ANNEX 4

Biofuel Applications in Internal Combustion Engines

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Only biodiesel and bioethanol are considered in this review due to their similar inherent properties to fossil-based fuels, especially auto-ignitibility. There is longer-term potential for other biofuels such as biobutanol, but little research effort has been seen in either regular or small engines.

The effects of replacing fossil-based fuels with regular fuels will depend on the inherent properties of the fuels and engine operating principles. In this review, aspects of combustion are reviewed; combustion characteristics of biofuels are different from those of regular fuels due to differences in fuel flow, physical phase change, fuel atomization to chemical reaction and heat exchange. In addition to combustion issues, replacing fossil-based fuels with biofuels can lead to other concerns about engine performance, durability and fuel storage.

Biodiesel Applications

Current diesel engines deliver higher engine efficiency with lower emissions than gasoline engines. The North American vehicular market is starting to see an increase in diesel engines, and diesel engines may play a significant role in the future small engine market as well.

The adoption of biodiesel/diesel blends is very promising since proper blends have proven to have better combustion efficiency and lower emissions than diesel fuel alone. However, some properties of biodiesel and engine durability problems limit the maximum fraction of biodiesel.

Biodiesel can also be used as the base oil for engine lubricants, primarily because of some inherent properties such as high lubricity.

Biodiesel as a Diesel Substitute

This section discusses biodiesel as a fuel in diesel (compression ignition engines). Biodiesel can be used as a direct substitute for diesel, or in a blend with diesel. Table 1 summarizes the recognized advantages and disadvantages of using biodiesel in this application. Several technical challenges and remedial improvements on both fuels and engines are required, leading to slightly higher costs of operating a diesel engine with biodiesels.

Table 1: Summary of benefits and drawbacks in using biodiesel as a diesel substitute.

Categories	Benefits		Drawbacks	
	Advantages	Reason	Disadvantages	Reason

Engine performance	Better combustion efficiency	Additional oxygen in fuel	Less power output	Lower power density (per mass)
			Poor atomization	Relatively higher viscosity and heavier molecular weight
Emissions	Reducing THC, CO	Better combustion due to additional oxygen Inherent properties	Increased NO_x	Hotter combustion due to additional oxygen
	Less sulfur content, compared to diesel	Less sulfur		
	Increase NO_x after-treatment efficiency	Derived from organic substances		
	Biodegradability			
Engine durability	Can be used in a new diesel without major modification	Same auto-ignitibility range as diesel	Broken seals	Oxy-polarity in esters makes biodiesel a good solvent
	Reduced wear of metallic components	Enhanced lubricity	Poor operability in cold weather	High pour point and cloud point temperatures
			Fuel system encumbrance	Dissolved residuals from a fuel tank that used to be filled with 100% diesel
			Engine oil degradability	Escaping fuel from a combustion chamber
			Injection tip	Decompose during ignition delay time and high cloud point temperature
Storage and Handling	More difficult to catch file	High flash point	Fuel degradability	Sensitive to water, temperature, microbial creatures and oxygen

Table XX: Causes and effects of under-standard biodiesel

Standardized properties	Cause	Effects
Total glycerin	Inefficient transesterification process	White sediments at the bottom of fuel tank and fuel system clogs
Free glycerin	Inefficient water washing process	Fuel injection system.
Flash point	Contamination of alcohol (methanol)	Expand lower temperature flammability limit
Sulfated ash	Residual soap and catalyst	Poison catalytic converter, health issues
Acid value	An increase in free fatty acids in old biodiesel due to hydrolysis	Corrode metalic parts of an engine
Water and Sediment	Moisture	Corrode metallic parts of an engine
Cloud point	The amount of saturated fats	Clogs fuel system
Carbon residue	Too high glycerin (reacted monoglycerides)	Fuel system encumbrance
Phosphorus	Contamination of phosphorus compounds called phospholipids or gums	Destroy some engine parts

Viscosity	Feedstock types (fatty acid chains)	Reduce the engine performance/ increase the potential
Sulfur	Present in some feedstock especially animal fats and recycled oil	Poison catalytic converter, health issues
Copper corrosion	Associated with acidic, sulfur-containing fuels	Corrode some parts of an engine
Cetane number	Feedstock dependency and oxidation (oxidized fuels tend to have higher cetane number due to peroxide compound)	Long ignition delay, engine knock
Vacuum distillation T90	Contamination of high boiling point material	Change in combustion behaviour

Advantages

The outstanding advantage of using biodiesel/biodiesel blends as engine fuel is the adaptability to a diesel engine without any major engine modification, especially when a limited fraction of biodiesel is introduced to the blend. The maximum amount of biodiesel blended with regular diesel depends on engine models. Newer engine models from large engine manufacturers (such as Caterpillar, Cummins, and John Deere) can tolerate (and warranty) as high as 20% biodiesel in the blend. However, use of B20 or higher fractions of biodiesel requires some precautions on fuel degradability, fuel filters, cold weather operation, and maintenance.

Additional oxygen in FAME biodiesels improves fuel oxidation (combustion), leading to more spontaneous combustion and better combustion efficiency. At the same time, it reduces the total energy content[1] of the fuel by ~10% (on a mass basis) primarily because oxygen carries less energy than heavy hydrocarbon molecules. This is the primary reason for reduction of engine power output when using 100% (neat) biodiesel. At lower biodiesel fractions, there is some discrepancy in the literature about the effect on power output – some studies show higher power output whilst others report a reduction. This is likely due to the combined effects of better efficiency and lower heating value. Furthermore, engine power output can be affected by other parameters (e.g. intake manifold conditions, fuel temperature, injection timing, flow inside a cylinder).

More complete combustion of biodiesel can substantially reduce unburned hydrocarbon and (HC) carbon monoxide emissions (CO). However, biodiesel can increase NO_x emissions as the combustion temperature is higher. NO_x emissions can be reduced by replacing some of the FAME biodiesel with kerosene or Fischer-Tropsch diesel (another form of biodiesel). In addition, for an engine with a catalytic converter, inherently low sulfur in biodiesel leads to a better NO_x catalytic conversion efficiency and therefore, after-treatment from a biodiesel engine probably emits less NO_x.

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[1] Also known as heating value (HV)

Fuel lubricity helps prevent engine wear and extends engine life. In regular diesel fuels, the natural sulfur content enhances lubricity. However, tight sulfur regulations (leading to low or ultra-low sulfur diesel) have caused lubricity problems. Fortuitously, biodiesels derived from vegetables oils[2] have an ultra low sulfur level yet also have high lubricity. Better lubricity is attributable to oxy-polarity of esters and high molecular weight fatty acid chains. The high lubricity of biodiesel extends the lifetime of fuel injection systems as well as metallic components that have sliding contacts with each other.

The low sulfur content in biodiesel also reduces emission of SO_2 and sulfate particulate matter. Further, as mentioned above, catalytic performance of exhaust after-treatment systems is enhanced.

Finally, it is safer to handle and store biodiesel at high temperature as biodiesel has a high flash point due to its composition of non-volatile fatty acid methyl esters (FAME).

Disadvantages and Problems

Engine durability is the real challenge of using biodiesel blends as an engine fuel. Oxy-polarity of esters makes biodiesel a good solvent, causing two major problems. First is elastomeric seal degradability, including swelling, shrinkage, embrittlement and changes in physical properties such as hardness and tensile strength. (It is notable that the problem of material compatibilities is worse when the biodiesel is already degraded and contains unstable hydroperoxides that can also attack elastomeric material). Second, high solubility of biodiesel could cause fuel system encumbrance especially when used in an engine normally operated with regular diesel fuels. During the use of the regular diesel fuels, deposits accumulate in the fuel tank. Addition of biodiesel loosens these additives and re-introduces them into the fuel stream.

High cloud point[3] and pour point[4] temperatures of biodiesel reduce thermal stability and limit the cold weather operability of both pure biodiesels and blends. The cloud point and pour point temperatures of biodiesels depend on the fraction of biodiesel present in the blends and the type of fatty acid methyl esters. It is notable that cloud and pour point temperatures also vary with the diesel base fuels. High cloud point causes filter clogging. In addition to engine operation, high cloud point temperature of pure biodiesels could lead to “shock crystallization” during the blending process of two fuels (regular- and bio- diesels) and therefore controlled conditions (e.g., temperature > 6°C) is mandatory.

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[2] Extracting biodiesel from animal oils or used oils could potentially lead to significantly higher sulfur content.

[3] Cloud point is the highest temperature at which the cluster of wax crystals is observable under specified conditions.

[4] Pour point is the lowest temperature at which the fuel still flows under specified conditions.

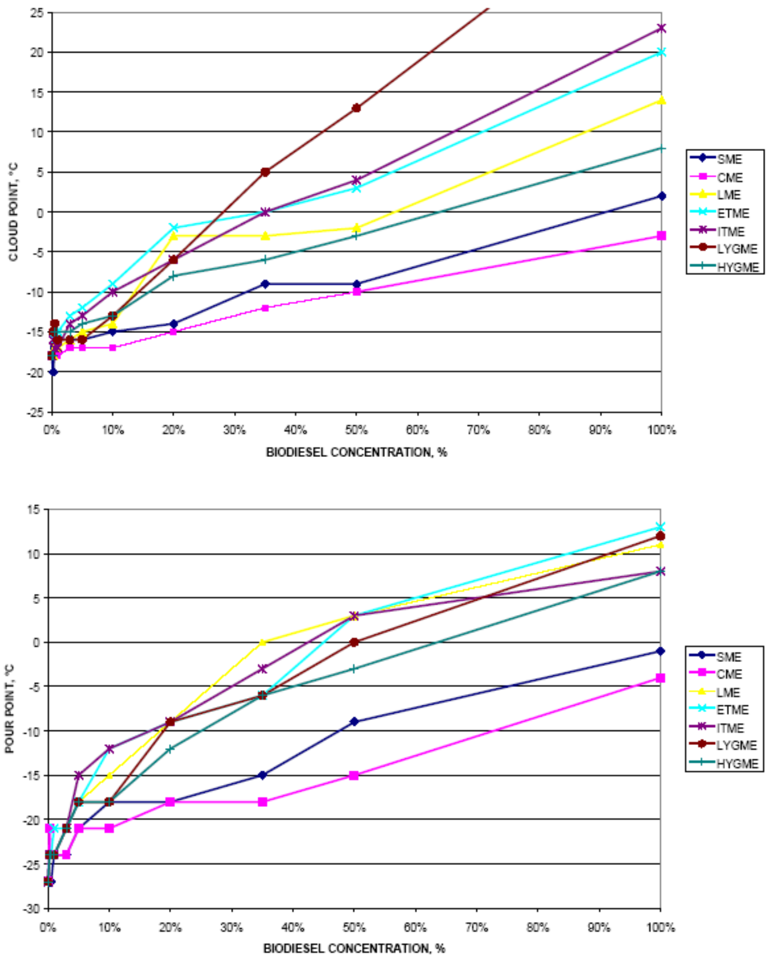

Figure 1: Biodiesel/diesel blend pour point test results

Some problems are caused by biodiesels' high viscosity, surface tension and molecular weight, which lead to poor atomization and generally larger spray droplets. This directly reduces engine performance. In addition, the bigger droplets tend to impinge on the wall. These impinged fuels can form deposits in the ring grooves and escape through the piston ring to the crank case during the compression stroke. This escaping oil is then dissolved with the engine oil, causing engine oil degradability (having some residual formation and viscosity decrease). Therefore, engine oil needs to be replaced more frequently.

Problems at the injector tip might occur when using biodiesel. Chol et al showed that soybean biodiesels can break down at 430°C to 480°C. This indicates the potential to decompose during ignition delay time which could cause deposits at the injector tip. This agrees with the FIE report which concluded that greater than 5% biodiesel blends can shorten the life time and could cause injector failures.

It is difficult to store biodiesel over a long period of time due to fuel degradability which can be divided into four main categories:

- Hydrolysis - normally occurs at polar bonds of esters, producing long chain free fatty acids.
- Thermal degradability - results from inherent properties of biodiesel such as pour point or cloud point as discussed earlier.
- Biological degradability – naturally derived biodiesel has straight carbon chains with two oxygens at one end (mono-alkyl ester), allowing microbial creatures[5] to metabolize and grow (especially with a presence of water).
- Chemical degradability – is caused by allylic methylene adjacent to double bonds of unsaturated fatty acid chains, (such as oleic acid (C18:1), linoleic acid (C18:2), linolenic acid (C18:3), etc.), reacting with oxygen, producing hydroperoxides which can further lead to other short chain fatty acids, aldehydes, ketones and products of polymerization.

Since biodiesel is very sensitive to water, temperature, microbial action and oxygen, unpleasant changes of biodiesel properties can occur rapidly (within a few months). The changing properties include acidic value (hydrolysis and biological), viscosity (thermal and chemical), the presence of some gases (biological), growing microbial creatures (biological) and the presence of other substances such as peroxides, acids, aldehydes and highly viscous polymers (chemical).

Potential Solutions

Engine power reduction due to biodiesel can be avoided by using a blend instead of neat biodiesel. In addition, some engine configurations (such as intake conditions and injection timing) can be adjusted to obtain the power output such that it satisfies the power requirements for particular applications. The problem of having poor atomization can be solved by redesigning an injector and reducing fuel viscosity. However solutions that do not require engine modification are yet to be developed, and could represent an opportunity.

Engine durability problems due to the use of biodiesel require some modifications on both engines and fuels. First, all elastomeric seals of an engine must be changed to synthetic material such as Viton or other compatible materials. Another major problem of engine durability is cold weather operability. Some additives might be used to improve low temperature properties[6] of biodiesel, which can be summarized in the following categories:

- Block copolymers of long-chain alkyl methacrylates and acrylates can be used as pour point suppressors and cold flow enhancers.
- Ethylene-vinyl acetate copolymers, polymethacrylates and styrene-maleic anhydride copolymers allegedly reduce cold filter plugging point (CFPP).

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[5] They are bacteria that normally break down fats and oils in the environment.

[6] Low temperature properties include solidification point, pour point and cold filter plugging point.

- For Palm Oil Methyl Ester (POME), the low temperature properties can be improved by Tween-80, dihydroxy fatty acid (DHFA), acrylated polyester prepolymer, palm-based polyol, a blend of DHFA and palm-based polyol, a synthesized DHAFA-ethyl hexanol and castor oil ricinoleate.
- Injector tip deposits can be reduced by surfactants such as a product from a succinic acylating agent and a polyamine and salt of a saturated carboxylic acid with an alkylated or alkoxylated amine.

Although some additives can improve some cold temperature properties of biodiesel, further improvement is still mandatory for use in cold weather areas.

The severity of crankcase oil degradability, caused by escaping biodiesel fuels from a cylinder, can obviously be decreased by reducing the amount of escaping fuels. In addition, adding some antioxidants and crankcase oil selection can help reduce the amount of residuals in crankcase oil. Although the problems of oil degradation can be partially dealt with by adding some antioxidants and selecting proper oil type, changing crankcase oil more often is still recommended to prevent any unexpected damage. Finally, the problem of injection tip is mitigated with the improvement of cloud point temperature.

Exposure of biodiesel to cold temperature, water, microbes and oxygen leads to rapid degradation of fuel properties and therefore some techniques are required to lengthen the preservation time. The stability of biodiesel in cold weather can be improved by some of the aforementioned additives, such as acrylates. Hydro-degradation can be eliminated and prevented by a water-removing process during biodiesel production and avoiding moisture exposure during the fuelling process. With decreasing water content in the fuel, biological stability is automatically enhanced since microbes need water to grow.

Since oxidative stabilities of biodiesel are subjected to unsaturated fatty acid chain compositions, reducing unsaturation can increase oxidative stability. This can be done by the technique called hydrogenation. Hydrogenation converts unsaturated fatty acid chains (unstable) to saturated molecules (stable) by adding hydrogen. The drawback of this method is that it reduces lubricity and raises pour point temperature. A better solution to reduce unsaturation of fatty acids is to genetically manipulate regular feedstock such that it contains high monounsaturated oil (such as oleic acid). The monounsaturated oleic oils are found to provide an optimum trade-off performance between oxidative stability and low temperature properties (pour point and cold flow properties). In addition to changing chemical structures of fatty acid chains, some antioxidants can also be used to resist oxidation of unsaturated fatty acid with air. The antioxidants that have been heavily tested with several kinds of akyl esters (such as rapeseed oil, sunflower oil, used frying oil, beef tallow) are pyrogallol (PY), propylgallate (PG), tert-butylhydroquinone (TBHQ) and butylated hydroxyanisole (BHA). Finally, preventing air exposure also reduces the chance of having unwanted oxidation.

Despite greater amounts of NO_x emissions produced from biodiesel combustion, they are not deemed problematic for an engine with a catalytic converter. In fact, NO_x emissions produced by a biodiesel engine with a catalytic converter might be lower than a regular diesel engine due to lower sulfur content of biodiesel.

Bioethanol

Bio-alcohol (mostly refers to bio-ethanol) can be produced from starch via fermentation. It is currently the most commonly used renewable fuel in an IC engine application and in fact, many states in the US and some countries around the world have gasoline fuel standards that require 10% and 20% ethanol blends [106]. The term, "Exx", is used to describe ethanol-gasoline blends, also known as gasohol, where xx indicates the fraction of ethanol present in the fuels. For instance, E15 means a blends of ethanol and gasoline that contains 15% ethanol.

Properties of Bioethanol

Depending on the controlled parameters in the manufacturing process, properties of fuel ethanol can be varied and therefore, a standard is required. The widely used ethanol standard in North America is ASTM D 4806. The details of this standard and testing method can be found in [107]. Inability to meet the standard requirements could result in several problems as indicated in Table C5.

Table YY: The effects of under-standard bioethanol

Standardized properties	Effects
Methanol content	MeOH is corrosive and can cause engine wear
Non-volatile content	Reduce the cold weather statibility
Water content	Blend separation/ metal corrosion
Denaturant content	Some denaturants can be harmful to engine operation
Copper	Active catalyst for low temperature
Acidity	Material incompatiblity
Sulphur	Causes sulfur-related emssions/ poisoning a catalytic converter
Phosphorus	Destroy some engine parts

Bioethanol Applications

Bioethanol is currently the most commonly used biofuel for spark ignition (gasoline) engine applications due to similar auto-ignitability properties to those of gasoline fuel. Currently, 5% of most gasoline fuels sold in the US have been blended with ethanol. In addition, unlike biodiesel, oxidative stability is not a major problem for bioethanol. Since most small engines are spark ignition, the future of bioethanol in small engine applications appears to be very promising.

Ethanol can also be used as an additive in diesel engines to enhance combustion and reduce some emissions in spite of differences in auto-ignitability as compared to diesel fuels. Therefore, this section is divided into two parts: 1) impact on SI engines and 2) impact on CI engines.

Before discussing the impacts of ethanol-diesel blends in an IC engine, it is noteworthy to compare the properties of ethanol to regular gasoline and diesel fuels. Ethanol generally has a higher auto-ignitability than gasoline, which is measured by octane number[7]. Ethanol has a greater ON than regular gasoline surrogates and incomparably higher ON than diesel fuels. In addition, ethanol has lower viscosity, wider flammability limit and lower flash point than those of both gasoline and diesel.

Table 2: Fuel properties comparison.

Highlighted portion indicates important parameters for auto-ignitability.

Property	Ethanol	Gasoline	No. 2 Diesel
Chemical Formula	C_2H_5OH	C_4 to C_{12}	C_3 to C_{25}
Molecular Weight	46.07	100–105	≈200
Carbon	52.2	85–88	84–87
Hydrogen	13.1	12–15	33–16
Oxygen	34.7	0	0
Specific gravity, 60° F/60° F	0.796	0.72–0.78	0.81–0.89
Density, lb/gal @ 60° F	6.61	6.0–6.5	6.7–7.4
Boiling temperature, °F	172	80–437	370–650
Research octane no.	108	90–100	--
Motor octane no.	92	81–90	--
(R + M)/2	100	86–94	N/A
Cetane no.(1)	--	5–20	40–55
Fuel in water, volume %	100	Negligible	Negligible
Water in fuel, volume %	100	Negligible	Negligible
Freezing point, °F	-173.2	-40	-40–30[b]
Centipoise @ 60° F	1.19	0.37–0.44[a]	2.6–4.1
Flash point, closed cup, °F	55	-45	165
Reid vapour pressure, psi	2.3-2.5	8-15	0.2
Blending Reid vapour pressure, psi	18-22	8-15	--
Heat of Vaporization, Btu/lb @ 60° F	362-400	140-170	≈100
Higher Heating Value, Btu/lb (liquid fuel-liquid water)	12,800	18,800–20,400	19,200–20000

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[7] Octane number is used to measure auto-ignitibility or knock resistance of fuels. A higher octane number fuel means it can tolerate more severe environment that leads to autoignition (or engine knock).

Lower Heating Value, Btu/lb (liquid fuel-water favor)	11,500	18,000–19,000	18,000–19,000
Autoignition temperature, °F	793	495	≈600
Flammability limits, vol%	3.3-19.0	1.0-8.0	-
Btu/lb air for stoichiometric mixture @ 60° F	44	≈10	≈8
Mixture in vapour state, Btu/cubic foot @ 68° F	92.9	95.2	96.9[c]
Fuel in liquid state, Btu/lb or air	1,280	1,290	–
Specific heat, Btu/lb °F	0.57	0.48	0.43
Stoichiometric air/fuel, weight	9	14.7[a]	14.7
Volume % fuel in vaporized stoichiometric mixture	6.5	2	–

Ethanol as a Gasoline Substitute

Ethanol in gasoline engine applications is currently the most practical and widely used biofuel and is potentially the most feasible renewable replacement for small gasoline engine applications. The fact that ethanol is oxygenate potentially makes it a better fuel than petroleum for an SI engine in terms of emission and efficiency. However, when all of the drawbacks are considered, the claim of ethanol as a better fuel can be questioned.

Advantages

The octane number (ON) of ethanol is greater than that of other gasoline surrogates, and contains no toxic additives such as MTBE. The higher ON property allows ethanol and ethanol-gasoline blends to be used in higher compression ratio engines, leading to better engine efficiencies. It was determined that a 5% increase in the portion of ethanol in the mixtures can enhance the ON of fuels by 10%. In addition, 3-5 times greater latent heat of evaporation significantly reduces the temperature inside the intake manifold system, enhancing volumetric efficiency. Furthermore, faster laminar flame speed of oxygenated fuels allows an engine to operate leaner. Although an ethanol engine seems to achieve better efficiency, power output is less than that from an engine fuelled with normal gasoline due to its lower heating value[8] (HV).

Emission performance is generally improved when using ethanol as a gasoline substitute. Hydrocarbon dilution and faster combustion due to additional oxygen lowers tail-pipe HC and CO emissions (especially CO) in combustion products. Several studies have confirmed the reduction in CO emissions of E10 and E20. In addition to inherent fuel characteristics, the presence of oxygen in the fuel allows leaner operation, ensuring that a significant amount of fuel will be oxidized, therefore further reducing CO and HC emissions. It is notable that decreasing HC emissions do not include ethylene, formaldehyde, acetaldehyde and acetone, which are

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[8] Similar to biodiesel, lower heating value in ethanol fuels is caused by oxygen components which replace high power hydrocarbon contents.

increased due to the unique oxidation path of ethanol. Blends containing more ethanol are generally expected to slightly increase NOx emissions because of more complete and hotter combustion. Several studies have indicated higher NOx emissions from the use of E10, although mixed results (both increasing and decreasing NOx) have also been reported. The mixed results of NOx emissions might be a result of better combustion efficiency and experimental fluctuation[9]. Sulfur related emissions are also expected to be lower as ethanol is derived from starch or lignocellulosic biomass which has far lower sulfur content than petroleum crude oils.

Because it is unnecessary to add aromatic compounds to enhance octane number, ethanol is found to reduce related emissions, such as toluene, xylene, benzene and iso-octane. These emissions are expected to be negligible, especially when using 100% ethanol fuels. However, the presence of such emissions does exist and is slightly reduced for gasoline-ethanol blends. Having said that, a number of studies have shown significant reduction in benzene when an engine was fuelled with E10 with one instance of increasing benzene. Additionally, VOC emissions are less when using ethanol blends.

Another advantage of using ethanol emerges when ethanol is used in a gasoline direct injection engine. Taniguchi found that a proper composition of ethanol-gasoline blends (E20) can reduce injector deposit formation due to the synergistic effects of high latent heat of vaporization and aromatic and sulfur content reductions.

Disadvantages and Problems

Power output from an SI engine fuelled with ethanol is likely to be lower than from an engine fuelled with gasoline. Although additional oxygen in ethanol can enhance combustion (resulting in higher efficiency), ethanol contains less energy density (per unit mass). In addition, phase separation of gasoline-ethanol blends can cause a substantial drop in engine efficiency.

Emissions of some hydrocarbons (acetaldehyde (ethanal), formaldehyde, methane, ethylene and acetone) were found to increase with the presence of more ethanol in the blends. These emissions were produced exclusively due to the oxidation path of ethanol. For instance, ethylene may be produced through the dehydration of ethanol during the combustion process. There are a number of studies that report 100-200% increase in acetaldehyde from the use of E10 and E20. A substantial increase in formaldehyde emissions was also found from an engine fueled with ethanol blends (possibly 5.12-13.8 times). It is notable that there are also a few studies that indicate contradictory results, i.e. a reduction in such emissions. This is probably because an engine was operating at optimized emission conditions or there were some experimental fluctuations.

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[9] NO_x emissions substantially depend on fuel-air ratio and operating conditions which might be varied during the experiments.

Carcinogenic evaporative emissions[10] are major concerns when using low-to-medium ethanol-fraction blends. The level of evaporative emissions depends on the fuel's volatility, measured by Reid Vapour Pressure (RVP)[11]. Unlike gasoline in which volatility can be controlled by changing hydrocarbon composition, ethanol has a constant volatility (less than that of standard gasoline). However, blending ethanol with gasoline tends to enhance fuel evaporation (increasing RVP). This is probably because ethanol reduces the boiling points of some aromatic compounds. Several studies have indicated approximately 20% to 80% more evaporative losses from the use of E10 and E20. In addition to RVP, the level of evaporative emissions also depends on the distillation temperature properties of the fuels. The source for evaporative emissions include gas tank venting, running losses and refueling loss during diurnal and engine cooling periods[12]. The diurnal evaporative losses are mostly caused by high RVP properties, whilst hot soak emissions result from distillation characteristics of ethanol. Including evaporative hydrocarbon losses, the total HC and air toxic emissions of an engine operating with ethanol/ethanol blends are higher compared to those produced from a gasoline engine.

Vapour lock[13] might be another problem resulting from the use of low-to-medium ethanol blends. When the intake system is too hot, highly volatile ethanol blends can promptly vaporize in a fuel system (fuel pumps, lines or carburetors). This substantially reduces the amount of fuel flow into the engine, causing power loss or sometimes complete stoppage. Nevertheless, no vapour lock incidents have been reported in the literature.

The fact that ethanol is completely soluble in water could lead to high water contamination problems in ethanol-gasoline blends. The presence of water can potentially cause corrosion on some metallic components (material compatibility problem). Moreover, it can separate from the homogeneous liquid phase of gasoline-ethanol-water mixtures. With significant amounts of water in the blends, the mixtures tend to separate easier (i.e. separation occurs at lower ethanol content), leading to fuel inhomogeneity, poor combustion, and cyclic variation. It is notable that phase separation is one of the major issues that limits the maximum fraction of ethanol that can be blended into gasoline. The natural water affinity of ethanol limits the use of this fuel in some applications (such as marine) unless proper procedures are implemented.

Material compatibility is another well-known issue. One of the reasons for corrosion is water contamination as discussed above. Another reason for material corrosion is electrical conductivity of ethanol/ethanol blends. High conductivity of the fuels also increases the chance

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[10] These evaporative emissions increase the potential of ground-level ozone formation.

[11] The Reid Vapour Pressure (RVP) test is used to measure the volatility of fuel. Higher RVP indicates greater volatilility.

[12] Evaporative emissions produced during engine cooling period after the engine is turned off are called hot soak emissions.

[13] Vapour lock is caused by too much evaporation of the fuel in the fuel system. This problem is usually found in tropical areas or during a hot summer time.

of having some ionic contamination, such as chloride, that could exaggerate metallic corrosion problems. These corrosive metals in fuel systems can lead to fuel system leakages and unsafe operation. The US Department of Energy has issued a warning on using "aluminum, zinc, tin, lead-based solder or brass" material in equipment that are in contact with ethanol related fuels. In addition to metallic material compatibility, oxy-polarity of ethanol is problematic to elastomeric materials which are normally used for hoses and valves.

A detailed study on material compatibility of engines fuelled with E5 and E10 can be found in the report conducted by Orbital Australia Pty Ltd. Several engine models ranging from the year 1984 to 2000 were selected for the test. It was found that new engine models (produced after the year 1999) did not have material compatibility problems with E5 blends; however, E10 blends did encounter such problems.

Cold weather operability is one of the most critical issues in certain northern climates. The problem is a major concern when pure ethanol or high ethanol content blends are used. It was found that at temperature below 11°C, it is difficult to form rich enough ethanol-air mixtures that can support combustion (i.e., not enough ethanol is evaporated and mixed with the air within an engine time-scale). Poor cold startability is a result of:

- poor volatility (this is only true for pure ethanol or rich ethanol blends) and
- high latent heat of evaporation[14].

Vapour pressure and latent heat of evaporation properties of ethanol compared to gasoline can be found in **Table**. High vapour pressure subdues ethanol volatility, resulting in higher energy demand to vaporize the fuels. High latent heat further increases the evaporating energy requirement. The cold start problem is reflected by the Distillation Index (DI)[15] in ASTM D4814. It was reported that replacing 5.7% by volume of gasoline hydrocarbon fuels with ethanol reduces calculated DI by 45 units due to the decreasing mid-range volatility.

With additional oxygen in its molecule and high auto-ignitability, ethanol/ethanol blends can provide advantages for engine efficiency and lower some emissions. However, the problems of evaporative emissions, cold engine operability, material compatibility and phase separation prevent the wide use of enriched ethanol blends in North America. These advantages and disadvantages as well as their reasons are summarized in Table.

Table 3: Summary of benefits and drawbacks in using ethanol as a gasoline substitute.

Categories	Benefits		Drawbacks	
	Advantages	Reason	Disadvantages	Reason
Engine performance	• Better combustion efficiency	• Operability in high compression ratio engine due to its high	• Less power output • Possibly poor	• Less heating value (per mass) • Phase separation

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[14] Heat of vaporization of E85 is 873kJ/kg as compared to gasoline (307kJ/kg).

[15] DI = $1.5T_{10}+3.0T_{50}+1.0T_{90}$, where T_{xx} is the distillation temperature at xx% evaporated.

		octane • Increases in volumetric efficiency from cold manifold • Faster laminar flame speed of oxygenated fuels • Possibly lean combustion	combustion characteristics	
Emissions	• Lower HC and CO (without consideration of evaporative emissions)	• More complete combustion/ lean – combustion	• Higher particular HC emissions, such as acetaldehyde (ethanal), formaldehyde, methane, ethylene and acetone	• Unique ethanol oxidation path
	• Lower emissions related to aromatic compounds	• Less aromatic octane enhancers		
	• Lower VOC emissions (for ethanol blends)	• Less volatile organic compounds	• Higher carcinogenic evaporative emisions (for the blends with small-to-medium ethanol fractions)	• High evaporative pressure/ Distillation temperature
	• Lower sulfur contents	• Derived from organic feedstocks		
Engine durability	• E20 can reduce injector tip for a gasoline direct injection engine.	• Synergistic effects of high latent heat and aromatic and sulfur content reductions	• Vapour lock (only for the blends with small-to-medium ethanol fractions)	• High volatility
			• Phase separation	• Presence of water
			• Material compatibility (both metal and elastromer)	• Oxy polarity/ Water contamination/ Ionic contamination such as chloride ions or acetic acid
Storage and Handling			• Leakage from storage corrosion	• Water content and electricity conductivity

Ethanol in Diesel Engines

Despite the cetane (inverse of octane) numbers of fuels ethanol and diesel are at the different extreme ends, (i.e., octane rating of ethanol is extremely high while that of diesel is extremely low), adding ethanol to diesel fuel has been done in order to enhance combustion efficiency and reduce some emissions. The ethanol-diesel blend is referred to as e-diesel.

The following sections discuss the impacts (both advantages and disadvantages) of e-diesel to a diesel engine.

Advantages

One of the main reasons for adding bioethanol to diesel fuels is to oxygenate the fuel in order to enhance combustion efficiency and reduce some emissions. Although increasing the oxygen content of the fuel can also be achieved with FAME biodiesel, which has an auto-ignitability range close to that of diesel fuels, the use of bioethanol cannot be ignored for three main reasons: 1) ethanol is more stable than biodiesel, 2) production cost/ simplicity of ethanol is better and 3) it is possible to extract ethanol from lignocellulosic (biomass) feedstock. However, the preferred type of blend (either ethanol-diesel or biodiesel-diesel) is still debatable due to the high auto-ignitability (low cetane number) of ethanol. The low cetane number of ethanol limits the ethanol fraction in the blends and some additives are required to shorten ignition delay.

There have been some studies that have confirmed the benefit of using oxygenate ethanol-diesel blends from the emission perspective, such as reduction of particulate matter and CO emission. However, there is no solid conclusion on NO_x emissions.

Disadvantages

Problems associated with using ethanol in SI engines also occur when using ethanol in CI engines - lower power output, phase separation and material compatibility. The phase separation problem tends to be more severe for ethanol-diesel blends, compared to those of ethanol-gasoline. Hansen et al has reviewed that phase separation can occur at temperatures below 10°C, which can be a major challenge for the use of these blends in Alberta. It is notable that the problems of phase separation decrease with the presence of aromatic content since polarity of ethanol can induce a dipole in aromatics forming strong interacting bonds.

There are three problems specific to ethanol-diesel mixtures:

- Low cetane ethanol can obviously lengthen ignition delay of a diesel engine. Without proper injection patterns and blend compositions, this could cause severe engine knock as the majority of the fuel ignites instantly.

- Replacing some portion of diesel with ethanol lowers fuel lubricities and viscosities. The consequence of decreasing lubricities is shorter life time of the fuel injection system (especially incorporating rotary distributor injection pumps and common rail fuel injection systems). Too low a viscosity affects the maximum amount of fuel delivery (power output) due to pump and injector leakage. It is notable that the viscosity of the blend also depends on the viscosity of the base diesel fuel.

- Since ethanol has a wider flammability limit and much lower flash point compared to regular diesel fuel (see **Table**), there is a better chance that ethanol-diesel fuels will catch fire. Therefore, special attention to fuel storage is required.

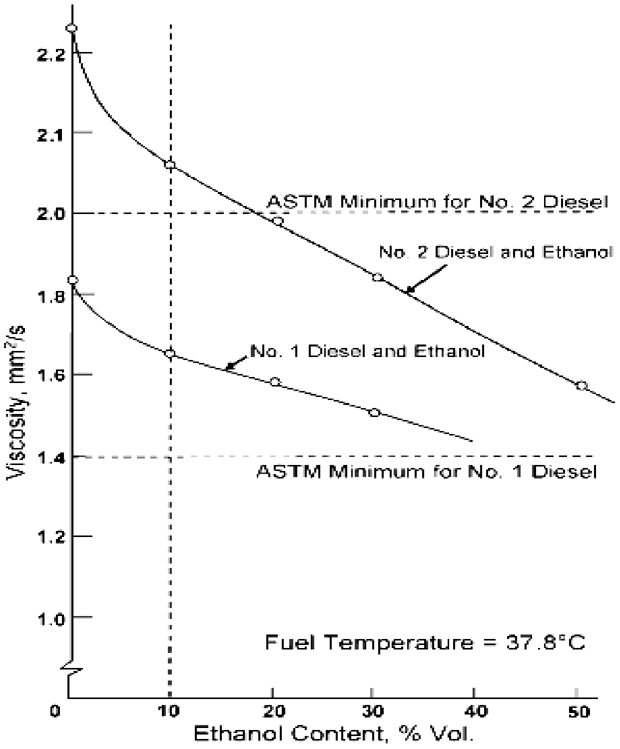

Figure 2: Effect of ethanol fraction on fuel viscosity

Table summarizes the advantages and disadvantages of using ethanol-diesel blends in a diesel engine. Although blending ethanol with regular fuels (both gasoline and diesel) could enhance engine efficiency and potentially reduce some emissions, several properties of blends lead to certain problems. Those properties include cetane number, blend stability, viscosity, lubricity, energy content, material compatibility and corrosiveness, fuel evaporation, flash point and fuel biodegradability. These problems require modification of fuel properties and/or engine design.

Table 4: Summary of benefits and drawbacks in using ethanol-diesel blends in a diesel engine.

Categories	Benefits		Drawbacks	
	Advantages	Reason	Disadvantages	Reason
Engine performance	• Better combustion efficiency	• Better diffusive flame due to additional oxygen	• Less power output	• Less heating value (per mass)
			• Instant combustion (could potentially cause engine damage)	• Longer ignition delay
			• Possibly poor combustion characteristics	• Phase separation
Emissions	• Lower HC and CO	• More complete combustion / lean – combustion	• Higher particular HC emissions, such as acetaldehyde (ethanal), formaldehyde, methane, ethylene and acetone **	• Unique ethanol oxidation path
	• Lower sulfur content	• Derived from organic feedstocks		

Engine durability		- Phase separation - Material compatibility (both metal and elastomer)	- Presence of water - Oxy polarity/ Water contamination/ Ionic contamination such as chloride ions or acetic acid
Storage and Handling		- Leakage from storage corrosion - More flammable	- Water contents and electricity conductivity - Wider flammability limit/ low flash point

** No reports on such emission have been yet published.

Potential Solutions – All Ethanol Applications

There have already been some solutions to address the challenges of using ethanol/ethanol blends in both SI and CI engines. Common disadvantages of applying ethanol to both SI and CI engines are lower power output, greater HC emissions (specific types), phase separation and material compatibility.

The lower energy content (of both FAME biodiesels and ethanol) can not be altered; however, the amount of injected fuels in each cycle can be increased by redesigning and presetting an engine so that load specification is satisfied.

HC emissions (especially acetaldehyde, formaldehyde, methane, ethylene and acetone) that occur due to the oxidation path of ethanol-related fuel can probably be reduced by lean combustion, which can be generated with either air enrichment or EGR dilution[16].

Phase separation is probably the most salient drawback to ethanol use, causing blend degradability and therefore poor combustion quality. The primary solution is to add either emulsifier or co-solvent additives. Real-time blending of separated ethanol and gasoline is another possibility to solve phase separation problems. This can be done by using a modified carburetor. Figure 3 shows schematic diagrams of (a) Carter carburetor and (b) redesigned carburetor, in which ethanol and gasoline are separated and blended in the fuel discharge tube. It is notable that the aromatic content in petroleum fuels also reduces the phase separation problems due to the chemical bonds.

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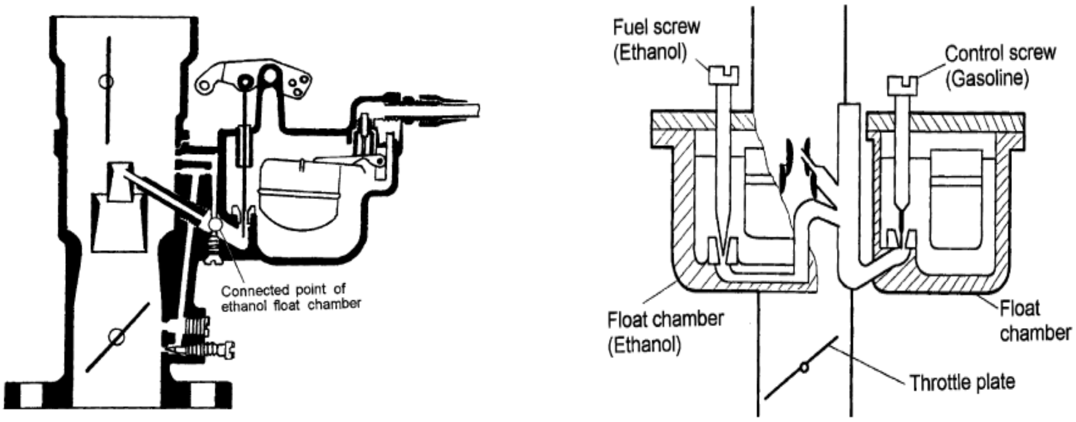
[16] It is more difficult to operate an SI engine with lean mixtures due to the flammability limit and therefore additional H_2 is probably required.



(a) (b)

Figure 3: Schematic diagrams of (a) Carter carburetor and (b) redesigned carburetor [68].

Material compatibility problems are caused by oxy-polarity of ethanol, which enhances dissolvability, electric conductivity and water affinity of the blends. Ethanol is incompatible with elastomeric and some metallic materials (such as aluminum, zinc, tin, lead-based solder or brass). Since material compatibility is caused by the polar nature of ethanol, the best solution to this problem is to avoid incompatible materials although selected lubricants might partially reduce the severity of the problem.

In SI engines, ethanol-gasoline blends have higher volatility, increasing vapour lock potential and evaporative emissions especially in the hot summer. One effective solution is to control the utilization period of ethanol blends. Another approach to reduce evaporative emissions is to avoid using plastic material for a fuel system as permeability of ethanol through plastic material is high. Finally, a canister can be used to purify the vented air through fuel. However, backfire of a canister is possible and troublesome, and occur especially with old canisters that have HC buildup.

Cold weather startability is another major problem of using enriched-to-pure ethanol blends in an SI engine, caused by inherently high latent heat of evaporation and low RVP. Adding VOC is one solution; however, it increases VOC related emissions. Another solution is to install a reliable heating device to a fuel system. The drawbacks to this solution are cost and start-up retardation.

In CI engines, pre-combustion and multi-injection can be used to mitigate the risk of having severe combustion caused by too long ignition delay time. Phase separation can be prevented by excluding water from the fuel. Also, adding some emulsifiers, additives and aromatics also prevents phase separation of diesel-ethanol blends. Preventing an external flame from entering a fuel tank is important due to the extended flammability limit and lower flash point. The risk can be mitigated by a flame arrestor.