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# The usage of bioethanol in light-duty SI vehicles – a brief overview

**Abstract**

Ethanol produced from fermentation of biomass has been of interest as a potential partial replacement for petroleum in SI engines for some time. The oxygenated nature of the ethanol molecule can aid combustion and reduce production of partial combustion products (HC, CO). Ethanol can be splash blended with petrol to produce blends. Blends with up to 10 % ethanol can be used with few problems in all but the oldest vehicles; up to 15 % ethanol has recently been deemed safe for use in light duty vehicles produced with the last decade. The E85 blend (85 % ethanol) requires specially designed vehicles, which are becoming more common in certain markets. The main issues associated with the use of ethanol and its blends are its corrosivity, affinity to water and its lower stoichiometric ratio. Increases in emission of aldehydes and a slight increase in emission of oxides of nitrogen have also been reported, and concern has been raised over the potential of increased aldehyde emissions to form more ground-level ozone. The potential for an improvement in air quality, engine performance and fuel supply security and sustainability makes work on the production and usage of ethanol and its blends a multidisciplinary research priority.
Key words: alternative fuels, biofuel, E85, emissions, ethanol blends, light-duty vehicles

## Ethanol and bioethanol as automotive fuels

Ethanol, a familiar organic compound, is employed in a wide variety of applications. Knowledge of its potential usage as a vehicular fuel dates to the conception of the automobile. Ethanol is the most widely-used biofuel, although geographically its usage is somewhat restricted. Ethanol can be produced using crude oil as a feedstock, but is more commonly sourced from conversion of biomass (‘bioethanol’). Since it is derived from biomass (and not fossil hydrocarbon deposits), bioethanol has been identified a fuel of great potential in efforts to make energy consumption in the transportation sector sustainable [1,2]. Bioethanol can potentially deliver greenhouse gas savings of up to 87 % over conventional fossil fuels [3]. First generation bioethanol is produced from the fermentation of sugar-rich edible crops, while second generation bioethanol uses inedible cellulosic material as a production feedstock. As with other biofuels, doubts over the sustainability and ethics of using edible crops as fuel mean that second-generation bioethanol is of great interest. Currently, almost all ethanol is produced from the fermentation of edible crops, most notably corn (in the USA) and sugar-cane (in Brazil). Authors analyzing the performance and potential of ethanol as a transport fuel almost invariably assume ethanol to be of plant origin, rather than from fossil hydrocarbon sources.

## Pysicochemical characteristics of ethanol and ethanol-petrol blends

Ethanol ($C_2H_5OH$), a primary alcohol, is the second simplest alcohol. Humankind has millennia of experience in its production, it evaporates quickly when spilled on land, and it is fully biodegradable [2,4].

Ethanol's properties such as density and octane number make it suitable for combustion in spark-ignition engines. Ethanol can also be mixed with Diesel to form blends for use in compression-ignition engines, although this application has received less attention in the literature. This paper focuses on applications for SI engines.

Ethanol can be splash blended with petrol to form ethanol-petrol blends, identified by an 'E' followed by the volumetric percentage of ethanol in the blend. E10 and E85 are common blends. In 2007, nearly 40 % of all petrol sold in the USA contained added ethanol [5]; blends up to E10 are permitted for sale in the European Union [3]. Ethanol is also fully water-miscible and readily absorbs water; any blend containing ethanol will likely also contain a small but significant proportion of water [2]. Ethanol and its blends occur as liquids, and therefore have energy densities superior to gaseous fuels. Ethanol has a higher density and viscosity than petrol [4,6,7], and lower lubricity [8].

One of the distinguishing characteristics of ethanol is that it is an oxygenated fuel, in comparison to petrol, diesel, LPG etc, which do not contain appreciable quantities of oxygen. The presence of an oxygen atom means that ethanol can be thought of as a partially oxidized fuel [9,10]. The O-H polar bond makes ethanol a polar molecule.

Complete combustion of pure hydrocarbons would produce only two products – carbon dioxide ($CO_2$) and water ($H_2O$). The ratio in which molecules of these two species are produced by a combustion reaction is controlled by the carbon to hydrogen ratio of the fuel. Fuels with lower carbon to hydrogen ratios are an attractive option for reducing $CO_2$ emissions, and thus ethanol and its blends are of interest (Table 1).

Table 1. The carbon to hydrogen ratio of various automotive fuels

| Fuel | Carbon:hydrogen ratio |
|---|---|
| Diesel | 0.54 |
| Petrol | 0.53 |
| E10 | 0.51 |
| LPG | 0.40 |
| E85 | 0.36 |
| E100 | 0.33 |
| CNG | 0.25-0.33 |
| Hydrogen | 0 |

Even the addition of relatively small proportions of ethanol to petrol lowers the C:H ratio and makes the resulting blend more competitive in this respect. Ethanol benefits from the absence of carbon-carbon double bonds, which enables the two carbon atoms to bond to more hydrogen atoms, this giving high ethanol blends a C:H ratio which approaches that of CNG/biomethane.

**Combustion characteristics**

The short length of the ethanol carbon chain, together with the presence of the oxygen atom, make the combustion of ethanol and its blends differ from the combustion of pure petrol in a number of ways.

As the fuel is already partially oxidized, the quantity of oxygen required for complete combustion of a given mass is reduced, and thus the stoichiometric ratio is lower than for pure petrol. For E10 the ratio is some 3.8 % lower; for E85 it is 32.8 % lower than for petrol alone. Due to this effect, a greater rate of fuel injection is required in order to maintain a stoichiometric mixture [11]. However, the oxygen content of ethanol and its blends can have a leaning effect on combustion [6,8]. Fuel consumption is usually considered to rise in response to increasing fuel ethanol content [4,6,11-17]; the E85 blend is invariably considered to cause higher volumetric fuel consumption than pure petrol [16-19]. When the difference in energy density is factored out, E85 has been reported to outperform petrol [18], due to improved thermodynamic efficiency. The potential for low and medium ethanol blends to deliver a small improvement in fuel economy – as reported in [20] – merits further investigation. A statistical analysis of data obtained by the EPA found that fuel consumption was controlled by the volumetric energy content of the blend employed [14,19]. The potential for smaller increases in the viscosity of engine lubricant, as suggested in [11], may also have a positive effect on fuel consumption via a reduction in frictional and pumping losses, and this may explain any variation is fuel consumption which is not accounted for by the energy content of the blend.

Flames from the combustion of pure ethanol propagate approximately 30 % faster than petrol [6], although the variation in flame propagation speed does not always appear to follow ethanol blend content in a linear fashion [21]. This reduces the total time of the combustion phase [22] and therefore could limit the time available for the formation of oxides of nitrogen. Additionally, the higher latent heat of vaporization of ethanol absorbs more heat and should thus inhibit $NO_x$ formation [23]. However, some authors have reported small increases in $NO_x$ emission when employing ethanol blends [24], although these trends are not consistent and may not be statistically significant [12]. Increased $NO_x$ emissions may be due to the effect of leaner mixtures ($\lambda>1$), which reduce $NO_x$ conversion efficiency in the three-way catalyst. Catalyst light-off may also occur slightly later when using an ethanol blend [25], due to the lower adiabatic flame temperature of ethanol [4].

The lower stoichiometric ratio makes complete oxidation of the fuel easier to achieve and consequently leads to lower emissions of HC and CO and higher emissions of $CO_2$. A large number of studies carried out on light-duty vehicles have concluded that emissions of HC and CO are generally lower (reviewed in [24]), due to more complete combustion and lower oxygen requirements. Emissions of carbon dioxide are greater, primarily due to the lower energetic content of the fuel, but also due to improved oxidation of HC and CO to $CO_2$. In his detailed and wide-ranging literature review [24], Hochhauser concluded that increasing the fuel oxygenate content reduces emission of HC and CO, but slightly increases emission of $NO_x$. Hochhauser's review looked at of a number of studies which added oxygenates (including ethanol) to standard petrol which showed that $NO_x$ emissions tend to increase for low blends, although the effect is not always significant and is generally small – up to around 5 %. As many studies compare only two or three blends over a narrow range of ethanol contents, extrapolation over the entire blend range from (i.e. from E0 to E100) is problematic. The profile of the boiling curve also affects $NO_x$ emission [24], and fuel additives which modify the mid- and back-end volatility ($T_{50}$ and $T_{90}$) of ethanol blends might mitigate against any increased emissions of $NO_x$.

As the RON of ethanol is higher than that of petrol, the addition of even small quantities of ethanol to petrol raises its knocking resistance. Each 10 % of ethanol added to petrol increases the RON of the blend by around 5 [4]. The anti-knock index (AKI) of the fuel is the arithmetic mean of the research and motor octane numbers. Ethanol and its blends have superior AKI values to standard petrol [24].

**Compatibility with petrol-fuelled vehicles**

The relatively small size and polar nature of the ethanol molecule, together with the likely presence of absorbed water, and other impurities make it more penetrating and corrosive than E0 petrol [26,27]. The most problematic impurities are water, chlorides and organic acids [8,28]. Metals (zinc, aluminium, magnesium, copper) and their alloys, certain coatings, and non-fluorinated rubbers and elastomers are all at risk [27,28], although it should be pointed out that E0 petrol also damages many of these components, albeit at a much slower rate [8]. The higher electrical conductivity of ethanol and its blends can contribute to galvanic corrosion [29]. Furthermore, ethanol and its blends can have adverse affects on some lubricating oils and even paintwork, where the two come into contact. However, it has been reported that the lower concentrations of reactive combustion products produced by ethanol and its blends may in fact slow chemical ageing of lubricating oils resulting from blow-by/oil interactions in the crankcase [11].

It is generally agreed that blends up to E10 may be used in unmodified port-injected SI engines with no problems. Beyond this point, vehicles not designed for use with ethanol blends may suffer damage, and intensive research into this area is ongoing [14]. Following a noteworthy positive assessment of the ability of recent models to adapt to E15 blends [29], the US Environmental Protection Agency (EPA) granted a waiver allowing the sale of E15 fuel, for use in vehicles from the 2007-2010 model years [30]. In January 2011 a further decision effectively extended this waiver to cover cars and light trucks from the 2001-2006 model years [30]. In Brazil, flexible-fuel vehicles capable of running on high ethanol blends are ubiquitous; they are also becoming more common in other markets. A US government website [16] lists around one hundred FFV vehicles as available in the USA for the 2010 model year, a roughly seven-fold increase on the range for the 2000 model year. Vehicles not designed for use with ethanol may be converted for use with these fuels; the type and number of changes required depends on the age of the vehicle and the blend to be employed.

Total protection from corrosion by ethanol blends in a light-duty vehicle would involve replacing or re-coating over three hundred components [28]. A number of studies have evaluated the feasibility of employing ethanol blends higher than E10 in unmodified vehicles. A recent report [29] concluded that the overall impact of using the E15 blend in vehicles for the model years 1994-2000 would be low, although other authors have insisted that usage of E15 and E20 blends causes engine damage [e.g. 31]. However, regardless of the compatibility of vehicles with ethanol blends higher than E10, much existing refuelling infrastructure may not be fully compatible with ethanol blends higher than E10-E15 [31]. Being highly hygroscopic, ethanol and its blends may not be compatible with existing fuel distribution pipelines [30,31], and this issue remains under investigation by the EPA [30].

Deposits formed from impurities in the fuel may be loosened by ethanol and lead to greater deposition on filters, valves etc. Deposition on the intake valves is higher when using ethanol blends than when using petrol alone [5,28]. The response is non-linear and dilution effects alone cannot explain this phenomenon [4]. This problem also occurs in FFVs, and FFVs show no real advantage in this area over their non-FFV counterparts, although the problem can largely be solved through the use of certain additives [28]. The lower lubricity of ethanol and its blends is not a major cause for concern; malfunctioning and fouling of injectors appears to be due to increased corrosivity, rather than reduced fuel lubricity [8].

Table 2. Modifications required for usage of ethanol blends in modern vehicles

| **Component / System Compatibility** | **1-15** | **15-25** | **25-85** | **85-100** |
|---|---|---|---|---|
| fuel injection | - | + | + | + |
| fuel pump | - | + | + | + |
| fuel pressure device | - | + | + | + |
| fuel filter | - | + | + | + |
| ignition system | - | + | + | + |
| evaporative system | - | + | + | + |
| fuel tank | - | + | + | + |
| catalytic converter | - | + | + | + |
| engine parts | - | - | + | + |
| motor oil | - | - | + | + |
| intake manifold | - | - | + | + |
| exhaust system | - | - | + | + |
| cold start system | - | - | - | + |

## Air quality, public health and toxicological aspects

A basic health and safety issue with ethanol and its blends is that ethanol burns with a near-transparent pale blue flame (unlike petrol), and its miscibility with water means that water is relatively ineffective at putting out ethanol fires [31]. Underground leaks or large spills of ethanol could cause it to enter groundwater, but its overall impact would be far less than that of a similar volume of standard petrol.

Any reduction in emissions of HC and CO has substantial positive implications for air quality. However, while the total HC emitted may be lower, emissions of oxygen-bearing organic compounds are substantially higher. While ethanol is a partially oxidized fuel, it can be further oxidized without combusting completely. Even relatively low blends such as E10 and E20 produce substantially greater emissions of aldehydes than standard petrol [31-34]. The aldehydes emitted (formaldehyde and acetaldehyde) are harmful, potentially carcinogenic gases [35] which are also well-known ozone precursor molecules [35,36]. As ground-level ozone has been identified as one of the biggest threats to public health in the EU [37], emission of ozone precursor molecules may be one area where ethanol's environmental credentials are inferior to those of petrol.

Increased evaporative emissions due to the corrosivity and penetrating ability of ethanol and its blends have been identified as a negative impact on air quality resulting from usage of such fuels [8,37]. Legacy vehicles fitted with carburetors are particularly prone to increased evaporative emissions. Materials which are effective at preventing evaporative emissions of petrol and its components are not always effective barriers to ethanol [37]. Research has indicated that fluorinated polymers provide the best protection from permeation and corrosion and therefore reduce evaporative emissions [39].
Considerations of air quality and health impacts of a switch to ethanol and its blends indicate that results could be mixed [40,41]; authors have found that that in certain areas the net effect of usage of E85 could be negative [e.g. 42]. Some reviewers have stressed that emissions from the use of ethanol blends are highly variable, and that the poor agreement between different studies prevents the drawing of firm conclusions regarding emissions inventories and air quality projections [e.g. 43]. Nevertheless, the benefits for air quality and public health resulting from reduced concentrations of HC and CO are self-evident; studies have found that overall public health could improve as a result of increased usage of ethanol and its blends [e.g. 38,44,45]. One recent paper expresses concern over increased emissions from ethanol-fuelled vehicles in cold climates and winter conditions [46].
It has been reported that standard TWCs are not particularly effective at oxidizing aldehydes. In addition, use of mid-high ethanol blends can cause certain aftertreatment systems to age prematurely and irrecoverably [47], thereby leading to significantly increased emissions of aldehydes, HC and possibly other regulated compounds. However, this effect is not observed in all vehicles, and is connected with the degree to which the stoichiometric ratio is adhered to [47]. The apparent trade-off between lower total HC emissions and significantly increased aldehyde emissions warrants further investigation into aftertreatment devices designed for ethanol-blend applications. Ethanol blend-specific TWC design and closer control over the equivalence ratio would enable the aftertreatment system to oxidize these compounds with greater efficiency.

## Conclusions

Despite variable data, ethanol blends have the potential to deliver benefits in the areas of HC and CO emission. The effect of ethanol blends on emission of $NO_x$, aldehydes and other compounds requires further investigation.

Any correlation between air quality improvement and the number of FFV vehicles in use is complicated by the fact that many motorists own a FFV and yet run it exclusively on standard petrol as they are unaware of the vehicle's FFV status [14] – indeed only 1 % of all the ethanol sold as fuel for SI vehicles in the USA occurs in E85 blends [48]. As of 2010, there are only ~1200 E85 stations in the USA [48] – approximately 1 % of all refuelling stations, although some countries have much higher E85 penetration – 10 % in Sweden [49] and close to 100 % in Brazil.

If appropriately marketed and legislated, ethanol could potentially be popular with consumers. Unusually for an alternative fuel, ethanol has the potential to increase performance [16]. Acceleration has been found to be better for Saab's FFV when running on E85 [15]. The allure of potential increases in performance could be an important marketing tool for both FFVs and ethanol blended fuel.

The use of higher compression ratios made possible by the high AKI of ethanol could go some way towards compensating for the lower volumetric energy density of this fuel [16]. Technology which enables varying the compression ratio according to the particular fuel or blend in use at the time would enable full exploitation of ethanol's superior knock-resistance characteristics [16].

Recent work suggests that certain ethanol blends may be suitable for use in gasoline direct injection engines [50,51], with an overall decrease in harmful engine out emissions reported in [51]. However, conventional aftertreatment systems are not adequate when using higher ethanol blends in this engine type [50].

Research priorities include:

- Continuing research into second generation bioethanol feedstocks and production pathways
- Clarifying the emissions benefits and the effects of load, speed and driving cycles from usage of low (E5-E15) blends of ethanol
- Further assessment of the safe usage of low-to-mid level blends (E10-E50) in unmodified vehicles from model years prior to 2007
- Formal investigations into the feasibility of adapting existing non-FFV vehicles to enable usage of E85, and the resulting emissions, fuel consumption and driveability benefits/penalties
- Further research into the direct and indirect effects of emissions from ethanol-fuelled vehicles on local, regional and global air quality scenarios
- Development of dependable, corrosion-resistant sensors, injectors and fuel delivery systems, engine calibrations and aftertreatment systems to allow full exploitation of the higher compression ratios permitted by higher ethanol blends, while maintaining strict emission standards

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