Nanoadditives: Propitious Alternative For Increase Biofuel Performance

Shanti Bhushan Mishra

Abstract In spite of the limited sources of fossil fuels, energy demand has been considerably increased since the last century. The problems associated with global warming due to rising atmospheric greenhouse gas levels and scarcity of fossil fuels makes it imperative to reduce our heavy dependency on fossil fuels. These reasons forced countries throughout the world to search for new fuel alternatives. Biofuel has gathered considerable attention due to their inherent benefits, like lower greenhouse gas emission, renewability, and sustainability. Commercially, biofuels are produced from vegetable oils, animal fats, and carbohydrates by using transesterification and fermentation. However, biofuel production suffers from high production costs and other technical barriers. Considering the environmental and economic issues, use of nanotechnology seems to be a viable solution. Nanoparticles have a number of interesting properties for the production of second-generation ethanol or transesterification of oils and fats to yield biodiesel. In this chapter highlighting the various available edible as well as nonedible vegetable feedstocks for biodiesel production, metal-based additives along with the variations in physiochemical properties.

Keywords Biodiesel · Biofuel · Nanometallic additives · Nanotechnology
Renewable resources

1 Introduction

Fuels are playing a major role in the economy of every country of this world and majority of the world energy needs are supplied by the petrochemical resources, coal, and natural gases, with the exception of hydroelectricity and nuclear energy (Shiu et al. 2010; Dennis et al. 2010). Among these mineral oils, petroleum plays a major role in the development of industrial growth, transportation, agricultural

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S. B. Mishra (✉)
United Institute of Pharmacy, Naini, Allahabad 211010, India
e-mail: shantipharma15@gmail.com

N. Srivastava et al. (eds.), *Green Nanotechnology for Biofuel Production*, Biofuel and Biorefinery Technologies 5,
https://doi.org/10.1007/978-3-319-75052-1_5

sector, and to meet many other basic needs of human being (Basha et al. 2009). Since 1970s, mineral-based fuel oil (i.e., petroleum, diesel, kerosene, natural gas, etc.) prices are increasing day by day due to depletion of fossil fuel reserves and rapid consumption of mineral oils. The main reason that caused the fast diminishing of energy resources is due to rapid population and industrialization growth globally (Lam et al. 2010). Moreover, petroleum-based fuels are creating negative impact on the ecosystem and burning of these fuels leads to emission of pollutant gases like CO_2, HC, NOx, SOx (Shahid and Jamal 2008). Due to the above and following reasons like rapidly increasing prices, uncertainties concerning petroleum availability, increased environmental concern and effect of greenhouse gases from industries have stimulated the search for alternative sources for petroleum-based fuel including diesel fuel (Balat and Balat 2008).

As a result, biodiesel and ethanol have been known as biofuel to substitute petroleum-derived cetane and octane fuel, respectively. These fuels have been attracting the attention since use of these oxygenated fuels in the engines clearly reducing the exhaust emission of greenhouse gases, particulate matters, unburned hydrocarbons, poly-aromatics, and oxides of sulfur (Lin et al. 2009).

Biodiesel, a processed fuel is derived from the vegetable oils and animal fats through the esterification and transesterification reactions of free fatty acids (FFAs) and triglycerides, respectively, that occur naturally in renewable biological sources (Clayton et al. 2008). In other words, we can define biodiesel as a mixture of alkyl esters of long-chain fatty acids, which are synthesized through esterification and transesterification of free fatty acids (FFAs) and triglycerides (TG) (Dennis et al. 2010; Clayton et al. 2008; Murugesan et al. 2009). The major feedstocks available for biodiesel are rapeseed, palm, canola, and soybean oils, though the process to grow nonfood grade oil is under process in the developing nations in tropic and subtropics. Many biodiesel industries have been set in the last decades worldwide, whereas most of these are not operational throughout the year due to the scarcity of cheap vegetable oils as feedstock for economic production of biodiesel.

In the production of biodiesel, more than 95% of feedstocks come from edible oils since they are mainly produced in many regions of the world and the properties of biodiesel produced from these oils are much suitable to be used as diesel fuel substitute. Use of such edible oil to produce biodiesel is not feasible in view of a big gap in demand and supply of such oils as food and they are far expensive to be used at present, and obviously, the use of nonedible vegetable oils compared to edible oils is very significant. Moreover, biodiesel does not contain any compounds like sulfur or aromatic compounds and burning of biodiesel results in the lower emission of hydrocarbons, carbon monoxides, and particulate matters (Karmakar et al. 2010; Shu et al. 2010). Since the cost of raw materials accounts about 60–80% of the total cost of biodiesel production, so choosing a right feedstock is very important and properties of biodiesel produced from different feedstocks would be quite different (Dennis et al. 2010). However, it may cause some problems such as the competition with the edible oil market, which increases both the cost of edible oils and biodiesel; moreover, it will cause deforestation in some countries because more and more forests have been felled for plantation purposes. In order to overcome these disadvantages, many researchers, scientists, technologists as well as industrialists are interested in nonedible oil source which are not suitable for human consumption because of the presence of some toxic components in the oils. Furthermore, nonedible oil crops can be grown in wastelands that are not suitable for food crops and the cost of cultivation is much lower because these crops can still sustain reasonably high yield without intensive care (Dennis et al. 2010; Balat and Balat 2008; Qian et al. 2010). However, most nonedible oils contain high free fatty acids. Thus, they may require multiple chemical steps or alternate approaches to produce biodiesel, which will increase the production cost, and may lower the ester yield of biodiesel below the standards.

Some of the common methods followed for improving the performance of diesel engine are engine modification, fuel modification, and exhaust gas retreatment. Fuel modification is carried out by adding catalysts or additives with the base fuel to optimize its physiochemical properties. The fuel additives are mixed thoroughly with diesel fuel for improving both performance and emission.

2 Importance of Additives

Biofuel is one of the best substitutes for petroleum diesel fuel. Biodiesel, mono-alkyl esters of long-chain fatty acids which are nontoxic in nature, nonexplosive, less flammable, and more importantly, it is biodegradable. Biodiesel is produced from various available natural sources namely palm, Jatropha, Pongamia, grape seed, mahua, castor, cotton seed, tobacco seed, rubber seed, rice bran, neem, coconut, sunflower oil, etc., Neat oil produced from these natural sources are chemically processed by "transesterification", in which the alcohol is added to the neat oil under mild condition in presence of a base catalyst. During esterification process, the triglycerides present in the oil get transformed into alkyl esters and glycerol. The transesterification process is carried out in the temperature range of around 50–80 °C with the addition of methanol or ethanol. The base catalysts commonly used are sodium hydroxide (NaOH) and potassium hydroxide (KOH). The methods used for biodiesel production are ultrasonic reactor method, supercritical process, lipase-catalyzed method and batch reactor method. Generally, the vegetable oil feedstock for biodiesel is categorized into two, namely edible and nonedible sources. Some of the prominent edible and nonedible feedstock available in India are as follows.

3 Edible Feedstocks

Corn belongs to the family of Poaceae with Zea mays as species name. Corn oil is extracted from the germinated maize. It is usually seen in tropical climates having a slow and sluggish growth upto a height of 6 m. With an oil content of around 40%, solvent extraction process using n-hexane or 2-methyl pentane extracts 85% of corn germ oil from its kernels. Soybean belongs to the family of Fabaceae with annuals as species. Soy is a leguminous and bushy plant producing beans for food and oil industry. It has of 18–20% of lipid and oil, 40% of protein along with minimal quantity of cellulose, glucose, ash, and fiber. Percolation extraction technique in the presence of n-hexane is used to extract oil from Soybean. *Brassica napus* (Canola) is capable of producing 75–240 gallons of oil in every hectare of cultivation. With oil content between 35 and 42%, solvent extraction method is widely adopted to extract oil.

Arachis hypogaea (Peanut also known as groundnut or goober) is widely grown in tropical and subtropical regions with a higher yield in light, sandy loan soil with pH between 5.9 and 7 and soil temperature of 20 and 35 °C. The oil content is estimated to be between 45 and 52% of which nearly 50% is extracted by pre-pressing and the remaining oil is extracted through solvent extraction method. *Chamaerops humilis* (Palm), a feedstock to extract edible oil from the mesocarp of the fruit, is usually seen in warm and tropical climates. The oil content is estimated to be between 48 and 52% along with high level of β-carotene. The oil extraction is based on screw pressing technique. *Cocos nucifera* (Coconut) belonging to the family of Arecaceae is widely grown in the coastal regions with hot and humid climatic conditions. The oil is extracted from the dried kernel (copra) of the coconut. The oil content is found to be between 65 and 72% and it is extracted by employing rotary chucks and oil expellers. Extract from grape seed of *Vitis vinifera* (Grape) is rich in polyunsaturated fat of about 69.6%. *Oryza sativa*, a type of Asian rice widely found in Asian countries including India is rich in carbohydrates. The oil extracted from the outer hard layer of rice husk is called rice bran oil. It mainly contains oleic acid which is used for edible purpose. Solvent extraction method is adopted to extract oil from the rice bran. *Helianthus Annuus* (Sunflower) belonging to the family of Asteraceae is a native of North America and presently widely cultivated as ornamental plant as well as food crop. The kernels of sunflower contain 44–50% of oil rich in oleic acid. Compression technique is used to extract oil from seeds of sunflower.

4 Nonedible Feed Stocks

Madhuca indica (Mahua), an origin of central and north India, belongs to the family of Sapotaceae. It is one of the most important tree species of Central India producing huge quantity of oleaginous seeds. The oil content of the seed is estimated around 33–43%. *Ricinus communis* (Castor) belonging to the family of Euphorbiaceae is a nonedible, high oil yielding crop mainly found in tropical regions. The castor bean is estimated to contain 40–50% of oil which is extracted through high-pressure continuous screw press technique with n-heptane as solvent. *Millettia pinnata* (Pongamia) of Fabaceae family is a semi-deciduous, drought-resistant, midsized tree found mainly in tropical and subtropical Asia. It is capable of growing in a wide range of soil and climatic conditions. It contains 30–40% of oil which is extracted through expeller and cold pressing, and solvent extraction method. *Jatropha curcas* (Jatropha) belonging to the family of Euphorbiaceae is a tropical and drought-resistant plant-producing seeds with oil content around 37–40%. Recently, Temasek life sciences laboratories and JOil Pte Ltd, Singapore developed strains of *Jatropha curcas* with 75% of oleic acid thereby making it as a more suitable biofuel. The oil is extracted by using mechanical press expeller as an oil extraction technique.

Azadirachta indica (Neem) of Meliaceae family, originated from India is found in all agro-climatic zones with soil pH value of 10 except in cold regions. Mechanical pressing, steam pressing, and solvent extraction techniques are used to extract 30–50% of oil from the seeds of neem. *Simmondsia chinensis* (Jojoba) belonging to the family of Simmondsiaceae is a species capable of growing in arid, semiarid with minimal water and extreme conditions but not suitable for soil prone to flooding and heavy waterlogging. The seed contains nearly 50% oil which is extracted using mechanical pressing followed by leaching and solvent extraction method. Nicotiana (Tobacco) belonging to Solanaceae family is a nonedible, green leafy plant grown in warm climates with its seed containing oil between 17 and 26%. Oil from the tobacco seed is extracted through solvent extraction and steam distillation methods. *Hevea brasiliensis* (Rubber tree) belonging to the family and subfamily of Euphorbiaceae and Crotonoideae have their nativity to African and Brazilian countries. Presently, it is widely cultivated in Southern Peninsular India. The rubber seed oil mainly contains linoleic and oleic acid which are extracted through mechanical expeller followed by soxhlet process. The various edible and nonedible biodiesel feedstock are shown in Fig. 1. Potential nonedible oil seeds plants of India have been mentioned in Table 1 and their physicochemical properties are described in Table 2.

5 Fuel Additives and Its Importance

Additives are organic based or metal-based substances which are easily soluble in fuel and its main purpose is to improve, maintain, and provide beneficial characteristics to the fuel without affecting the performance and combustion parameters. The fuel additives are added in smaller quantities ranging from 100 ppm to several thousand ppm. The fuel additives are broadly classified as refinery products, distribution system products, and automotive performance enhancement products. They are again subdivided into following categories namely antioxidants, cetane improvers, antiknocking agents, antifreezing agents, stability improvers, additives to prevent corrosion, cold flow improvers, fuel borne catalysts, antiwear agents, etc.

Fig. 1 Various edible and nonedible biofuels feedstock

6 Antioxidants

Biodiesels are fatty acid methyl esters produced by transesterification process which are ready to react with oxygen by the process called auto-oxidation. To avoid auto-oxidation of biodiesel in the diesel blend, additives like BHT (Butylated hydroxytoluene), TBHQ (Tert-butyl hydroquinone), BHA (Butylated hydroxyanisole), PG (Propyl gallate), and PA (Pyrogallol) are mixed with diesel–biodiesel blends.

7 Oxygenated Additives

To improve the burning characteristics of fuel with more ignition delay, chemical compounds having more oxygen content are added to that fuel at a trivial quantity. Oxygenated components like ethanol, methanol, biodiesel, dimethyl ether, dimethyl

Table 1 Potential nonedible oil seed plants in India

Botanical name	Common name	Distribution	Potential (metric/annum)	Oil %	Use
Cyanobacteria	Algae	Few places in India	157.4–629.8	20–40	Human nutrition, animal feed, aquaculture, biofertilizer, source of polyunsaturated fatty acids, and recombinant proteins, etc
Ricinus communis	Castor	All over India	790,000	46–55	Adhesives, coatings, soaps, lubricant, paints, and dyes, etc
Gossypium hirsutum	Cotton	All over India	851,000	18–25	Dairy cattle feeding, alternative biofuel source, etc
Jatropha curcus	Jatropha	All over India	15,000	40–60	Biodiesel, manufacture of candles, soap, and cosmetics
Simmondsia chinensis	Jojoba	Few places in India	–	45–55	Cosmetics, skin softeners, lubricants
Pongamia pinnata	Karanja	Maharashtra, Karnataka, Assam	200,000	30–40	Tanning leather, soap, lubricant and pesticides
Garcinia indica	Kokum	Western Ghats region, Andaman and Nicobar	55,000	–	Ideal feedstock for biodiesel
Linum usitatissimum L.	Linseed	Few places in India	150,000	35–45	Textiles, oil crops, stem fibers, geotextiles, filters, absorbents
Madhuka indica	Mahua	Maharashtra, Gujarat, West Bengal, Tamil Nadu, Orissa	520,000	35–40	Ointments, rheumatism, lighting, soaps, etc
Moringa oleifera	Moringa	Himalayan regions	_	33–41	Skin diseases
Mesua ferra	Nahor	North-eastern state of India	_	58–75	Production of biodiesel, boat buildings, mine props, tool handles
Azadirachta indica	Neem	All over India	500,000	35–45	Preservation of stored grains, Ayurvedic medicines, Unani and Homeopathic medicines
Erythea salvadorensis	Palm	_	<70,000	20–21	Cosmetics, soaps, lubricant for biodiesel engine

(continued)

Table 1 (continued)

Botanical name	Common name	Distribution	Potential (metric/ annum)	Oil %	Use
Simarouba glauca	Simarouba	Gujarat, Maharashtra, Tamil Nadu	1.1–2.2 oil/ha yr	55–65	Manufacture of soap, vegetable, fat lubricant, paints, polishes
Sapindus mukurossi	Soapnut	Andhra Pradesh, Karnataka, Delhi	6.61	51.8	Medicinal soap, surfactant, fabric, bathing
Citrullus colocynthis	Tumba waste cooking oil and animal fats	Few places in India, Restaurants and household	21,000 tons 1,135,000	–	Medicinal biodiesel production

carbonate, diethylene glycol diethyl ether, sorbitan monooleate, etc., which easily mixes and blends with diesel are used as an additive.

8 Additives to Improve Cold Flow Behavior

During cold conditions, the wax content present in the biodiesel begins to freeze and results in crystal-like structure which affects the cold filter plug point (CFPP). This situation may be avoided by using additives like ethylene vinyl acetate copolymer, glycerol ketals, glycerol acetates, phthalimide, and succinimide copolymers which improves the cloud point property of the fuel.

9 Additives to Improve Cetane Number

Cetane number is one of the major factors which determines the fuel quality by representing the ignition capability of the fuel. Fuels with high cetane number provide better performance with respect to compression ignition engine. Nitrates, nitroalkanes, nitro carbonates, peroxides, etc., are used as additives which improve the cetane number of the fuel.

Table 2 Physiochemical properties of biofuel feed stocks

Chemical properties	Castor oil	Cotton seed	Jatropha	Jojoba	Karanja	Kokum	Linseed	Mahua	Moringa	Nahor	Neem	Palm	Rice bran	Simarouba	Soap nut	Tumba	Waste cooking
Unsaponifiable matter(w/w)	–	–	–	–	3.3	–	–	1	–	2.7	–	–	–	0.40	–	–	–
Specific gravity	0.96	0.9148 at 15°c	0.912 at 15°c	0.8635–0.8640 at 40°c	0.882 at 15.5°c	0.895 at 40°c	0.931–0.938 at 15.5°c	0.856 at 15°c	0.907	0.92 at 30°c	–	0.9180 at 15°c	0.92 at 30°c	–	–	0.924–0.927 at 28°c	0.925
Kinematic viscosity at 30° c (mm^2/s)	29.7	33.5 at 38°c	29.4	11.82 at 40°c	27.8	–	22.2 at 40°c	24.5 at 40°c	43.4 at 38°c	4.1 at 40°c	50.3	5.7	36.68 at 40° c	–	–	–	36.4 at 40°c
Calorific value MJ/kg	39.5	39.648	39.23	42.17	34.000	–	–	38.863	–	36	–	36.510	39.500	–	–	–	–
Iodine value (g/I2/100gm)	88.72	104.7	108.4	82–89	29.9	25–38	156.74	58–70	73	89.4	65–80	35–61	90–108	53.8	64.5	118–122	141.5
Acidic value (mg KOH/g)	–	0.16	28	–	5.06	–	–	38	1.194	34	–	6.9	0.45	–	–	–	0.15
Saponification value (mgKOH/g)	191	198.5	200.8	92-167	188.5	187–192	187.6	190.5	199.7	190.6	209.66	208.6	201.27	191	195	172–174	188.2
Flash point (°c)	260	234	225	292	205	–	241	232	–	172	–	164	316	–	–	–	212
Aniline point (°c)	–	–	–	52.9	–	–	–	–	–	–	–	–	–	–	–	–	–
Cetane no.	42.3	54	61–63	–	60–61	65.6	34.6	56.61	56.66	54.6	57.83	62	50.1	59.32	59.77	–	49
Pour point (°c)	–32	258 k	2	6	–3	–	–15	15	–	–1.2	–	–31.7	1	–	–	–	11
Carbon residue (wt%)	0.21	0.42	0.44	–	0.71	–	<0.001	0.42	–	–	–	–	0.6	–	–	–	0.46
Moisture content (wt%)	0.15–1.30	–	–	–	19%	–	–	1.6	7.9 ± 1	0.1	–	0.02	0.02	–	–	–	0.42

10 Metal-Based Additives

The burning characteristics of the fuel can also be improved by the addition of metals and metal oxides to the fuel in the range of micro- or nanosizes through ppm or percentage by weight ratios. Metals like iron (Fe), aluminum (Al), magnesium (Mg), manganese (Mn), silver (Ag), gold (Au), copper (Cu), boron (B), graphene, silica (Si), etc., and metal oxides like aluminum oxide (Al_2O_3), cobalt oxide (Co_3O_4), cerium oxide (CeO_2), titanium oxide (TiO_2), zinc oxide (ZnO), copper oxide (CuO) etc., are used as additives to improve the fuel physiochemical properties. Alloys of metals like magnalium (Mg-Al), Carbon nanotubes (CNT) are also used as metal-based additive which improves the performance of fuels by changing its physiochemical properties. Figure 2 shows some of the metals and metal oxides nanoadditives used as performance enhancers.

After several studies, researchers have found that the modification of fuel with respect to its physiochemical properties yields better results in enhancing the engine performance and controlling the exhaust emissions rather than carrying out engine modifications. With reduced exhaust emissions, ignition delay, cold flow characteristics, etc., along with comparable performance characteristics, using biodiesel as fuel is found to be favorable. A few literature also reported about the reduction in lifespan using biodiesel as fuel which can be overcome with the use of fuel additives.

The main focus of this chapter is to comprehend the knowledge and information related to fuel modification by the addition of metal and metal oxide nanoadditives to improve the performance and reduce the emissions of the diesel engine. There are

Fig. 2 Metal and metal oxide nanoadditives as a performance enhancer

the outcome of several studies carried out by various researchers on the impact of nanofuel additives on fuel properties, its effect on performance and exhaust emissions at different operating conditions.

11 Effect of Nanometallic Additive on Fuel's PhysioChemical Properties

Attia et al. (2014) investigated the effect of B20-Jojoba methyl ester with the addition of aluminum oxide nanoparticle on properties of fuel, performance, and emission characteristics of the diesel engine. The result showed that there was a considerable change in fuel properties. It was also noticed that the addition of Al_2O_3 reduced the kinematic viscosity of the fuel along with an increase in density and cetane number. Arockiasamy and Anand (2015) mentioned that the addition of 30 ppm Al_2O_3 and CeO_2 with Jatropha methyl ester improved the kinematic viscosity, density, and calorific value as 4.25 Cst, 875 kg/m3 and 38.9 MJ/kg for JBD30A blend. JBD30C blend was found to have similar fuel property values as 4.30 Cst, 876 kg/m3, and 38.7 MJ/kg, respectively. The addition of alumina with Jatropha biodiesel improved the fuel properties. Aalam and Saravanan (2015) also obtained similar improved fuel properties for B20-Mahua biodiesel by adding aluminum nanoparticles.

Syed Aalam et al. (2015) evidently exhibited the enhancement in ZJME 25 fuel properties with the addition of alumina nanoparticles. AONP 50 gave better results with ZJME 25 than AONP 25 blend with increased flash point and cetane number. Shaafi and Velraj (2015) used alumina, ethanol, and isopropanol as a fuel additive for B20-Soybean biodiesel. They mixed 100 mg/l of AONP in D80SBD15E4S1 blend and noticed a drastic decrease in viscosity and calorific value along with an increase in cetane number. Anbarasu et al. (2016) and Bharathiraja et al. (2015) studied the effect of blending AONP with Canola methyl ester emulsion and straight diesel, and noticed a significant increase in flash point, density along with a significant decrease in viscosity.

Sadhik Basha and Anand (2013) compared the fuel properties of JME with and without the presence of AONP and CNT. The result indicated that the addition of CNT with JBD yielded better results with enhanced fuel properties. The flash point of CNT-blended Jatropha biodiesel was lowest when compared with neat JBD- and AONP-blended JBD.

Balaji and Cheralathan (2015) and Singh and Bharj (2015) mentioned that the addition of CNT with biodiesel resulted in increased flash point, viscosity, calorific value, and cetane number. The values were found to be increasing with increase in the amount of CNT concentration. Tewari et al. (2013) discussed about the change in properties of HOME with the addition of CNT. The author concluded that HOME + 50 ppm CNT showed better results than HOME + 25 ppm CNT.

Sadhik Basha and Anand (2014) studied the CNT-blended JME water emulsion and found that flash point for 100 CNT blend was 1220C, which was lowest among all the blends. With the increase in CNT concentration, viscosity, density, calorific value, and cetane number also showed an increased trend.

Karthikeyan et al. (2014a) mentioned that the addition of ZnO with B 20-Grape seed oil methyl ester increased the flash point, fire point, density, and viscosity.

Rao and Rao (2015) and Karthikeyan et al. (2014b) showed that the addition of ZnO and CeO_2 nanoparticles with straight diesel and B20-Pomoline stearin wax biodiesel resulted in increase of calorific value and decrease in flash/fire point.

Gan et al. (2012) investigated the burning characteristics of various nanoparticles at dilute and dense concentrations. Iron nanoparticle spherical in shape of size 15–80 nm (coated with thin layer of carbon between 2 and 6 nm) and boron nanoparticle nonspherical in shape of size 80 nm were studied.

Kannan et al. (2011) highlighted about the addition of FBC ($FeCl_3$) in waste cooking palm oil biodiesel which decreased the flash point, fire point, and density values, whereas the kinematic viscosity, calorific value, and cetane number showed a significant increase. Banapurmath et al. (2014), found that the addition of AgNP with HOME decreased the flash point value, whereas it increased the viscosity, density, and calorific values. HOME + 50 ppm of Ag showed good results compared to properties of HOME.

Vishwajit et al. (2015) found that the addition of graphene NP improved the properties of HOME. Among all the blends, HOME + 50 ppm graphene showed an enhanced properties.

Ansari et al. (2014) elaborated the recent trends in nanofluids, its preparation, and its applications. Nanofluid synthesis was classified into two types as one-step process and two-step process.

Bafghi et al. (2015) studied the performance and emission characteristics of a single-cylinder four-stroke air-cooled diesel engine fuelled with nanoceria added diesel–biodiesel extracted from waste fried oil. CeO_2 of size 10–30 nm were mixed with diesel–biodiesel blends in the range of 5–25 ppm.

Sharma et al. (2015) discussed about the addition of CeO_2 and CNT in JME + TPO blend and found that CeO_2 addition decreased the viscosity and density, whereas the same was increased with CNT addition.

Caynak et al. (2009) found that the addition of Mn (12 µmol/L) in B25 of pomace oil reduced the viscosity by upto 20.37% and flash point by upto 7%. The pour point got reduced from 0 to −15 °C.

Studies by Ayhan (2002) and Jayed et al. (2009) also showed the importance of adding nanometal additives in biodiesel and its effect in improving the physio-chemical properties of the nanometal-blended biodiesel.

12 Change in PhysioChemical Properties upon Addition of Nanometal Additives

Addition of CuO and Al_2O_3 nanoparticles with neat diesel increased the flash point and cetane number, whereas ZnO and CeO_2 reduced the values of flash point (Bharathiraja et al. 2015; Rao and Rao 2015). Addition of nanoparticles to the emulsified fuel increased the values of viscosity, density, calorific value, and cetane number (Singh and Bharj 2015; Sadhik Basha and Anand 2014). Addition of CeO_2, Al_2O_3, CNT, Al, Ag, and graphene nanoparticles with neat biodiesel reduced the flash point values, whereas the same increased the viscosity and density values [14, 20, and 29]. Calorific value of neat biodiesel increased with the addition of FBC, CNT, graphene, and Al nanoparticles [21, 29, and 30]. Addition of ZnO nanoparticles increased the flash point, viscosity, density, and calorific value of the fuel. Mn, Mg, and aluminum nanoparticles in diesel–biodiesel blends reduced the flash point values [15, 38, and 39].

The reason for adding metal-based nanoadditives to the diesel/biodiesel is to enhance the performance of the engine by improving the properties of the fuel. The addition of nanoparticles with diesel/biodiesel blends increased the calorific value and cetane number of the fuel. In some cases, it also reduced the sulfur content present in the fuel. Addition of CuO and Al_2O_3 with neat diesel reduced the sulfur content (Gumus et al. 2016). Aluminum nanoparticle with mahua methyl ester reduced the flash point and increased the calorific value and cetane number Aalam and Saravanan (2015). Addition of ZnO with biofuel blends increased the flash and fire point, calorific value, and cetane number (Karthikeyan et al. 2014a, c). Addition of fuel-borne catalysts also reduced the flash and fire point of the fuel (Arockiasamy and Anand 2015; Aalam and Saravanan 2015; Sadhik Basha and Anand 2013). ZnO with neat diesel reduced the flash and fire point values (Rao and Rao 2015). The calorific value increased with the addition of ZnO in all the cases. Addition of CNT with emulsified fuels improved the properties of fuels, whereas Al_2O_3 with emulsified fuels increased the flash and fire point and decreased the calorific value (Singh and Bharj 2015; Sadhik Basha and Anand 2014). Graphene nanoparticles gave better fuel improvements in HOME compared to silver nanoparticles (Vishwajit et al. 2015).

13 Conclusion

It is understood that the addition of nanoparticles plays a major role in improving the fuel properties and enhancing the performance of CI engine as well as reducing the exhaust emissions. Addition of nanoparticles increases BTE which depends upon the base fuel used, amount of nanoparticle added, how well they are mixed with the base fuel, and operating condition of the CI engine. Nanoparticles like Al_2O_3, Al, CNT, and CeO_2 show good results as additives with diesel and biodiesel blends in all aspects. ZnO also gives better results, but more amount of ZnO should be added than other nanoparticles to get an equivalent performance and the use of ZnO as fuel additive increases the cost of fuel. The performance enhancement cannot be achieved with every amount of nanoparticle addition. Therefore, selecting optimal range of nanoparticles addition is key to get good results on enhanced performance and reduced emission in a CI engine. Some nanoparticles give good results with every base fuel with which it is added, but in some cases, it fails to improve neither performance nor emissions. Size of the nanoparticle is also a criterion to be considered in using nanometal additives for improving the fuel properties. Therefore, selecting the nanoparticles based on the properties of the fuel to be improved.

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