Present Developments and the Research of Biodiesel fuel: A Review

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Abstract
CI engines are important power producers for on road and off road vehicles. Most of the heavy duty vehicles and trucks are powered by a diesel engine due to reliability, high fuel economy and high torque output. Diesel powered vehicles have shown 30-40 percent fuel economy advantage over gasoline powered vehicles. Because of this, the consumption of diesel is increasing drastically. Further, CI engine emits toxic pollutants such as particulate matter, smoke, oxides of nitrogen, hydrocarbon, carbon monoxide and carbon dioxide. These pollutants adversely affect human health, environment and contribute to acid rain, ground level ozone, global warming and reduced visibility. The fast depletion of crude oil and environmental degradation makes us to go for an alternate source of fuel. Biodiesel is one of the promising alternate fuel for CI engiane depending on their heat content and combustion. Biodiesel is an oxygenated, non-toxic, sulfur free, biodegradable and renewable fuel. It can be used in CI engines in any proportion blended with diesel without any major modification in the engine. Biodiesel is typically produced from vegetable oils and / or animal fats with an alcohol and a catalyst to make it suitable for CI engines. Biodiesel blends are used in cars, trucks, buses, off-road equipment and oil furnaces. The use of biodiesel can reduce a CI engine's overall emission by up to 75 percent. It can also reduce engine wear and tear and help a CI engine vehicle last longer due to its high lubricity. Lot of research studies have been made with several biodiesels as diesel substitute which includes karanja, jatropha, mango seed, mahua, pungamia etc. Hence, in the present review a detailed study the possibility of renewable fuels this can perform better than that of diesel fuel in terms of performance, combustion and emission characteristics. The renewable fuels such as mango seed, mahua and pongamia biodiesels are used as diesel fuel substitute in the present work.

Keywords: Biodiesel fuel, Present, Development, Performance, Emission, Combustion.

1. Introduction

CI engines are widely used in light, medium and heavy duty vehicles, load carriers and power generation, because of their higher fuel efficiency and ability to lean burn operation. Further, the lean burn capability helps to lower carbon-monoxide and hydrocarbon emission compared to that of gasoline engines. The major pollutants emitted in CI engines are CO, HC, NOx, particulate matter and smoke. These are harmful and often interact with other pollutants and leading to ozone depletion, global warming, photochemical smog and acid rain, which will disturb the ecological balance.

1.2Problems associated with CI engine

The high levels of particulate matter and oxides of nitrogen (NOx) emission make the CI engines difficult to pass through the strict emission norms. The high level particulate emission is due to the diffusive combustion chamber temperature and dissociation. It is very difficult to control simultaneously both the particulate matter and oxides of nitrogen (NOx) emission in a CI engine due to their trade off. Apart from the emissions, the fossil fuel is going to deplete too shortly and the world will face fuel crisis. In order to meet the demand in future, it is essential to go for alternate fuel to diesel fuel.

1.3Need of biodiesel

The world energy supply has relied heavily on non-renewable crude oil derived fuels, out of which 90% is estimated to be consumed for energy generation and transportation. It is known that emission from the combustion of these fuels are the principal causes for environmental issues and many countries have passed legislation to arrest their adverse effect on environment consequent to the rapid increase in population. Worldwide energy demand is increasing and crude oil reserves could be depleted in less than 30 years at the present rate of consumption. Biodiesel refers to a vegetable or animal fat consisting of long chain alkyl (methyl, propyl or ethyl) esters. Biodiesel is typically made by chemically reacting lipids with alcohol. It can be used alone or blended with diesel with minor modification in the diesel engine. The choice of biodiesel is depending on availability in particular area, its heating value and also its other physical properties.

1.4 Sources of biodiesel

India is the leading producer of biodiesel in the world, and it can be harvested and sourced from non-edible oils like jatrophacurcas, pungamiapinnata, neem, mahua, castor, linseed, kusum, etc. Some of these oils produced even now are not being properly utilized. Out of these, India is focusing on jatrophacurcas and pongamiapinnata, which can grow in arid and wastelands. Oil content in the jatropha and pongamia seed is around 30 – 40 %.

1.5 Thermal barrier coating (LHR)

CI engine lost two third of the heat energy of fuel, one-third to the coolant, one third to the exhaust and about one-third as worthwhile power output. According to the theoretical study, if heat rejection could be reduced, then the thermal efficiency will be improved. The main aim of the Low Heat Rejection (LHR) engine is to reduce the amount of heat transferred from the engine combustion chamber to the coolant by providing insulation. Application of thermal barrier coatings on the engine combustion chamber can improve the efficiency of CI engine with several limitations. There are number of coating techniques such as Air Plasma Spray (APS), Suspension Plasma Spray (SPS) or Liquid solution precursor plasma spray (LSPPS), Vacuum Plasma Spraying (VPS), Plasma spraying physical vapour deposition (PS-PVD) and Plasma spraying chemical vapour deposition (PS-CVD) are used in CI engines.Among these plasma spray is the most common method for coating on C.I engines. It creates a splat structure with 10-20 % volume fraction of voids and cracks. High porosity of this structure makes it an ideal choice for LHR coating in CI engines.

1.6 Antioxidant Additive

Oxygen oxidise the fuel and inhibits a chain of oxidation reactions which can result in formation of hydro peroxides (ROOH) and peroxides (ROOR`). They are high oxidizing agent, which results in oxidation of metals in the fuel system and also suppress the combustion quality of the fuel. These problems can be avoided by adding antioxidant additive with the biodiesel. Recent studies have reported that the use of antioxidant fuel additives can reduce the NOx emission from biodiesel fuelled CI engine effectively. Antioxidant will suppress the oxidation of unsaturated fuels at the double bond sites by terminating the liberation of free radicals. Free radicals play a major role in the formation of prompt NOx during the combustion of biodiesel. Addition of antioxidants can possibly inhibit the participation of these free radicals in the sequence of NOx forming reactions.

1.7 Present work

The objective of the review is to identify the possibility of renewable fuels which can perform better than that of diesel fuel in terms of performance, combustion and emission characteristics. The renewable fuels such as mango seed, mahua and pongamia biodiesels are used as diesel fuel substitute in the present work. These biodiesels are widely used in CI engines and having the drawback of lower performance and higher NOx emission. These problems can be prevented by means of providing LHR mode in CI engine and addition of additive with biodiesel. The LHR engine will enhance the combustion leading to improved performance and the addition of additive in biodiesel will improve the biodiesel properties and reduces NO_x emission significantly. Hence, an attempt is made to study the effect of mango seed, mahua and pongamia biodiesels with LHR engine and additive with different proportions on the engine performance, combustion and emission characteristics in a single cylinder direct injection CI engine.

2. The effect of antioxidant additive along with biodiesel operated in a conventional engine and LHR engine on the emission and performance characteristics

Depletion of fossil fuel, ever increasing demand for the fuel and serious environmental issues leads us to go for alternate fuel to CI engines. This chapter reviews the available open literature about the biodiesels for the CI engine application. The recent studies in the field of performance and emission characteristics of the biodiesel and biodiesel – diesel blend as a fuel in CI engine are also reviewed. Further, the application of Low Heat Rejection engine (LHR) with diesel and biodiesel blend as a fuel is studied elaborately.

2.1Biodiesel

Among the various alternate fuels, biodiesel is found to be the most promising alternate fuel in CI engine because of its availability, simplicity in processing and distribution. This section reviews the various studies conducted about the feed stocks for biodiesel preparation, processing of biodiesel, performance and emission studies using biodiesel as fuel in a CI engine.

Perumal & Ilangkumaran (2017) experimentally analyzed the combustion, emission and performance characteristics of PME blends. The CO and HC emission of PME is reduced to a maximum of 8.2% and 8.9% respectively compared to diesel. They also mentioned that there is a considerable reduction in oxides of nitrogen. The BSFC of PME increase by 4.2% and the BTE reduced by 2.4%. They found that ID period of PME is lower than diesel and it decreases with the increase in the proportion of biodiesel.

Tamil selvan et al. (2013) have investigated the performance and emission characteristics of the biodiesel having varying fatty acid composition. It is observed that the higher cetane index will reduce the ignition delay. Compared to other fuels, pongamia biodiesel has slightly higher BTE than diesel and other biodiesel having slightly higher NOx, reduced CO and HC emissions.

Senthil et al. (2014) have investigated the combustion, performance and emission characteristics of the different blends of Annona Methyl Ester (AME) with diesel. The BTE of the blends are lower than that of diesel but for A20, it is very much close to that of diesel.

Islam et al. (2014) have studied the emission and performance of castor biodiesel blends from 0% to 40% with diesel in a CI engine. The B40 has the lower smoke emission compared to that of the other blends. There is a reduction in CO, HC and PM emissions with the increase in the blend proportion. It is observed that there is an increase in the NOx emission and SFC at maximum load.

Ergenc et al. (2013) have investigated the performance, emission and heat release characteristics of soyabean methyl ester and diesel in a DI CI engine. They also found that the NOx emission of the blends are slightly higher than diesel due to higher combustion temperature. Further, the heat release in the premixed combustion phase of the diesel is slightly higher than that of other biodiesel blends.

Swarup Kumar Nayak et al (2022) have the effects of adding t-butyl peroxide (TB) additive with diesel fuel and biodiesel originated from Mahua oil and waste Palm oil in form of quaternary blends with varying injection timing (21^{o}bTDC (before Top Dead Centre), 23^{o}bTDC, and 25^{o}bTDC) on performance, emission, and combustion characteristics of a diesel engine. In this experimentation, all the quaternary blends were prepared by keeping the volume percentage of diesel fuel at 48% v/v, while concentrations of Mahua oil-based biodiesel, waste Palm oil-based biodiesel, and t-butyl peroxide were varied by volume.

Summary

From the above literature survey it is seen that a number of biodiesels were tested in the CI engine. It has been reported that the brake thermal efficiency was reduced for all biodiesel and the optimum blend ratio is 20%. Further, all researches pointed that the NOx emission increases for all biodiesel blends. At the same time, emissions like HC, CO and smoke were decreased considerably at all conditions. It is further reported that most commonly used biodiesels in the CI engine are mahua oil, mango seed, karanjajatropha, pongamiapinnata, etc.

Table 1 shows the engine performance such as brake thermal efficiency (BTE), brake specific fuel consumption (BSFC), exhaust gas temperature (EGT) and exhaust emissions such as hydro carbon (HC), carbon monoxide (CO), oxides of nitrogen (NOx), and smoke of biodiesel fuel engine as compared to diesel engine.

Table 1 Effect of biodiesel-diesel blends on engine performance and emissions.

Type of engine and test conditions	Feed stock of biodiesel	Performance (Compared to diesel)		Emission (Compared to diesel)				References
		BTE	BSFC	HC	CO	NOx	smoke	
Single cylinder, 4 stroke diesel engine at 1500 rpm	Pongamia biodiesel	Decrease	-	Decrease	Decrease	Increase	Decrease	Rao &Anand (2015)
Single cylinder, 4 stroke diesel engine at 1500 rpm	Mahua methyl ester (MOME),	Decrease	-	Decrease	Decrease	Increase	Increase	Nayak et al. (2014)
Single cylinder, 4 stroke diesel engine at 2000 rpm	Pongamia Methyl Ester	-	Decrease	Decrease	Decrease	Increase	-	Gopal&ThundilKarupparaj (2014)
Single cylinder, 4 stroke diesel engine at 1500 rpm	Pongamia Methyl Ester	Decrease	Increase	Decrease	Decrease	Decrease	-	Perumal&Ilangkumaran (2017)
Single cylinder, 4 stroke diesel engine at 1500 rpm	Methyl Ester Mango Seed Oil (MEMSO)	Decrease	Increase	Decrease	Decrease	Increase	Decrease	Vijayaraj et al. (2015)
Single cylinder, 4 stroke diesel engine at 1500 rpm	Pongamia, Ricebran, Sunflower And Palm Oil	Increase	Decrease	Decrease	Decrease	Increase	Decrease	Tamil selvan et al. (2013)
Single cylinder, 4	Neem Oil Methyl Ester	Decrease	Increase	Decrease	Decrease	Increase	Decrease	Senthil et al. (2014)

stroke diesel engine at 1500 rpm	(NOME)							
Single cylinder, 4 stroke diesel engine at 1500 rpm	Castor biodiesel	Decrease	Increase	Decrease	Decrease	Increase	Decrease	Islam et al. (2014)
Single cylinder, 4 stroke diesel engine at 1500 rpm	Soyabean Methyl Ester	Decrease	Increase	Decrease	Decrease	Increase	Decrease	Ergenc et al. (2013)
Single cylinder, 4 stroke diesel engine at 1500 rpm	Jatropha Methyl Ester	Decrease	Increase	Decrease	Decrease	Increase	Decrease	Paul et al. (2014)
Single cylinder, 4 stroke diesel engine at 1500 rpm	Citrus Sinensis Biodiesel (CSB)	Decrease	Increase	Decrease	Decrease	Increase	Decrease	Tuccar et al. (2014)
Single cylinder, 4 stroke diesel engine at 1500 rpm	Biodiesel	Decrease	Increase	Decrease	Decrease	Increase	Decrease	Lahane et al. (2015)
Single cylinder, 4 stroke diesel engine at 1500 rpm	Biodiesel	Decrease	Increase	Decrease	Decrease	Increase	Decrease	Hasan Ali et al. (2013)
Single cylinder, 4 stroke diesel engine at 1500 rpm	Corn Oil, Rapeseed Oil And Waste Oil	Decrease	Increase	Decrease	Decrease	Increase	Decrease	Tesfa et al. (2014)

2.2Low heat rejection engine (LHR)

In this section, reviews have been made to study about the performance and emission characteristics of the different coatings on the diesel engine components and effects of using biodiesel in a LHR engine.

Taymaz (2014) has investigated the effect of thermal barrier coating on performance and emission characteristics of the diesel engine. The cylinder head, valves and piston crown are coated with LHR materials such as $CaZrO_3$ and $MgZrO_3$ using plasma spray coating onto the base coating of NiCrAl for better adherence of coating over the substrate. There is a considerable increase in BTE and reduction in SFC of the engine due to higher in-cylinder temperature.

Siva kumar et al. (2014) have investigated the effect of YSZ coated piston crown on performance and emission characteristics of diesel engine. They also found that there is an increase in volumetric efficiency in TBC coated engine and residual gas reduces the density of inducted air. It is concluded that NOx emission of coated engine is higher due to the increased combustion temperature which facilitates the reaction between oxygen and nitrogen during combustion.

Senthil et al. (2015) have investigated the performance and emission characteristics of a LHR engine using nerium biodiesel and its blends. The BTE of coated engine fuelled with is 3.8% higher than that of uncoated engine at full load. The various emissions for the coated engine with MEON are lower, except NOx emission at all loads.

Basavaraj M Shrigiri, et al. (2016), have investigated the performance, emission and combustion characteristics of cotton seed (CSOME) and neem kernel oil (NKOME) methyl esters in a semi-adiabatic diesel engine. It is stated that CO and HC emissions of biodiesel in LHR engine are higher than that of diesel due to higher viscosity and poor atomization. It is also stated that NOx of biodiesel with LHR engine is higher than that of the diesel due to the presence of oxygen in fuel and higher combustion temperature of the LHR engine.

Summary

It has been seen from the literature survey that the many experimental investigations are conducted using different ceramic materials like alumina, cerium oxide, partially stabilized zirconia, aluminium, titanium and yttria stabilized zirconia as coating material in a diesel engine, but very limited literature studies have been undertaken using lanthanum as coating material in CI engine. The use of LHR engine results increase in the BTE of the engine and reduced SFC. It also increases the peak in-cylinder pressure and combustion temperature of the diesel engine which in turn increases the NOx. Most of the researches are proved that use of LHR engine has better combustion even though when the engine is operated with biodiesels.

Table 2 shows the effect of low heat rejection on engine performance and emissions of biodiesel fuel engine as compared to diesel engine.

Table 2 Effect of LHR on engine performance and emissions.

Type of engine and test conditions	Feed stock of biodiesel	Type of coating material	Performance (Compared to diesel)			Emission (Compared to diesel)				References
			BTE	BSFC	EGT	HC	CO	NOx	Smoke	
Single cylinder, 4 stroke diesel engine at 1500 rpm	Biodiesel	$CaZrO_3$ and $MgZrO_3$	Increase	Decrease	-	-	-	-	-	Taymaz (2014)
Single cylinder, 4 stroke diesel engine at 1500 rpm	Biodiesel	$3Al_2O_3 .2SiO_2$ (mullite)	Increase	Decrease	Increase	Decrease	Decrease	Increase	-	Shrirao et al. (2011)
Single cylinder, 4 stroke diesel engine at 1500 rpm	Biodiesel	Lanthanum zirconium oxide (La2Zr2O7)	Increase	Decrease	-	-	-	Increase	-	Thomas et al. (2014)
Single cylinder, 4 stroke diesel engine at 1500 rpm	Biodiesel	YSZ	Increase	Decrease	-	Decrease	Decrease	Increase	-	Siva kumar et al. (2014)
Single cylinder, 4 stroke diesel engine at 1500 rpm	Jatropha seed oil biodiesel	Partially stabilized zirconia	Increase	Decrease	-	Decrease	Decrease	Decrease	Decrease	RajendraPrasath et al. (2010)
Single cylinder, 4 stroke diesel engine at 1500 rpm	Various biodiesel and vegetable oils	PSZ	Increase	Decrease	-	-	-	Increase	-	Abedin et al. (2014)
Single cylinder, 4 stroke diesel engine at 1500 rpm	Vegetable oils	Zirconium Oxide (ZrO_2)	Increase	Decrease	-	Decrease	Decrease	Increase	Decrease	Hüseyin Aydin (2013)
Single cylinder, 4 stroke diesel engine at	Waste cooking oil biodiesel	88% ZrO_2, 4% MgO and 8% Al_2O_3	Increase	Decrease	-	Decrease	Decrease	Increase	Decrease	Selman Aydin et al. (2014)

1500 rpm										
Single cylinder, 4 stroke diesel engine at 1500 rpm	Pongamia Methyl Ester (PME)	Al_2O_3	Increase	Decrease	-	Decrease	Decrease	Increase	Decrease	Mohamed musthafa et al. (2011)
Single cylinder, 4 stroke diesel engine at 1500 rpm	Pongamia and rice bran oil methyl ester	Fly ash	Increase	Decrease	-	Decrease	Decrease	Increase	-	Mohamed musthafa et al. (2011a),
Single cylinder, 4 stroke diesel engine at 1500 rpm	Nerium biodiesel	Partially stabilised zirconia (PSZ)	Increase	Decrease	-	Decrease	Decrease	Increase	Decrease	Senthil et al. (2015)
Single cylinder, 4 stroke diesel engine at 1500 rpm	Palm oil methyl ester (POME)	Yattria-stabilized zirconia (Y2O3-ZrO3)	Increase	Decrease	Increase	Decrease	Decrease	Increase	Decrease	Karthikeyan et al. (2014)
Single cylinder, 4 stroke diesel engine at 1500 rpm	PME	Titanium oxide	Increase	Decrease	-	Decrease	Decrease	Increase	-	Prabhahar et al. (2013)
Single cylinder, 4 stroke diesel engine at 1500 rpm	Vegetable oil blends	ZrO_2	Increase	Increase	-	Decrease	Decrease	Increase	-	Iscan et al. (2014),
Single cylinder, 4 stroke diesel engine at 1500 rpm	Cotton seed (CSOME) and neem kernel oil (NKOME)	LHR coating	Increase	Increase	-	Increase	Increase	Increase	-	Basavaraj M Shrigiri, et al. (2016)
Single cylinder, 4 stroke diesel engine at 1500 rpm	Methyl ester of mahua oil (MEMO)	Al_2O_3	Increase	Decrease	Increase	Decrease	Decrease	Increase	Decrease	Santhanakrishnan et al. (2013)
Single cylinder, 4 stroke	Annona methyl ester	88% of ZrO2, 4% of MgO,	Increase	Decrease	-	Decrease	Decrease	Increase	-	Ramalingam et al. (2016)

diesel engine at 1500 rpm	(AME)	and 8% of Al2O3								
Single cylinder, 4 stroke diesel engine at 1500 rpm	Carburetted methanol and crude jatropha oil	LHR coating	Increase	Decrease	Decrease	-	-	Increase	-	Murali Krishna et al. (2014)

2.3 Antioxidant additive

Biodiesel is prone to oxidation due to the presence of unsaturated and poly unsaturated fatty esters which will undergo oxidation during storage. The oxidation of biodiesel results in formation of fuel degrading compounds which would have different physiochemical properties. The antioxidants addition results in the improvement of oxidation stability of the biodiesel. Antioxidant will also have potential to suppress the NO_x emission when mixed in a small proportion with biodiesel and diesel. The present section will give clear view about the recent research works done in the antioxidant additive along with biodiesel in CI engines.

Zengshe Liu et al. (2016), have synthesised epoxidizedcardanol (ECD) and evaluated its antioxidative properties with vegetable oils and biodiesel by using pressurized differential scanning calorimetry (PDSC) and Rancimat method. The cardanol is a product obtained from the cashew nut shell oil. TGA (Thermo Gravimetric Analysis) of cardanol and ECD shows that the decomposition temperature of ECD is higher than cardanol.

Velmurugan et al. (2015), have studied the effect of antioxidant additive on NOx emission from a mango oil biodiesel fuelled engine. Among the antioxidants tested, the phenolic derived additive showed maximum reduction of NOx emission compared to that of DEA and TBHQ. It is also seen that addition of antioxidant is insignificant in BTE and SFC but there is an increase in CO, smoke and HC emission.

Rashed et al. (2016), have compared the effect of N,N’-diphenyl-1,4-phenylenediamine (DPPD), N-phenyl-1,4-phenylenediamine (NPPD) and 2-ethylhexyl nitrate (EHN) on the performance and emission behaviour of the 20% blend of calophyllumininophyllum biodiesel with diesel. The B20 has lesser BTE and higher BSFC compared to diesel. It is seen that additive has a positive effect in reducing the NOx emission at the expense of increase in CO and HC emission.

Ramalingam et al. (2016), have investigated the effect of natural and synthetic antioxidants on oxidation stability, performance and emission characteristics of diesel engine operated with 20% blend of sapota oil methyl ester. They have found that LE and PY are the best antioxidants in terms of increasing the oxidation stability of the biodiesel. From the emission analysis, B20 has the lower emission comparing to diesel except NOx while addition of LE has reduced the NOx emission considerably.

2.3.1 Summary

Literature review shows the investigation on various antioxidants such as Butylated Hydroxyl Anisole (BHA), Butylated Hydroxyl Toluene (BHT), tertbutylhydroquinone (TBHQ), 2-ethylhexyl nitrate (EHN), Pyrogallol (PG), Propylgallate (PA), L-ascorbic Acid (LA) and carotene antioxidant with biodiesel. All the antioxidants have improved the oxidation stability of the biodiesel above the standard induction period of 6 hours without affecting the physiochemical properties of the biodiesel by suppressing the free radicals. All the antioxidants showed better reduction of the NOx emission, when it is fuelled with biodiesel.

Conclusion

From the literature it is clear that neat biodiesel cannot be used as a fuel in a diesel engine without any fuel or engine modification. The neem oil, mango seed oil, mahua, pongamiapenatea and nerium are the feed stocks available in abundance in India. Most of the researchers pointed out that use of biodiesel increases the NOx emission due to the presence of more oxygen content. It is also pointed out that BTE has been reduced invariably for all biodiesels at all blend ratios.It has been seen that one of the best way to increase the efficiency of biodiesel operated CI engine is to adopt LHR mode engine. Studies revealed that LHR engine has increased BTE at the expense of NOx emission. Alumina (Al2O3), Zirconia (ZrO2), Titanium oxide, Partially Stabilized Zirconia (PSZ), Magnesium Oxide (MgO), fly ash and etc., are used as coating material in CI engine and very little studies were reported on Lanthanum Oxide as a coating material for CI engine. It has been reported that Lanthanum Oxide has higher thermal stability and lower thermal conductivity compared to that of PSZ. Lower thermal conductivity of the lanthanum oxide results in lower heat loss to the coolant and higher in-cylinder gas temperature, which may increase the BTE of the engine.

It is reported that the higher in-cylinder gas temperature is due to LHR coating and leads to increase in NOx emission and the use of biodiesel will further increase the NOx emission.It has also been reported that the antioxidant additive are the best way to suppress the NOx emissions while using biodiesel. Most of researchers suggested that BHA, BHT, TBHQ, Pyrogallol, Propylgalate, L-Ascorbic acid, n-Butyl amine, PhosphorateCardnol are effective antioxidants to control the NOx emissions. The antioxidant activity of the additive are exhibited by the number of phenolic groups present in the additive. Among the various additives L-ascorbic acid contains four phenolic group (OH) and also it is readily available at a lower cost. Further very limited studies have been carried out and it can be tried in the present investigation.

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