

Review of fuel ethanol impacts on local air quality

A literature review of available evidence for effects of ethanol fuels on air pollutant emissions from motor vehicles

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Summary

One of the aims of the Bioethanol for Sustainable Transport (BEST) project is to demonstrate the environmental benefits of ethanol as an alternative to fossil-based transport fuels. The BEST Evaluation Plan provides a systematic framework for monitoring and assessment of those benefits, based on a detailed set of evaluation requirements for the demonstration activities in the project. These requirements include monitoring of ethanol usage at the project sites, reviewing the available evidence for the environmental impacts of ethanol use, and where necessary, carrying out new analyses to improve our understanding of those impacts. This report is a review of the available evidence for the air quality impacts of using ethanol fuels in transport. The report focuses on regulated and unregulated air pollutant emissions from vehicles running on ethanol fuels, but does not cover greenhouse gas emissions¹.

The review begins with a general overview of the air quality impacts of burning fuels in vehicle engines, listing the types of pollutants normally produced and their impacts on human health and the environment. The factors influencing air pollutant formation and standard methods of limiting pollutant production and emission are described. The specific impacts of using ethanol in both petrol and diesel engines are then considered, both from the perspective of what current knowledge indicates those impacts should be, and through considering the reported results of recent studies.

¹The Evaluation work package is currently developing life-cycle assessments of the greenhouse gas emissions from production and use of ethanol at the different BEST sites, and will report on these separately.

Air pollution from motor vehicles

Combustion of fuels in internal combustion engines always generates some undesirable products in the engine exhaust systems. Additionally, vehicle fuel systems give off unburnt fuel vapours, and open-vented engine crankcases give off escaped combustion products and vaporized lubricating oil. In high enough concentrations, these emissions can be harmful to human health and the environment, and modern vehicle systems and fuels are designed to prevent these emissions exceeding specified limits. The main pollutant components of vehicle emissions are:

- **carbon monoxide (CO)**, a toxic compound which reduces the blood's ability to carry oxygen to tissues and is associated with a number of adverse health effects, particularly in people with cardiovascular disease (WHO 2005)
- **hydrocarbons** – these contribute to formation of ground-level ozone and in some cases are known to have direct adverse effects on human health;
- **oxides of nitrogen (NOx)**, which are linked to respiratory illnesses and are involved in production of ground-level ozone
- **particulate matter**, which are usually complex, heterogeneous mixtures of solid or liquid particles suspended in the air, and are linked to adverse respiratory and cardiovascular impacts in humans
- **toxic pollutants**, which are specific compounds that are known or suspected to cause cancer or other serious health effects; these are mainly hydrocarbons and related organic compounds and include
 - o **benzene**
 - o **1,3 butadiene**
 - o **acetaldehyde**
 - o **formaldehyde**
 - o **polycyclic aromatic compounds**

In addition to the direct pollutant emissions, motor vehicle use also results in production of secondary pollutants, formed in the atmosphere by reactions involving direct or primary emissions. These include secondary particulate matter, with characteristics and risks described above and **ground-level ozone**, which causes pulmonary and cardiovascular problems in humans, as well as damage and yield reduction in plants.

Exhaust emissions

Exhaust emissions refer to substances exiting the tailpipe of motor vehicles. The composition of tailpipe emissions depends on the composition of the exhaust streams leaving the engine after combustion and on the effectiveness of any pollutant-reducing measures employed in the exhaust system downstream of the engine. Most of the pollutant components of exhaust emissions originate in the process of fuel combustion in the engine.

Perfect combustion of any sample of fuel would involve complete oxidation of the entire sample with maximum heat production and no pollutant emissions. This would require complete mixing of exactly reacting quantities of the pure fuel and oxygen with the addition of an appropriate amount of heat. For hydrocarbon fuels, the only products of combustion would be carbon dioxide¹, water vapour and heat. The combustion of fuels in practical internal combustion engines is not perfect for a number of reasons:

- the fuel is burned in air, which contains other elements in addition to oxygen; in particular, nitrogen present in the air (78% by volume) can react with oxygen to produce NOx

¹ Note that carbon dioxide was traditionally not viewed as a pollutant. However, with more recent recognition of the role of human-induced emissions of greenhouse gases such as carbon dioxide in promoting global climate change, emissions of carbon dioxide which do not form part of a closed cycle cannot be considered to be non-polluting.

- the ratio of the quantities of air and fuel cannot be exactly controlled at every moment during the combustion process
- the fuel may contain impurities which can react or pass through the process to produce pollutant emissions
- the heat for combustion may at certain times be insufficient (such as when starting up a cold engine)
- the control of fuel ignition or injection timing may not always achieve combustion at optimal conditions

As a result, exhaust gases leaving the engines of motor vehicles always contain some pollutant compounds. The conditions and processes that lead to formation of the major pollutants are summarised below.

Carbon monoxide

Carbon monoxide emissions are caused by incomplete combustion of fuels. This most often occurs when the ratio of air to fuel in the combustion chamber is too low for complete combustion, or when there is inadequate mixing of fuel and air, leading to isolated pockets where the air-fuel ratio is too low for complete combustion. When the air-fuel ratio is too low, there is insufficient oxygen to convert all the carbon in the fuel to carbon dioxide. A small amount of carbon monoxide is also formed when there is much more air than required for complete combustion (i.e., very weak fuel-air mixtures), due to chemical kinetic effects.

Hydrocarbons

Hydrocarbons emitted with engine exhaust gases are composed of unburned fuel and products of partial combustion (such as ethylene) that were still present (i.e., not yet combusted) in engine cylinders at the beginnings of the engine exhaust strokes. This failure to complete combustion during the power stroke is generally related to the movement of fuel mixtures and speed of propagation of the flame in the engine cylinders during the power stroke. Abnormal engine operation, such as cylinder misfiring, can also cause significant quantities of hydrocarbons to be introduced into the engine exhaust stream.

Nitrogen oxides (NO_x)

Nitric oxide (NO) is the main form of NO_x produced by internal combustion engines, although nitrogen dioxide (NO₂) is also produced in significant quantities. Nitric oxide is formed from the reaction of nitrogen and free oxygen at high temperatures. The rate of formation of NO is a function of oxygen availability, and increases exponentially with flame temperature.

Particulate matter (PM)

Particulate matter emissions are produced more by diesel engines than by spark-ignition engines. They are formed mainly from carbon particles (soot) produced in fuel-rich zones of the combusting gases and hydrocarbons adsorbed on to the carbon particles. Particulate matter also contains unburned lubricating oil and ash-forming fuel and oil additives. PM emissions from spark-ignition engines result mainly from condensation of lubricating oil in the exhaust.

Toxic pollutants

Benzene in engine exhausts originates as a fuel component that has escaped the combustion process and is produced by dealkylation of other aromatic compounds.

1, 3 butadiene is a product of partial hydrocarbon combustion.

Aldehydes are formed as intermediate products of hydrocarbon and alcohol fuel combustion. They usually end up in exhaust emissions as a result of some portion of the partially reacted combustion mixture being subjected to lower temperature (for example by coming into contact with a colder surface). The primary oxidation reactions of alcohol fuels proceed through formation of aldehydes, so these compounds are often found in significant concentrations in the exhaust gases of engines burning alcohols.

Polycyclic aromatic hydrocarbons (PAHs) in engine exhausts result from PAH components of the fuel that survive combustion, or are produced during the combustion process from non-PAH fuel components.

Evaporative and refuelling emissions

Evaporative emissions refer to fuel vapours given off by vehicle fuel systems. Refuelling emissions are fuel vapours displaced from vehicle fuel tanks and emitted to the atmosphere during vehicle refuelling. Evaporative and refuelling emissions can be significant for volatile fuels such as petrol and ethanol.

Evaporative emissions are generally classified as:

- **breathing or diurnal losses** from fuel tanks through venting after expansion of gas in the fuel tank as the temperature increases
- **running losses** or evaporation from the fuel system when the engine is running
- **hot soak emissions** or evaporation from fuel systems after a warm engine is turned off
- **resting losses** or evaporation of fuel after permeation through plastic and rubber components of fuel systems

The levels of emissions occurring through evaporation are heavily dependent on fuel volatility, ambient temperature and fuel system design.

Crankcase emissions

Crankcase emissions refer to leakage of compressed combustion gases past the piston rings in reciprocating engines. These gases have to be vented from the crankcase, but consist largely of unburned or partially burned fuel-air mixture, and therefore contain significant levels of pollutants. Most modern engines (and all modern spark-ignition engines) therefore have closed crankcase ventilation systems which vent their crankcases back to the air intake system. However, many turbocharged, aftercooled heavy duty diesel engines still vent their crankcases to atmosphere, usually through basic mesh filters that still allow significant particulate matter to be emitted.

Strategies for controlling emissions

To reduce the air pollution impacts of motor vehicle use, national and international standards set limits on the levels of specific pollutant emissions that may be emitted by new car models during standard emissions testing for new car type approval. Over time, these standards are revised, making them increasingly stringent. For example, the European standards for regulated emissions from passenger cars are given in Table 1 below. Note that when a later standard has a maximum limit value greater than an earlier one, the later standard is still more stringent, as a result of more demanding test conditions.

Table 1: Euro emission standards for passenger cars

| Standard | Date of introduction | Fuel | Limit values (g/km) | | | | |
|----------|----------------------|-----------------------------|---------------------|------|------|--------|-------|
| | | | CO | HC | NOx | HC+NOx | PM |
| Euro I | July 1992 | Petrol | 2.72 | - | - | 0.97 | - |
| | | Diesel | 2.72 | - | - | 0.97 | 0.14 |
| Euro II | January 1996 | Petrol | 2.2 | - | - | 0.5 | - |
| | | Diesel (indirect injection) | 1.0 | - | - | 0.7 | 0.08 |
| | | Diesel (direct injection) | 1.0 | - | - | 0.9 | 0.10 |
| Euro III | January 2000 | Petrol | 2.3 | 0.20 | 0.15 | - | - |
| | | Diesel | 0.64 | - | 0.50 | 0.56 | 0.05 |
| Euro IV | January 2005 | Petrol | 1.0 | 0.10 | 0.08 | - | - |
| | | Diesel | 0.50 | - | 0.25 | 0.30 | 0.025 |

Emissions standards do not specify technologies for achieving required emissions performance, and vehicle manufacturers can decide on the technological options for achieving required emissions performance. Table 2 lists design features used in modern motor vehicles to control regulated emissions.

Design and Fitment Options

Table 2: Vehicle design for emissions control

| Pollutant emissions | Vehicle design features for emissions control |
|----------------------------|---|
| Carbon monoxide (CO) | Precise control of air/fuel ratio, especially under slow-running and cold start conditions; achieved by advanced engine management systems |
| | Improved fuel distribution through multi-point injection |
| | Precise engine tuning under control of engine management system to prevent incorrect adjustment during maintenance |
| | Compact combustion chambers tend produce lower CO emissions |
| | Throttle positioner system for slight opening of throttle at idle or during deceleration |
| | Precise ignition timing through advanced engine management system |
| | Catalytic converters |
| Hydrocarbons | Positive crankcase ventilations systems, which return crankcase gases to the air induction system |
| | Fuel evaporative emission control that seals the fuel tank and passes fuel vapours via a charcoal canister to the air induction manifold |
| | Accurate ignition timing control to allow retarding of ignition timing for slow-running or decelerating engine |
| | Precise air/fuel ratio adjustment during deceleration |
| | Catalytic converters |
| Oxides of nitrogen (NOx) | Exhaust gas recirculation to slow down combustion when the engine is under high load |
| | Combustion chamber shape alteration in combination with reduced compression ratios |
| | Engine designed to operate on weak mixture (peak NOx content at about 12% richer than stoichiometric) |
| | Computer-controlled ignition timing alteration to prevent advance in ignition timing for given time when throttle is snapped open |
| | Varying valve timing to optimize overlap period between inlet and exhaust, inducing some exhaust gas into intake port and lowering combustion temperature |
| | Fitting intercoolers to turbocharged engines to reduce intake air temperature and therefore combustion temperature |
| | Fitting three-way catalytic converter |
| | |
| Particulates | Diesel particulate filters or partial filters |

Fuel Options

Control of fuel composition and characteristics provides an important option for limiting pollutant emissions from motor vehicles. By reducing fuel components known to contribute to particular pollutant emissions, it is possible to produce reductions in those pollutants. However, changes to fuel specifications may require design changes to different vehicle subsystems such as engine, fuel system and emission controls. Additionally, changes that reduce emissions of one pollutant may increase emissions of others.

Fuel options for reducing emissions include reformulating conventional fuels to reduce or increase particular components, or use of alternative fuels such as ethanol.

Impacts of ethanol fuel and blends on pollutant emissions

Fuel properties of ethanol

Ethanol may be used as a fuel itself or in blends with petrol or diesel. It has a lower energy density than petrol or diesel, a higher octane number than petrol, and a much lower cetane number than diesel. It is highly miscible with petrol but not miscible with diesel. Ethanol-diesel blends use cetane enhancers and solubility improvers. Table 3 lists the important fuel properties of ethanol and compares these with petrol and diesel fuel.

Table 3: Fuel properties of anhydrous ethanol and comparison with petrol and diesel fuel

| Property | Ethanol | Petrol | Diesel |
|---------------------------------------|---------|--------|---------|
| Composition, weight % | | | |
| C | 52.2 | 85-88 | 84-87 |
| H | 13.1 | 12-15 | 13-16 |
| O | 34.7 | 0 | 0 |
| Density, kg/m ³ | 794 | 750 | 825 |
| Lower heating value, MJ/kg | 26.7 | 42.9 | 43 |
| Octane number | 100 | 86-94 | - |
| Cetane number | 8 | 5-20 | 40-55 |
| Reid vapour pressure (kPa) | 15.6 | 55-103 | 1.4 |
| Stoichiometric air/fuel ratio, weight | 9:1 | 14.7:1 | 14.7:1 |
| Boiling temperature, °C | 78 | 80-225 | 188-343 |
| Flash point, closed cup, °C | 13 | -42 | 74 |

Sources: JEC, 2005; Joseph, 2007; EERC, 2008

Addition of ethanol to petrol at low blend ratios results in a blend with increased vapour pressure. This vapour pressure increase rises to about 7 kPa above the base petrol vapour pressure for ethanol contents between 2% and 10% (Martini, 2007). As ethanol content increases beyond this range, the vapour pressure of the blend decreases (Figure 1).

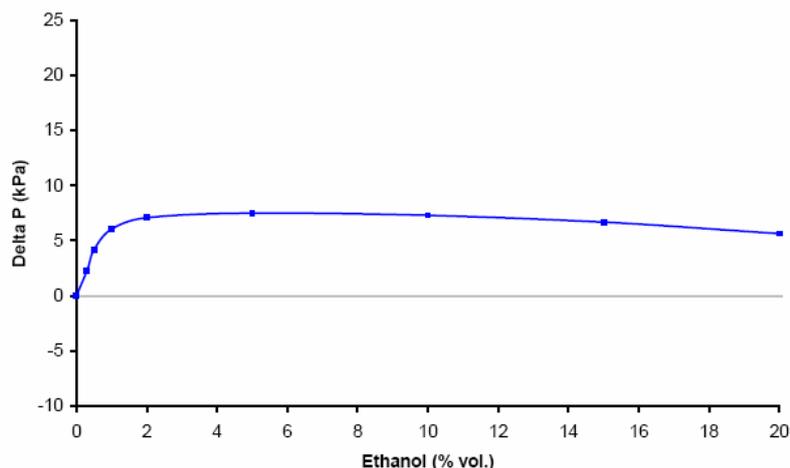


Figure 1: Vapour pressure increase vs ethanol content in ethanol-petrol blends (Source: Martini, 2007)

Expected air quality impacts of ethanol fuel

Ethanol has a number of properties that suggest that burning it either as a pure fuel or in blends with petrol or diesel should result in reductions in emissions of a number of the common pollutants generated by petrol and diesel combustion. Ethanol is commonly added to petrol as an oxygenate, as the oxygen content of ethanol is believed to promote easier and more complete combustion, leading to generally lower emissions of carbon monoxide and unburnt hydrocarbons in vehicle exhausts. Ethanol does not contain olefins, aromatics or sulphur (although ethanol denaturants may contain these components). These are all present in gasoline and diesel and are known to have negative impacts on air quality. Ethanol in blends may be expected to reduce some of the harmful effects of these pollution sources through dilution.

The improved availability of oxygen in the combustion zone of engines using ethanol may, however, lead to increased combustion temperatures and therefore increased NO_x emissions.

The higher volatility of low blends of ethanol in petrol can be expected to result in increased evaporative emissions of those blends compared with petrol.

Emissions of aldehydes, which are intermediates in alcohol combustion, would be expected to increase when burning ethanol compared with petrol or diesel.

Reported air quality impacts of ethanol fuel

Coinciding with the dramatic growth in fuel ethanol production and use over the past decade, a number of studies have been carried out in different countries into the air quality impacts of pure and blended fuel ethanol. Unfortunately, there is little consistency in the impacts reported. The International Energy Agency's 2004 publication "Biofuels for Transport – An International Perspective" reviewed studies on air quality impacts of E10 blends and found that E10 reduced emissions of carbon monoxide, exhaust volatile organic compounds (VOCs), particulate matter and some unregulated pollutants, while increasing evaporative and total VOCs, NO_x and some unregulated pollutants. In fact, the IEA's review found evidence for both increases and decreases in NO_x emissions with E10, with the magnitude of the effect small in most cases.

Table 4: Changes in Emissions when Ethanol is Blended with conventional gasoline (IEA 2004)

| Pollutant | Effect of ethanol on emissions |
|--|--------------------------------|
| Commonly regulated air pollutants | |
| CO | decrease |
| NO _x | increase |
| Tailpipe VOC | decrease |
| Evaporative VOC | increase |
| Total VOC | increase |
| Particulate matter | decrease |
| Toxic/other air pollutants | |
| Acetaldehyde | increase |
| Benzene | decrease |
| 1,3 Butadiene | decrease |
| Formaldehyde | increase |
| Peroxyacetyl nitrates | increase |
| Isobutene | decrease |
| Toluene | decrease |
| Xylene | decrease |

A 2004 literature survey carried out by TNO for Senternovem in the Netherlands (Smokers and Smit, 2004) concentrated on studies primarily from the period 2000-2004.

Table 5: Effect of ethanol on regulated and unregulated emissions from reference petrol or diesel (Smokers and Smit 2004)

| Ethanol Blend (P - petrol, D - diesel) ^a | Ethanol Effect on Regulated Emissions ^b | | | | Ethanol Effect on Unregulated Emissions ^b | Reference |
|--|--|------|-----------------|------|--|----------------------|
| | CO | HC | NO _x | PM | | |
| E100P | dec. | dec. | dec. | | | Brusstart 2002 |
| E85P | dec. | | dec. | dec. | inc. | US EPA 2002 |
| E85P | | | | | dec. & inc. | NREL 2002 |
| E12-E95 | dec. | dec. | dec. & inc. | | inc. | NREL 2002 |
| E??P | dec. | dec. | dec. | | inc. | Amaral 2001 |
| E85P | inc. | inc. | dec. | dec. | dec. & inc. | EC 2000 |
| E95P | inc. | inc. | dec. | dec. | | Beer 2000 |
| E85P | inc. | | dec. | | dec. & inc. | Dodge 1998 |
| E10P | dec. | dec. | 0 | | dec. & inc. | Apace & NSW EPA 1998 |
| E50/85P | dec. | dec. | dec. | | dec. & inc. | Kelly 1996 |
| E42P | dec. | dec. | | | dec. & 0 | Guerrieri 1995 |
| E85P | 0 | inc. | dec. | | inc. | Benson 1995 |
| E??D | inc. | inc. | 0 | dec. | inc. | Corkwell 2003 |
| E10/30D | inc. | inc. | dec. | dec. | inc. | He 2003 |
| E10/15D | dec. & inc. | inc. | dec. & inc. | | | Hansen 2001 |
| E15D | 0 | inc. | dec. | dec. | dec. & inc. | EC 2000 |

^a Designation refers to volumetric blend percentage of ethanol in petrol or diesel. For example, E85P is an 85% volumetric blend of ethanol in petrol, and E15D is a 15% volumetric blend of ethanol in diesel. E??P and E??D refer to unspecified blend percentages.

^b “inc.” indicates an increase in emissions, “dec.” indicates a decrease in emissions and “0” indicates no effect

These apparent inconsistencies in reported emissions impacts of ethanol fuel make it difficult to draw firm conclusions from the body of available study reports. In all the studies analysed by TNO, particulate matter was the only pollutant category consistently shown to decrease. However, it is always necessary to consider comparisons among results of large numbers of studies with much care. The levels of transparency of the study reports differ considerably, and it is not always clear whether the comparisons are meaningful. The specifications for the ethanol, petrol and diesel fuels used in the different studies were likely to have been different. Perhaps more importantly, the specifications for the emissions control measures (e.g., catalytic converters, engine design features) employed on the test vehicles were likely to have been different. Variations in methodology (such as drive cycles used and test procedures) could also account for much of the apparent inconsistencies. Nevertheless, analysis of the different studies does suggest that, depending on particular conditions, both increases and decreases in emissions of some major air pollutants may be observed when substituting ethanol for petrol or diesel. It is of great importance to understand what those particular circumstances are. Further research is very clearly needed in this area.

Conclusions

Although studies carried out by major national and international agencies (IEA, 2004; US EPA, 2002; Faiz, et. al., 1996 for World Bank) have reported that ethanol fuel combustion results in reduced emissions of carbon monoxide and exhaust hydrocarbons compared with petrol and diesel, a number of other studies have reported that burning ethanol results in increases in these emissions. It is clear that different studies have been carried out under different conditions and further work needs to be carried out in order to understand these.

The studies reviewed consistently reported reductions in particular matter and increases in evaporative hydrocarbon emissions and aldehydes when ethanol fuels are used in place of petrol or diesel. Both increases and decrease in emissions of nitrogen oxides are reported to result from replacing petrol or diesel with ethanol fuels.

It is possible that analysis of the reasons for the apparent inconsistencies between the various study results will bring improved understanding of the requirements for ensuring that pollutant emissions are always minimized when running vehicles on ethanol fuels. The current state of knowledge makes it possible to say that ethanol fuels can provide some air quality benefits, but, especially as ethanol use continues to grow worldwide, further emission control measures may be necessary to ensure that all air pollutants emissions of concern are kept within acceptable limits.

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