Prospects of Biodiesel from Rubber Seed Oil in India- A Review

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ABSTRACT

Rubber (Hevea brasilienis) is a plantation tree and its seeds contain non edible oil which have huge potential of biodiesel production. Being a non-edible oil it helps fight the food versus fuel crisis that India may face due to utilization of edible oils for biodiesel production. Indian states like Kerala have huge rubber plantations and production thus providing the essential raw material for biodiesel production. The rubber seeds have around 35 to 60 % oil content. Biodiesel yield of around 96.8% is obtained through transesterification by use of 1 wt% KOH as catalyst and 6:1 alcohol to oil ratio at a reaction temperature of around 55 degree Celsius. The fuel properties of biodiesel manufactured from rubber seed oil is similar to that of diesel. In low blends of biodiesel the hydrocarbon (HC) and carbon monoxide (CO) emissions are quite low as compared to pure diesel. This review paper describes rubber seed oil as a potential alternative fuel candidate for India.

Keywords - Rubber seed oil, Biodiesel, Alternative fuel, Engine, Transesterification.

1. INTRODUCTION

With the decrease in the reserves of non-renewable resources and rising of the environmental concerns there is a need for a better fuel source. The UN Sustainable development goals (goal 7) also promote governments to provide affordable and clean energy. Considering these requirements biofuel is a very promising option. Fig. 1 shows the share of bioenergy in total final energy consumption. Bioenergy is the biggest contributor of the renewable source accounting for about 12.8% of the total. Biofuel is the largest contributor in renewable transport sector, with around 2.8% of the total [1].

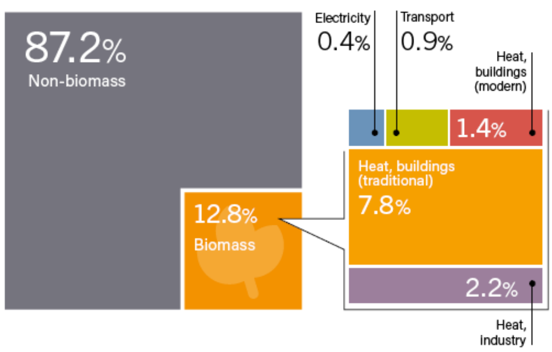

Fig. 1 Share of bioenergy in total final energy consumption [2]

One of the important features of biodiesel is that it is 'carbon neutral'. This means that the net release of CO_2 is zero because the amount of CO_2 released on combustion is absorbed by the plants grown for production. It also has been pointed out that although the emissions of biofuels are lesser than petrol, the indirect release of gases is more when emissions from changed land usage is took under consideration. The air quality benefits from biofuels relative to fossil fuels vary according to the fuel used and the vehicle type; however, analysis indicates that biofuels can reduce carbon monoxide, hydrocarbons and particulate matter emissions. In many countries biofuels also reduce the need for fuel imports, promoting energy security and reducing cost and vulnerability to fluctuations in the international fuels market. Presently around 95% of world's biodiesel is produced from edible oil source [3]. Despite the effectiveness of fuels from edible oils, its consumption is a major concern due to the food versus fuel crisis in a country like India. The solution to this problem is non-edible oil. The main feed stock for biodiesel production in India is non-edible oils obtained from plant species such as Jatropha (Jatropha curcas), Pongamia (Pongamiapinnata) and Polanga [4]. The availability of the non-edible resources makes biodiesel a viable option. In this paper our main focus will be on biodiesel production from Rubber seed oil.

Hevea brasilienis (Rubber tree) is indigenous to Brazil. Although the amount of rubber oil in seeds varies from country to country, the average extraction is 40% [5]. The extraction from rubber seed oil is 80-120 kg/ha [6]. Some of the other uses of rubber are in soap, alkyd resin, printing ink, lubricant, paints and coatings. Rubber seed oil is a semi-dried substance that is a rich source of fatty acids such as oleic acid, linoleic acid, linolenic acid, palmitic acid, and stearic acid (about 52% of total fatty acid composition) [7]. Table 1 shows the top 10 natural rubber producing countries.

Table 1 Top 10 natural rubber producing countries [8]

Position	Country	Production of Rubber
1	Thailand	3120000
2	Indonesia	2540000
3	Malaysia	1270000
4	India	803000
5	Vietnam	550000
6	China	545000
7	Philippines	360000
8	Nigeria	143000
9	Cote-d'Ivore	128000

2. RUBBER OIL IN INDIA

Table 2 shows the import and export quantities of natural rubber for India. In India the largest amount of rubber is grown in Kerala. In the year 2001-02 the rubber grown in Kerala accounted for about 91% of the total, but over the years the production has decreased and the production accounts for about 69% [10]. Table 3 shows the state wise distribution of rubber in India. Table 4 shows the physiochemical properties of crude rubber oil.

3. RUBBER SEED OIL EXTRACTION METHODS

3.1 Aqueous Enzymatic Method

In this method certain enzymes are used to rupture the cell walls of the rubber seed without the help of any solvents and thus help in extracting the oil. It is an eco-friendly method and low cost in nature. [13] This method is generally used to extract oil from oil rich seeds of various plants. Enzymes like cellulases, proteases and pectinases are mostly used in such aqueous enzymatic extraction.

Table 2 The import and export quantities of natural rubber [9]

	April 2014	April 2013	April 2013 to March 2014	April 2012 to March 2013
Import				
Natural Rubber	29140	14396	325190	217364
Synthetic Rubber	30700	28797	371839	329585
Total NR&SR	59840	43193	697029	546949
Export				
Natural Rubber	28	1538	5398	30594

Table 3 State wise distribution of rubber [11]

Position	State	Area under cultivation (ha)
1	Kerala	545000
2	Tripura	63223
3	Karnataka	32415
4	Assam	23705
5	Tamil Nadu	18115
6	Meghalaya	4834
7	Nagaland	3515
8	Manipur	2400
9	Goa	1010
10	Andaman & Nicobar islands	880

3.2 Ultrasonic Assisted Method

In this method macroscopic bubbles are formed which when collapse cause energy and mechanical shear thus causing the rupture of the cell wall of the rubber seed.[14,15] In microbiology ultrasound is mostly related to cell disruption. In sonicating liquids the sound waves produce alternate high pressure and low pressure cycles with different rates. During the low pressure cycle ultrasonic waves create bubbles which when attain enough volume they collapse violently during the cycle. During such collapse very high temperature and very high pressure is created locally and also velocity jets are created which results in shearing of the cell walls thereby extracting the oil.

Table 4 Physiochemical properties of Crude rubber oil [4, 12]

Properties	Crude RSO	Crude Pongamia oil
Color	Dark brown	Yellowish orange
State	Liquid	Liquid
Viscosity (mm^2/s)	40.86	27.84-38.2
Specific gravity	0.91	0.912-0.940
Peroxide value (Mg/g)	3.42	-
Moisture content (wt %)	0.37	-
High heating Value HHV (MJ/kg)	39.71	34-38.5
Acid Value (mg KOH/g)	83.76	3.8-5.06
Free Fatty acids (wt %)	41.64	2.53-20
Iodine Value (mg/I_2/g oil)	118.8	-
Sulfur content (wt %)	None	-

3.3 Conventional Method

This method generally employs the usage of mechanical presses oil expellers which are considered to be somewhat inefficient as it leaves about 7 to 15 % of available oil in the de oiled cake. The mechanical method has high quality [16]. According to researchers double stage compression expellers are recommended for better oil recovery. [17] If the pressure applied is increased, pretreating the seed is reported to give better oil extraction. The chemical method employs the use of chemicals as the n hexane and/or other organic solvents however the method tends to extract unwanted components along with the oil. Solvent to seed ratio, drying time, boiling point of solvent are some parameters that affect the extraction process. As reported by Gimbun J et al. [18] extraction of 100g of rubber seeds was carried out using 250 ml of n-hexane at a temperature of 60degree Celsius and for 4 hrs.

3.4 Microwave Assisted Method

This method involves the use of an electromagnetic field which accelerated the extraction process. As reported by Gimbun J et al. [18] extraction of rubber seed oil from 250g of crushed rubber with 500ml of n hexane for 30 min at 64 degree Celsius using the Milestone Micro synth ATC-FO 300 and separated the oil/hexane mixture using a rotary evaporator.

3.5 Gas Assisted Method

In this method supercritical CO_2 is dissolved into the milled steel followed by screw pressing process. [16] This method can be used for low pressure extraction.

4. RUBBER OIL PRODUCTION METHODOLOGY

The seeds are dried and are milled to reduce their size and to make them ready for further treatment and conditioning process. The milled seeds are treated by putting into gas heated dryer for 10–20 min at a temperature of 60–70 degree Celsius. After this the resulting meal is put in mechanical press to extract the oil. The wastes are filtered using filtration unit and some more rubber oil is extracted. Further treatment the oil cake is treated with n-hexane. The oil cake is stored whereas the seed oil and n hexane mixture is separated using vacuum evaporator. The diagram has been shown in Fig 2.

On basis of the Table 5, it can be concluded that the rubber seed oil has higher value of unsaturated fatty acids, however the values reported by various scholars can be a bit different owing to different extraction methods, related processes and the geographical location of the rubber tree.

5. TRANSESTERIFICATION METHODS FOR RUBBER SEED OIL

To produce biodiesel from rubber seed oil various transesterification methods are available and are used such as conventional method, in situ method, ultrasonic method and enzymatic method. TABLE 6 shows the biodiesel yield and optimum reaction conditions for biodiesel production from rubber oil.

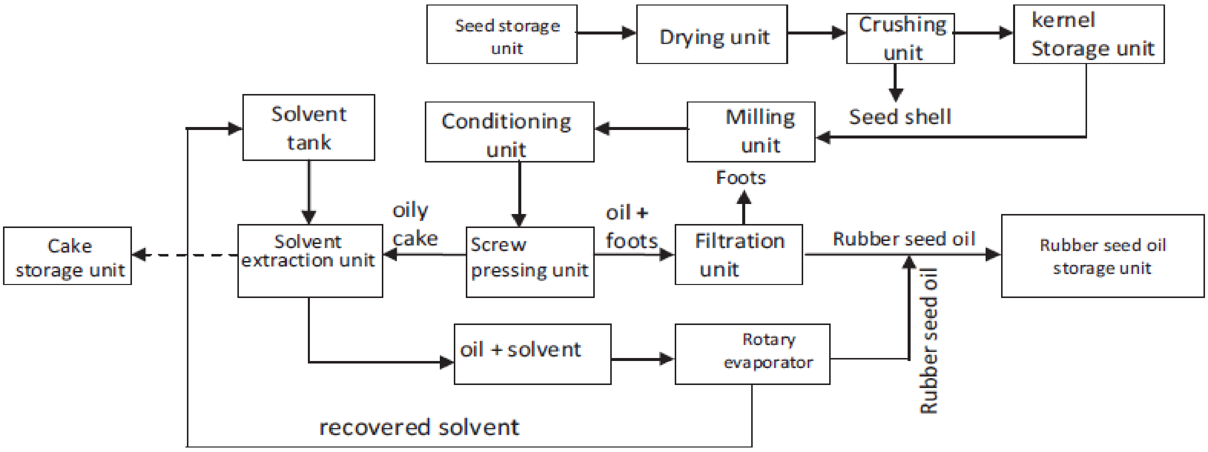

Fig. 2 Rubber seed oil production adapted from [19]

Table 5 Fatty Acid composition of various oils [7, 18, 20-24]

Fatty acid	Chemical Formulae	Rubber	Jatropha	Karanja
Stearic acid	$C_{18}H_{36}O_2$	5.6-12	5.9-7.3	2.4-8.9
Oleic acid	$C_{18}H_{34}O_2$	12.7-44.8	34.2-44.6	44.3-71.3
Palmtic acid	$C_{16}H_{32}O_2$	0.23-10.6	12.6-16	3.6-9.7
Myristic acid	$C_{14}H_{28}O_2$	2.2	0.2-1.5	-
Linoleic acid	$C_{18}H_{32}O_2$	37.6-51.8	30.5-40.1	10.6-18.2
Arachidonic acid	$C_{20}H_{40}O_2$	0.66-0.97	0.16-0.3	2.1-4.2
Oil content (wt %)	-	35-60	20-60	25-40

5.1 Conventional Method

Through the use of NaOH, KOH, alkoxides and carbonates as the homogenous base catalysts and the biodiesel yields were obtained in range of 86.5-97.3% via conventional method [27, 29, 30, 31]. It was also suggested that the use of homogenous acid catalysts such as $H_2SO_4$for pretreatment of rubber seed oil before transesterification process. Certain heterogeneous catalysts such as metal oxides in solid state can also be used for transesterification of rubber seed oil. [30]

5.2 The Supercritical Method

Sanjel N. et al. [32] suggested the use of this method where high FFA content is present, in this alcohol generally becomes a super acid and the use of catalysts is thereby removed. This method utilizes high temperature and high pressure and has low reaction time.

5.3 Microwave- Method and Co-Solvent Method

Microwaves are a type of radiation having low energy and is non-ionizing in nature. The microwaves help in re aligning the dipoles of the reactants thus increasing the yield of biodiesel in a very short time [33]. Co solvent method is a very environmentally friendly method due to its low energy requirements, and causes the formation of biodiesel in a very short time. A single phase is generally produced in this technique. Tetrahydrofuran is a co solvent that has been widely used [22].

5.4 The In-Situ Method

In this method instead of reaction between the extracted oil and alcohol, directly the milled seeds are made to react with alcohol in presence of a catalyst. Abdul Kadir et al. [34] generated biodiesel with 91.05% yield using this method. TABLE 6 shows Biodiesel yield and optimum reaction conditions for biodiesel production from rubber oil.

6. RUBBER BIODIESEL (RB)

Rubber biodiesel is a promising fuel for the existing designs of engines. Moreover, biodiesel can be used with petro diesel in the form of blends [51]. The presence of biodiesel in petro diesel enhances some properties of diesel such as storage properties, flash point, and cetane number [27].

FAME, or fatty acid methyl esters, is the term used for biodiesel produced by methanol [4]. Methanol is used as a solvent in the synthesis of biodiesel hence it must be used in excess. However, the amount of methanol should not be much exaggerated because it leads to lowering of flash point of the biodiesel [54]. TABLE 7 shows various properties of rubber oil and its biodiesel along with other esters and diesel. (Table 7 Physiochemical properties of rubber seed oil methyl esters, other methyl esters and diesel [5, 6, 27-29, 35-38, 40, 44, 45-50, 52, 54, 55]).

The comparison shows that rubber seed oil esters have similar properties to other esters which have been recognized as potential alternative to diesel. It can also be seen that after the transesterification process, the properties of RB became comparable to that of diesel. One of the biggest barriers in usage of crude rubber oil as a fuel in IC engines is the high kinematic viscosity of the oil which significantly reduces by 40-80% after transesterification [27, 51, 54]. Ramdhas et al. [42] reported that at high temperature operations of engine (above 60 degree Celsius) the viscosity of the biodiesel decreases even more and becomes almost equal to that of diesel. Although a thorough study of the blending of RSO biodiesel in petroleum diesel is yet to be done. The heating value of the biodiesel is around 91% of that of diesel [36]. The presence of oxygen in the fuel enhances the combustion characteristics of the fuel. Widayat et al. [28] reported that one of the main issues with non-edible oils is the high acid value (or acid number). Acid value is the measure of amount of carboxylic acid groups present in the chemical substance like fatty acids. High acid value means that the biodiesel still contains a lot of free fatty acids which are yet to be converted to methyl esters which leads to deposits in the fuel systems. Process optimization of the transesterification process reduces the acid value significantly which prevents the possible occurrence of saponification reaction [27, 35]. Iodine number is used to determine the amount of unsaturated fatty acid in the fuel. High iodine number indicates higher number of C=C bonds in the oil. RSO biodiesel contains less amount of unsaturated fatty acid and hence has a lower iodine number [28].

Another important parameter for fuels is the cetane number. It tells about the ignition quality of the fuel. RSO biodiesel has a cetane number higher than that of diesel and hence it would enhance the ignition quality of diesel in blends [59]. The flash point of the RSO biodiesel is higher than that of diesel. Hence, it is easier to store the biodiesel. Moreover, the flash points of the blends are improved and increase the storage stability of diesel [27, 39, 46, 54]. All the properties of a sellable biodiesel have to pass the standard specifications such as ASTM and EN and the RB meet these standards

6.1 Oxidation stability and cold flow properties of rubber seed oil

Oxidation stability is an important parameter to judge the fuel stability and its performance in engines. It is the ability of the biodiesel to remain unchanged when it is stored for a long period of time [48]. The reaction of atmospheric oxygen with unsaturated fatty acid leads to formation of hydrogen peroxides and gums which affects the engine performance of the fuel. Rancimat method is used to determine the oxidation stability of oils. The specification adopted in this method is a minimum of 6-h induction period at 110^{o}C [55]. Ikwuagwu et al. [5] reported that the induction period of crude RSO (13.7-h) was higher than that of RSO biodiesel 8.7-h). This decrease in the oxidation stability of methyl esters is due to the drastic decrement of the kinematic viscosity of the oil on esterification. The decrement in viscosity leads to higher oxygen diffusion rate which increases contact of the esters with oxygen. Despite the decrease in IP, RSO biodiesel meets the standard values [29].

The three major parameters to determine the cold flow properties of biodiesel are cloud point (CP), pour point (PP) and cloud filter plugging point (CFPP) [27]. Cloud point is the temperature at which solid crystals begin to appear in the fuel when cooled continuously which may lead to filter clogging. Pour point is the temperature at which the free flow of the fuel is ceased

[49]. Cloud filter plugging point is the lowest temperature at which a given quantity of fuel can still pass through a standard filtration device, when cooled under specified conditions [50]. The cold flow properties in biodiesel are related to molecular structural features of fatty acids such as carbon chain length, degree of un-saturation, double-bond orientation [29]. Due to its high un-saturated fatty acid concentration, RSO biodiesel show better cold flow properties than many other fuels.

Table 6 Biodiesel yield and optimum reaction conditions for biodiesel production from RSO

Type of catalyst	Production method	Reaction Temperature (°C)	Reaction time (hours)	Alcohol to oil ratio	Weight of catalyst used	Biodiesel Yield (%)	References
Esterification							
H_2SO_4	Conventional	65	3h	10:1	10 wt%	-	[25]
H_2SO_4	Conventional	45	1.5h	15:1	10 wt%	-	[26,27]
Transesterification							
CaO	Conventional	65	4h	5:1	5 wt%	96.9	[18]
KOH	Conventional	55	6.75h	6:1	1 wt%	96.8	[27]
H_2SO_4	In-situ	60	2h	3:1	0.5% (v/v)	91.05	[28]

Table 7 Physio chemical properties of rubber seed oil methyl esters, other methyl esters and diesel [5, 6, 27-29, 35-38, 40, 43- 45, 47-50, 52, 54, 55].

Fuel properties	Rubber seed oil methyl esters	Pongamia methyl esters	Rapeseed oil methyl esters	Cotton seed oil methyl esters	Diesel
Specific gravity	0.86-0.887	0.876-0.94	0.882	0.874-0.911	0.816-0.84
Kinematic viscosity(mm^2/s) at 40^oC	3.7-6.29	3.99-11.82	4.5	4.0-6.0	2-5.7
Calorific value (MJ/kg)	32.6-41.07	35.56-42.17	37	39.5-40.32	42-45.9
Flash point (^oC)	110-235	147-196	170	210-243	45-98
Cetane number	43-54	47.78-57.9	52	41.2-59.5	45-47
Oxidation stability at 110^oC, h	6.5-14.55	2.3-11.6	-	-	-
Cloud point(^oC)	0.4 to 5	-3 to 22.5	-4 to – 6.57	-2 to 1.7	-10 to 2
Pour point(^oC)	-8 to -2	-4 to 15	-12 to -14	15 to -4	-20 to -16
Cloud filter plugging point (^oC)	0	-	-	-	-
Acid value (mg KOH/g)	0.18-0.9	0.62-0.80	-	-	0.062
Iodine number	82.9-146	-	-	-	38.3
Carbon residue (%)	0.14-0.22	-	-	-	2-4.5

Table 8 Properties of blends of rubber seed oil biodiesel [45].

Fuel properties	**B10**	**B20**	**B30**
Density (kg/m^3)	853.8	854.4	856.8
Viscosity (mm^2/s)	3.54	3.57	3.59
Calorific value (MJ/kg)	41.885	41.448	40.247
Flash point (^{o}C)	80.5	82.5	84.5
Oxidation stability at 110^{o}C, h	14.55	13.59	13.25
Pour point (^{o}C)	0.0	1.0	1.6
Cloud point(^{o}C)	1.0	1.0	1.8

Table 9 Engine performance and emission characteristics of RSO biodiesel and its blends as a fuel.

S. No	**Engine specification**	**Fuel**	**Engine performance**	**Emission characteristics**	**References**
1	DI Engine: Rated speed: 1500 rpm Rated power: 5.5 kW Stroke: 110 mm Bore: 88 mm Number of cylinders:1	RSO biodiesel (B20, B40, B60, B80, B100), Diesel	1. BSFC for B20 and B40 is comparable to that of diesel. 2. Brake thermal efficiency of B60 and B80 is comparable to diesel.	1. Smoke density is decreased for B60 and B80. 2. Carbon deposit increased on the walls of combustion chamber.	[42]
2	Diesel Engine: Rated speed: 1500 rpm Rated power: 4.4 kW Stroke: 110 mm Bore: 87.5 mm Compression ratio: 17.5:1 Number of cylinders:1 Air cooled	RSO, RSO biodiesel, Diesel	1. Brake thermal efficiency: Diesel >RSO Biodiesel > RSO. 2. BSEC: RSO > RSO biodiesel > Diesel. 3. Cylinder peak pressure: Diesel > RSO biodiesel > RSO 4. Ignition delay: RSO > RSO Biodiesel > Diesel	1. Exhaust gas temperature, smoke density, CO and HC emissions: RSO > RSO Biodiesel > Diesel. 2. NOx emissions: Diesel > RSO biodiesel > RSO.	[45]
3	CI Engine: Rated speed: 1500 rpm Rated power: 3.7 kW Stroke: 110 mm Bore: 80 mm Compression ratio: 16.5:1 Number of cylinders:1 Water cooled	RSO biodiesel (B20, B60, B80, B100), Diesel	1. Brake thermal efficiency is decreased with higher concentration of biodiesel. 2. BSEC increased by 7.3-20.3% than diesel.	1. NOx emission is decreased by 10.1% for B100 and 4.6% for B80. 2. Exhaust gas temperatures are increased by 1.4-11.8% than diesel. 3. Smoke opacity is lesser than diesel for B20 and B60 and it is higher than diesel for B80 and B100. 4. CO and HC levels are higher in biodiesel than diesel.	[53]

4	CI Engine: Rated speed: 1500 rpm Rated power: 5.5 kW Stroke: 110 mm Bore: 88 mm Number of cylinders:1	RSO biodiesel (B10, B20, B50, B75, B100), Diesel	1. Brake thermal efficiency is increased by 3% for B10. 2. BSFC is reduced at lower concentrations of biodiesel.	1. CO, CO_2 emissions are reduced at lower concentrations of biodiesel. 2. Smoke density is decreased as biodiesel concentration increased. 3. Exhaust gas temperature and NOx is increased as biodiesel concentration increased.	[54]
5	CI Engine: Rated speed: 1500 rpm Rated power: 5.5 kW Stroke: 110 mm Bore: 88 mm Number of cylinders:1 Compression ratio: 16.5:1 Water cooled	RSO biodiesel, diesel	1. Brake thermal efficiency for RSO biodiesel is lesser than diesel. 2. BSFC for RSO biodiesel is higher than diesel.	1. CO emissions for RSO biodiesel are lesser than diesel at higher loads and greater at lower loads. 2. HC emissions for RSO biodiesel are lower than diesel at all loads. 3. NOx emissions for RSO biodiesel are comparable to diesel at lower loads but greater at higher loads.	[56]

6.2 Engine Performance of RB

Table 9 shows engine performance and emission characteristics of rubber biodiesel (RB) and its blends as a fuel. This biodiesel has the prospect of being used as an alternative to diesel in compression ignition engine without any extra engine modifications. The emissions in case of diesel and RB are comparable for lower blends of rubber biodiesel.

7. CONCLUSION

The crude oil properties of Rubber seed oil is similar to that of crude Pongamia oil from which vast majority of biodiesels are made. The availability of varied oil extraction methods have helped in the economics and extraction yield of the crude rubber oil with the conventional method of oil extraction being the one which is widely used. KOH and H_2SO_4 catalysts have shown to give the highest yield of biodiesel from rubber seed oil of around 96.8 and 91.05 % respectively. Two step esterification reaction is employed to produce the biodiesel from RSO due to its high free fatty acid content. The physiochemical properties of rubber seed oil methyl esters are comparable to those of diesel. Blending of RSO biodiesel in petro diesel improves the flash point, cetane number and certain emission characteristics such as smoke opacity, CO and HC concentration at low levels of biodiesel. For blends with biodiesel concentration below 20%, the engine characteristics such as BSFC, BSEC and brake thermal efficiency are comparable with diesel. The exhaust gas temperature is increased with increase in biodiesel concentration which in turn leads to increase in NOx emissions.

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