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Iranian (Iranica) Journal of Energy & Environment
Journal Homepage: www.ijee.net
IJEE an official peer review journal of Babol Noshirvani University of Technology, ISSN:2079-2115

Role of Nanoparticles as Performance and Emission Improver of Compression Ignition Engine Fuels: An Overview

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P A P E R I N F O

Paper history:
Received 02 May 2019
Accepted in revised form 24 June 2019

Keywords:
Compression Ignition Engine Fuels
Emission Characteristics
Nanoparticles
Performance

A B S T R A C T

Applications of nano-scaled energetic materials in diesel and diesel-biodiesel blends as catalytic agents have emerged contemporarily in pace to develop an efficient and eco-friendly alternative fuel for compression ignition (CI) engines. Inclusion of nanoparticles as additives for CI engine fuels promises as overall improver of engine performance and emission characteristics. However, simultaneous control on engine performance parameters and emission characteristics is usually difficult. Dispersion of nano-additives improves combustion efficiency by altering specific fuel properties of diesel. Average particle size of 40-50 nm facilitate greater surface-to-volume ratio, hence ensure more complete combustion through further chain reactions during combustion. Nanoparticles as catalytic agents in diesel and its proportionate blends have recently emerged as game changer but their potential is in-fact not fully explored for market acceptability. The following are the major challenges that are to be considered in future researches: (a) There is a need of on-road testing in real ambient conditions, (b) Effects of exhaust emission fuelled with nanocatalysts on human breathing, (c) Overall effects on diesel engines of agricultural tractors and other heavy earth moving machines which are designed for high load factors, and (d) Effects of such modified fuels on driving habits of consumers.

doi: *10.5829/ijee.2019.10.02.06*

INTRODUCTION

Performance of diesel-powered vehicles is remarkable which made diesel engines (D-engines) became popular in past two decades. D-engines have shown their importance in all the major sectors, such as transportation, power industries, agricultural tractors and machines etc., owing to their fuel economy, reliability, sturdiness and rigidity [1]. In present, most of the medium and heavy-duty vehicles are powered by diesel fuel worldwide [2]. This is no-more surprise to state that the life of diesel fuel on earth is finite. Moreover, the usage of diesel has some devastating effects on our environment due to harmful exhaust emissions such as unburned hydrocarbon (HC), carbon-monoxide (CO), sulphur oxides (SO_x) and soot carbon (C_{soot}) [3]. Therefore, researches are more intended to develop alternative fuels these days.

Over the past three decades, several efforts have been made to develop alternative fuels from the plantation of agricultural based energy crops and other feed-stocks [1]. Biofuels produced from vegetable oils and non-edible plants has provided a vital alternative against diesel. Production of biodiesel and their proportionate blending with base fuel (diesel) have drawn researchers' attention in recent years [4] which has also proven successful to replace the dependency solely on diesel fuel at some extent. Liquid biofuels (e.g., bioethanol, biobuthanol and biodiesel) are capable of propelling both on-road and off-road transporting vehicles with considerable reduction of harmful emissions like HC, CO, SO_x and C_{soot} [5]. However, usage of biodiesel has also exhibited lower engine performance, in terms of torque and power, due to its lower net calorific values as compared to conventional diesel [6]. Moreover, the use of biodiesel promotes nitrogen oxide (NO_x) emission due to high peak temperature during the combustion process inside the engine cylinder (Figure 1) [7].

Xue et al. [8] suggested blending of biofuels with neat diesel in suitable proportion to improve performance and

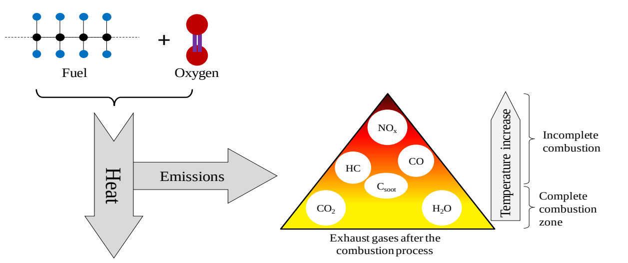

Figure 1. Formation of exhaust gases during combustion

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exhaust gas emissions from compression ignition (CI) engines which require slight modifications in engine designs. Abu-zaid [7] studied the performance of a direct injection (DI), single-cylinder D-engine using water-in-diesel emulsion with 5, 10, 15 and 20 water-to-diesel ratio and reported that the increase in brake thermal efficiency (BTE) of D-engine proportional to the concentration of water-diesel ratio. The improved overall emission characteristics were also achieved, including lower NO_x emission, due to lower exhaust gas temperature [9]. Similarly, additives are also used with diesel and biodiesel blends which improve the ignition quality essentially by altering specific fuel properties. For example, Inclusion of organic based synthesized manganese (Mn) improve the cetane number, flash point and viscosity of diesel, hence ensures more complete ignition of diesel during combustion [10].

Ambrozik et al. [11] enlisted basic requirements of fuel additives which are as follows: (a) Catalysts added to fuels should reduce overall emission of harmful gases during the combustion. (b) Catalysts should maintain the chemical stability of fuel. (c) Catalysts use in fuel should not affect engine operating conditions. (d) Catalysts should improve specific fuel properties. Keskin et al. [12] investigated the effect of metal based-biodiesel blend B60 (containing 40 and 60% conventional diesel and tall oil, respectively) additives as combustion catalysts. A considerable improvement was reported in some specific fuel properties, such as flash point, pour point and viscosity, depending on the concentration of additives mixed with prepared fuel blend. Moreover, a significant decrease in CO and NO_x emission with reduced smoke opacity.

In the pace of developing efficient and eco-friendly fuels for CI engines, applications of nano-scaled energetic materials in diesel and diesel-biodiesel blends as catalytic agents have also emerged contemporarily. Use of nanoparticles as fuel additives are in-fact unexplored today. However, many researchers have investigated performance and emissions characteristics of D-engines by using the inclusion of both individual nanoparticles and also with numerous combinations of more than one type of nanoparticles. Kao et al. [13] investigated change in combustion process due to inclusion of aqueous aluminium (Al) nano-additive, covered with oxide layers, in diesel fuel and reported an overall improvement in exhaust emission. Mehta et al. [14] formed oxides of Al, Fe and B as nano-catalysts dispersed with neat diesel fuel and concluded that nanofuels reduced ignition delay with a significant increase and decrease of BTE and overall emissions, respectively. Prabu [15] investigated the effect of inclusion nanocatalysts of more than one type i.e., alumina (Al_2O_3) and carbon nanotubes (CNTs), with neat diesel and diesel-biodiesel blends in different proportions. In addition to nanocatalysts based diesel fuel blends, researches have tested numerous combinations of hybrid fuels as summarised in Table 1.

EFFECTS OF NANOCATALYSTS ON SPECIFIC FUEL PROPERTIES

Determination of diesel fuel properties contributes a very crucial role to examine the acceptability of diesel in CI engines during combustion [16]. Cetane number (CN) is an indicator of ignition delay (time between the fuel injection and the spontaneous ignition of fuel) of diesel [17]. CN value of a diesel fuel depends primarily on its chemical composition. In D-engine, the desirable CN value is established by the requirements of good ignition quality at light loads and low temperatures [18]. De et al. [19] observed that the presence of ethanol and ethyl ter-butyl ether (ETBE) significantly alters the characteristics of volatility and reduces the Cetane number, impairing the fuel's performance in engine tests.

Yang et al. [20] reported that emulsion fuels 10 and 15 (water-in-diesel, 10% and 15%, respectively) exhibit higher viscosity index of 8.8 cSt and 11.4 cSt at 40ºC, respectively. Due to the same, engine power drops down significantly and consequently affects customers' driving habits. Use of nanocatalysts in emulsion fuel having 5% water displayed a significant decrease in kinematic viscosity of 7.6 cSt at 40ºC. Viscosity of emulsion fuels is higher than pure diesel but drops down faster with an increase in temperature as compared to that of diesel. Basha et al. [21] observed an increase in viscosity of 5.36 cSt in modified fuel blend consisting JBD, Al_2O_3 and CNT, as compared to pure JBD (5.25 cSt).

Density is a significant property for diesel engines, which affects the performance characteristics of engines and the other many performance characteristics like higher heating value. Cetane number is correlated against density [۲2-28]. Furthermore, the amount of fuel in the fuel injection systems is measured volumetrically, and the changes in density affect the engine output power and fuel consumption [29, 30]. Table 2 has displayed variations in essential fuel properties due to the inclusion of nanocatalysts in different diesel and diesel-biodiesel fuel blends. Chief characteristics of nanocatalysts have improved oxidation intensity due to having higher surface-to-volume ratio. The dispersion of nanocatalysts in fuel/fuel blends improve combustion characteristics mainly due to better fuel atomisation and rapid evaporation, which allow more surface area of fuel to react with oxygen molecules [15].

METHODS TO PREPARE NANOCATALYSTS MIXED FUEL BLENDS

Generally, the preparation of nanocatalysts mixed fuel blends is a two step process: (a) treatment of nanoparticles, and (b) their dispersion into fuel blends. Kao et al. [13], at first step, made an attempt on nano-scaled (40-60nm) aqueous alumina coated with thin oxide layer due to high oxidation activity of pure aluminum (Al). In second step, the oxide coated nanocatalysts were dispersed in the diesel fuel with the aid of ultrasonicator. Studies have shown that water can react with nano-scaled 'Al' powder during combustion to generate hydrogen, hence increase the combustion heat of aqueous 'Al' fuel. Hydrogen is clearly a promising alternative to hydrocarbon fossil fuels since it has higher energy efficiencies with lower emissions [31]. The catalytic activity of a metal-oxide catalyst Fe/Al_2O_3 can cause water to yield hydrogen through decomposition [32].

TABLE 1. Summery of fuel hybrids prepared using nanocatalyst(s)

Author (s)	Fuel hybrids	
	Notation	**Composition**
Keskin et al. [12]	B60	40% pure diesel and 60% biodiesel prepared from tall oil
	B60 – 4Mg	Magnesium (Mg) with B60 @ 4 µmol/L
	B60 – 8Mg	‘Mg’ with B60 fuel blend @ 8 µmol/L
	B60 – 12Mg	‘Mg’ with B60 fuel blend @ 12 µmol/L
	B60 – 4Mo	Molybdenum (Mo) with B60 @ 4 µmol/L
	B60 – 8Mo	‘Mo’ with B60 fuel blend @ 8 µmol/L
	B60 – 12Mo	‘Mo’ with B60 fuel blend @ 12 µmol/L
Tewari et al. [33]	Diesel	Pure diesel
	MOME	Honge Oil Methyl Ester (biodiesel)
	HOME + 25CNT	Carbon nanotubes (CNT) blended with HOME having concentration of 25 ppm
	HOME + 50CNT	CNT blended with HOME having concentration of 50 ppm
Basha et al. [21]	JBD	Pure Jatropha biodiesel
	JBD+25 Al_2O_3	JBD with Alumina (Al_2O_3) having concentration of 25 ppm
	JBD+50 Al_2O_3	JBD with Al_2O_3 having concentration of 50 ppm
	JBD+25 CNT	JBD with carbon nanotubes (CNT) having concentration of 25 ppm
	JBD+50 CNT	JBD with Al_2O_3 having concentration of 25 ppm
	JBD+25 Al_2O_3+25 CNT	JBD with Al_2O_3 and CNT having concentration of 25 ppm of each
Basha et al. [21]	JME	Pure Jatropha methyl esters
	JME2S5W	93% JME + 2% surfactant + 5% water
	JME2S5W25CNT	93% JME + 2% surfactant + 5% water + 25 ppm CNT
	JME2S5W50CNT	93% JME + 2% surfactant + 5% water + 50 ppm CNT
	JME2S5W100CNT	93% JME + 2% surfactant + 5% water + 100 ppm CNT
Mirzajanzadeh et al. [34]	B5	95% pure diesel and 5% biodiesel prepared from waste cooking oil (WCO)
	B20	80% pure diesel and 20% WCO-biodiesel
	B5+(CeO_2-MWNTs) @ 30 ppm	B5 with hybrid of cerium oxide (CeO_2) nanoparticles and multi-walled carbon nanotubes (MWNTs) having concentration of 30 ppm
	B5+(CeO_2-MWNTs) @ 60 ppm	B5 hybrid of (CeO_2+MWNTs) having concentration of 60 ppm
	B5+(CeO2-MWNTs) @ 90 ppm	B5 with hybrid of (CeO_2+MWNTs) having concentration of 90 ppm
	B20+(CeO_2-MWNTs) @ 30 ppm	B20 with hybrid of (CeO_2+MWNTs) having concentration of 30 ppm
	B20+(CeO_2-MWNTs) @ 60 ppm	B20 with hybrid of (CeO_2+MWNTs) having concentration of 60 ppm
	B20+(CeO_2-MWNTs) @ 90 ppm	B20 with hybrid of (CeO_2+ MWNTs) having concentration of 90 ppm
Shaffi et al. [35]	Diesel	Pure diesel
	Soybean biodiesel	Pure biodiesel made of soybean
	B20 (soybean)	Diesel and soybean biodiesel in the ratio of 4:1
	D80SBD15E4S1+Al_2O_3	80% diesel, 15% soybean biodiesel, 4% ethanol and 1% iso-propanol with Al_2O_3 having concentration of 100 mg/L
Aalam et al. [36]	Neat diesel	100% pure conventional diesel fuel
	Mahua Methyl Ester (MME)	100% biodiesel prepared by vegetable oil
	MME20	Blend of 80% pure diesel and 20% MME oil (by volume)
	MME20 + ANP50	
	MME20 + ANP100	MME20 with 100 ppm of aluminum oxide nanoparticles
Prabu [15]	Diesel	Pure diesel fuel
	B100 (Jatropha)	Pure Jatropha biodiesel
	B20	Fuel blends containing 20% biodiesel and 80% diesel by volume
	B100A30C30	Fuel blends containing 100% biodiesel, 30 ppm Al_2O_3 and 30 ppm CeO_2
	B20A30C30	Fuel blends containing 20% biodiesel, 30 ppm Al_2O_3 and 30 ppm CeO_2

TABLE 2. Changes in fuel properties and performance and emission parameters due to inclusion of nanocatalyst(s)

Nanocatalyst(s) based fuel blends	Fuel properties					Performance and emission			
	Cetane No.	Kinematic viscosity at 40 °C, cSt	Flash point, °C	Density, kg/m^3	Calorific value, MJ kg^{-1}	BTE, %	bsfc, kg kW^{-1} h^{-1}	HC, ppm	NO_x, ppm
Basha et al. [21]									
JBD	53	5.25	85	895	38.88	24.9	0.37	60	1282
JBD+25 Al_2O_3	54	5.31	84	896	39.22				
JBD+50 Al_2O_3	56	5.35	82	897	39.53	27.9	0.32	52	1015
JBD+25 CNT	55	5.29	83	895.5	39.5				
JBD+50 CNT	57	5.33	81	897.9	39.78	27.1	0.33	49	1001
JBD+25 Al_2O_3+25CNT	57	5.36	81	895.2	39.99	28.9	0.31	46	985
Tewari et al. [33]									
Diesel	-	2.3	56	840	43	28	-	32	800
HOME	-	5.6	170	880	36.016	23	-	82	580
HOME + 25 CNT	-	5.7	166	898	34.56	24	-	70	600
HOME + 50 CNT	-	5.8	164	900	35.10	25	-	58	750
Basha et al. [21]									
JME	53	5.05	85	895	38.88	24.80		59	1282
JME2S5W	51	5.4	140	899.8	37.05	26.34	0.346	63	1001
JME2S5W25CNT	54	5.43	130	897.2	37.28	27.89	0.315	60	973
JME2S5W50CNT	55	5.76	125	897.8	37.35	28.13	0.308	60	961
JME2S5W100CNT	56	5.91	122	899.4	37.85	28.45	0.301	57	910
Shaffi et al. [35]									
Diesel	57	2.61	-	825	44.7	-	0.349	-	1792
Soybean biodiesel	49	4.78	-	865	41.2	-			
B20 (soybean)	42	3.7	-	847	43	-	0.312	-	1921
D80SBD15E4S1+Al_2O_3	52	3.37	-	840	42.59	-	0.309	-	1971
Aalam et al. [36]									
Neat diesel	47	3	56	815	42	-	-	-	-
Mahua Methyl Ester (MME)	56	3.9	136	869	39.95	-	-	-	-
MME20	49	3.4	76	826	41.62	-	-	-	-
MME20 + ANP50	49.5	3.37	71	827.5	41.67	-	-	-	-
MME20 + ANP100	51	3.33	65	829	41.69	-	-	-	-
Prabu [15]									
Diesel	-	2.20	48	835	42.3	32.3	-	25	1320
B100	-	4.10	85	873	39.5	28.5	-	18	1390
B20	-	2.58	55	843	41.7	30.3	-	13	1300
B100A30C30	-	4.10	83	874	40.2	31	-	12	1208
B20A30C30	-	2.59	52	844	42.2	32.5	-	10	978

Yang et al. [20] prepared an emulsion fuel with diesel, water and water soluble oxygenated fuel additives, consisting glycerine and polyethoxy-ester, in the proportion of 82.5, 5 and 12.5%, respectively. In order to tranquilise oil-water surface tension, surfactant (LP-9) was also added. The addition of surfactants can reduce the pooling of nanoparticles and their accumulation in nanoparticles as demonstrated by many studies [37]. Chaichan et al. [17] prepared a nano-soluble diesel emulsion by adding distilled water containing nanoparticles and mixed with diesel by using ultra sonic shaker one hour to ensure the complete mixing of water with diesel fuel. Shaffi et al. [35] attempted two-step method to prepare modified fuel blends. First, 100 mg of Al_2O_3 were mixed in 99.9% pure ethanol and then, mixed with the diesel-soybean biodiesel blend. The phase separation is prevented by the addition of iso-propanol as a surfactant. The fuel sample was transferred to the ultrasonicator to intensively disperse the particles and to reduce their agglomeration.

Sarvestany et al. [31] prepared emulsified diesel fuels of ferrofluid which consist Fe_3O_4 nanoparticles dispersed in diesel having concentration of 0.4 and 0.8% by volume, respectively. One of the most important features of ferrofluids is their stability, which means that particles in the fluid do not agglomerate and phase-separate, even in the presence of strong magnetic fields [32]. Moreover, nanoparticles have higher suspension period of more than one week when dispersed into test fuels [26]. Mirzajanzadeh et al. [34] prepared a novel fuel blend by synthesising CeO_2 and carbon nanotubes (multi-walled) and dispersed into biodiesel prepared by waste cooking oil by means of ultrasonic bath.

EFFECTS OF NANOCATALYSTS BASED FUELS ON ENGINE PERFORMANCE

Inclusion of nanoparticles in diesel, biodiesel and diesel-biodiesel blends have influenced the overall engine performance. Keskin et al. [12] observed non-significant improvement in performance with slightly less specific fuel consumption of single cylinder diesel engine when fuelled with metal based nanocatalysts. Basha et al. [21] observed higher BTE in nanoparticles blended JBD fuel at all the loads when tested with single cylinder 4.4 kW of air-cooled stationary engine. The lower brake specific fuel consumption (BSFC) was probably attributed to catalytic effects of Al-oxide and CNT nanoparticles due to their enhanced surface-area/volume ratio. Nanocatalysts as fuel additives help to boost combustion efficiency of diesel engine by shortening the ignition delay [23]. Tewari et al. [33] studied variations in BTE due to the inclusion of multi-walled CNT nanocatalysts, under different concentrations of 25 and 50 ppm, mixed in indigenously prepared biodiesel (HOME). Variations in BTE were found proportional to the concentration of CNT added to the fuel, greater for 50 ppm concentration as compared to either 25 ppm or without inclusion of CNT.

Basha et al. [21] investigated performance of single cylinder 4.4 kW engine due to inclusion of nanocatalysts consisting both Al_2O_3 and CNT. Reduction in peak pressure, heat release rate and ignition delay was observed due to the inclusion of nanocatalysts (Al_2O_3 + CNT) in pure JBD. BTE and BSFC were found maximum and minimum, respectively, when both Al_2O_3 and CNT nanocatalysts were dispersed in JBD. Mirzajanzadeh et al. [34] investigated the effects on engine power and torque due to inclusion of a hybrid nanocatalyst containing CeO_2 on amide-functionalized MWNTs with two types of diesel biodiesel blends (B5 and B20) at three concentrations (30, 60 and 90 ppm). Under constant speed and full load conditions, engine power and torque were increased with increasing the concentration of hybrid nanocatalysts in B5 and B20, respectively. Prabu [15] reported a significant improvement of 12% in BTE of diesel engine for the nanoparticles dispersed test fuel (B20A30C30) as compared to B100.

EFFECTS OF NANOCATALYSTS BASED FUELS ON EMISSIONS

Generally, engine emissions are divided into two categories: emissions produced as results of high flame temperature in chamber like NO_x and emissions produced resulting from incomplete combustion of fuel and lower flame temperature like HC and CO_2. Simultaneous control of the pollutants is difficult since different pollutants form at different temperatures [23]. CO is produced as a result of incomplete combustion of air–fuel mixture, low combustion cycle time in the engine or lower temperature of the combustion chamber [34]. Figure 2 has summarized the effects on exhaust gas emissions with and without the inclusion of nano-additives with fuel during combustion inside the engine cylinder. Fuel usually burns locally instead propagating uniformly into the cylinder, chiefly due to poor atomisation of fuel. Inclusion of nanoparticles in fuel spreads in the form of millions of clusters uniformly and facilitates more complete burning of fuel, hence reduces emission of harmful exhaust gases with improved combustion efficiency.

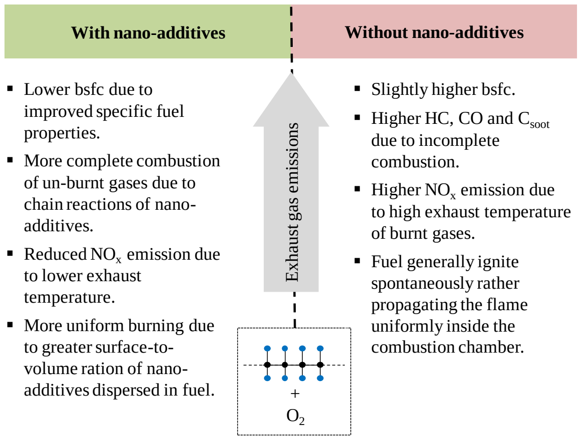

Figure 2. Effects on exhaust gas emissions (with and without the inclusion of nano-additives)

CONCLUSION

So far studies done by researchers all across the world, inclusion of nanoparticles as additives in diesel and diesel-biodiesel blends have shown significant improvement in CI engine performance with overall reduced emissions. Today, application of nanotechnology is expected to play a vital role in order to develop an innovative fuel hybrid for CI engines that may revolutionize the automobile sector worldwide. However, the development of such nanocatalyst(s) based CI-engine fuel is still a matter of concern due to limited and not fully explored R and D. The following are the major challenges that are to be considered in future researches: (a) There is a need of on-road testing in real ambient conditions, (b) Effects of exhaust emission fuelled with nanocatalysts on human breathing, (c) Overall effects on diesel engines of agricultural tractors and other heavy earth moving machines which are designed for high load factors, and (d) Effects of such modified fuels on driving habits of consumers.

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Persian Abstract

DOI: 10.5829/ijee.2019.10.02.06

چکیده

استفاده از مواد پر انرژی نانوکامپوزیت در دیزل و سوخت دیزل - بیودیزل مخلوط شده به عنوان کاتالیزورها به طور همزمان با سرعت در حال توسعه یک سوخت جایگزین کارآمد و سازگار با محیط زیست برای موتورهای احتراق فشرده (CI) ظهور کرده است. استفاده از نانوذرات به عنوان افزودنی برای سوخت های موتور CI قابل اعتماد بوده و به طور کلی بهبود عملکرد موتور و ویژگی های انتشار محدود. با این حال، کنترل همزمان بر پارامترهای عملکرد موتور و خصوصیات انتشار معمولا مشکل است. پراکندگی نانو مواد افزودنی باعث بهبود راندمان احتراق توسط تغییر خواص سوخت مخصوص دیزل می شود. متوسط اندازه ذرات ۴۰-۵۰ نانومتر، نسبت حجم به حجم را تسهیل می دهد، از اینرو احتراق کامل تر از واکنش های زنجیره ای بیشتری در طی احتراق را تضمین می کند. نانو ذرات به عنوان کاتالیزوری در دیزل و مخلوط متناسب آن به تازگی به عنوان مبادله بازی ظاهر شد، اما پتانسیل آن در واقع به دلیل عدم پذیرش بازار مورد بررسی قرار نمی گیرد. چالش های اصلی زیر در تحقیقات آینده مورد توجه قرار می گیرند: الف) نیاز به آزمایش در جاده ها در شرایط واقعی وجود دارد؛ ب) تأثیر خروجی اگزوز ناشی از نانوکاتالیزورها بر تنفس انسان؛ ج) اثرات بر روی موتورهای دیزلی تراکتورهای کشاورزی و سایر ماشین آلات سنگین زمین که برای عوامل بار بالا طراحی شده اند، و د) تأثیر چنین سوخت های اصلاح شده بر تطبیق پذیری با رانندگی مصرف کنندگان.