Fuel 262 (2020) 116609

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Experimental investigation of the distinct effects of nanoparticles addition and urea-SCR after-treatment system on NO_x emissions in a blended-biodiesel fueled internal combustion engine

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A R T I C L E I N F O

Keywords:
Nanoparticles
$DeNO_x$ efficiency
Urea-SCR catalyst
Diesel engines
Biodiesels

A B S T R A C T

The present study reports an investigation about the distinct effects of nanoparticles addition and urea-SCR system on NO_x emissions. Also nano-additives influence on pollutants (NO_x and CO) reduction performance of a urea-SCR system is investigated. B20 blended biodiesel which contains of 20% waste frying oil biodiesel and 80% diesel has been used as the base fuel in this work. Manganese oxide and cobalt oxide nanoparticles with the mass fractions of 25 and 50 ppm were dispersed in the base fuel as nano-fuel additives. The findings showed that both studied nano-additives reduce NO_x emissions. However, the reduction level is lower compared to urea-SCR system. As well as, the results revealed that the pollutants reduction efficiency of the urea-SCR system was appreciably enhanced due to nanoparticles addition.

1. Introduction

With the considerations of fossil fuels resources and petroleum prices, alternative sources for internal combustion engines especially biodiesel-based fuels have gained much attention recently due to their availability, non-toxicity and environment-friendly properties [1,2]. However, one of their serious drawbacks is the higher NO_x emissions because of the high oxygen content [3].

NO_x is known as one of the most harmful pollutants which affects the environment through humans and animals diseases, damages to vegetation, buildings, etc. Therefore NO_x mitigation in diesel engines is currently a critical element of clean air regulations [4,5].

Studies have pointed out that it is very challenging for diesel engines alone to achieve NO_x emission levels satisfying vehicle exhaust regulations worldwide and exhaust gas after-treatment systems are typically necessary for most diesel engines powered vehicles [6]. Among the exhaust after-treatment techniques, urea-SCR (selective catalytic reduction) is one of the most promising systems which is capable of reducing NO_x emissions efficiently in diesel engines [7]. In this system, urea solution is sprayed into the hot exhaust gas stream and then decomposes into ammonia. The main NO_x reduction reaction with ammonia is given in the following formula [7]:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad (1)$$

Almost three decades ago, Seto and Yokoyama proposed using urea as the reducing agent together with a selective catalytic reduction system to reduce NO_x emissions [8]. Many researches have been conducted ever since to develop this technique in order to enhance the NO_x reduction performance of this system [4,7,9]. Koebel et al. revealed that perfect mixing between exhaust gas stream and urea solution may lead to very high levels of NO_x reduction [10]. Hirata et al. developed the catalyst material to enhance the catalytic performance of the urea-SCR system [11]. According to Gowthaman and Velmurugan, injecting the optimum percentage of urea solution into the hot exhaust gas resulted in maximum NO_x reduction in a biodiesel-fueled diesel engine [12]. Mehregan and Moghiman obtained the optimum design conditions for urea injection parameters in order to achieve minimum NO_x emissions from a blended biodiesel-fueled diesel engine [13].

Apart from urea-SCR system as one of the most efficient technologies to reduce NO_x emissions, nano-additives are nowadays considered as one of the best fuel additives in order to improve exhaust emissions in diesel engines [5,14]. A bunch of investigations about effect of nanoparticles addition on emissions characteristics of diesel engines fueled with biodiesel have been carried out. Basha and Anand reported that Al_2O_3 and CNT nanoparticles addition to Jatropha biodiesel fuel resulted in reduced exhaust emissions [15]. According to Selvan et al., the combined effect of CeO_2 and CNT nano-additives to biodiesel blends was to reduce harmful exhaust emissions [16]. Özgür et al. revealed that the addition of SiO_2 and MgO nanoparticles to RME (rapeseed oil methyl ester) biodiesel fuel resulted in lower NO_x and CO emissions

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https://doi.org/10.1016/j.fuel.2019.116609
Received 17 June 2019; Received in revised form 31 August 2019; Accepted 6 November 2019
Available online 15 November 2019

Table 1
Technical specifications of the engine.

Engine type	Inline, 4-cylinder, 4-stroke, water-cooled
Bore (mm)	104
Stroke (mm)	118
Displacement (cc)	4009
Compression ratio	17.9:1
Rated power (kW/rpm)	38/1500

[17]. Sharma et al. findings indicated that lower exhaust emissions were achieved with the addition of CeO_2 and CNT nanoparticles to biodiesel blended fuels [18]. According to Chandrasekaran et al., adding copper oxide (CuO) nanoparticles to Mahua Oil biodiesel-blends led to the reduction of exhaust emissions from a single cylinder diesel engine [19]. Wu et al. reported that using carbon coated aluminum (Al@C) nanoparticles as additives in palm oil biodiesel could reduce NO_x and CO emission significantly [20]. Ramesh et al. revealed that alumina nanoparticles addition to poultry litter oil B20 biodiesel blend resulted in a significant reduction in CO and NO_x emissions [21]. According to Muthusamy et al., iron oxide (Fe_3O_4) nanoparticles addition to B20 blended biodiesel reduced the harmful emissions from diesel engines [22].

Mehregan and Moghiman studied the influence of the simultaneous use of urea-SCR system (as a post-combustion technique) and nanoparticles addition (as a pre-combustion method) on NO_x emissions at the optimum urea injection parameters in a blended-biodiesel fueled diesel engine [23]. They reported that using nano-additives together with urea-SCR system resulted in less NO_x emission from a diesel engine. However, the amount of each technique influence on NO_x reduction was not clear. It was likely that the studied nanoparticles would not have the desirable effect on NO_x reduction solely and acted only as catalysts in urea-SCR system to accelerate the NO_x conversion in this system. Moreover, the influence of nanoparticles addition on NO_x reduction efficiency of urea-SCR system had not been quantified. On the other hand, according to the literature, the CO emission at downstream of the urea-SCR system is slightly higher compared to the upstream emission [24]. Therefore, if nano-addition is going to be considered as an efficient technique to develop the urea-SCR system in order to obtain a higher NO_x reduction performance, it would be challenging if this method could also enhance the CO conversion efficiency of the system.

Table 2
Specifications of diesel and biodiesel.

Property	Fuel type	
	Diesel	Biodiesel
Density at 15 °C (kg/m^3)	818	880
Kinematic viscosity at 40 °C (mm^2/s)	2.65	4.79
Net calorific value (MJ/kg)	42.3	38.7
Cetane number	47.3	62
Flash point (°C)	61	147
Cloud point (°C)	− 7	− 3.4

Table 3
Properties of the nanoparticles.

Nanoparticle	Symbol	Particle size (nm)	Purity (%)
Cobalt oxide	Co_3O_4	10–30	99
Manganese oxide	Mn_2O_3	30	99.2

This study aims to distinct the effectiveness of nanoparticles addition as pre-combustion method and urea-SCR system as post-combustion technique on NO_x emissions. As well as, another objective of this research is to evaluate the nanoparticles addition influence on pollutants (NO_x and CO) reduction efficiency of urea-SCR system which has not yet been investigated.

2. Experimental setup and procedure

2.1. Test setup

The engine used in this study was a 4-cylinder, water-cooled diesel engine mounted to an electrical generator. The generator was then connected to a loading device to apply load on the engine. A K-type thermocouple was used to record exhaust gas temperature, while the

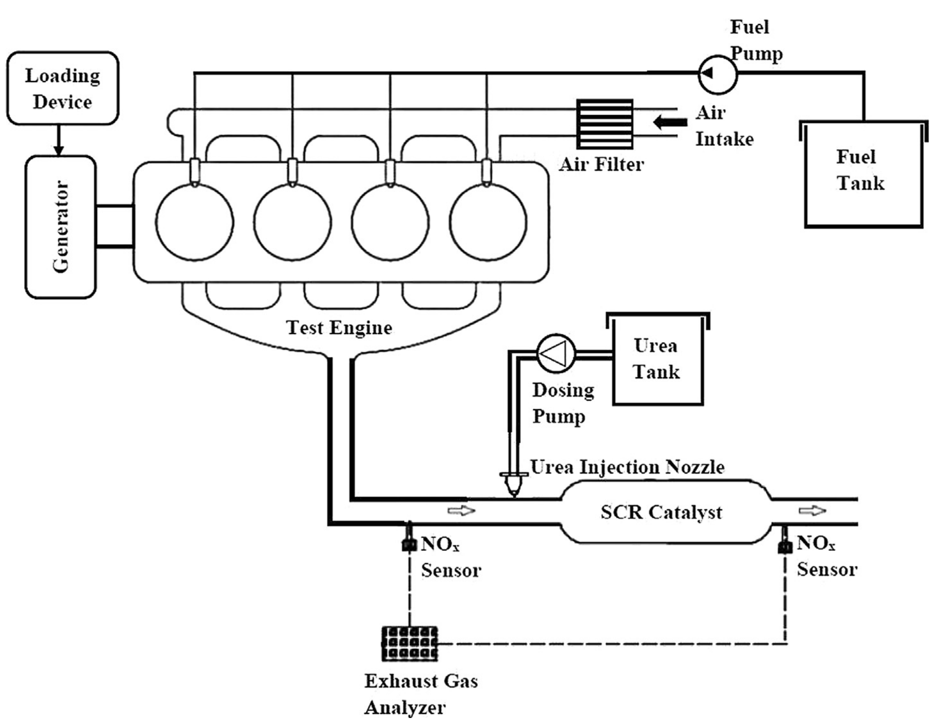

Fig. 1. Schematic layout of the test setup.

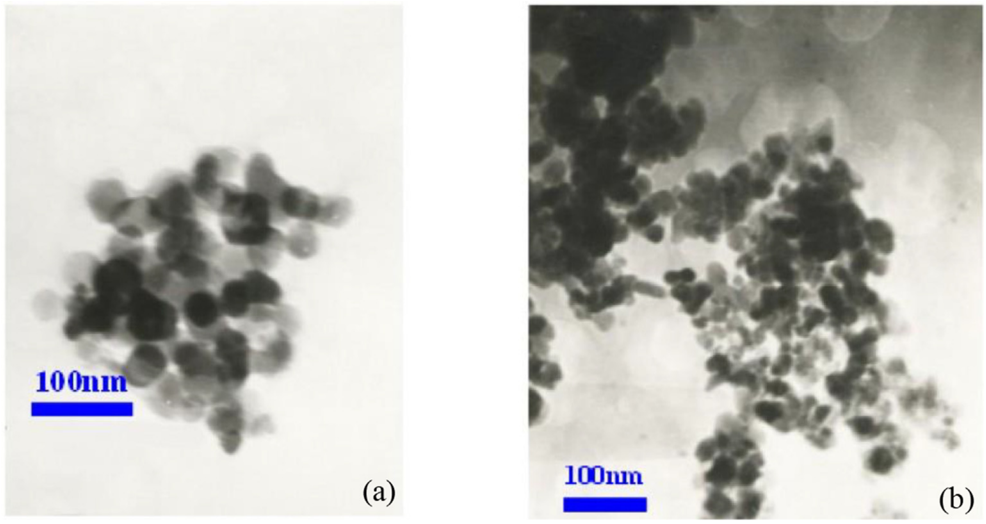

Fig. 2. TEM image of the nano-additives (a) Cobalt oxide (b) Manganese oxide.

Table 4
The uncertainty for the measured quantities.

Quantity	Range	Resolution	Uncertainty
Engine speed	10 – 99,999 rpm	1 rpm	± (0.04% +2)
Exhaust gases temperature	0 – 1000 °C	0.5 °C	± 2 °C
NO	0 – 4000 ppm	1 ppm	± 5%
NO_2	0 – 500 ppm	0.1 ppm	± 5%
CO	0 – 10,000 ppm	1 ppm	± 5%

exhaust emissions were measured utilizing a Testo 350 flue gas analyzer. In order to measure the distinct effects of nano-additives and urea-SCR system on NO_x emission and also to calculate the pollutants reduction efficiency, exhaust emission was measured both upstream and downstream of the urea-SCR. Technical specifications of the engine are listed in Table 1.

The test engine has been equipped with an urea-SCR after-treatment system, while urea injection parameters were set at the optimum working conditions determined by Mehregan and Moghiman [13]. The schematic diagram of the experimental setup is depicted in Fig. 1.

2.2. Fuel preparation

Biodiesel and its blends have received much interest recently owing to their potential to be used as alternative fuels in diesel engines [1,2,25]. Biodiesel blends are named with a letter B followed by the volume percentage of biodiesel fuel [26]. The most common blends are B2, B5 and B20 [27]. It is generally believed that blends of up to 20% biodiesel with diesel fuel (B20) can be used in internal combustion engines without any modifications made [26].

Biodiesel can be produced from various feedstocks which these sources differ from region to region. The main raw materials to produce biodiesel are vegetable oils, animal fats and waste oils [27]. Used cooking oil is one of the cost-effective sources for biodiesel production. Using wastes as the biodiesel feedstock not only reduces the raw material cost, but also solves the waste disposal issue [28].

B20 blended biodiesel which contains of 20% waste frying oil biodiesel and 80% ultra-low sulfur diesel fuel was used as the base fuel in this study. The main properties of the fuels are presented in Table 2.

2.3. Nanomaterials

Two oxygenated nanoparticles, manganese oxide (Mn_2O_3) and cobalt oxide (Co_3O_4), were used as nano-additives in the present investigation. The nanoparticles have been procured from US Research Nanomaterials, Inc. The main properties of nanoparticles are listed in Table 3. Also, the TEM images of nano-additives are presented in Fig. 2.

In this study, two-step method was used for preparing nanofluids. First, manganese oxide and cobalt oxide nanoparticles were dispersed with the mass fractions of 25 and 50 ppm to the base fuel. Then, the suspensions were kept in an ultrasonic bath for around half an hour to enhance the stability of the fuel blends. In order to avoid any sedimentation of nanoparticles, the prepared nanofuels were used right after preparation. However, no obvious sedimentation was observed after several hours.

2.4. Test procedure

Each test was performed by starting the engine with neat diesel fuel at zero load condition and allowing to warm up. Then, after switching the fuel to test fuel, the experiments were carried out by applying the load progressively at constant speed of 1500 rpm. After reaching a stable condition, the appropriate quantities have been measured. To ensure the repeatability of the observed results, each test has been performed three times under the identical conditions and each recorded data was the average value of three quantities. The uncertainty values are presented in Table 4.

3. Results and discussions

The distinct and combined effects of nanoparticles addition and urea-SCR system on NO_x emission are depicted in Fig. 3. From this Figure, it is evident that in the absence of urea-SCR system, the studied nanoparticles have the potential of reducing NO_x emissions. The reason is that metallic-base structures of Mn_2O_3 and Co_3O_4 nanoparticles enhance heat transfer in the combustion chamber and consequently decrease the peak temperature which leads to NO_x reduction [17]. However according to this figure, urea-SCR system is more effective in reducing NO_x emissions compared to studied nano-additives. The NO_x reduction in this system occurs according to Eq. (1). It is evident that the simultaneous use of nanoparticles addition and urea-SCR system has a greater effect on NO_x reduction than either of the methods alone. The reason is that metal oxides nanoparticles of Mn_2O_3 and Co_3O_4 act as catalysts in urea-SCR system and enhance the NO_x conversion in this system. Fig. 3 also reveals that increasing the dosing level of both nanoparticles in the base fuel results in further reduction of NO_x emissions. As well as according to this figure, cobalt oxide nanoparticles show better NO_x reduction compared to manganese oxide nano-

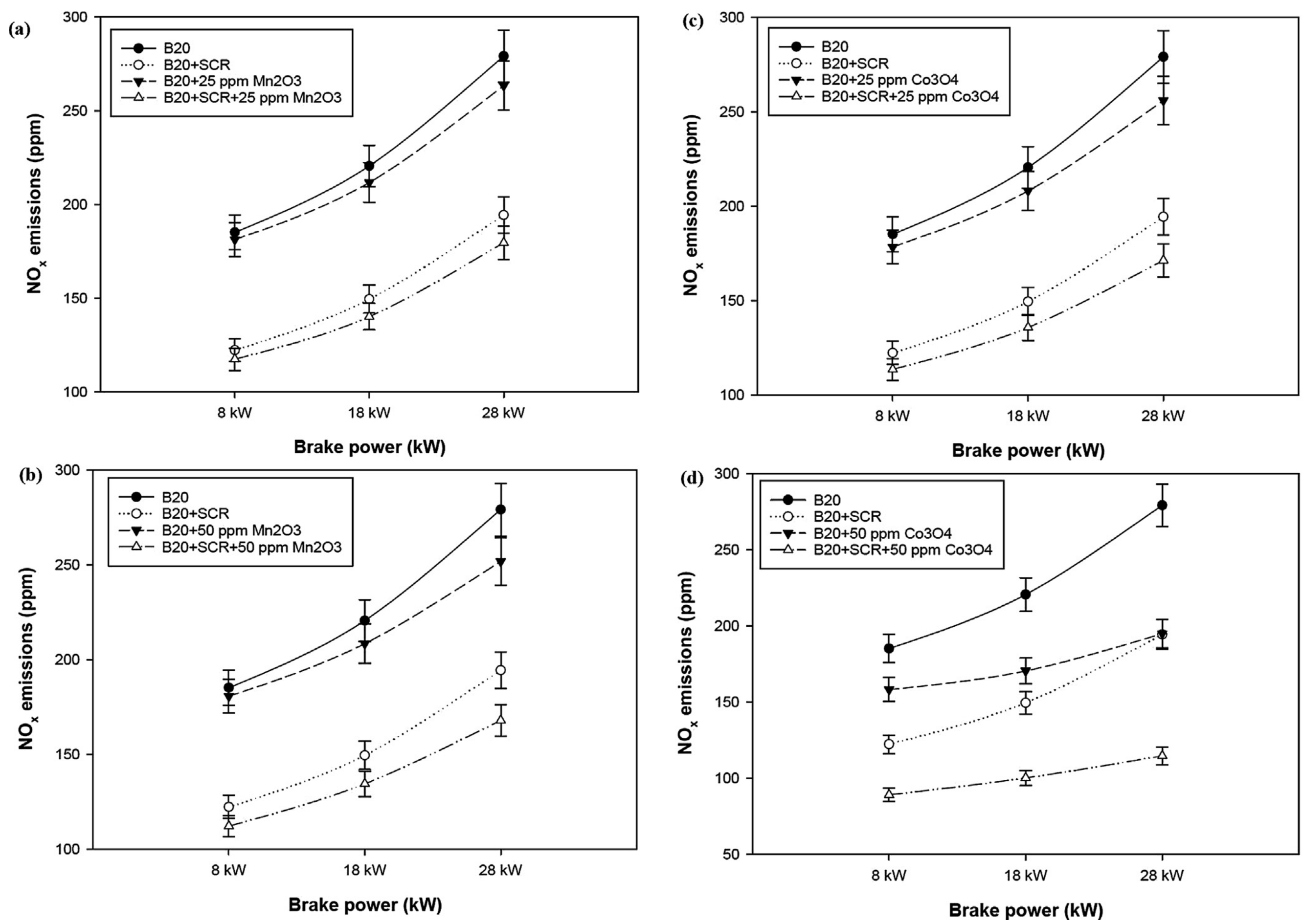

Fig. 3. The distinct and combined effects of nanoparticles addition and urea-SCR system on NO_x emission: a) 25 ppm Mn_2O_3, b) 50 ppm Mn_2O_3, c) 25 ppm Co_3O_4, d) 50 ppm Co_3O_4.

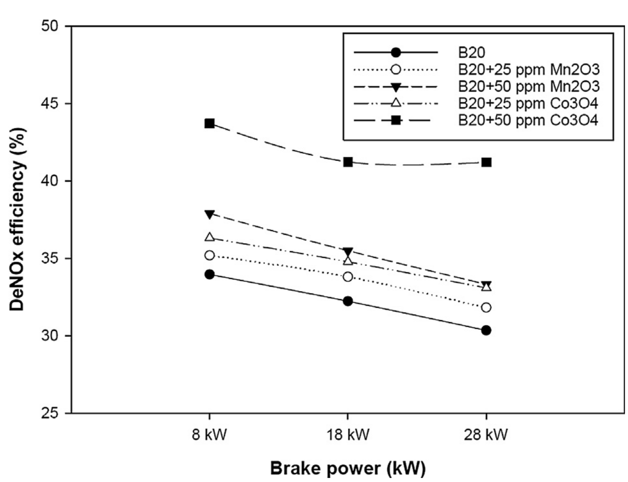

Fig. 4. Variation of $DeNO_x$ efficiency with load for different fuel blends.

additives. This is because of the remarkable thermal properties of cobalt oxide resulting in more heat transfer and lower peak temperature which leads to less NO_x emissions [29].

In order to measure the influence of nano-additives on NO_x reduction efficiency of urea-SCR system, the $DeNO_x$ performance - the efficiency of removing nitrogen oxides - of the system has to be calculated. The pollutant conversion efficiency of the SCR system is given by following equation [24,30]:

$$\textit{Pollutant conversrion performance} = \frac{\textit{Upstream emission} - \textit{Downstream emission}}{\textit{Upstream emission}} \times 100 \tag{2}$$

The comparison of $DeNO_x$ efficiency at different load conditions for B20 and B20 with nano-additives is illustrated in Fig. 4. It has been observed that the addition of both nanoparticles to B20 led to an effective increment in the $DeNO_x$ efficiency. This is because Mn_2O_3 and Co_3O_4 nanoparticles act as catalysts and enhance the NO_x conversion reaction inside urea-SCR by absorbing oxygen [23]. Thus, nanoparticles addition to the base fuel can be considered as an efficient method to enhance the $DeNO_x$ efficiency of the urea-SCR system. At each engine load condition, the $DeNO_x$ efficiency enhances more with increasing the mass fraction of nanoparticles in the base fuel.

Fig. 5 presents the percentage improvement of $DeNO_x$ efficiency of nano-fuels compared to B20 at different load conditions. From this figure, it is clear that cobalt oxide nanoparticles show better improvement in $DeNO_x$ efficiency compared to manganese oxide nano-additive. Adding 50 ppm Co_3O_4 to B20 resulted in about 35% enhancement in $DeNO_x$ efficiency at maximum load condition while the improvement in $DeNO_x$ efficiency was around 12% at the same concentration of Mn_2O_3.

The CO pollutant conversion efficiency of B20 and B20 with nano-additives at different load conditions are compared in Fig. 6. As illustrated in this figure, the reduction efficiency of CO emissions for B20 is negative, because the downstream CO emission is slightly higher compared to the upstream emission. This is ascribed to the fact that very few hydrocarbons inside SCR produce CO instead of CO_2 during their oxidation [24]. It is evident from Fig. 6 that by adding Mn_2O_3 and Co_3O_4 nanoparticles to B20, the reduction efficiency of CO emissions is

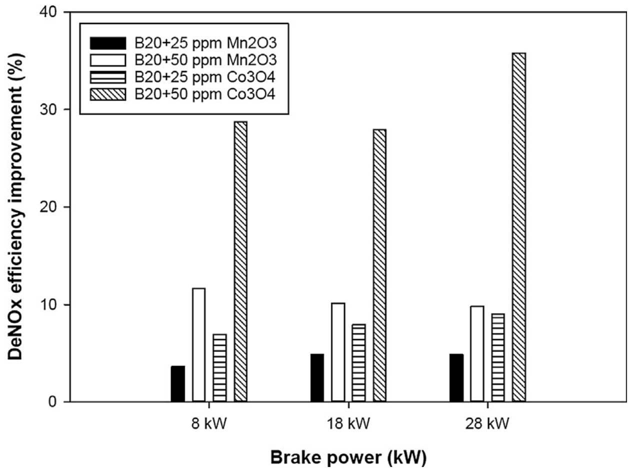

Fig. 5. Percentage improvement of $DeNO_x$ efficiency for different nano-fuels compared to B20.

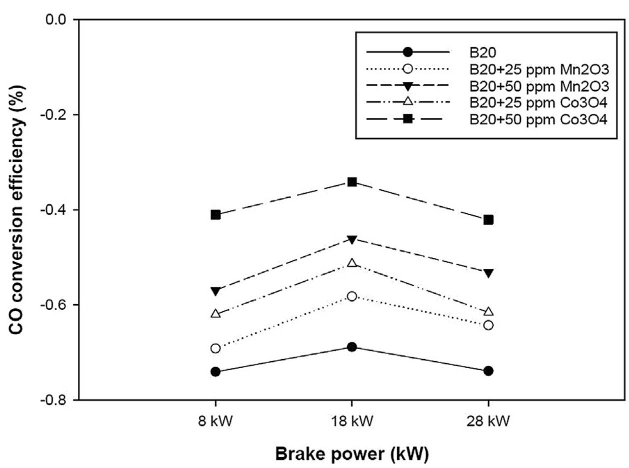

Fig. 6. Variation of CO conversion efficiency with load for different fuel blends.

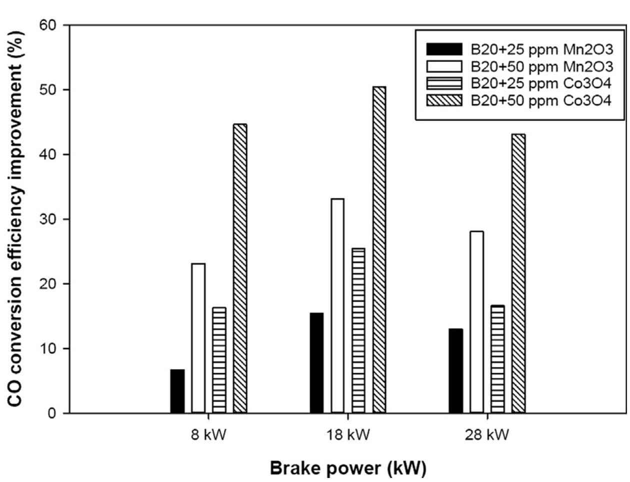

Fig. 7. Percentage improvement of CO conversion efficiency for different nano-fuels compared to B20.

enhanced. The reason is that nanoparticles behave as oxygen donating catalyst and reduce CO emissions by the oxidation of CO inside the urea-SCR system [23]. Further improvement of CO conversion efficiency is occurred by increasing the dosing level of nanoparticles in the base fuel.

Fig. 7 shows the percentage improvement of CO conversion efficiency of different blends with respect to B20 for different brake powers. As illustrated in this figure, Co_3O_4 nanoparticles have the stronger influence on CO conversion improvement at all brake powers compared to Mn_2O_3 nanoparticles. According to Fig. 7, at maximum load condition there is nearly 45% improvement in CO conversion efficiency at 50 ppm concentration of Co_3O_4, while the enhancement efficiency is about 30% for Mn_2O_3 at the same concentration.

4. Conclusions

The distinct effects of Mn_2O_3 and Co_3O_4 nanoparticles addition (as pre-combustion method) and urea-SCR system (as post-combustion technique) on NO_x emissions have been investigated experimentally. As well as, the influence of nanoparticles addition on the pollutants (NO_x and CO) reduction efficiency of the urea-SCR system has been studied.

The results indicate that manganese oxide and cobalt oxide nanoparticles addition to B20 blended biodiesel leads to lower NO_x emissions due to heat transfer enhancement and decreasing the peak temperature. However, the effectiveness of urea-SCR system in NO_x reduction is more appreciable. Results confirmed that the simultaneous use of nanoparticles addition and urea-SCR technology has a stronger influence on NO_x reduction than either of the techniques alone. This is due to the catalytic effect of the studied nanoparticles which enhances the NO_x conversion reaction inside the SCR system. As well as, the findings show that nanoparticles addition has considerable effect on pollutants reduction performance of the urea-SCR system. According to the test results, both nanoparticles improve the pollutants reduction efficiency of the SCR system and increasing the dosing level of nanoparticles results in more improvement in the reduction performance. However under all conditions, Co_3O_4 nano-additives show better enhancement in comparison with Mn_2O_3 nanoparticles because of its remarkable thermal properties.

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