon radicals in the ambient during combustion as well as the end-combustion temperature. Increasing the amount of O₂ included in the combustion reaction means more N molecules to react and thus more NO_x formation [34]. The presence of O₂ in the content of biodiesel fuels caused some increase in NO_x emissions (Figs. 9 and 11). Also, lower compressibility, lower soot formation and higher adiabatic flame temperature of biodiesel compared to diesel increase NO_x formation [16,17]. Compared to diesel fuel, the average rate of increase in NO_x emission with the use of B20, B40 and B60 fuels was measured as 5.26%, 8.36% and 11.39% respectively. It has been observed that the reductions in NO_x (NO and NO₂) emissions are similar in other studies performed [35–38].

NO_x conversion rates for Va/SCR and Ag/SCR catalysts are presented in Fig. 10 and Fig. 12, respectively. When NO_x conversion graphics are compared, it has been seen that Ag/SCR catalyst shows better NO_x conversion performance at lower engine loads than Va/SCR catalyst. Maximum NO_x conversion rates in both catalysts were achieved at an engine load of 18 Nm. The use of biodiesel did not have a significant impact on NO_x conversion efficiency. NO_x conversion efficiency of blends was determined to be similar to that of diesel in general.

Compared to Va/SCR catalyst, the increase in conversion rates with Ag/SCR catalyst at 6 Nm obtained as 5.71%, 3.33%, 3.82% and 4.35% for D, B20, B40 and B60 respectively. Although the curves of conversion efficiencies of catalysts were converging at 18 Nm engine torque, the conversion efficiency of the Va catalyst was higher than the Ag catalyst over 18 Nm. Considering Ag/SCR catalyst, the conversion rates of Va/SCR catalyst at 24 Nm were measured higher as 0.71%, 0.68%, 0.50% and 0.48% for D, B20, B40 and B60 respectively. Maximum conversion rates of Va/SCR and Ag/SCR catalysts were obtained as 70.25% and 70.48% respectively for diesel at 18 Nm. Even though the lower conversion rates of Ag/SCR catalyst at 24 and 27 Nm compared to Va/SCR

catalyst, Ag/SCR catalyst performed well in reduction of NO_x in general.

4. Conclusion

In this study, diesel and 20%, 40% and 60% mixtures of biodiesel were prepared and after the fuel properties of each fuel were determined, they tested in diesel engine. In the tests, SCR catalyst (Va/SCR or Ag/SCR), and a DOC placed before the SCR catalyst were used at the exhaust outlet. The effects of test fuels on exhaust gas temperature, O₂, CO, NO, NO_x emissions and efficiencies of DOC/SCR catalysts were examined. The conclusions of this experimental study are listed below.

- In terms of fuel properties, the use of biodiesel led to an increase in density, viscosity, flash point values, and decrease in calorific value and Cetane number values compared to diesel.
- Exhaust gas temperatures of blends showed a downward trend, especially due to lower volatility and higher thermal efficiencies of biodiesel with lower calorific value
- The fact that the biodiesel contains O₂ and has lower stoichiometric air/fuel ratio gave rise to more O₂ in the combustion process and therefore the amount of O₂ in the exhaust gas also increases. O₂ in exhaust gas played an important role especially in converting of CO emissions by DOC.
- CO emissions decreased significantly with the use of biodiesel. Compared to diesel, the biodiesel does not contain sulphur and aromatics, contains oxygen in its content and has a lower C/H ratio, thus improving the combustion efficiency and reducing CO emissions of diesel engine.
- Biodiesel led to slightly increase in NO_x (NO, NO₂) emission.
- Improvements in DOC activity have been observed with the use of biodiesel while a significant change was not obtained in activity of SCR catalysts in general.
- The higher activity of silver catalysts at low temperatures compared to vanadium-based catalysts enabled the performance of Ag/SCR catalyst at low engine loads to be more effective than Va/SCR catalyst. In contrast, higher activity and conversion efficiency have been demonstrated with the Va/SCR catalyst at high engine loads.

Credit author statement

Ibrahim Aslan Resitoglu: achieved all contribution (Conceptualization, Methodology, Investigation, Visualization, Analysis and/or

interpretation of data, Preparation of the manuscript).

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: This work was supported by Mersin University Scientific Research Projects Unit. (Project Code: 2018-2-AP3-2964).

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References

- [1] European Environment Agency. Air quality in Europe - 2020 report. Luxembourg: EEA; 2020.
- [2] World Health Organization. Healthy environments for healthier populations: why do they matter, and what can we do? Geneva: WHO; 2019.
- [3] Resitoglu IA. NO_x pollutants from diesel vehicles and trends in the control technologies. In: Viskup R, editor. Diesel and gasoline engines. London: Intechopen; 2020. p. 161–76.
- [4] Cummins. Diesel exhaust fluid. (DEF) Q & A. Bulletin; 2009.
- [5] Palash SM, Kalam MA, Masjuki HH, Masum BM, Rizwanul Fattah IM, Mofijur M. Impacts of biodiesel combustion on NO_x emissions and their reduction approaches. *Renew Sustain Energy Rev* 2013;23:473–90.
- [6] Cho CP, Pyo YD, Jang JY, Kim GC, Shin YJ. NO_x reduction and N₂O emissions in a diesel engine exhaust using Fe-zeolite and vanadium based SCR catalysts. *Appl Therm Eng* 2017;110:18–24.
- [7] Zhang Q, Wu Y, Yuan H. Recycling strategies of spent V₂O₅-WO₃/TiO₂ catalyst: a review. *Resour Conserv Recycl* 2020;161:104983.
- [8] Doronkin DE, Khan TS, Bligaard T, Fogel S, Gabriellson P, Dahl S. Sulfur poisoning and regeneration of the Ag/γ-Al₂O₃ catalyst for H₂-assisted SCR of NO_x by ammonia. *Appl Catal B Environ* 2012;117–118:49–58.
- [9] Rogoz R, Kapusta LJ, Bachanek J, Vankan J, Teodorczyk A. Improved urea-water solution spray model for simulations of selective catalytic reduction systems. *Renew Sustain Energy Rev* 2020;120:109616.
- [10] Zhang Y, Lou D, Tan P, Hu Z. Experimental study on the durability of biodiesel-powered engine equipped with a diesel oxidation catalyst and a selective catalytic reduction system. *Energy* 2018;159:1024–34.
- [11] Kim JH, Kang SW, Nah IW, Oh I. Synthesis and characterization of Fe-modified zeolite for spin conversion of hydrogen at cryogenic temperature. *Int J Hydrogen Energy* 2015;40:15529–33.
- [12] Ström L, Carlsson P, Skoglund M, Harelind H. Hydrogen-assisted SCR of NO_x over alumina-supported silver and indium catalysts using C₂-hydrocarbons and oxygenates. *Appl Catal B Environ* 2016;181:403–12.
- [13] Resitoglu IA, Altınışık K, Keskin A. The pollutant emissions from diesel-engine vehicles and exhaust aftertreatment systems. *Clean Technol Environ Policy* 2015; 17:15–27.
- [14] Lapuerta M, Armas O, Rodriguez-Fernandez J. Effect of biodiesel fuels on diesel engine emissions. *Prog Energy Combust Sci* 2008;34(2):198–223.
- [15] Hoekman SK, Robbins C. Review of the effects of biodiesel on NO_x emissions. *Fuel Process Technol* 2012;96:237–49.
- [16] Jeevananthama AK, Nanthagopala K, Ashok B, Al-Muhtaseb AH, Thiyagarajan S, Geo E, et al. Impact of addition of two ether additives with high speed diesel-Calophyllum Inophyllum biodiesel blends on NO_x reduction in CI engine. *Energy* 2019;185:39–54.
- [17] Rajendran S. Effect of antioxidant additives on oxides of nitrogen (NO_x) emission reduction from Annona biodiesel operated diesel engine. *Renew Energy* 2020;148: 1321–6.
- [18] Ghareghani A, Asiaei S, Khalife E, Najafi B, Tabatabaei M. Simultaneous reduction of CO and NO_x emissions as well as fuel consumption by using water and nano particles in Diesel–Biodiesel blend. *J Clean Prod* 2019;210:1164–70.
- [19] Rashed MM, Kalam MA, Masjuki HH, Habibullah M, Imdadul HK, Shanin MM, et al. Improving oxidation stability and NO_x reduction of biodiesel blends using aromatic and synthetic antioxidant in a light duty diesel engine. *Ind Crop Prod* 2016;89:273–84.
- [20] Shi X, Yu Y, He H, Shuai S, Dong H, Li R. Combination of biodiesel-ethanol-diesel fuel blend and SCR catalyst assembly to reduce emissions from a heavy-duty diesel engine. *J Environ Sci* 2008;20:177–82.
- [21] Vallinayagam R, Vedharaj S, Yang WM, Saravanan CG, Lee PS, Chua KJE, et al. Emission reduction from a diesel engine fueled by pine oil biofuel using SCR and catalytic converter. *Atmos Environ* 2013;80:190–7.
- [22] Zhang Y, Lou D, Tan P, Hu Z. Experimental study on the particulate matter and nitrogenous compounds from diesel engine retrofitted with DOC+CDPF+SCR. *Atmos Environ* 2018;177:45–53.
- [23] Iojoiu E, Lauga V, Abboud J, Legros G, Bonnetty J, Da Costa P, et al. Biofuel impact on diesel engine after-treatment: deactivation mechanisms and soot reactivity. *Emission Science and Technology* 2018;4:15–32.
- [24] Williams A, Luecke J, McCormick R, Luecke J, Brezny R, Geisselmann A, et al. Impact of biodiesel impurities on the performance and durability of DOC, DPF and SCR technologies. *SAE International Journal of Fuels and Lubricants* 2011;4(1): 110–24.
- [25] Fayad MA, Herreros JM, Martos FJ, Tsolakis A. Role of alternative fuels on particulate matter (PM) characteristics and influence of the diesel oxidation catalyst. *Environ Sci Technol* 2015;49(19):11967–73.
- [26] Brookshear DW, Nguyen K, Toops TJ, Bunting BG, Rohr WF, Howe J. Investigation of the effects of biodiesel-based Na on emissions control components. *Catal Today* 2012;184:205–18.
- [27] Granstrand J, Paris RS, Nilsson M, Regali F, Pettersson LJ. Assessment of the impact of trace elements in FAME biodiesel on diesel oxidation catalyst activity after full lifetime of operation in A heavy-duty truck. *Catalysts* 2020;10:1439.
- [28] Anguita P, García-Vargas JM, Gaillard F, Iojoiu E, Gil S, Giroir-Fendler A. Effect of Na, K, Ca and P-impurities on diesel oxidation catalysts (DOCs). *Chem Eng J* 2018; 352:333–42.
- [29] Emiroğlu AO, Keskin A, Şen M. Experimental investigation of the effects of Turkey rendering fat biodiesel on combustion, performance and exhaust emissions of a diesel engine. *Fuel* 2018;216:266–73.
- [30] Al-Iwayzy SH, Yusaf T. Diesel engine performance and exhaust gas emissions using Microalgae *Chlorella protothecoides* biodiesel. *Renew Energy* 2017;101:690–701.
- [31] Anwar M, Rasul MG, Ashwath N. A pragmatic and critical analysis of engine emissions for biodiesel blended fuels. *Fuel* 2020;270:117513.
- [32] Erdoğan S, Balki MK, Aydın S, Sayın C. Performance, emission and combustion characteristic assessment of biodiesels derived from beef bone marrow in a diesel generator. *Energy* 2020;207:118300.
- [33] Ogunkunle O, Ahmed NA. Exhaust emissions and engine performance analysis of a marine diesel engine fuelled with Parinari polyandra biodiesel–diesel blends. *Energy Rep* 2020;6:2999–3007.
- [34] Khalife E, Tabatabaei M, Demirbaş A, Aghbashlo M. Impacts of additives on performance and emission characteristics of diesel engines during steady state operation. *Prog Energy Combust Sci* 2017;59:32–78.
- [35] Xue J, Grift TE, Hansen AC. Effect of biodiesel on engine performances and emissions. *Renew Sustain Energy Rev* 2011;15:1098–116.
- [36] Büyükkaya E, Benli S, Karaaslan S, Gürü M. Effects of trout-oil methyl ester on a diesel engine performance and emission characteristics. *Energy Convers Manag* 2013;69:41–8.
- [37] Gokalp B, Buyukkaya E, Soyhan H. Performance and emissions of a diesel tractor engine fuelled with marine diesel and soybean methyl ester. *Biomass Bioenergy* 2011;35:3575–83.
- [38] Hazar H. Effects of biodiesel on a low heat loss diesel engine. *Renew Energy* 2009; 34:1533–7.