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Review

Properties, performance, and applications of biofuel blends: a review

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Abstract: Biofuels such as ethanol and biodiesel derived from living plants or animal matter can be used directly in their neat forms or as blends with their fossil counterparts in internal combustion engines. Although the properties and performance of neat biofuels have been extensively reported, this is not the case for many blends. The purpose of this review is to analyze different forms of biofuel blends that are under research and development comparing their utility and performance in the two primary classes of engines, i.e., spark ignition and compression ignition engines. The fuel properties, performance and emission characteristics, advantages and disadvantages of various fuel blends are compared and discussed. The analysis reveals certain blends possess better overall fuel properties and yield better overall performance than the neat or fossil forms.

Keywords: biodiesel blends; ethanol blends; gasohol; E-diesel; EB-diesel; gasoline-ethanol-methanol; bio-oil/biodiesel

1. Introduction to Biodiesel and Biodiesel Blends

1.1. Biodiesel

Biodiesel is a type of renewable fuel produced from biological resources [1,2] that conforms to the ASTM D6751 standard (also comparable in general to the European standard EN 14214 and the National Standard of Canada CAN/CGSB-3.524). Biodiesel is produced from triglycerides that may be found in different sources, such as vegetable oils, animal fats [3], and algae [4]. In the United States, the most common source of feedstock for biodiesel is soybean oil [5]. Other types of oils can also be used including palm oil which is predominantly used in Asia and canola oil which is

predominantly used in Europe [6,7,8]. The fast-paced evolution of biodiesel and other types of biofuels is due to many reasons, including the ability to utilize renewable resources (unlike fossil fuels), price stability compared to crude oil, eco-friendliness, and its contribution to reducing US dependence on foreign oil. Biodiesel is produced through a process called transesterification, which produces fatty acid alkyl esters via breakage of ester linkages in triglyceride in the presence of acid (H_2SO_4) or base catalysts (NaOH or KOH), and common alcohols (such as methanol or ethanol). This process results in biodiesel and glycerol as byproducts [2].

Table 1. ASTM D6751 biodiesel specifications summarized [9].

Property	Test Method	Grade No.1-B S15
Sulfur, % mass (ppm), max	D5453	0.0015 (15)
Cold soak filterability, s, max	D7501	200
Monoglycerides, % mass, max	D6584	0.4
Calcium and Magnesium, combined, ppm, max	EN14538	5
Flash point (closed cup), °C, min	D93	93
(1) Methanol content, % mass, max	EN14110	0.2
(2) Flashpoint, °C, min	D93	130
Water and sediment, % volume, max	D2709	0.05
Kinematic viscosity, mm^2/s , 40 °C	D445	1.9–6.0
Sulfated ash, % mass, max	D874	0.02
Copper strip corrosion	D130	No. 3
Cetane number min	D613	47
Cloud point, °C	D2500	Report
Carbon residue, % mass, max	D4530	0.05
Acid number, mg KOH/g, max	D664	0.5
Free glycerin, % mass, max	D6584	0.02
Total glycerin, % mass, max	D6584	0.24
Phosphorus content, % mass, max	D4951	0.001
Distillation temperature, 90% recovered (T90) ^b , °C, max	D1160	360
Sodium and potassium, combined, ppm, max	EN14538	5
Oxidation stability, hrs, min	EN15751	3

Biodiesel can be mixed or used as 100% “neat” form in diesel engines to generate power [10]; however, biodiesel cannot be used in gasoline engines because the fuel’s flash point is higher than gasoline, and it has a high cetane index (or low octane index). Thus, it will not ignite as fast as gasoline within the combustion chamber. When mixed, the ratio of mixing or blending biofuel depends on the final purpose. There are different types of blends with fossil fuel such as B-20, where B is biodiesel, and the number represents the blending proportion. For example, a B-20 blend would possess 20% biodiesel, and the remainder would be fossil diesel [10].

Neat (B100) biodiesel can only be used in modified engines that have compatible parts. Since biodiesel esters have good solvent capability, parts made of rubber and plastic are known to dissolve in biodiesel [11].

It should be noted that biodiesel properties change with the raw material used. However, the term biodiesel is used only for fatty acid alkyl esters that conform to aforementioned standards. Accordingly, this review analyses biodiesel that conforms to these standards.

1.1.1. Properties of B-100

Select properties of biodiesel fuel blends are depicted in Table 2. Comparisons of some critical parameters are also depicted in Figure 1.

Table 2. Biodiesel blends properties compared to diesel.

Properties	Fossil Diesel	Biodiesel B-100	B-20 Blend	B-5 Blend	Remarks	Ref.
	2.8271	4.2691	-	-	Fossil Diesel is (no.2),	[12]
	3.53	4.89	3.75	3.56	biodiesel is from soybean.	[13]
	3.06	5.75	-	4.45		[14]
Viscosity mm ² /s	4.3*	11*	-	-	*FAME	[15]
	2.71	6.17	3.21	2.92	40 °C/70 °C,	[16]
	2.4	4.92	2.74	2.48	At 40 °C	[17]
	2.5				At 40 °C	[18]
Flash point °C	69	120	82	74		[13]
	53	168*	-	57	*FAME	[14]
	71.5	-	-	-		[8]
	59	111	67	64		[17]
Cetane number min	42.6	51.5	-	-	Fossil diesel is no.2,	[12]
	50.9	56*	52.2–52.3*	51.5*	*FAME	[14]
	46					[18]
Cloud point °C	0	3	0	0		[13]
	2	-	-	-		[8]
	-	-	-	(-24--28)	Range	[19]
Pour point °C		0	-9	-12		[13]
	<-12*1	-	-	-	* Less than Range	[8]
Calorific value MJ/Kg	-	-	-	(-36--39)		[19]
	-	-	44.41	45.37		[13]
	43.35	39.76	-	-		[15]
	46.35	39.87	44.98	46.00	At 40 °C,	[16]
	45.38	-	-	At 20 °C	[8]	
	43.15	39.95	42.01	42.19		[17]
Sulfur Content	15–500	-	-	-	mg/Kg	[20]
	300 ppm	-	-	-	ppm	[18]
	3.59–12.29	10.94–11.69	-	-	µg/g	[21]
Lubricity (groove diameter mm)	-	-	0.07	-	(6.6 mg/Kg sulfur) in fuel	[22]
	0.83	0.72	-	-		[23]
Acid Number mg KOH/g	-	0.275	0.057	0.008		[24]

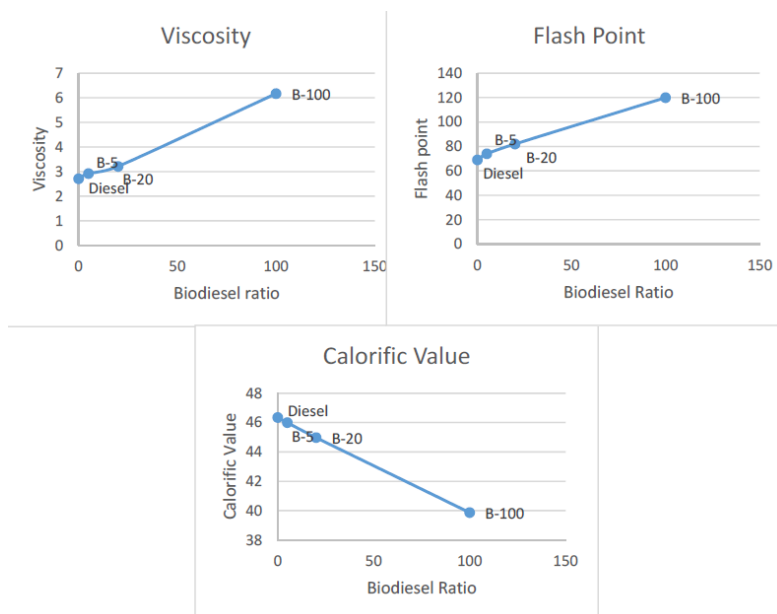


Figure 1. Comparison of select key properties of biodiesel blends and fossil diesel.

1.1.2. Kinematic viscosity

Kinematic viscosity is the liquid's resistance to flow, which basically measures how thick the fuel would be. High viscosity would clog the fuel injection system, and low viscosity may not facilitate complete combustion. However, viscosity might vary depending on feedstock and the method of measurement. The American Society for Testing and Materials (ASTM) has determined viscosity to occur in a range of 1.9–6.0 mm²/s by ASTM D445 (Test of Kinematic Viscosity for Transparent and Opaque Liquids) for pure biodiesel from the various feedstock. It has been reported that the viscosity of biodiesel is higher than that of fossil diesel (Table 2). In fact, one of the key reasons for transesterification is to reduce the viscosity of vegetable oil; the resulting biodiesel has a drastic reduction of viscosity as compared to the starting triglycerides. Generally, increasing the number of double bonds in the carbon chains causes the biodiesel to be more viscous [8]. Values of viscosity for diesel and biodiesel blends are compared in Table 2.

1.1.3. Flash point

Flash point is defined as the temperature at which the fuel ignites when it is exposed to a flame or spark. It varies from one fuel to another and from one blend to another. The higher the flash point, the higher the temperature required to ignite the fuel. On the one hand, it is better to lower the flash point for combustion purposes. However, the higher flash point means the fuel is safer to transport. Usually, the biodiesel flash point is higher than conventional diesel. In biodiesel, the flash point is around 110–180 °C, whereas in conventional diesel it is around 55–60 °C. The reason for the high flash point is the presence of unsaturated chains C 18:1 and longer. The proposed empirical model for flash point estimation made by Catoire and Naudet [26], clarifies the reason for the high flash point for longer carbon chain compounds [25,26]:

$$FP = 1.477 T_b^{0.74686} * \Delta H_{vap}^{0.16845} * C^{0.05948}$$

Where:

FP: is the Flash Point (K)

T_b : is the boiling point of the compound (K)

ΔH_{vap}° : is the standard enthalpy of vaporization of the compound at 298.15 K, expressed in KJ/mol

C: is the number of carbon atoms in the fuel molecule

1.1.4. Cetane number (CN)

CN is the measure of the ignition quality of the fuel after it is introduced to a diesel engine, which is measured by ASTM D613 (Standard Test Method for Cetane Number of Diesel Fuel Oil). CN measures the ignition timing (or ignition delay) in the combustion chamber of a diesel engine [27]. The higher the CN, the better and faster the fuel becomes for combustion or ignition. This means that the fuel needs less time to ignite if the CN is higher. Usually, longer and saturated carbon chains have a higher CN. Thus, the higher the hydrocarbon content in the feedstock, the higher the CN will be; for example, biodiesel derived from animal fat would have higher CNs than other feedstock [28].

1.1.5. Cloud point and pour point

Two of the important physical properties of biodiesel fuel are cloud point and pour point. Cloud point is defined as the temperature at which the fuel will become cloudy, due to wax crystals [10]. Crystallization occurs when the fuel is cooled. Cloud point is measured by ASTM D2500 (Test Method for Cloud Point of Petroleum Products), and related test methods D5771, D5772, or D5773 [10]. On the other hand, the pour point is the temperature at which the liquid will start to lose its fluidity and begins to turn into a solid [10]. Pour point is measured by ASTM D97 (Standard Test Method for Pour Point of Petroleum Products) and D5950 or D5949 [10]. Cloud and pour points are related to the amount of saturated fatty acids. In general, higher amounts of saturated fatty acids increase cloud and pour points. Generally, biodiesel has higher cloud and pour points than conventional diesel. The values of cloud and pour points for B-100 range from -15 to 16 °C [29]. A recent study showed that cloud point is 3 °C whereas the value varied between 1 and 2 °C in conventional fuel [13]. This increase in cloud and pour points could be a result of the natural occurrence of saturated fatty acids in biodiesel as compared to none in petroleum diesel.

1.1.6. Calorific value (CV)

CV is also referred to as the heating value in literature and is measured by ASTM D240 (Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter). The amount of energy released when a known volume of the fuel is fully combusted is an indication of the energy content of the fuel. Generally, biodiesel has a lower heating value than conventional diesel because of the higher oxygen content. The maximum heating value reported for

biodiesel has a minimum limit of 35 MJ/kg, whereas the majority of conventional fuels have a higher limit of 45 MJ/Kg [8].

1.1.7. Lubricity

Lubricity is a key property of biodiesel, which gives it an advantage when compared to fossil diesel. Lubricity is referred to as the lubrication ability of a substance. In fact, as little as 2% of biodiesel added to regular diesel has been known to solve lubricity problems [30]. Regular diesel manufacturers were forced to remove sulfur (an additive that enhanced lubricity) by the EPA in 1993 and again in 2006 when severe hydrotreating was required to meet the US EPA 15 ppm sulfur maximum rule. When that happened, fuel lubricity was reduced to the point of causing damage to engine parts. Muñoz et al. [31] found that the sulfur removal damage could be reversed by adding biodiesel. Lubricity can be determined through viscosity measurement [31,32] and is done by evaluating the ability of a thin film of the liquid to protect two metal surfaces from severe corrosion [31,32]. The most common methods for lubricity evaluation are a high-frequency reciprocating rig test (HFRR), a ball-on-cylinder lubricity evaluator test (BOCLE), and a four-ball wear test which was developed in 1933 [23]. The standards for the wear test are ASTM D2266 for greases and ASTM D4172 B for lubricants. Fernando [23] had explained and conducted the four-ball wear test based on ASTM D4172 standard for biodiesel B-100 and diesel fuels from the different feedstock. In the four-ball test, the metal balls are forced to move on a metal surface under a specific load—which causes a groove on the metal's surface. The diameter of the groove is measured and compared to a standard measurement. The greater the diameter of the groove, the lower the lubrication ability (or lubricity) the liquid has. As can be seen from Table 2, biodiesel has a significantly higher lubricity than diesel fuel.

1.1.8. Acid number

The Acid number is known as the amount of KOH in mg required to neutralize the acids in a 1 g sample [33]. In the biodiesel area, it is a measurement of the extent of hydrolysis and oxidation for biodiesel [34]. It is measured according to ASTM D6751, and EN 14214, both of which have emphasized the acid number for biodiesel should not exceed 0.5 mg KOH/g for B-100 due to the formation of free fatty acids during the production process [35]. Apparently, the acid number is affected by the storage and the age of the biodiesel which will become more acidic with age [35]. Baig [24] determined the acid number of biodiesel B-100 using the titration method according to ASTM D974 (using 0.02 M KOH in 10 ml titration solvent). The results are shown in Table 2.

1.1.9. Sulfur content

Sulfur is one important property in biodiesel, which has a great impact on engine performance and emissions. The presence of sulfur increases the particulate matter emissions in the exhaust causing more pollution [22,36]. The excess amounts of sulfur in the fuel will cause corrosion inside the engine cylinder [22]. The excess amount of sulfur will be oxidized during combustion into SO₂. Sulfur dioxide will then be further oxidized into SO₃ forming sulfuric acid eventually after reacting with water. Furthermore, sulfuric acid will condensate on the metal parts in the engine, which will

cause corrosion, damage, and failure to the engine parts [37]. There are also other effects in the exhaust emissions from sulfur on the environment and health. The exposure to sulfur gaseous emissions can create breathing problems, and longtime exposure will cause heart diseases and eventually death [22]. Therefore, the less sulfur content in the fuel, the better. Results were collected from different sources and are shown in Table 2.

1.1.10. Emissions

Emissions measurements including smoke concentration, CO content, CO₂ content, NO_x, and sulfur emissions of biodiesel combustion, have been compared with conventional diesel using parallel criteria, i.e., smoke concentration/particulate matter, CO content, and CO₂ content (Table 3). Biodiesel produces less smoke, and CO emissions are reduced as well as CO₂ emissions when compared to conventional diesel. In fact, it has been reported that particles emissions were 33% less than conventional diesel for B-100. Also, levels of CO and CO₂ were reduced by 10%, compared to conventional diesel. However, this ratio may vary when using biodiesel blends [38].

Table 3. Emission comparison of diesel and biodiesel blends.

Emission	Diesel	B-100	B-20	B-5	Remarks	Ref.
CO ₂	12.9%	-	12.9%	-		[39]
	173.6	172.9	-	-	g/km	[40]
	3892.5*	-	3664.2*	3488.7*	*g/kW-h @ 16.3 N.m	[41]
CO	30	-	32	-	ppm	[39]
	0.153	0.067	-	-	g/km	[40]
	3.6*	-	2.8*	2.9*	*g/kW-h @ 16.3 N.m	[41]
Particulate Matter			12.5 ± 0.9	-		[38]
Concentration	12.9 ± 0.9	8.6 ± 1.3	13.38	-		[39]
(mg/m ³)	14.92	-				
SO _x	96	-	77	-	SO ₂ , unit is ppm	[39]
	6.8*	-	0.8*	1.4*	*g/kW-h @ 16.3 N.m	[41]
NO _x	104 ppm	-	109 ppm	-	NO ₂	[39]
	0.367	0.454	-	-	g/km	[40]
	-	-	-	571 ppm	Average	[42]
	21.5*	-	16.8*	16.2*	*g/kW-h @ 16.3 N.m	[41]

1.1.11. Performance

Generally, biodiesel produced from different oils has about the same performance for the short term as the diesel fuel. For example, A single cylinder engine with various types of vegetable oils (raw sunflower oil, raw soybean oil, and opium poppy oil fuels) operated at 1300 rpm only observed maximum torque differences of about 10% between the diesel reference and peak values of vegetable oil fuels. The maximum power difference between the reference value and peak values of the vegetable oil fuels was about 18% obtained from raw cottonseed oil and raw soybean oil fuels. The minimum torque and power difference was about 3% between the reference value and oils [15]. These results may be due to the higher viscosity and lower heating values of vegetable oils.

1.1.12. Engine efficiency

One of the effective factors of engines efficiency is brake specific fuel consumption (BSFC). It is a measure of fuel efficiency that burns and produces rotational motion. BSFC with biodiesel was measured at the engine's full load and 1400 rpm with No.2 diesel as a baseline. It was found that biodiesel had a higher BSFC, almost 13.5% increase because biodiesel is having a 12% lower heating value than No.2 diesel by 12% [12].

1.1.13. Thermal efficiency

Another factor that dictates engine performance is thermal efficiency. Thermal efficiency and brake specific fuel consumption are inversely proportional. Thus, BSFC is the inverse of thermal efficiency. The thermal efficiency of biodiesel is about 0.5% higher as compared to No.2 diesel (Table 4) [12].

Table 4. Performance efficiency comparison of #2 diesel and biodiesel.

Fuel type	BSFC (g/kw-hr)	% change in BSFC	Thermal efficiency%	% change in thermal efficiency
No.2 Diesel	228.42	-	36.96	-
Soy Methyl Ester	259.33	13.53	37.13	0.45

1.1.14. Advantages of B-100

- (1) Renewable and thus carbon neutral.
- (2) Fewer price fluctuations as compared to fossil diesel
- (3) Delivers higher thermal efficiency.
- (4) Biodiesel has higher CNs as compared to conventional diesel; thus, biodiesel is a better fuel for compression ignition engines.
- (5) Affords a better emissions profile than diesel fuel making it environmentally friendly.

1.1.15. Disadvantages of B-100

- (1) Long-term storage causes oxidation and thus degrades fuel quality.
- (2) Elicits a higher brake specific fuel consumption compared to fossil fuel.
- (3) Can have high levels of insoluble materials.
- (4) Cold flow properties may be not as attractive as fossil diesel.
- (5) Requires engines modification to accommodate neat biodiesel.
- (6) May cause increased NOx emissions.

1.2. Biodiesel blends

Biodiesel is miscible in diesel fuel at any ratio. However, there are several standardized blends including B2, B6, B10, and B20 (other intermediate blends are also available, but used less frequently). Table 5 presents summarized requirements for 6% biodiesel (B6) to 20% biodiesel (B20) as listed in ASTM D7467-13.

Table 5. Summarized requirements for 6% biodiesel (B6) to 20% biodiesel (B20) as listed in ASTM D7467-13 [9].

Property	Test Method	Grade		
		B6 to B20 S15	B6 to B20 S500 j	B6 to B20 S5000
Acid number, mg KOH/g, max.	D664	0.3	0.3	0.3
Viscosity, mm ² /s at 40 °C	D445	1.9–4.1 ^a	1.9–4.1 ^a	1.9–4.1 ^a
Flash point, °C, min	D93	52 ^b	52 ^b	52 ^b
Cloud point, °C, max or LTFT/CFPP, °C, max	D2500	c	c	c
Sulfur Content, (µg/g or ppm)	D5453	15	-	-
mass%, max.	D2622	-	0.05	-
mass%, max.	D129	-	-	0.5
Distillation temperature, °C, 90% evaporated, max	D86	343	343	343
Ram's bottom carbon residue on 10% bottoms, mass%, max.	D524	0.35	0.35	0.35
Cetane number, min	D613	40	40	40
One of the following must be met:				
(1) Cetane index, min	D976-80	40	40	40
(2) Aromaticity, vol%, max.	D1319-03	35	35	-
Ash Content, mass%, max.	D482	0.01	0.01	0.01
Water and Sediment, vol%, max.	D2709	0.05	0.05	0.05
Copper Corrosion, 3 h @ 50 °C, max	D130	No.3	No.3	No.3
Biodiesel Content, % (V/V)	D7371	6.–20.	6.–20.	6.–20.
Oxidation Stability, hours, min.	EN15751	6	6	6
Lubricity, HFRR @ 60 °C, (micron µm), max.	D6079	520	520	520

Biodiesel blends are added to fossil diesel to improve certain physical properties—such as lubricity, efficiency, cetane number, and oxygen content of the final blend. Some of these property improvements are attributed to the high degree of oxygenation. The degree to which fuel properties change depends on the blend composition and the key characteristics of some common biodiesel blends (i.e., B-20 and B-5), which are discussed below. Biodiesel and diesel are blended such that the desired properties of both biodiesel and fossil diesel are enhanced.

1.2.1. B-20

B-20 is a mixture of 20% biodiesel and 80% conventional fuel. This is a key blend in that it is widely considered as the highest amount of biodiesel that can be used in compression ignition engines without engine modification. [8].

(1) Properties

Properties of B-20 are generally only slightly different from that of B-100. A comparison of key properties of B-20 along with B-100 and #2 diesel fuel are depicted in Table 2.

(2) Viscosity

As can be seen from Table 2, neat biodiesel and blends of biodiesel have viscosity values that are close to the diesel fuel. In general, the viscosity of diesel fuel is lower than neat biodiesel. The viscosity of B-20 was between neat biodiesel and diesel fuel and ranged from 3.416 mm²/s [13] to 3.416 mm²/s at 25 °C [39].

(3) Flashpoint

It is known that the lower the flash point is for a fuel, the faster and more efficient that fuel would be in terms of combustion [27]. In this case, the flash point of B-20 is 67 °C, which is lower than B-100; however, it is still higher than pure fossil diesel. Therefore, B-20 would combust faster as compared to B-100.

(4) Cetane number (CN)

The value of CN for B-20 has not been specifically measured; however, the values of other blends such as B-15 and B-25 have been reported [14]; Thus, the value of B-20 is likely to be ~52.2–52.3. This value is still higher than that of diesel (50.9).

(5) Cloud and pour point

Cloud point of B-20 is reported to be 0 °C whereas the pour point is –9 °C by some accounts [13]; however, others [39] report values at –3.6 °C, and –24 °C, respectively. Regardless of the variation, it is clear that the cloud point and pour point are lower than diesel fuel and neat biodiesel [38]. Studies indicate B-20 to be superior in its cold flow/start properties as compared to neat biodiesel or diesel fuel.

(6) Heating value (calorific value)

Since B-100 has a lower calorific value than conventional diesel, blending biodiesel with diesel will increase the calorific value of the blends as compared to using neat biodiesel. The calorific value of B-20 is approximately 44 MJ/kg, which is quite close to that of conventional diesel (45 MJ/Kg). Heating value is related to fuel consumption because a cylinder must be charged with more fuel in order to produce the same power [39]; and in this measure, B-20 outperforms neat biodiesel with minimal impact on energy density or fuel consumption.

(7) Emissions

Generally, blending will decrease the positive effects of neat biodiesel on emissions as blends only contain a fraction of the biodiesel that contributes to improved emissions; however, blends do improve the emission profile significantly as compared to diesel fuel. For example, B-20 decreased SO_2 by $19.7 \pm 2.5\%$ compared to diesel fuel. Also, particle emissions were $15.7 \pm 7.5\%$ lower than No.2 diesel [39]. Lower emissions are attributed to the lower sulfur content of biodiesel as compared to fossil diesel and the higher oxygen content, which facilitates a complete combustion.

(8) Performance

Engine performance of B-20 fuel is only slightly different from either B-100 or diesel fuel. Under identical tests, BSFC, which is one indicator of the engine's fuel consumption efficiency (ratio of fuel consumption rate to power), B-20 resulted in 234.55 (g/kW-hr) which was 2.69% higher than fossil diesel [12]. Nevertheless, B-100 resulted in 259.33 (g/kW-hr) which was even higher. The increase of BSFC could be attributed to the higher oxygen content of biodiesel fuel blends. It should be noted that the oxygenation, although increasing fuel consumption efficiency, reduces power slightly since the heating value of B-100 is less than diesel fuel. Similarly, the thermal efficiency of B-20 is slightly less than the conventional diesel (by 0.16%), which is already less than B-100 [12].

(9) B-20 advantages

1. The ability to use B-20 blends without any engine modification.
2. Possesses closest energy density to fossil diesel and thus has minimal impact on fuel consumption.
3. Burns cleaner than fossil diesel.
4. B-20 has better cold flow and cold start properties than diesel or neat biodiesel.

(10) B-20 disadvantages

1. No significant reduction of toxic and pollutant emissions as compared to neat biodiesel; even though, SO_2 is reduced to some extent.
2. The blend still relies on conventional diesel; thus it has a lesser impact on energy security and the environment compared to neat biodiesel.

1.2.2. Biodiesel B-5

B-5 is another biodiesel blend that consists of 5% biodiesel and 95% fossil diesel. It is considered the minimum effective blend of biodiesel and diesel that does not cause any problems for the engine [12]. Minimal biodiesel blends of this sort are only used to enhance certain properties of the conventional diesel fuels that diesel fuel alone cannot provide such as lubricity.

(1) Properties

Key properties of B-5 compared with other biodiesel blends and fossil diesel are depicted in Table 2.

(2) Kinematic viscosity

Several studies were conducted to determine the viscosity of the B-5 blend. The viscosity was predicted to be closer to the diesel fuel's viscosity when compared to pure biodiesel due to the low biodiesel-to-diesel blend ratio. This prediction was confirmed by several studies. The viscosity of B-5 was reported to be between 2.48 and 4.45 mm²/s. Whereas the diesel fuel's viscosity was between 2.40 and 4.3 mm²/s [17].

(3) Flashpoint

The flashpoint of this blend (B-5) was not close to biodiesel; however, it was not as high as fossil diesel either. Overall, the flashpoint, 64 °C, was closest to that of B-20 (and higher than diesel fuel, which is 55 °C) [17]. This implies that the addition of even a small amount of biodiesel improves fuel safety during storage and handling.

(4) Cetane number

The B-5 biodiesel blend did not show significant variance from B-20 on CN. In fact, the CN of B-5 (53.5) was closer to B-20 (52.2) than pure diesel (42.6–50.9) [43]. This indicates that even a slight addition of biodiesel can improve cetane rating of the fuel enhancing combustion properties under compression ignition.

(5) Cloud and pour points

The value of the B-5 cloud point was between -24 °C and -28 °C, which is close to that of diesel No.1 (-26 °C). Also, the pour point of B-5 ranged between -36 °C and -39 °C, which is higher compared to diesel No.1, (-42 °C) [19]. The cloud point and pour point of B-5 and low biodiesel blends are closer to that of diesel fuel than high biodiesel concentration blends. Thus, B-5 and almost all low ratio biodiesel/diesel blends tend to behave more like diesel fuel in cold weather [44].

(6) Calorific value

It was reported that the calorific value of B-5 is closer to diesel fuel than B-20. Since the calorific value of biodiesel is lower than that of fossil diesel, the blends were expected to vary the calorific values proportionately. The calorific value of B-5 was 42.19 MJ/kg which laid between that of B-100 (39.95 MJ/kg) and pure diesel (43.15 MJ/Kg) [17].

(7) Emissions

As with other properties, the emissions profile also tends to change proportionately with the strength of the blend and in general, B-5 biodiesel blends have better emissions profiles as compared to fossil diesel but not as good compared to neat or B-20 biodiesel as shown in Table 3 [16].

(8) Performance

The performance of B-5 is not significantly different from that of fossil diesel primarily due to the low blending ratio, which results in domination of diesel fuel performance and properties. For example, BSFC for B-5, from rapeseed oil, was almost the same as the diesel fuel [45]. Experiments on fuel consumption with B-5 in place of diesel fuel resulted in a consumption increase of 7–8% [46]. The thermal efficiency of B-5 was reported to be slightly higher than that of diesel fuel [16]. However, this increase cannot be considered as significant as that of B-100, which ranged between –0.8% and +5.8% [16].

(9) B-5 advantages

B-5 blends can be used as lubricity enhancers without changing performance characteristics of the diesel fuel.

B-5 has an improved cetane rating compared to fossil diesel, which in turn helps improve efficiency characteristics.

(10) B-5 disadvantages

B-5 emissions are closer to that of fossil diesel.

B-5 blends are not considered adequate renewable substitutes to diesel fuel, and thus the environmental benefits are not that significant.

2. Ethanol and Ethanol Blends

2.1. Ethanol E-100

Ethanol is an important renewable fuel that is targeted for spark ignition engines [47] and produced primarily via carbohydrate fermentation (primarily corn in the temperate regions and sugar cane in the tropics) and more recently from cellulose [48]. Regardless of the source, the backbone for ethanol is glucose sugar [48]. Ethanol can be used in its pure form called E-100 or blended with fossil gasoline at any ratio. Like biodiesel, the percentage amount of ethanol in ethanol-gasoline blends are represented by the number that follows the prefix E. The most common blends in the United States are E85 and E10 [49].

2.1.1. Properties

Key properties of ethanol and ethanol-gasoline blends are depicted in Table 6 and compiled in Figure 2.

It can be seen from Figure 2 that the octane number increases with the amount of ethanol in the blend while pure ethanol has the highest octane rating [59] suggesting that pure ethanol has the highest antiknock properties of any of the blends or gasoline. Flashpoint of ethanol is also the highest of all the blends considered. It is also clear that the heating value of pure ethanol is lowest primarily due to the high oxygen content. It is also reported that viscosity increases with higher ethanol content with pure ethanol eliciting the highest viscosity [60]. Ethanol also has higher ignition and flashpoints than gasoline and, thus, is safer during handling and transport.

Table 6. Comparison of key properties of ethanol and ethanol-gasoline blends.

Properties	Gasoline	E-100	E-85	E-35	E-10	Remarks	Ref.
Viscosity mm ² /s	0.84	1.57	1.42	-	-	@ 20 °C	[50]
	0.48	-	-	0.69	0.53	@ 30 °C	[51]
Flash Point °C	-65	13	5-8.5	(-13.5)-(-15)	-40		[52]
	-	-	(-20)-(-28)	-	-		[53]
	-	-	-	31	-		[51]
*RON °C	88-100	108.6	-	-	-	Research Octane	[54]
	91	114	107-110	97-98	94	number	[52]
	86.4	-	-	-	87.4		[55]
**MON °C	80-90	89.7	-	-	-	Motor Octane number	[54]
	85	112	102.5-105	89-92	86		[52]
	98.8	-	-	-	99.9		[55]
***Octane number (ON) °C	86-94	98-100	105	-	-	The average of RON and MON is ON	[50]
	93.2	-	-	104.1	97.1		[51]
Cloud point °C	-	-	-30	-	-	Not above	[56]
	-22	-	-	8*	8*	*Above	[51]
Pour point °C	(-17)-(-19)	-	-	0*	0*	*Above	[51]
Calorific value MJ/Kg	30-33	21.1	-	-	-	Lower Heating Value	[54]
	44.4	30	30.1-33.8	38.5-40.4	44.22		[52]
	42.5	26.9	29.2	-	40.9	Lower Heating value	[57]
	41.9-44.2	26.8	29.1	-	-	Lower heating value	[50]
	34.84	-	-	30.92	33.19		[51]
	44	26	-	-	-		[58]

2.1.2. Performance

It should be noted that similar to biodiesel, using pure ethanol warrants engine modifications [59]. Water being miscible with pure ethanol elicits corrosion issues [54]. Nevertheless, research suggests that once blended with gasoline; no engine modifications are necessary [61]. The heating value of ethanol is lower than gasoline; and thus, a higher amount of ethanol is required to achieve the same power output. Nevertheless, the amount of air required to get a full combustion is

less for ethanol [61] due to its high oxygen content. Moreover, the latent heat of evaporation for ethanol is higher than gasoline, reducing the temperature of engine intake pipes and increasing volumetric efficiency.

2.1.3. Brake thermal efficiency (BTE)

BTE is a function of the input heat to the engine in the form of fuel. It is used as a criterion for engine's efficiency to convert the amount of heat from the fuel to mechanical energy and motion [62]. It was found that the 5% ethanol presence in the fuel increases the BTE by 4–12% [63]. Turner et al. used the E-85 blends to measure the performance of the high compression ratio spark ignition engine. The result was an increase in the BTE with an increase in the knock effect due to the higher octane number of ethanol compared to gasoline [64].

2.1.4. Brake specific fuel consumption (BSFC)

Calorific value and density of the fuel are important factors in BSFC measurement [62]. Koc et al. [54] found that BSFC values for E-50 and E85 were higher than the gasoline values by 16.1% and 36.4%, respectively. This increment depends on the ratio of ethanol. Because the heating value of ethanol is less than the value of gasoline by 35%, more ethanol needs to be burned to produce the same power [65]. This is the reason why the BSFC of E-85 was higher than E-50.

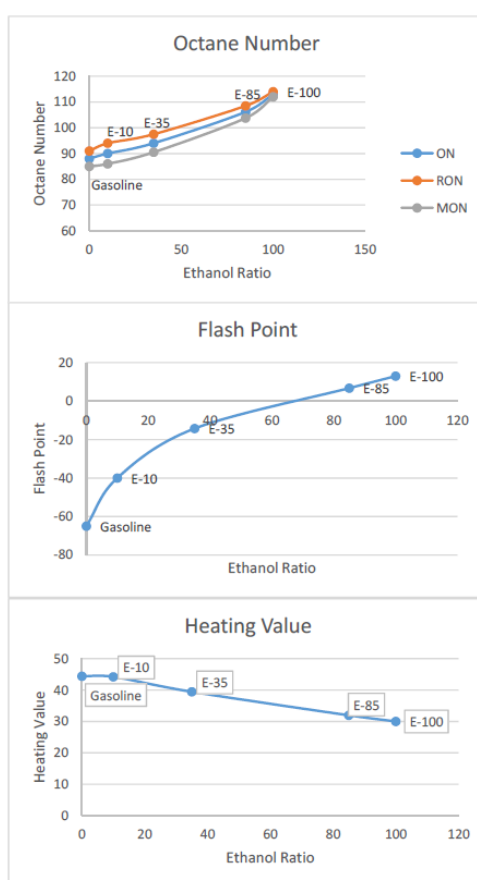


Figure 2. Comparison of key properties of ethanol and ethanol-gasoline blends.

2.1.5. Emissions

Several studies were conducted to elucidate the effect of ethanol blends on the emissions. It was shown that blending ethanol with fuels in especially low concentration ethanol enhances the engine performance and reduces emissions such as CO and NO_x [55,66]. He et al. [67] showed that emissions of CO, HC, and NO_x were drastically reduced with E-30 at idle and increased acetaldehyde emissions in the meantime. Hsieh et al. [61] found a dramatic decrease in CO and HC emissions due to the leaning effect for different ratios of ethanol in ethanol-gasoline blends. The results were that CO emissions are less than 0.6% when the engine is working at 2000 rpm with a compression ratio 10:1. On the other hand, CO₂ emissions were increased due to improvement in combustion characteristics. He et al. [67] also stated that NO_x emissions depend on the operational conditions of the engine and not on the fuel conditions. NO_x emissions were around 1000 ppm with the same engine conditions and parameters [61].

2.2. Ethanol E-85 blend

E-85 is one of the most common blends used in the U.S. and consists of 85% ethanol in gasoline. E-85 is typically used in Flex Fuel engines that have been manufactured to tolerate a range of (ethanol-based) fuel blends [68]. It should be noted that usage of E-85 in a non-flex fuel vehicle can lead to poor acceleration, a substantial increase in maintenance costs, and eventual component failure [68].

2.2.1. Properties of E85

Properties of E-85 are primarily dictated by the presence of molecular oxygen.

2.2.2. Kinematic viscosity

The viscosity of E-85 is higher than gasoline, lower than E-100, and is attributed to the presence of hydrogen bonding [50].

2.2.3. Flashpoint

The flashpoint of E-85 is slightly above 5 °C [52] and is higher than pure gasoline but lower than E-100. However, according to the Renewable Fuel Association (RFA) [53], the flashpoint of E-85 could go significantly lower. This low flashpoint is favorable for engine performance and efficiency but poses some risks for fuel handling and safety.

2.2.4. Octane number

Octane number is a measure of gasoline fuel performance in spark ignition engines and provides an indication of the anti-knocking behavior of the fuel. Anti-knocking is an important parameter for gasoline engines [69]. If the fuel ignites before the piston reaches the desired point, i.e., top-dead-center, the combustion will generate a counter-power that will force the piston to move down when it

is supposed to move up. This phenomenon is known as a knock, and it occurs when the octane number is low. There are two common forms of octane ratings, i.e., Research Octane Number (RON), and Motor Octane Number (MON). Both types depend on the composition of the fuel blend. Also, a combined octane number can be added to the list of important octanes. It is the average of both (RON) and (MON) $((R+M)/2)$ [70]. Reported octane numbers ranged from 105 [50] to 94–96 [53] and thus E-85 has excellent octane boosting properties.

2.2.5. Cloud point and pour point

Kheiralla [51] compared both E10 and E35 values of cloud and pour points with pure gasoline. In all cases, the cloud and pour points of both blends, E10 and E35, were the same and they were higher than cloud and pour points of gasoline. Results are shown in Table 6.

2.2.6. Calorific value

For ethanol blends, the lower heating value is generally reported, and, the calorific value is slightly lower than the normal heating value [71]. The lower heating value of E-85 was reported at around 29.1 MJ/kg which is higher compared to other blends [50]; however, the calorific value is lower than gasoline—again due to the presence of structural oxygen.

2.2.7. The performance of E-85

In general E-85 is reported to yield better engine performance than other lower concentration blends [54]. The performance of ethanol blends is proportional to the blends ratio—and increases as ethanol concentration increase in the blend [59]. E-85 has more different compositions from gasoline than any other ethanol blend [72]. It was shown that brake specific fuel consumption (BSFC) for E-85 was 36.4% higher as compared to pure gasoline at a compression ratio 11:1 [59]. The thermal efficiency of E-85 also increased by more than 3–10% as compared to gasoline.

2.2.8. Emissions of E-85

Studies report that emissions of NO_x reduced when using E85 as opposed to gasoline; however, CO₂ emissions were the same [66]. Also, Hydrocarbon emissions were the lowest when using E-85. It was also reported that CO emissions were lowered by significantly when using E-85 as compared to gasoline [54]. Another study confirmed reduction of CO, NO_x, and non-methane hydrocarbon emissions by 72%, 48%, and 55% respectively when using E-85 [72].

2.2.9. E-85 advantages

- (1) E-85 contains a higher ratio of ethanol than other blends thereby increasing the amount of heat absorbed to spread the fuel for injection. The latent heat of vaporization is 2.5 times higher than gasoline which reduces the temperature of the air charge at the intake. As such, air density increase allows more engine output [73,74].
- (2) E-85 delivers higher octane ratings and thus allows higher knock resistance [74,75].

- (3) E-85 could be used with higher compression ratio engines resulting in higher thermal efficiencies than gasoline [76].
- (4) E-85 reduces greenhouse gasses.
- (5) E-85 yields a better performance due to a higher flash point than other blends and gasoline.

2.2.10. E-85 disadvantages

- (1) E-85 has a higher ratio of ethanol than any other blends that allows water solubility, which makes the fuel more corrosive warranting engine modifications [74].
- (2) Handling E-85 blend is more difficult due to its corrosiveness and higher flash point.
- (3) Storage problems can occur due to susceptibility to microorganism growth which can lead to deterioration of fuel quality.
- (4) E-85 is susceptible to cold start problems.
- (5) The heating value of E-85 is lower than gasoline. Thus, engines that run on E-85 require higher amounts of fuel compared to gasoline.

2.3. Gasohol

Gasohol is a general term used for alcohol-gasoline blends that contain at least 10% ethanol by volume [77]. However, the term also refers to blends of alcohol with alcohol ratios between 10% and 85% (Flex Fuel) [78]. Most of the gasohol blends do not require major engine modifications due to the small ratio of ethanol to gasoline. In fact, Al-Hasan [58] reported the possibility of using up to 20% ethanol on spark ignition engines without any issues; however, Najafi [79] reported that spark ignition engines would not run as usual when the ratio of ethanol exceeds 20%.

2.3.1. E-35

E-35 is an ethanol-gasoline blend that has 35% ethanol and 65% gasoline. The reason to consider E-35 is that this blend has proven to provide the highest ratio of ethanol that an engine can handle without any modifications [51].

(1) Kinematic viscosity

Generally, the viscosity increased about $0.006 \text{ mm}^2/\text{s}$ for each 1% increment of ethanol and thus, the viscosity of E-35 has been reported to be 41% higher than that of gasoline. E-35 is less viscous than E-85 flex fuel.

(2) Flashpoint

The flashpoint of E-35 is higher than pure gasoline due to the presence of ethanol. Nuevo [52], reported the flash point ranges between $-15 \text{ }^\circ\text{C}$ and $-13 \text{ }^\circ\text{C}$; however, Kheiralla [51] reported that value was closer to $\pm 0 \text{ }^\circ\text{C}$.

(3) Octane number

The MON and RON of E-35 were reported to be ~10% higher than that of gasoline [51] and was between 89 and 92 and between 97 and 98, respectively [52].

(4) Cloud and pour point

The cloud point of for E-35 was reported to be 8 °C [51]. It was also reported that the cloud point for this blend is approximately 5 to 8 °C above the pour point. Cloud point is more important than pour point for heavy fuels with high boiling points.

(5) Heating value

The heating value of E-35 was reported in the range of 38–40 MJ/Kg and thus ~11% lower than that of gasoline. It is reported that the heating value decreases by 0.1069 for every 1% increment of ethanol [51].

2.3.2. E-10

E-10 is the most common blend and has been widely adopted in more than 35 countries around the world including the USA, Canada, France, and many countries in Asia including Thailand and the Philippines [66,80]. E-10 is commonly used in the United States; 21% of the fuel used for transportation is E-10.

(1) Viscosity

It has been reported that the viscosity of the E-10 blend increases continuously and linearly by 0.006 mm²/s @ 30 °C for every 1% increment of ethanol [66]. The viscosity of E-10 was reported to be 0.5383 mm²/s @ 30 °C, which is slightly higher than the gasoline viscosity 0.4872 mm²/s @ 30 °C [81]. However, Kheiralla also reported in another work that the viscosity of E-10 was 10.4% higher than gasoline [51].

(2) Flashpoint

Nwufo [52] reported that the flash point of E-10 was higher than pure gasoline, and it increases as the ethanol ratio increases. Kheiralla [51] was not able to determine the flash point of E-10 as the fuel starts to ignite before its flash point can be determined due to the differences of the flash points between ethanol and gasoline. Consequently, the flash point of E-10 and other blends would depend on and would be dictated by the flashpoint of the more volatile substance.

(3) Octane number

The octane number of E-10 was found to be 93.2 which was 4% higher than that of gasoline. However, E-10 has the lowest octane number among ethanol blends. The octane number increases by 0.29 for every 1% increment of ethanol [51,52].

(4) Cloud and pour point

According to Kheiralla [51], E-10 will have the same values of cloud and pour points as E-35; which are ~8, and 5–8 °C respectively. However, the cloud point of E-10 is still higher than that of gasoline [66].

(5) Calorific value

The heating value of ethanol is 1.6 times lower than that of gasoline, which creates a need for 1.5–1.8 times more ethanol to elicit the same energy output. The heating value for E-10 is around 9511 cal/g [61].

(6) Performance

The fuel economy of E-10 is the same as gasoline but offers better environmental benefits [82]. It is considered the optimum blend that can work under different compression ratios [61]. Generally, ethanol blends improve engine performance [59] with an increase of power produced by 5% [83,84]. Ethanol affects the intake temperature due to its almost 3x higher latent heat of vaporization than gasoline decreasing the intake manifold's temperature; and thereby increasing the engine efficiency [58,85]. However, the BSFC of E-10 is lower than E-85, which makes it slightly higher than pure gasoline, which means BSFC can be improved by increasing the compression ratio [67].

(7) Emissions

It was reported that E-10 could reduce CO emissions by up to 30% [86]. In fact, the addition of ethanol up to 20% would help decrease CO and HC emissions; nevertheless, these emissions would be increased if the ratio of ethanol goes higher. In contrast, CO₂ elicits an opposite behavior. This is because ethanol increases the engine's efficiency by allowing a more complete combustion—increasing CO₂ emission eventually [58]. It was also reported that NO_x emissions decrease with the increase of ethanol content [87]. Also, NO_x was lower for E-10 compared with gasoline [87]. However, it was higher than other blends like E-30 [67].

(8) Advantages of gasohol

- 1) Gasohol blends can be used without any major engine modifications.
- 2) Increased flashpoint enhances combustion properties.
- 3) Gasohol blends efficiently reduce exhaust emissions such as CO and NO_x [77].

- 4) Gasohol increases the overall efficiency of engines.
- 5) Gasohol improves power [87].
- 6) Fuel economy does not change compared to gasoline [82].

(9) Disadvantages

- 1) Gasohol is miscible in water, which could promote corrosion of the engine/fuel system metal parts.
- 2) It is not that effective for displacing fossil fuels due to the low blend concentration.
- 3) The high flash point raises safety concerns during handling, storage, and transportation.

3. Ethanol-Diesel Blends (E-Diesel)

Ethanol-Diesel also referred to as E-Diesel is another fuel blend that uses ethanol in diesel targeted for compression ignition engines. Initial work started with methanol (M-100) as a substitute for diesel fuel [88,89]; however, as methanol prices started to increase, ethanol was tested as a substitute due to its low price [89]. Anhydrous ethanol is miscible with diesel fuel making stable solutions. However, ethanol-diesel blends are reported to be less stable than ethanol- gasoline and other blends. In fact, the blends would separate below 10 °C when 20% ethanol is blended with diesel [89]. Two approaches can be used to maintain the stability of the blend: adding emulsifiers that produce stable emulsions or adding co-solvents that produce stable solutions. Nonetheless, the current approach is to prepare ethanol-diesel blends with less than 20% ethanol. E-diesel has been a successful replacement for M-100 and has been successfully demonstrated in transit buses.

3.1. Properties

Table 7 presents properties of a common blend E-diesel blended with 10% ethanol. It could be seen that the viscosity of E-diesel is lower than diesel. The flash and pour points of E-diesel are 65% (~10–20 °C) lower than that of diesel fuel. Interestingly, the cloud points of both fuels remain the same. The heating value of E-diesel is 90% that of diesel [80].

Table 7. Select properties of E-diesel 10 and diesel.

Type of fuel	Viscosity mm ² /s @ 20 °C	Flash Point C	Cloud Point C	Pour Point C	Heating Value MJ/Kg	Ref.
Diesel	5.61	74	5	5	44.51	[80]
E-D 10*	5.46	25	5	-10	43.19	[80]

*ethanol-diesel blend with 10% ethanol

3.2. Performance

It is reported that usage of E-diesel generally in diesel engines presents some concerns—primarily the risk fire or explosion due to the lower flash point of ethanol as compared to diesel [90]. The engine performance is also adversely affected due to lower heating values of the

blend that leads to a higher fuel consumption as compared to diesel. Also, the efficiency has been reported lowered because of the decreased cetane number of the diesel blend (as ethanol is an octane enhancer which has a very different mission than that of the high-ignition-delay-seeking cetane). A low cetane number could cause some engine start-up problems. There has to be a balance, which is difficult to achieve when blending ethanol with diesel. Moreover, using alcohol in high ratios will have corrosion effects which can cause engine deterioration [91].

Nevertheless, some of these drawbacks could be addressed: First, using low ratios of alcohol would help eliminate issues associated with corrosion and compatibility. Second, performance can possibly be improved by using fuel pumps with higher capacity. Additionally, the cetane number could be improved by using cetane enhancers as additives to the blend [91].

3.3. Advantages of E-diesel

- (1) Ability to use renewable ethanol as an additive in compression ignition engines.
- (2) Oxygenation that assists combustion.

3.4. Disadvantages of E-diesel

- (1) Cannot eliminate the reliance on fossil fuels completely since only minor quantities of ethanol could be blended.
- (2) Fire and explosion hazard.
- (3) Adverse impact on engine performance due to lowering of cetane number.
- (4) Lower energy content compels higher fuel consumption.

4. Ethanol-Biodiesel (E-Biodiesel)

Generally, blending ethanol to biodiesel is meant to improve oxygenation properties of biodiesel. These blends follow the common nomenclature with the number following prefix E depicting the percentage of ethanol and that following prefix B representing the percentage of biodiesel. The most common E-Biodiesel blends are E5B95, E10B90, and E15B85 representing 5%, 10%, and 15% of ethanol blended with 95%, 90%, and 85% of biodiesel, respectively.

The purpose of blending ethanol is to improve most important fuel properties related to the injection process, i.e., flash point, pour point, cloud point, and viscosity. It was found that adding 3% ethanol to biodiesel reduces the flash point of the blend almost to ethanol's flash point. Also, when the ratio of ethanol increases, kinematic viscosity decreases because ethanol's viscosity is lower than that of biodiesel. The pour point of the blend follows the same behavior as ethanol's pour point, which is significantly low compared to that of biodiesel. However, pour point improvements are not notable beyond E10B90—when the pour point decreases only by less than 3 °C with ethanol addition. Since ethanol has a better behavior in low temperatures than biodiesel, ethanol addition improves cold-flow properties such as cloud point, pour point and cold filter plugging point [92].

Properties related to performance also improve because of ethanol addition. Viscosity has a direct effect on atomization of the fuel in the combustion chamber, and atomization affects the combustion process thereby impacting the overall efficiency. In general increased viscosity negatively affects fuel atomization and thus efficiency [93]. By adding ethanol to biodiesel, viscosity

is decreased enhancing efficiency. Consequently, combustion is improved and in turn, the formation of engine deposits is reduced [92].

The most recommended blend among E-Biodiesel blends is E15B85. This is because E15B85 results in the most improved engine performance and emissions profile. Some drawbacks include lowering of lubricity compared to other blending ratios, and the low flashpoint that causes safety concerns. Nevertheless, these issues can be addressed by using additives that help increase flashpoint and lubricity within acceptable limits [92].

5. Other Blends

There are several less common renewable fuel and fossil fuel blends that are still under research. Some of these blends are binary while others are ternary.

5.1. Bio-oil/Biodiesel blends

Bio-oil is derived from thermal depolymerization of biomass under pyrolytic conditions in the absence of oxygen. The resulting product consists of two phases, an oily phase termed bio-oil and an aqueous phase [94].

Bio-oil was found to be compatible with biodiesel; however, using bio-oil in its neat form in diesel engines might not be effective due to significant variability of properties resulting from complex structure and composition. Nevertheless, the use of bio-oil as an additive has been investigated. The oily phase is more soluble than the aqueous phase in biodiesel due to the low water content [94]. The aqueous phase once processed to be compatible with biodiesel is called polar oil. It has been demonstrated that modified diesel engines can successfully run on bio-oil [95].

Properties of the two phases were studied separately, obtained from and compared to the properties of biodiesel. The properties studied were viscosity and heating value.

Table 8 shows properties of bio-oil obtained by pine chips and pine pellet pyrolysis. It could be seen that the viscosity of the oily bottom phase is higher than polar oil for both feedstock, and viscosity of the oily phase of pine chip is the highest. This indicates that only a small quantity of bio-oil could be used as an additive without adversely affecting fuel properties of the blend. It could also be seen that the heating value of the oily bottom phase is higher than polar oil for both feedstock; however, the heating value for biodiesel is the highest [94]. The likely reason for low heating values of bio-oil is the significant presence of structural oxygen and presence of some moisture.

Table 8. Properties of bio-oil and biodiesel.

Properties	Pine Chips		Pine Pellets		Biodiesel
	Polar oil	Oily bottom	Polar oil	Oily bottom	
Viscosity mm ² /s @ 25 °C	125.6	140.2	44.8	76.8	6.4
Heating Value MJ/Kg	17.9	23.8	19.5	24.8	39

5.2. Methanol-gasoline

Methanol in gasoline, also sometimes referred to as gasohol, is another blend targeted for spark ignition engines [78]. The most common methanol-gasoline blends are M10 and M20.

5.2.1. Properties

Methanol has a high octane number (108.7). It has been reported that the high octane number and oxygen content leads to more efficient combustion and thus higher efficiency [78]. As such, Zaid [96] has suggested that methanol-gasoline blends can be used as an alternative to engines with higher compression ratio due to superior performance of the fuel blend. Due to oxygenation, the emissions profile is also improved [97,98].

5.2.2. Performance

Using methanol with gasoline is reported to result in better engine performance. Methanol addition improved brake thermal efficiency (BTE) as compared to other alcohol-gasoline blends. Methanol has about 50% more oxygen per mass basis than other common alcohols, which leads to improved combustion quality and a higher BTE [78]. Also, the latent heat of methanol vaporization (1103 KJ/Kg) is higher than other alcohols and gasoline (305 KJ/Kg) [99,100,101] leading to a decrease in the intake manifold's temperature (as methanol absorbing more heat). As a result, the density of the incoming charge increases thereby increasing the efficiency. It has been concluded by Agarwal [78] that BTE for M20 was higher than M10. On the other hand, Bardaie and Janius [102] reported that the engine's power decreased by 4–5% when pure methanol was used. The BSFC of the methanol blend was also reported to be higher under some engine operating conditions compared to gasoline [100,101].

5.2.3. Emissions

It was reported that methanol addition results in better emission profiles as compared to other alcohols or gasoline due to higher oxygen content allowing for more complete combustion. Arapatsakos' [103] work with M10, M20 and M30 found that by increasing methanol ratios, fuel consumption increased, and CO and HC emissions decreased. However, HC emissions significantly increased using the pure M100 methanol [104]. Also, HC emissions from this blend were higher than gasoline at low engine speeds. Therefore, HC emissions differ depending on engine operating conditions. Yanju [101] reported that CO and NO_x emissions decreased with the increase of methanol/gasoline ratio. In particular, M85 reduced CO and NO_x by 25% and 80%, respectively.

5.2.4. Methanol advantages

- (1) Methanol can be used for light to mid-duty engines due to the presence of structural oxygen that improves the octane number of the fuel and thus efficiency.
- (2) Methanol has lower emission rates of CO, NO_x, and HC as compared to gasoline fuels.

5.2.5. Methanol disadvantages

Methanol is corrosive and is not safe unless engine modifications are done.

5.3. Gasoline-ethanol-methanol (GEM)

Tertiary blends combine two renewable additives such as alcohols or esters with fossil fuels; and in the case, ethanol and methanol are added to gasoline. The letters stand for respective components, i.e., G for gasoline, E for Ethanol, and M for Methanol. The number that follows each letter represents the percentage of each component in the blend. EM 10, for example, is the most common blend, which means ethanol and methanol are 10% of the GEM blend and so on. This specific blend combines ethanol and methanol with gasoline in order to have an iso-stoichiometry of air: fuel which is geared toward generating a balanced and reduced amount of emissions [99].

5.3.1. Performance

It was mentioned earlier that the latent vaporization heat of ethanol is almost three times that of gasoline. Apparently, methanol has a latent vaporization heat 3.5 times higher than that of gasoline. The higher latent vaporization heat reduces intake manifold temperature, which increases the volumetric efficiency leading to better combustion and an increase in the output torque, especially, at high engine speeds. Since methanol has a latent vaporization heat even higher than that of ethanol, engine performance is even better. Elfasakhany [99] reported that brake power, torque, and efficiency were higher for GEM than gasoline especially at high speeds; nevertheless, the increase was non-significant at low engine speeds.

5.3.2. Emissions

Turner [105] studied the effects of GEM blends on emissions, NO_x, and CO₂, and showed that these blends could reduce emissions moderately compared to pure gasoline. Slieghem [106] studied the effects of GEM blends on emissions of NO_x and CO and found that these blends produce fewer emissions than pure gasoline, but more emissions than pure methanol. Elfasakhany [99] found that EM10 gives lower CO and NO_x emissions than ethanol, but higher than methanol. GEM blends also resulted in moderate performance compared to M or E blends. It was also reported that emissions and performance of GEM blends depend on the engine's speed and load.

The higher latent heat of vaporization leads to complete combustion of incoming fuel leading to fewer emissions. Therefore, methanol produces the lowest CO and HC emissions due to the lean effect, which refers to the burning of the fuel with an excess amount of air. This is because of the high (50%) oxygen content in methanol. The oxygen ratio in ethanol is around 34.8% which is also helpful in improving the lean effect. Generally, GEM 10 reduces emissions moderately at all engine speeds.

5.3.3. GEM advantages

(1) Emissions profiles from the GEM blends are better than pure gasoline.

(2) The engine performance (efficiency, torque, and power) is improved especially at higher speeds.

5.3.4. GEM disadvantages

(1) Only lower (renewable) blend ratios are effective (up to 20%); thus, cannot displace significant amounts of fossil fuels.

(2) Emissions and performance are not as good as when using pure alcohol-based fuels.

5.4. Ethanol-biodiesel-diesel (EB-Diesel)

This is another ternary blend targeted for compression ignition engines. The diesel engine cannot run properly on E-diesel without modifications due to immiscibility issues of ethanol in diesel [107] and the cetane lowering effect of ethanol [108]. Nevertheless, ethanol can improve cold start properties once mixed with diesel. Also, ethanol has a relatively high oxygen content, which is known to improve emissions profile. To rectify issues with ethanol, the addition of biodiesel has been attempted and the fuel blend EB-diesel is proposed that consists of ethanol, biodiesel, and diesel targeting compression ignition engines [11,107]. It was reported that biodiesel works as an emulsifier with enhancing lubricity properties of the fuel [107,109]. Some blends of EB-diesel reported are Fernando D76 E4 B20 [107] and Hulwan [109] D70 E20 B10, D50 E30 B20, and D50 E40 B10.

5.4.1. Properties

Table 9 illustrates some key properties of select EB-Diesel. As can be seen, EB-Diesel blends significantly improved cold flow properties and oxygenation as compared to diesel fuel. The best results were obtained with D50 E40 B10 with biodiesel derived from *Jatropha* [109]. It was also reported that the D76 E4 B20 blend can stay as a stable microemulsion even in the presence of some moisture [107] while improving the lubricity of the fuel.

Table 9. Properties of EB-diesel.

Fuel Properties	Diesel D100	Ethanol E100	Biodiesel B100	D70 E20 B10	D50 E30 B20	D50 E40 B10
Viscosity mm ² /s	2.64	1.10	4.64	2.380	2.40	2.01
Heating Value MJ/Kg	44.89	28.18	38.08	39.930	38.96	36.33
Cetane Number	54	8	-	50	50	41
Flash Point C	50	12	-	14	12.50	12
Pour Point C	0	-	0	-3	-9	-12
Oxygen content % w	0	34.73	10.79	7.77	12.21	14.53

5.4.2. Performance

EB-Diesel blends display comparable or sometimes better performance as compared to diesel. Studies reported an increase in brake thermal efficiency (BTE) at high loads and speeds of 1200 and 1600 rpm with increasing ethanol proportions in the blend. However, this also led to an increase in BSFC requiring more fuel to produce the same power [109,110,111].

The increased presence of ethanol impacts injection timing, which creates an ignition delay. The delay allows the charge to mix well before it ignites, producing more power. The advantage of the ethanol and biodiesel presence is the ability to modulate the cetane number of the fuel by changing the ratios of the two oxygenates. Oxygen enrichment is also reported to help the mixing process [109,112].

5.4.3. Emissions

Generally, NO_x emissions depend on internal temperature in the cylinder, the oxygen content in the fuel, and residence time of the charge in the combustion chamber. NO_x emissions, therefore, will be decreased for the EB-diesel blends compared to diesel at low loads at both 1200 and 1600 rpm. CO emissions depend on air/fuel ratios in any blend as well as combustion temperature. CO emissions increase drastically at lower loads and decrease at high loads for EB-diesel blends compared to diesel fuel [109].

6. Conclusions

This paper reviews properties, emissions profiles, and performance of different biofuel blends that have been attempted for spark ignition and compression ignition engines. The most common biofuel blends targeted for compression ignition engines are biodiesel-diesel blends while ethanol-gasoline blends are targeted for spark-ignition engines. Less common fuel blends for gasoline engines include methanol-gasoline (M-gasoline) and gasoline-ethanol-methanol (GEM); bio-oil/biodiesel, ethanol-diesel (E-diesel), and ethanol-biodiesel-diesel (EB-diesel)—all of which are targeted for compression ignition engines.

In general, emissions profile improves with the addition of oxygenates (regardless of the engine type). Addition of oxygenates also improves combustion properties leading to increased efficiency and power in general. However, due to increased oxygen content, the addition of oxygenated fuels into fossil fuels reduces the energy content also increasing break specific fuel consumption as compared to using fossil fuel counterpart(s) alone.

The addition of biodiesel to diesel fuel improves the cetane number of the final blend while also improving its lubricity properties. The addition of ethanol to diesel in moderation improves the cold-flow properties of the blend; however, it also reduces the cetane rating. The addition of biodiesel to ethanol-diesel blends can counter the cetane reduction while also improving the miscibility of ethanol in diesel fuel—enhancing the quality of the final fuel blend.

The addition of alcohols to gasoline increases the octane rating of the final blend. The addition of oxygenated renewable alcohols to gasoline improves the cold-flow properties of the blend.

From this meta-analysis, it is surmised that E-10 is the most pragmatic fuel blend for unmodified spark-ignition engines and B-20 is the preferred choice for compression ignition engines. GEM seems to have significant promise as a spark-ignition alternative blend while EB-diesel (with low ethanol content) seems to be the best choice for compression ignition engines; however, all of these alternative biofuels need to be thoroughly investigated for engine performance and safety before being adopted for commercial use.

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Conflict of Interest

All authors declare no conflicts of interest in this paper.

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