



Ethanol as a Future Fuel for Road Transportation

Main report

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EFP06



IEA Implementing Agreement on **Advanced Motor Fuels**

Ethanol as a Fuel for Road Transportation

Main Report

Ulrik Larsen
Troels Johansen
Jesper Schramm



Technical University of Denmark



May 2009

Preface

This report is financed by the Danish Energy Authority (EFP 2006 — Ethanol som motorbrændstof) and made in cooperation with the International Energy Agency — Advanced Motor Fuels Agreement. The report is a contribution to Annex XXXV: “Ethanol as a Motor Fuel — Subtask 1: Ethanol as a Fuel in Road Vehicles.” The work has been carried out by The Technical University of Denmark, Department of Mechanical Engineering.

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Acronyms

AEBIOM	European Biomass Association
AFDC	Alternative Fuels and Advanced Vehicles Data Center
AFR	air–fuel ratio
ANFAVEA	Brazilian Automotive Industry Association Energy & Environment Commission
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
BE-diesel	biodiesel–ethanol–diesel blend
Btu	British thermal unit
CAI	controlled auto-ignition
CERC	Combustion Engine Research Center, Chalmers University
CH ₄	methane
CHP	combined heat and power
CI	compression Ignition
CO	carbon monoxide
CO ₂	carbon dioxide
CO ₂ eq	carbon dioxide equivalent
CONCAWE	European Oil Company Organisation for Environment, Health and Safety
CRC	Coordinating Research Council
DDGS	dried distillers grains with solubles
DI	direct fuel injection
DOE	U.S. Department of Energy
E10	gasoline containing 10 percent ethanol by volume
E85	gasoline containing 70–85 percent ethanol by volume
E93	ethanol containing 7 percent water
EBS	ethanol-boosting system
ECU	engine control unit
E-diesel	specific ethanol–diesel blend
EEPS	Engine Exhaust Particle Sizer
EERE	U.S. Office of Energy Efficiency and Renewable Energy
EGR	exhaust gas recirculation
EJ	Exa Joule (10 ¹⁸)
ELPI	Electrical Low Pressure Impactor
EMPA	Swiss Federal Laboratories for Materials Testing and Research
EPA	U.S. Environmental Protection Agency
ETBE	ethyl tertiary butyl ether
EU	European Union
EUCAR	The European Council for Automotive R&D

FAME	fatty acid methyl esters
FAO	Food and Agriculture Organization (U.N.)
FCAI	Federal Chamber of Automotive Industries (Australia)
FFV	flex fuel vehicles
GDI	gasoline direct injection
GHG	greenhouse gas
GM	General Motors
GREET	The Greenhouse gases, Regulated Emissions and Energy use in Transportation model
HC	hydrocarbon
HCCI	Homogenous Charge Compression Ignition
IBUS	Integrated Biomass Utilization System
IEA	International Energy Agency
IFP	French Petroleum Institute
IMF	International Monetary Fund
IPCC	Intergovernmental Panel on Climate Change
JRC	Joint Research Center
KL	knock-limited ignition timing
kWh	kilowatt-hour
LCA	Life Cycle Assessment
LEV	low-emission vehicle
MBT	maximum brake torque ignition timing
MTBE	methyl tertiary butyl ether
N ₂ O	nitrous oxide
NEV	net energy value
NO ₂	nitrogen dioxide
NO _x	nitrogen oxides
NREL	National Renewable Energy Laboratory (U.S.)
O ₂ -diesel	brand of ethanol–diesel blend
OBDS	on-board distillation system
OECD	Organisation for Economic Co-operation and Development
PAH	polyaromatic hydrocarbons
PCCI	partial premixed controlled combustion
PFI	port fuel injection
pHCCI	partial homogenous charge compression ignition

PM	particulate matter
PVC	polyvinyl chloride
PZEV	partial zero-emissions vehicle
RFG	reformulated gasoline
RON	research octane number
RVP	Reid Vapor Pressure
SADE	spark-assisted diesel engine
SAE	Society of Automotive Engineers
SI	spark-ignited
SUV	sport utility vehicle
USDA-ARS	U.S. Department of Agriculture Agricultural Research Service
VOC	volatile organic fractions
VVT	variable valve timing
VW	Volkswagen
WTW	well-to-wheels (assessment)

Summary

Bioethanol as a motor fuel in the transportation sector, mainly for road transportation, has been subject to many studies and much discussion. Furthermore, the topic involves not only the application and engine technical aspects, but also the understanding of the entire life cycle of the fuel, well-to-wheels, including economical, environmental, and social aspects. It is not, however, the aim of this report to assess every single one of these aspects. The present report aims to address the technical potential and problems as well as the central issues related to the general application of bioethanol as an energy carrier in the near future.

A suitable place to start studying a fuel is at the production stage, and bioethanol has been found to have a potential to mitigate greenhouse gases, depending on the production method. This and a potential for replacing fossil fuel-based oil (and being renewable) are the main reasons why ethanol is considered and implemented. Therefore, we must focus on two central questions related to ethanol implementation: how much carbon dioxide (CO₂) can be mitigated and how much fossil fuel can be replaced? A number of life cycle assessments have been performed in order to provide estimates. These assessments have generally shown that bioethanol has very good potential and can mitigate CO₂ emissions very effectively, but it has also been shown that the potential for both fossil fuel replacement and CO₂ mitigation is totally dependent on the method used to produce the fuel. Bioethanol can be made from a wide range of biomass resources, not all equally effective at mitigating CO₂ emissions and replacing fossil fuel. The Brazilian ethanol experience has in many ways shown the way for the rest of the world, not least in the production stage. Brazil was the first and biggest producer of bioethanol, but the United States, China, India, and European Union have since then increased their production dramatically.

Overall, bioethanol represents the best alternative transportation fuel; its use is projected to increase significantly and remain high. As transportation fuel is a very big sector globally, a shift toward more bioethanol usage will potentially have great consequences in many areas of life, driving the need for more comprehensive evaluation methods and regulations. Among the concerns are the principles of sustainable development, particularly the need for the definition of indicators, regulations, and criteria; not unlike those implemented in the forestry sector.

The most apparent problems in producing the biomass and then processing it to bioethanol are pollution and usage of water, use of fossil fuels in production, soil degradation, and land use conflicts. At the layman's level, perhaps the most intensely discussed concern to date has been the *food versus fuel* problem. Clearly, we should not deprive people of food in order to produce transportation fuels. As has been stated by the United Nations Food and Agriculture Organization, the problem at the present time seems not to be a lack of food production capability, but rather, economical politics — namely, trade barriers. Aside from that, it has been discussed whether any real potential for greenhouse gas mitigation potential exists with the current forms of ethanol

production, especially outside Brazil, since another greenhouse gas, nitrous oxide (N_2O), seems to be emitted when the feedstock crops are grown. This gas is a very powerful greenhouse gas, about 300 times stronger than CO_2 . There have been investigations showing a negative potential; that is, bioethanol would be a greater contributor to global warming than regular fossil fuels (gasoline). Another very important issue is the conservation of the natural carbon reservoirs. When land is converted into farm land, there is a possibility of releasing more CO_2 into the atmosphere than the biofuel would be able to mitigate, even over a long time.

Currently, much effort is being put in to solving the problems of the second-generation ethanol technology, the way of producing bioethanol from cellulosic biomass. There is wide agreement about the advantages of this technology, for example, the use of much cheaper feedstock, because several highly efficient (energy) crops can be used, as well as biomass waste such as straw and corn cobs. Another advantage is a very high efficiency, that is, a high yield per area of land used. Lately there has even been talk about using algae as feedstock, thereby avoiding land use conflicts. Nevertheless, many remain to be resolved before this technology can be used on a wider scale, mainly improvement of cost efficiency as well as process efficiency.

Ethanol has been shown to suit different kinds of integrated production scenarios. In Brazil the processes of producing ethanol and power have now been integrated at many locations with success. Previously the excess biomass, that is, bagasse, was burned under open air rather than being converted to power. This has a significant effect on the overall efficiency of the fuel production. In the United States, massive corn-based ethanol production creates opportunities for production of animal feed. In Denmark integrated production of second-generation bioethanol, biogas, hydrogen, and solid fuel pellets has been demonstrated to be exceptionally efficient at utilizing the biomass waste product straw, as well as reusing process water. The idea behind this method is to imitate nature by reusing the waste products from one process as feed for another process. Yet another facility has demonstrated the integrated production of power, district heating, and first-generation and second-generation bioethanol. The solid carbon that remains from the ethanol production is burned in an efficient power plant, which then supplies the ethanol process with cheap, low-grade steam.

The fuel properties of ethanol differ from those of gasoline. Depending on the application, that is, the type of blend used or whether it is used neat, the vehicle needs special specifications for some parts to function properly. First, ethanol is hygroscopic, and an effort is required to avoid water contamination and the ensuing problems. Moreover, production methods favor a content of water, because water can be removed only to a certain degree by normal distillation (up to about 95percent purity), and then another relatively energy costly process removes the remaining water. This makes an argument for using the fuel containing some amount of water. Unfortunately, ethanol has poor blending properties when mixed with either diesel or gasoline, if the ethanol contains more than a very small amount of water. Phase separation occurs and can, in the worst-case scenario, make the fuel inapplicable or, in other cases, cause all

kinds of fuel system and engine problems. These blending problems depend on ambient temperatures and the blending ratios of ethanol, gasoline, and water, and therefore determine the choice of technology for a particular region or country. The worst blending problems occur when low-percentage-ethanol blends containing water are used in cold climates. Mid-and high-percentage blends can contain much more water, posing fewer problems, and in Brazil, ethanol containing 7 percent water is used widely. The strategy behind this Brazilian watery ethanol fuel is to minimize production costs, because less effort/energy is needed for removing water from the ethanol.

Another issue related to cold climate markets is cold starting or, more precisely, engine start problems and excessive start-up emissions. These problems are related to the use of high-percentage-ethanol blends such as E85 and are even more pronounced using neat ethanol. Ethanol does not contain the light hydrocarbon compounds that make gasoline a relatively good fuel at cold ambient temperatures. The evaporative and flammability properties also contribute to this problem. Nevertheless, there are solutions to these problems. The evaporative properties are also problematic regarding safety and pollution of the environment. Ethanol is more flammable at conditions normally occurring in the fuel system of vehicles and can therefore pose a danger, but preventive measures can be taken. The evaporative properties and the chemical properties can in many cases cause high evaporative emissions from the fuel system, compared to gasoline application, and even higher emissions for diesel vehicles. However, this problem is worse for low-percentage-ethanol blends, and high-percentage-ethanol blends and neat ethanol seem to offer improvement compared to gasoline (but not diesel).

In terms of engine technical possibilities, almost all ethanol is used in gasoline vehicles, because gasoline blends well with ethanol, compared to diesel. In Brazil ethanol application is mandatory in gasoline vehicles, with the use of E25 and E100. In Sweden the use of E85 is fairly widespread and in several other countries the use of E5 and E10 is mandatory. Further increases in ethanol applications are somewhat limited by the unfortunate properties of ethanol use in regular gasoline vehicles. The general limit for these vehicles is set at about 5–10 percent ethanol in gasoline. In the United States and Sweden, the flex fuel vehicles (FFVs) currently on the road are compatible with blends ranging from 0 to 85 percent ethanol content. These vehicles have demonstrated the technical feasibility of running on ethanol fuels with a high renewable content, without higher cost. Certainly, there are fuel compatibility issues, especially for older vehicles. Corrosion and other types of damages can occur in the fuel system, ultimately resulting in engine failure. Ethanol fuels are therefore not recommended for vehicles made before 1986.

Many experimental studies have confirmed that ethanol in gasoline engines increases engine (energy) efficiency, torque, and power compared to baseline gasoline tests, mainly because of a superior fuel octane rating. On the other hand, ethanol contains much less energy per liter of fuel, very often resulting in lower mileage. However, the engine efficiency has in some cases been improved to a degree; that is, mileage was

improved compared to that for gasoline. There is little doubt that ethanol, especially high-percentage-ethanol fuels or neat ethanol, can improve the overall energy efficiency of the vehicle fleet.

In terms of current trends in engine development, ethanol appears to be a good candidate, complimenting these trends well, both for gasoline and diesel engines. Technologies such as downsizing, direct injection, increased pressure charging, and also advanced ignition strategies (homogeneous charge compression ignition [HCCI] and controlled auto-ignition [CAI]) are all compatible with ethanol.

Tailpipe emissions from vehicles running on ethanol fuels are generally cleaner than those from gasoline. However, evaporative emissions generally seem worse for ethanol fuels, namely, low-percentage blends. Investigations and models have shown that ethanol application does improve the overall health impact of the so-called air toxics, that is, carcinogenic compounds such as benzene and butadiene, even though aldehyde emissions increased with ethanol

Ethanol can be applied in diesel vehicles with some limitations. In general, ethanol does not mix well with diesel oil, but with the use of additives, ethanol can be used more or less immediately. With the use of biodiesel (fatty acid methyl esters [FAME]), ethanol has been shown to blend quite well with diesel, thus representing a fuel with a potential for a high degree of renewability, easily up to 30 percent. Neat ethanol has been used in diesel engines, improving the tailpipe emissions significantly. Even relatively small amounts of ethanol seem to improve the emissions of particulate matter. Questions remain, however, about the impact of ethanol on the size of the particulate and emission reduction systems. Many types of application techniques have been tried with relatively high degrees of success, making it possible to apply ethanol in diesel vehicles. Again, ethanol seems to suit engine development trends. Ethanol promotes a higher tolerance for engine gas recirculation ratios, which reduces nitrogen oxides (NO_x) emissions. The lower emissions of particulate matter make it possible to reduce NO_x further, and ethanol can also be used in future HCCI engines.

In discussions of the advantages and drawbacks of ethanol, the type of application is important. Generalization is not possible, because ethanol can be used in many forms. Furthermore, a wide range of ethanol/gasoline blends has not yet been investigated sufficiently. The most favorable type of application is determined by infrastructural factors, especially vehicle fleet configuration. From a technical point of view, optimal usage involves a high degree of water content in the ethanol, and this excludes low-percentage-ethanol fuels. The benefits seem strongly related to the amount of ethanol in a given blend, that is, the more the better. Both engine efficiencies and emissions improve with more ethanol in the fuel. Wet ethanol constitutes an even cleaner fuel in both the production and application phases. In summary, ethanol application has many possibilities, but with each type of application comes a set of challenges. Nevertheless, technical solutions for each challenge are available.

Introduction

This report examines the application of pure ethanol alone, even though for smaller concentrations of ethanol conversion to ethyl tertiary butyl ether (ETBE) can be advantageous due to better compatibility with gasoline.

The past few years have seen a veritable explosion in the advocacy and use of bioethanol as a fuel in the industrialized world. In a remarkable way, this cause — as it has almost become — seems to transcend normal political divisions, appealing to environmental concerns over global warming and promising oil-importing countries a greater independence from oil-exporting ones.

Since the *hydrogen society* has yet to materialize, bioethanol seems to be a possible way of dealing with the rise in both oil prices and carbon dioxide (CO₂) emissions. Bioethanol has been the subject of much discussion, research, and development in recent years and literature on it is abundant. Several other reports and reviews of ethanol studies viewed from various perspectives are incorporated where appropriate. This report is based on scientific articles and literature from the United Nations, the U.S. Department of Energy (DOE), and the International Energy Agency (IEA), as well as technical papers published by the Society of Automotive Engineers (SAE). This approach carries the risk of a main stream perspective; to counter that, the views of many debate forums and conference presentations have been considered as well. In general, discussions on the topic of ethanol seem subject to a great deal of half-truths, and we hope to present a report based on technically sound argumentation and differentiation on which proper decisions can be based.

Ethanol from biomass can provide substantial benefits to local, regional, and global societies, provided the methods by which ethanol is produced and used, are considered carefully. The IEA report “Biofuels for Transport” (2004) has summarized the potential benefits and costs of biofuels, ethanol included. See Table 1. The benefits and costs listed in Table 1 and others are discussed in more detail in the following sections.

Table 1: Potential Benefits and Costs of Biofuels (Source: IEA, 2004¹)

Potential benefits	Potential costs
<ul style="list-style-type: none">• Energy security• Balance of trade• Lower GHG emissions• Reduced air pollution emissions• Vehicle performance• Agricultural sector income, jobs and community development• Waste reduction	<ul style="list-style-type: none">• Higher fuel costs• Increases in some air emissions• Higher crop (and crop product) prices• Other environmental impacts, such as land use change and loss of habitat

Security of Fuel Supply

Fossil oil reserves are predicted to be limited, and they will be fading at some point in the future, if not already. Recent dramatic fluctuations in oil prices indicate a steadily increasing demand. The time horizon for oil depletion is very difficult to predict, but it is quite certain that the supply/demand situation will worsen as time passes. It is likely that the oil price will rise significantly in the coming decades, possibly with very dramatic impacts on all levels of society. At some point it will make much less economical sense to fuel cars with fuels produced from fossil oil, because it will be cheaper to produce fuel from other sources, such as coal, gas, biomass, wind or water energy, or even nuclear power. Ethanol offers an immediate possibility to reduce the dependency on fossil oil, and this is perhaps the most important reason for using ethanol in the transportation sector today. If ethanol is chosen as part of the solution to the problem of fading oil reserves, it is important to ensure a sustainable ethanol production that can satisfy the need continuously.

Global Warming

CO₂ is a so-called greenhouse gas (GHG); that is, the gas limits the earth's ability to radiate thermal energy from the sun back to the universe. It is more or less agreed, that we, as humans, now need to be very cautious of changes we make regarding the ecosystem and atmospheric system in this regard. In its "Climate Change 2007: Synthesis Report,"² the IPCC (Intergovernmental Panel on Climate Change) states that significant regional and global temperature increases have been observed. Furthermore the panel has found that it is "very likely" that these increases are caused by increased anthropogenic GHG emissions. It is therefore important to find ways to minimize the introduction of more GHG into the atmosphere, particularly those caused by combustion of fossil fuels. The transportation sector is a large GHG contributor, with about 13 percent (2004 numbers) of all anthropogenic GHG emissions.² The sector is highly dependent on fossil fuels, and not many realistic alternatives exist at the moment, as compared to the rest of the energy sector, which has numerous alternatives for producing electricity, for example, wind and water energy, nuclear power, solar energy, and more.

Rather than focusing entirely on one aspect of the GHG issue related to ethanol, for example, applications, it is more appropriate to view the situation as a whole and include all aspects of the fuel life cycle. Durante and Miltenberger (2004) claimed that little or no GHG benefit is obtained when bioethanol is used for transportation in its current form, in terms of production of the fuel.³ They recommend considering the perspectives of using biomass not for ethanol and transportation, but for other possible CO₂-mitigating applications as well, since biomass is a limited (yearly) resource. In Denmark, for example, the efficiency of burning waste and biomass is very high. The biomass is utilized significantly more efficiently this way, compared to ethanol usage as a biofuel, but realistically alternatives for the transportation sector are relatively few.

Bioethanol as Energy Carrier — General Issues

This section draws attention to some of the most important issues of large-scale ethanol production. An in-depth discussion of ethanol production is beyond the scope of this report, but review of the literature indicated several important issues that should be addressed here.

Distribution

In the distribution of ethanol, especially gasoline/ethanol blends, the problems are mainly those associated with using existing gasoline pipelines because of the corrosive and watery nature of ethanol. Furthermore, fuel stations present safety and storing issues. Nevertheless, years of practical experience have shown that ethanol can be distributed without major problems, using different procedures than those used for gasoline. Ethanol is usually distributed in a system specifically designed for it, so that blending issues, for example, water and dirt problems, are avoided, at least until the fuels are mixed at the service stations.

Production

Ethanol is the largest biofuel in the world and is expected to remain so. Figure 1 shows how ethanol accounts for a relatively small fraction of the total fuel demand globally. The main suppliers of ethanol are the United States and Brazil.

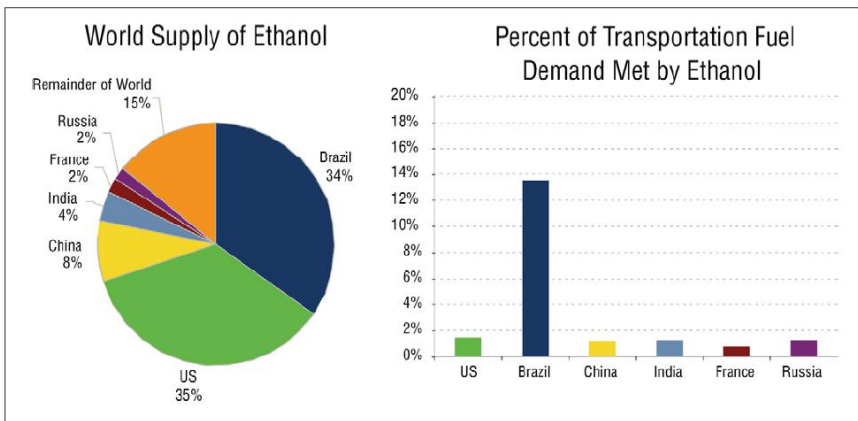


Figure 1: World Supply and Demand Met Figures (Source: Fichera and Kueter, 2006,⁵ Energy Information Administration, 2003, and Renewable Fuels Association, 2005)

The production of ethanol increased dramatically from 1975 to 2003, and it therefore seems important to discuss how ethanol is used most rationally. Figure 2 shows how ethanol production, mainly for fuel purposes, has risen in these years.

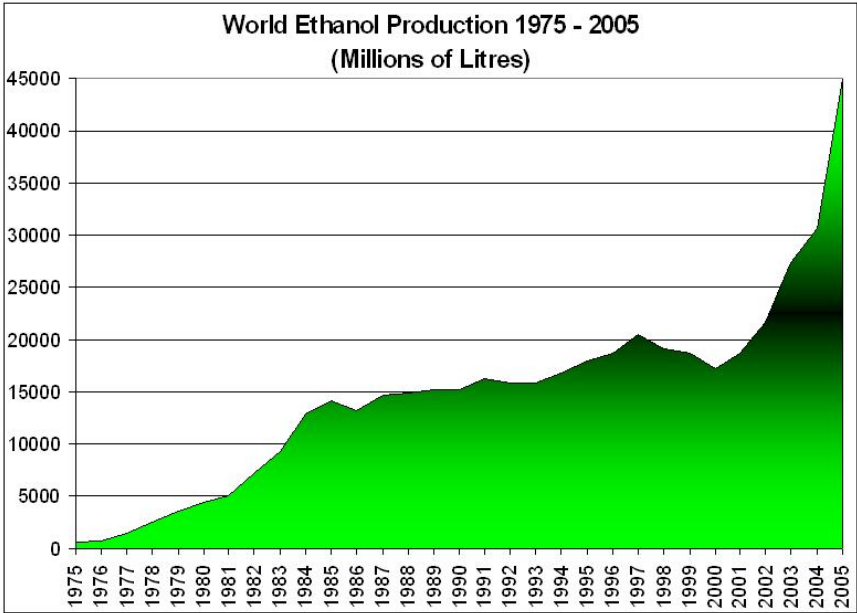


Figure 2: World Ethanol Production (Source: RISE⁶)

First, a continued massive increase in ethanol production and usage will have tremendous effects on the people, economy, and ecosystems of the planet. The IEA projects an average annual growth rate of 6.3 percent for consumption of liquid biofuels from 2005 to 2030, most of that being ethanol.¹⁵ Second, an increasing dependency on the fuel will demand reliable production. Therefore, growing of the feedstock crops used for ethanol production must be done in a sustainable way. Sustainability, according to findings reported at the Rio Conference 1992, includes economical, social, and ecological concerns, and it seems necessary to consider all three concerns when deciding whether to use ethanol as a motor fuel extensively. According to the Brundtland report definition of sustainability (1987), sustainable ethanol must provide a solution that "satisfies the needs of today without compromising the needs of future generations."⁸

Economics strongly influences the technical solutions a community or region chooses and thus influences the environment in different ways. At present, it makes more economical sense to keep producing ethanol using first-generation technology, even though the actual GHG gas mitigation and emission benefits in some cases seem rather limited.⁹ Socially there are heated discussions, at many levels around the world, about

the *food or fuel* issue, but other issues such as regional agricultural development and international trade relations are also important. In terms of ecosystems, the discussions concern topics such as the need to preserve valuable ecosystems, for example, the Amazon rainforests of Brazil, and to ensure the quality of local soil and water.

Feedstock

Bioethanol is usually made by fermenting sugar contained in various kinds of biomass:

- Sugar-rich biomass, mainly sugar beet and sugarcane;
- Starch-rich biomass, grain (e.g., barley, wheat, corn, rice), potatoes, sorghum, cassava; and
- Cellulose-rich biomass, straw, wood (residues), corn cobs and stalks, grass, paper and more.

About half the world's bioethanol production uses sugar crops as feedstock, mostly sugarcane but also beets. The majority of the remaining ethanol is produced from starch crops, mainly grains such as corn and wheat.¹⁵ Practically no ethanol is produced from cellulose-rich biomass commercially, but commercial plants are planned.¹⁰

Not surprisingly, the most efficient way to produce ethanol today (in terms of cost and CO₂ mitigation) is via Brazilian sugarcane. The feedstock, which is the major contributor to the cost, grows very fast there, and production methods have been refined. Furthermore, it is relatively easy to make ethanol from sugar crops, since the fermentable sugars are more readily accessible than other feedstocks.¹⁵

Cellulosic ethanol production is now at a stage where trials of different feedstocks are being conducted. The aim is to find crops that increase the biomass output as well as reduce the negative environmental impacts. Also of interest are the types of land (quality) the feedstock can grow on because of land use issues. Agricultural fertilizers have significant environmental impacts, such as marine eutrophication, global warming, resource depletion, groundwater contamination, and stratospheric ozone destruction.¹¹ Thus since the purpose of using ethanol is partly to mitigate global warming, the use of synthetic fertilizers in the production of feedstock for ethanol should be reduced.

Some crops can naturally fixate nitrogen from the air, for example, peas, and thus reduce the need for fertilizers. Growing these crops alongside other crops is called intercropping, which has been found to reduce the need for both fertilizers and pesticides in the case of a wheat and peas combination.⁷ Other crops do not need as much fertilizer and will still provide very good yields. Switchgrass (or prairie grass) is one of the more promising examples of feedstock crops for second-generation ethanol production because of its high yield, low fertilizer requirements, soil-restoring properties, good disease and pest resistance, and low cost of production.^{12,13} A joint

USDA-ARS (U.S. Department of Agriculture, Agricultural Research Service) and Institute of Agriculture and Natural Resources (U.S.) study¹² has found, that cellulosic ethanol production from switchgrass could reduce GHG emissions up to 94 percent compared to gasoline. The switchgrass is intended for growing on marginal lands, and the researchers estimated an ethanol yield of 85 percent of what is currently achieved on class 1 farm land with corn ethanol in the United States. The study was based on a 20-acre trial. Switchgrass is not a solution for first-generation ethanol production, however, since it is almost purely cellulosic.

The development of feedstock for ethanol is at a stage where new methods are on the way, while the old practices still exist alongside. In order for the new methods to gain a foothold, a prerequisite is maturation of second-generation ethanol production processes and, in particular, methods for cost-effective breakdown of the strong ligno-cellulosic molecules of biomass.

Production Methods

As discussed later, the production method is the key factor determining the degree of sustainability of ethanol. There are great differences in the life cycle effects of ethanol produced by different feedstocks and by different methods.

First Generation Technology

The traditional production of ethanol follows these general steps:

1. Milling of biomass to break it down to finer parts, a substance called the *meal*; (This stage can be done either wet or dry; dry processing in some cases can save nearly 50 percent of the total energy used to produce the ethanol.¹⁵)
2. Cooking and liquefaction, in which the *meal* is mixed with water and enzymes and cooked into a *mash*;
3. Saccharification, - a secondary enzyme is used to produce sugars that can be fermented.;
4. Fermentation of sugars with yeast to form CO₂ and watery ethanol (about 10 percent pure);
5. Distillation of the wet ethanol to concentrate the ethanol up to 95 percent;
6. Dehydration of the remaining 5 percent water to make fuel-grade ethanol; and
7. Denaturing, usually with gasoline to make the ethanol undrinkable.

The main inputs are feedstock, enzymes, yeast, energy, water, and denaturant. The main outputs are ethanol, CO₂ and co-products, which are used as animal feed called

distillers' grain (DDGS). The CO₂ is often captured and purified to be sold to other industries.¹⁴

In some places, in Brazil, for example, the energy input for ethanol production comes from the crop used as feedstock. To provide heat for the boiling and distillation processes, the leftover biomass (bagasse) from the sugarcane is combusted. In many other cases the energy comes from fossil sources, typically natural gas or coal. Thus, the impact on the effective CO₂ mitigation benefit of the fuel depends on whether the first or second option is used.

Low temperatures generally characterize the majority of the energy used in ethanol production. The cooking process normally happens at about 80°C and distillation at about 100°C.¹⁴ From an energy-efficient viewpoint, it therefore seems appropriate to use waste heat from other processes such as electricity generation instead of high worthy/quality energy such as natural gas, coal, or even biomass.

Second Generation Technology

Second-generation ethanol, also called cellulosic ethanol, is produced in almost the same way as first-generation ethanol. The pre-treatment needed to access the fermentable sugars in the ligno-cellulosic plant materials, however, is much more difficult and may, depending on the feedstock, require acid, pressurized steam, special enzymes, or a combination. These methods can result in undesirable toxins that inhibit the following fermentation process. Once decomposed, the biomass requires a fermentation process in which both hemicellulose (C5) and cellulose (C6) sugars must be processed.

A state-of-the-art report¹⁵ has identified important research tasks for second-generation ethanol production:

- Pre-treatment and decomposition processes that create a minimum of toxic fermentation inhibitors and use fewer chemicals;
- Reduction of enzyme costs; (The price of enzymes has gone down significantly recently, but this is still a problematic issue for full-scale commercialization.)
- Techniques for processing at high solid levels (i.e., minimizing water and thus energy use);
- Development of microorganisms that can tolerate inhibitors and ethanol and can process both C5 and C6 sugars;
- Higher degree of process integration to reduce water consumption; and
- Recovery of lignin waste products for use in power production, for example.

Almost all ethanol is currently produced by the first-generation technology. Second-generation technology is at a stage where a great deal of research is being conducted. Pilot and demonstration plants are running, but commercial plants are not in operation, although several are in the planning phase. The status of commercialization of cellulosic ethanol (by 2007) is as follows:

- 15–20 pilot plants worldwide, mostly small-batch operations;
- two demonstration plants open (Ottawa and Japan) with 2–3 others to open later in 2007;
- 15–20 commercial plants being built worldwide; and
- Large range of feedstocks being investigated (Reed¹⁰).

The major advantage of cellulosic ethanol is the low cost of feedstock, which as mentioned can be agricultural or forestry residues or more dedicated energy crops such as willow and switchgrass. Another advantage is that second-generation production does not conflict, in the same way as first-generation ethanol, with production of human food. Unfortunately, the economics of cellulosic ethanol are currently at a stage where the low cost of feedstock does not outweigh the high cost of production.

The advantages of second-generation technology over first-generation technology are mainly as follows:

- Much higher utilization of the individual plant, providing higher production efficiency and yield per hectare;
- Fewer or no conflicts between food and fuel interests because other types of crops or even agricultural waste can be used; (There can be a conflict due to the use of arable land.)
- Cheaper feedstock;
- Possibly more sustainable feedstock production; and
- Very high CO₂ mitigation, up to 94 percent.

The IEA projects that widespread usage of second-generation technology will be a reality after the year 2020.¹⁶ Integrated Approaches

Ultimately production of ethanol could be combined the production of chemicals, power, heat, food, animal food, and fuel.¹⁷ Ethanol production could also use various resources such as household waste and agricultural waste. Gasification and gas-to-liquid fuel processes could be used in the production of ethanol and other fuels.¹⁸ Another option would be to integrate the production of biodiesel and ethanol to minimize the transportation of biomass. As discussed later, biodiesel has shown promising properties for blends of ethanol and diesel. If the biodiesel is made from, for example, palm oil, only the palm fruit is used. Integrated biofuel production could include cellulosic ethanol production from the biomass left over from the palm tree, thus utilizing more of

the palm, or electric power could be co-produced by using mostly waste heat for fuel production.

On a global basis, electricity production from thermal power plants generally loses 55–65 percent of the fuel energy as relatively low-temperature waste heat, although there are cases in which the heat is recovered and used for district heating or other purposes. Thus a huge potential exists and incentives exist for process integration of ethanol and power production, in order to reduce CO₂ emissions simply because the low temperature waste heat principally does not cause extra CO₂ emissions.

The few second-generation ethanol pilot plants worldwide provide examples of interesting concepts that might also inspire other industries. Among these are two Danish concepts; Maxifuel and IBUS (Integrated Biomass Utilization System, the Venzin vision). Maxifuel integrates the production of ethanol, biogas, hydrogen, and solid fuel pellets. The concept aims to reuse or recirculate process streams in order to reduce the environmental impact. The biogas production is added as a way of cleaning and reusing the process water, but is also beneficial to the overall energy balance and economy.¹⁹ The philosophy is that the waste or coproduct of one process must be used as input for the next so that the waste streams are minimized.

The IBUS concept integrates a biomass/coal-fired power plant (CHP) with first- and second-generation ethanol production. The products are ethanol, solid biofuel, animal feed (DDGS), and fertilizer. The ethanol process receives low-cost steam and efficiently produced power from the power plant, while the power plant receives high-quality solid biomass fuel, a leftover from the ethanol process. Integrating these two processes achieves a reduction in investments, because no power/steam unit is needed for the ethanol plant.²⁰ Both the IBUS and Maxifuel concepts claim to have solved all major bottlenecks and barriers for cellulosic ethanol production; the only challenge remaining is the upscaling of the process into a cost-effective industrial production.

In a future scenario, a carbon capture and storage (CCS) system might remove CO₂ emissions completely from the integrated processes, that is, the power plant with the ethanol plant, lowering the GHG emissions so much that CO₂ is in fact removed from the atmosphere, over the life cycle of ethanol.

Life Cycle Assessment

To ensure the long-term benefits of ethanol, one of the tools for evaluating environmental effects is the life cycle assessment (LCA), in which the life cycle of the fuel is divided into phases — production, usage, and disposal. As shown, the main benefit of ethanol is its production.

Net Energy Value and Greenhouse Gasses

One of the main reasons for using biofuels, including ethanol, is to reduce GHG emissions. GHGs are gasses that impair the earth's ability to radiate thermal energy to space. The amount of GHGs in the atmosphere is depends on the circulation of carbon; that is, the amount of carbon is relatively constant. Important GHGs are CO₂, methane (CH₄), nitrous oxide (N₂O), and water vapor. In order to assess GHG potentials, the term of measure CO₂ equivalent (CO₂eq) is used to express the amount of global warming potential as an equal amount of CO₂.²¹ The CO₂eq's for methane and nitrous oxide are 23 and 296, respectively, meaning methane has a 23 times stronger GHG potential than CO₂.³ The term CO₂-neutral is sometimes used to describe ethanol, but the term is misleading, because production of ethanol at present cannot be done without introducing fossil-based CO₂ or other GHGs into the atmosphere.

Currently there is a great deal of debate on whether usage of ethanol in the transportation sector really reduces GHG emissions. The predominant tool used to assess this is LCA or, in fuel terms, a well-to-wheels (WTW) assessment. In this case WTW assessments most often aim at estimating the net output of GHGs and usage of fossil fuels by accounting for various inputs and outputs associated with the entire life cycle of a given fuel. International standards (ISO 14000 series) dictate how to perform this kind of assessment, but critics²² claim that using the standards can lead to perspectives that are too narrow.

An often used, but also criticized, term for evaluating ethanol is the net energy value (NEV). NEV is defined as the difference in energy content between the fuel product (output) and the energy used to produce it (input).²³ A more relevant way of evaluating ethanol is to compare only the non-renewable, or fossil fuel, input used with output energy. (The energy input from the sun should in any case not be included.)

LCA Reviews

This section discusses some LCA studies and reviews of LCA studies on ethanol. Table 2 shows the results from a number of major LCA studies.

There seems to be an ongoing debate about whether production of ethanol has a positive NEV; that is, less energy is used to produce the ethanol than the actual energy content in the ethanol. However, Table 2 clearly shows that most of the major studies find a positive NEV. Dr. Wang and Eric Larsson reviewed a variety of LCA studies and established that with current production and vehicle technologies, ethanol offers the potential to achieve at least minor CO₂ (or CO₂eq) emission reduction and to reduce fossil energy usage compared to gasoline. These investigations should be seen as worst-case scenario analyses, because they consider first-generation technologies using traditional crop growing and as such are not representative of cutting-edge and future

Table 2: Summary of Major LCA Studies (Source: Durante and Miltenberger³)

Ethanol's Net Energy Value: A Summary of Major Studies	
Authors and Date	NEV (Btu)
Shapouri, et. al (1995) - USDA	+20,436 (HHV)
Lorenz and Morris (1995) - Institute for Local Self-Reliance	+30,589 (HHV)
Agri. and Agri-Food, CAN (1999)	+29,826 (LHV)
Wang, et. al. (1999) – Argonne National Laboratory	+22,500 (LHV)
Pimentel (2001) - Cornell University	-33,562 (LHV)
Shapouri, et. al, Update (2002) – USDA	+21,105 (HHV)
Kim and Dale (2002) - Michigan State University	+23,866 to +35,463 (LHV)
Shapouri, et. al, (2004) – USDA	+30,258 (LHV)

scenarios. Studies on second-generation production shows significant improvements in both GHG emissions and fossil fuel usage.

Examples of things that would potentially improve the life cycle GHG and fossil energy economy of ethanol:

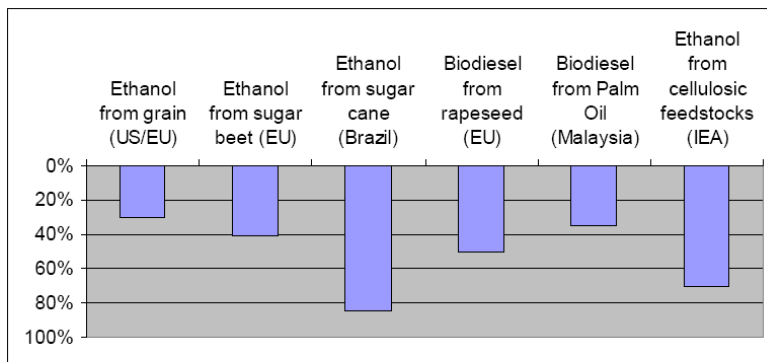
- Implementation of second-generation technologies;
- Process integration of power and ethanol production;
- Process heat used in ethanol production coming from biomass power coproduction; and
- General production efficiency improvements.

LCA studies⁹ show that GHG emission reductions for different gasoline–ethanol blends made by corn, on first-generation technologies, are 18–26 percent and 21–29 percent for E10 and E85 gasoline, respectively. For cellulosic-based ethanol, it is estimated that GHG emissions will be reduced by about 85 percent for E10 and E85. These numbers are based on displacement of gasoline, on an energy equivalent basis using the GREETⁱ model. Similar results have been found by Larson,²² who has reviewed LCA studies and has concluded that ethanol made from corn reduces GHG emissions by 10–50 percent, while ethanol from grass (cellulose) reduces GHG emissions by 40–100 percent.

There are significant differences in GHG reduction with different feedstocks; corn, sugarcane or sugar beets. An OECD study,²⁴ based on figures from IEA and EMPA (Swiss Federal Laboratories for Materials Testing and Research), found that the CO₂-equivalent

ⁱ The Greenhouse gases, Regulated Emissions and Energy use in Transportation model (GREET). The model is an industry standard model used to evaluate various fuel and vehicle combinations methodically. The model was developed by Dr. Michael Wang, at the Argonne National Laboratory Center for Transportation Research, with support from the U.S. DOE Office of Energy Efficiency and Renewable Energy (EERE).

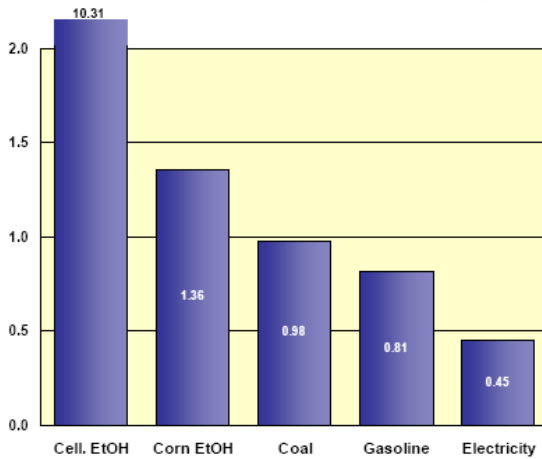
well-to-wheels GHG emission reduction per driven kilometer varies from about 30 percent for grain ethanol in the European Union (EU) and United States to 40 percent for sugar beet in the EU and 93 percent for sugar cane in Brazil. respectively. See Figure 3. The IEA biofuels report (2004) provides figures that would rank the GHG emission reductions potential similarly.



Source: IEA, 2005 and EMPA (biodiesel from Palm oil). Note: Reduction in well-to-wheels CO₂-equivalent GHG emissions per kilometre.

Figure 3: GHG WTW CO₂ Equivalent Reductions (Source: Doornbosch and Steenblik²⁴)

Wang et al. at Argonne National Laboratory have demonstrated that looking at the energy balance of a fuel (or energy product) isolated is not entirely meaningful. The second law of thermodynamics states that energy conversion always causes a loss, which in practice is seen in, for example, coal-fired power plants. Coal is converted into electricity, and about half of the energy in the coal is lost as heat (if not used as district heating). Wang et al. instead focus on the fossil energy input. Figure 4 shows the so-called Fossil Energy Ratio, the ratio between the energy in an energy end product and the fossil energy input. First-generation ethanol performs quite well compared to existing energy products, and second-generation ethanol has a great potential in this regard.



**Figure 4: Energy Output Compared to Fossil Input
(Source: Wang²⁵)**

Discussion on LCA Studies and Results

LCA and WTW studies present results from modeling tools, based on a number of assumptions and methods that can vary and influence the results. Among the most important WTW variables in relation to ethanol are the following:

1. Feedstock, for example, corn, wheat, sugarcanes, switchgrass, and more.
2. Allocation of coproducts, that is, how they are accounted for. Ethanol production leads to by-products which can be accounted for differently, such as no allocation, allocation by energy content in certain coproducts, or allocation by share of process energy consumed to make coproducts. The most important coproduct in the U.S. corn-based ethanol production is called DDGS, a protein-rich substance used for animal feed. About one-third of the corn kernel ends up as DDGS, so this is a significant post in the LCA.²⁴
3. N₂O, which is discussed later.
4. Soil carbon sequestration, which concerns the long-term storage of carbon in soils. If, for example, previously unfarmed land is brought into feedstock production, the end result could easily be decreased carbon storage in the soil. The net life cycle result might thus be increased carbon (CO₂) emissions to the atmosphere, even though the biofuel is produced efficiently. Not all LCA studies include this issue.^{22,26}

Because of these variables, it is not surprising that WTW assessments made around the globe have different results.

Related to crop production is the emission of N_2O , a powerful GHG, about 300 times stronger than CO_2 . N_2O emission from farming depends on a variety of conditions, such as soil, climate, and crop and farming practice. Uncertainties in predicting N_2O emission are relatively large, possibly so large that they can affect the outcome of a LCA decisively, if included in the LCA inventory.²⁷ Wang²⁸ states that N_2O originating from nitrogen fertilizer can account for up to 25 percent of the total GHG emissions from U.S. corn ethanol.

A recent study,²⁹ led by the Nobel-prize-winning chemist Paul Crutzen, claims that commonly used biofuel crops may in fact lead to increased GHG emissions due to N_2O . Corn-based ethanol was found to cause 0.9–1.5 times GHG emissions, compared to what is saved in CO_2 emissions. Sugarcane ethanol was found to be a viable option with a factor of 0.5-0.9. The study has been criticized for its basic assumptions and numbers for crop-to-ethanol conversion, but a report from OECD²⁴ supports Crutzen's skepticism.

Many researchers have pointed out that more comprehensive and holistic approaches are needed, in addition to the standard LCA methods. Replacing fossil fuel with biofuel has, as discussed here, many consequences on different local and global-scale levels.

Accordingly, ethanol has great potential for mitigating GNGs in the near future, but pitfalls do exist. Recommending ethanol on a larger scale can only be done if exact knowledge of the effects are well-documented and effective reductions of GHG outputs and fossil fuel inputs are ensured in the production.

Hydrous Ethanol

Ethanol that contains water can be used as a fuel. The purpose is mainly to minimize costs of the fuel. The application of hydrous ethanol is not without challenges, but applications have been shown to overcome all obstacles and proven by operation on a daily basis in Brazil and Sweden. From an environmental perspective, maintaining water in ethanol minimizes the energy consumption in the production phase. Figure 5 shows the net energy balance of ethanol from US corn.

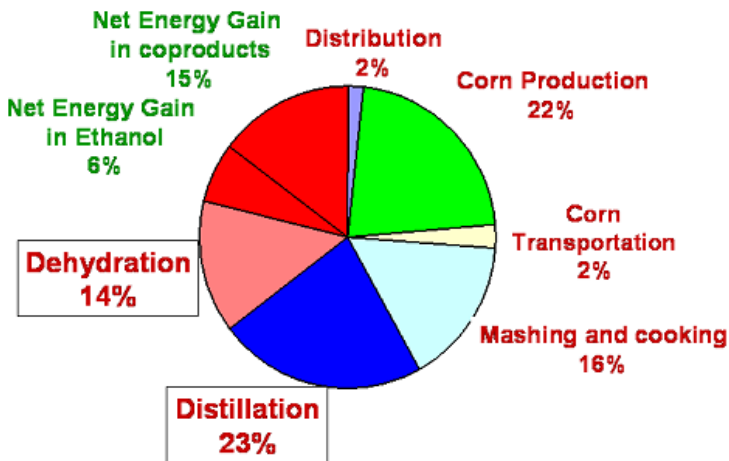


Figure 5: Net Energy Balance of U.S. Ethanol Produced from Corn
 (Source: U.S. DOE³⁰)

The circle in Figure 5 represents all the energy of ethanol and coproducts. U.S. corn-based anhydrous ethanol has a net energy gain of only 21 percent including the coproducts of production, while hydrous ethanol, with about a 5 percent water content, would gain another 14 percent.

An effective way of using wet ethanol in internal combustion engines is homogenous charge compression ignition (HCCI), and a few studies show that it might be possible to use ethanol containing up to 70 percent water in ethanol.^{31,32} According to Flowers and Aceves,³² this would require a rather special application including a heat exchanger to vaporize the very wet ethanol. This concept still needs to be proven but could well be realized in transportation applications, for example, in a hybrid vehicle with batteries, electric motor, and a combustion engine. Distillation energy, when ethanol with 65 percent water is used, would be reduced from 23 percent to only 3 percent, providing a net energy gain of 55 percent instead of 21 percent% with anhydrous ethanol.³² Other investigations of ethanol production may have different results, but energy savings will in any case be significant using wet ethanol.

Combustion engines, in general, suffer from a relatively low efficiency, that is, utilization of the fuel energy. Even though the combustion engine has undergone many years of optimization and development, the compression Ignition (CI), that is, diesel, engine, which represents the most efficient application, still utilizes only about 25–35 percent of the fuel energy. The rest of the fuel energy is wasted, a large part being heat emitted in the exhaust gas and cooling water. Waste heat from the engine is used to compensate for the high water content of the fuel instead of being wasted. In that way, waste energy from the vehicle replaces energy of relatively high quality or usefulness, be that coal, natural gas, or biomass. See Figure 6.

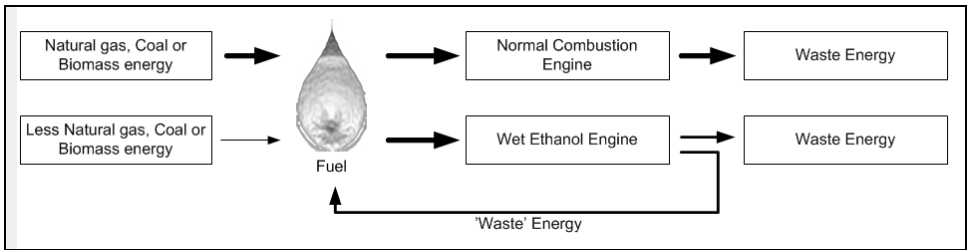


Figure 6: Schematic Overview of Energy Flow Using the ‘Wet Ethanol Engine’ Concept

While relatively radical new-thinking is required to implement this kind of solution on a large scale, the potential for energy savings (and CO₂ mitigation) on a global, regional, or national scale will most probably make it worth the effort. Less radical solutions are also possible and perhaps more realistic and would still provide significant benefits. An example is Brazil, where hydrous ethanol (E93, ethanol with a water content of 7 percent) is used on a large scale with huge energy savings (not to mention economical savings). The technical aspects of using wet ethanol are discussed later in this report, but the utilization of wet ethanol generally requires dedicated technical solutions, that is, alternative to the current vehicle market.

Sustainability

Since one of the main purposes of bioethanol is to mitigate environmental impacts, especially GHGs, it is important to ensure certainty about the actual effects of ethanol production. Furthermore, as ethanol usage increases on a global level, there will be increasing pressure on ecosystems and thus a need for principles of sustainable agricultural production. There will be great dependency on large amounts of biomass feedstock crops for many years to come. Thus it is essential to ensure safe, long-term social, environmental, and economical impacts of a relatively new industrial/agricultural sector with significant growth. One report states, "...there is no point in replacing one unsustainable system with another.." ³³

It is logical to expect a higher degree of environmental impacts on ecosystems, soil, and water due to biofuels, compared to fossil fuels, since the latter do not need large cultivated land areas. Therefore the two fuels cannot be directly compared in this regard; any comparison will have to be a (subjective) weighing of different environmental effects. EMPA ³⁴ has compiled an index accounting environmental impacts as damages to human health, ecosystems, and depletion of natural resources, the so-called UBP indicator. See Figure 7.

Figure 7 shows that the impact from cultivation activities are significant in the life cycle of ethanol (and biodiesel) made from different crops. The figure also shows that it would be a mistake to consider only vehicle operation emissions.

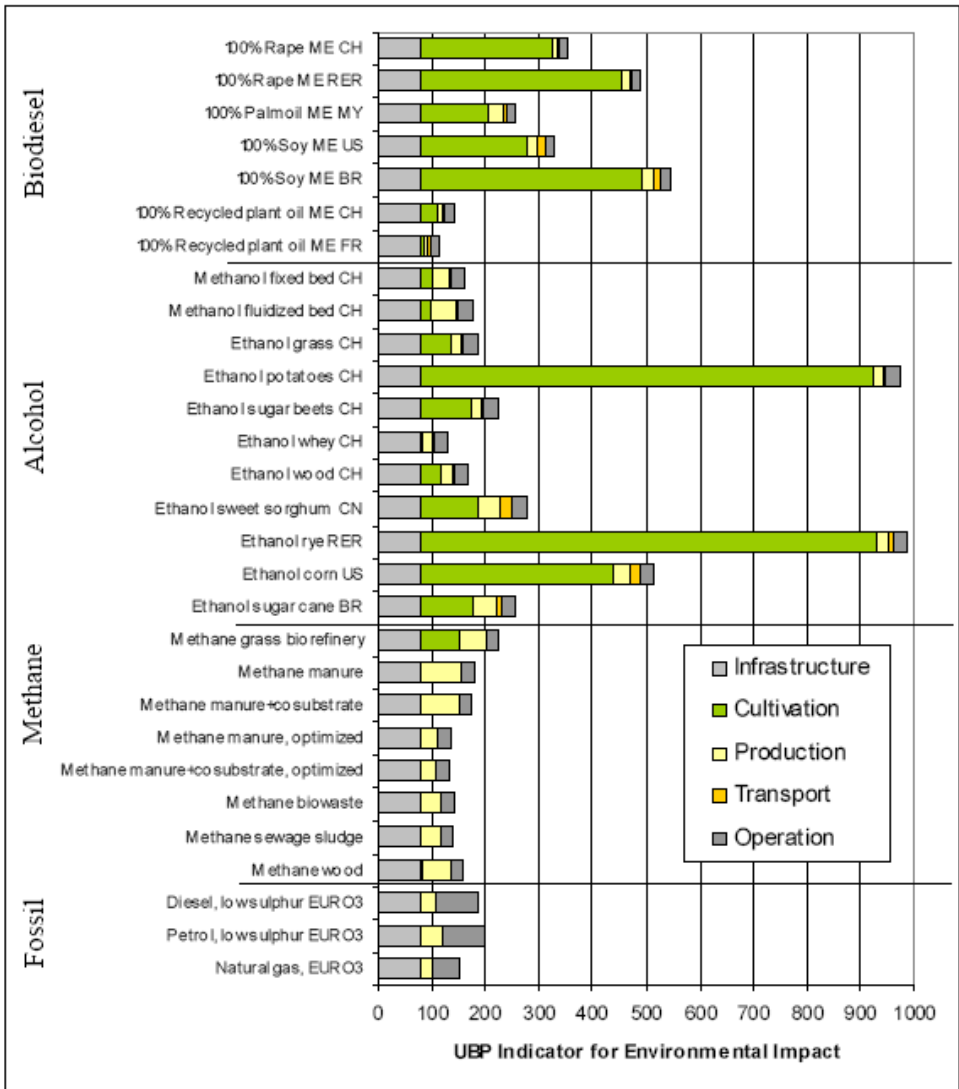


Figure 7: Environmental Impact for Ethanol and Other Fuel Options (Source: EMPA³⁴).
 Note: CH = China, RER = European Union, MY = Malaysia, US = United States,
 BR = Brazil, FR = France, and CN = Canada.

The Roundtable on Sustainable Biofuels, consisting of nongovernmental organizations, companies, governments, intergovernmental organizations, experts, and others, is developing four criteria to form a tool to ensure a degree of sustainability in the production and use of biofuels. The criteria concern life cycle GHG efficiency, environmental impacts (namely, biodiversity, soil issues, and water resources), social impacts (mainly food supply security), and implementation. Currently many activities at the highest levels of influence, for example, national governments, the European Commission, and the IEA, are trying to find ways to ensure sustainability. One example is work commissioned by the Dutch government, which suggests that criteria of sustainability should be satisfied in order to justify subsidies.²⁴ Another suggested approach is to learn from experience with certification of forest products.

The European Biomass Association (AEBIOM)³⁴ supports the idea of sustainability but points out the importance of making all agricultural production sustainable, not only biofuels. Because there already are policies to ensure some degree of sustainability in Europe, including biofuel crop growing, AEBIOM states that certification should target imported biofuels.

Review of the literature on sustainability of ethanol production indicated the following general concerns (not in prioritized order):

- GHG emissions, over the entire life cycle of ethanol, must be significantly lower than those for fossil fuels.
- Nutrients from the biomass must be returned to the soil.
- There should be no harm to valuable ecosystems, and biodiversity must (at least) be maintained.
- Carbon stored in the soil and above ground should be strongly considered in starting new biomass production.
- Soil erosion and degradation, as well as water resources and quality, are major concerns.
- Food security and prices, locally and globally, must be considered.
- Because biofuels are an international commodity, international sustainability certification and labeling standards should be developed to ensure a minimum level of sustainability.

Land Use Issues

An important concern for ethanol production is that the planet has only a limited potential for producing biomass. The main interests for arable land are food, animal feed, materials, energy, nature conservation, and biodiversity. That being said, production in one sector does not always conflict with that in another. For ethanol, examples have been outlined; because animal feed usually is a coproduct of ethanol production, it can in fact produce opportunities for at least the livestock industry.³³ Other examples are coproduction of food and fuel with the use of second-generation technologies and improvement of biodiversity with inter-cropping.

Global Biofuel Potential

It is very difficult to accurately assess the global energy potential for fuel biomass production. First, what is technically possible? Second, what is the reality and what are the boundary conditions for fuel production? There are many factors to consider, perhaps most importantly, biomass need for food and other sectors, trade barriers, agricultural policies, economy, agricultural and ethanol production efficiency, new technology advances, and new crop types.

Currently, the annual energy use for transportation is roughly 100 EJ (Exa Joule), a number that will increase by more than 50 percent by 2030, if the current annual growth rate remains unchanged.³⁵ With the recent increases in crude oil prices and the likely decrease in oil production,³⁶ the growth might slow down. Rapid growth in world consumption of transport fuels will require more rapid growth in the production of biofuels in order for the net CO₂ emissions from the transport sector to decrease or just stabilize. In recent years, this has indeed been the case: biofuel production doubled between 2000 and 2007, while crude oil production increased by 7.7 percent.¹⁶ A quadrupling of worldwide biofuel production by 2020 (a plausible scenario) would correspond to the displacement of roughly 7 percent of fossil fuels for road transportation worldwide. Beyond 2020, the potential of second-generation ethanol opens up and with it a greater usage of the land available, because of the use of waste products such as agricultural and forest residues and animal and other organic waste. Several studies have attempted to establish plausible values for the fossil transport fuel displacement in the distant future (2050).

Doornbosch,²⁴ using conservative figures, estimated the potential for displacement of fossil transport fuels at about 23 percent in 2050. Hoogwijk³⁷ charted four future scenarios with different estimates of the energy production potential from biomass compared to fossil fuels. The scenarios range from values of 20 percent to approximately 50 percent fossil transport fuel displacement. Also, the IEA has made a forecast¹⁶ for 2050 that indicates that a fossil transportation fuel displacement of 100 percent is feasible, if the entire global energy biomass production is converted into

liquid fuel, with none reserved for electricity generation or heating. Such an exclusive use for transport fuels might be an unrealistic assumption, however.

In contrast to the projection for 2020, these estimates assume improvements in the technology for producing and converting biofuels, such as those heralded by the advent of second-generation biofuels. Also, they offer opportunities, understood as goals that can be reached only by being actively pursued. Unless governments, organizations, and research institutions actively strive to support and develop biofuels, the future displacement of fossil transportation fuels will certainly be much lower.

Note that the above scenarios consider only land-based biomass. With ocean as 70 percent of the Earth's surface, the potential for sea-based biomass is clearly enormous. Some researchers and companies are currently working in this field, but the technologies and infrastructure needed for any large-scale marine biomass production are still in the development stage.

Although these scenarios for the future are fraught with uncertainties and contingencies, they all show that not only do ethanol and other biofuels have a large potential, but also they are by no means an easy and effective solution for a sustainable transportation sector. Fossil fuels will provide a major part of the global transportation energy for some years to come, indicating a period in which different fuels and engine technologies, fossil-based and renewable, will exist side by side.

Biomass for Transport or Power

An important aspect of the ethanol discussion is biomass. A recent study⁴ at The Technical University of Denmark assessed a number of environmental impacts, such as GHG emissions, waste generation, ozone formation, and acidification, related to ethanol production. IBUS is supposedly state-of-the-art second-generation technology, integrated with a coal-fired combined heat and power plant (CHP) in Denmark. The central question posed in the study was whether land as a limited resource should be used for transportation energy purposes in order to reduce GHG emissions and replace fossil fuel usage. The conclusion was that even using the currently best available ethanol production technology, there is (in Denmark) a better use for the limited biomass than ethanol, that is, using it in CHP production. Based on a life cycle analysis of the scenario, with production of ethanol nutrients are to some degree kept in the agricultural system due to the main coproduct, animal feed. Reversely burning biomass in the power plant makes it harder to recycle nutrients to keep the soil sustainable for growing future crops and minimizing fertilizer usage.

The report compares CHP with ethanol production, and this is substance for a relevant debate. As for land use, it is relevant that the global usage of limited biomass is optimal and irrelevant how GHG emissions are reduced. Regarding fossil fuel scarcity, the report concludes, higher displacement is achieved with CHP. It is questionable, however, to

compare fossil fuel displacement of coal in CHP production with fossil oil displacement in transportation, since coal reserves are not running scarce at this time, compared to oil, which seems much closer to scarcity. It could also be argued that there are not that many viable and GHG-mitigating alternatives for transportation fuels, while there are a number of viable options for GHG-mitigating electricity production, such as wind-, hydro, solar, and nuclear power, not to mention CO₂ storage at coal-fired power plants. As the optimal utilization of biomass, the report suggests electric cars in combination with CHP as a solution.

CHP is not an option in many countries since there is simply no need or economical viability for district heating, for example, in tropical countries. Thus CHP is by far the most ideal usage of biomass and should be pursued where possible, but in other cases it remains an unrealistic application. It is furthermore not entirely *fair* to compare energy efficiencies (and thus GHG emissions) in stationary units, with those in moving applications. Even with highly efficient electric motors, the moving application always *loses* in comparison to the power plant (wind turbine or other electricity-producing unit) simply because the electric motor represents an extra link in a chain of processes with less than 100 percent energy conversion efficiency.

In terms of the quality (or usefulness) of the energy, low-temperature heat energy is categorized as lower quality than liquid fuels; thus the comparison again is not *fair*. Integration of productions, technologies, and processes appears to be a better overall solution. This LCA is one example that does not consider all aspects of the energy situation, as the report itself recognizes. This is of course understandable but not entirely satisfactory, and as suggested by Larson and others, studies including all aspects of the biofuel and energy situation seem relevant and necessary at this point.

Biomass for Food or Biofuels

Because this topic is very fundamental, complex, and controversial, the following discussion provides only selected perspectives and arguments, not any conclusions. There are many stakeholders and competing interests, and argumentation seems naturally to depend on these interests.

The United Nations Foundation report, *Biofuels FAQ*,³⁸ states that according to the United Nations Food and Agriculture Organization (FAO), increased food production will be able to keep up with a growing population. Furthermore the report states that the malnutrition on global scale is not caused by lack of food. Rather, the world could easily produce more food, if there was a demand, that is, if the poor could pay for the food and create the demand. Because most of the poorest people live off the land in rural areas, they could in fact be benefiting from biofuel crop production, and many poor countries (mainly in Africa) are fairly well suited (climatically) to biofuel crop production. Biofuels seem (according to the *Biofuels FAQ* report) to offer potential if poor countries could produce and export biofuels. Thus it might be political, infrastructural, and

perhaps international restrictions and trade relations that would keep the poorest people starving, not biofuels. That being said, rising food crop prices will unavoidably have a negative impact on some of the world's poorer people's ability to afford food.

An AEBIOM report³⁴ acknowledges that there is a linkage between food prices and biofuel production, but also states that the food-versus-fuel dilemma has often been overestimated. The organization claims, first, that there is land enough to grow both food and fuel crops and, second, that there is an overproduction of food in the EU. AEBIOM furthermore points out that surplus food production is *dumped* in developing countries and results in local markets not being able to compete. Furthermore, AEBIOM finds that crop prices have little influence on the final product price. Wheat, for example, represents less than 10 percent of the bread price. AEBIOM therefore recommends that the EU should not limit biofuels due to land use concerns or food prices, while recognizing that there might be short-term local impacts for countries depending on food imports. However, AEBIOM is an organization with a vested interest in this matter.

In a December 2007 article,³⁹ Simon Johnson, economic counselor and director of the IMF (International Monetary Fund) research department, discusses the relations between higher food prices and biofuels. He mentions reasons for increasing food prices, such as rising prosperity worldwide, especially in the emerging markets, the weather (droughts), animal disease, and, recently, biofuels. Corn prices have doubled in the United States and worldwide from 2005 to 2007, and there have been rapeseed price increases as well. A significant part of the price increases for food is due to biofuels policies, according to the IMF staff's assessment. Importantly, the effect is moderate for people in rich countries, because food represents only about 10–15 percent of consumption and the raw material represents a relatively small part of the actual food price. In less rich countries, food represents 30–50 percent of consumption or even more in very poor countries. Thus, the impact is felt more keenly by poor. The people who experience the hardest and most direct impact are those living in urban areas in poor countries, because they have to pay for the food and do not have the means to grow it themselves. Furthermore, Johnson states that biofuels production does not take place where it can be done cheapest, due to trade barriers and subsidies. Those who gain from the situation are farmers, also in the poor countries. He recommends using the current high food prices to remove subsidies and bring down import tariffs on biofuels, thus giving the poor countries an opportunity for development through freer trade of biofuels.

Currently there seems to be room for crop growing of biomass for fuel, but it will not be without unfortunate consequences. The literature repeatedly stated that cellulosic ethanol is a solution to the food versus fuel issue. This is only partly true; the feedstock is not in direct competition with food sources. and waste from food production can be used for fuel production. However, the situation could turn into a competition for productive arable land using, for example, grasses for fuel production instead of for food production. Therefore interference with free market forces and a common step to

prevent major fuel versus food conflicts or tragedies probably will be required. With this perspective it seems important to work on a radical reduction of fuel usage (i.e., more efficient cars or fewer cars), since unfortunate consequences of massive biofuel production appear nearly unavoidable.

Fuel Properties

This section deals with the chemical and physical properties of ethanol, especially those relevant to its use in automotive vehicles. The more engine specific properties such as energy density, octane rating, and so on are discussed in later sections.

Basic Chemistry

The chemical formula for ethanol is C_2H_5OH , sometimes written $EtOH$ or C_2H_6O . It is also known under the names ethyl alcohol or hydroxyethane and is the type of alcohol found in alcoholic beverages. Ethanol is a rather simple organic molecule consisting of a group of carbon and hydrogen atoms, with a hydroxyl group (an oxygen and a hydrogen atom) attached. Compared to most gasoline components, the ethanol molecule is small and light, having a molecular weight of just 46 g/mol (see Table 3 for relevant properties of ethanol, gasoline and diesel).

Ethanol is somewhat special in its electrochemistry, the molecule being polar at one end and nonpolar at the other. The polarity of a molecule refers to the distribution of electric load in the molecule and is a significant factor in the physical and chemical behavior of substances. The presence of a hydroxyl group in the ethanol molecule allows it to participate in hydrogen bonding with other ethanol molecules or other polar substances. The bond is relatively weak but strong enough to make ethanol more viscous and less volatile than other similar but less polar substances. The fact that the ethanol molecule has both a polar and a nonpolar end makes ethanol soluble in both polar and nonpolar substances. The polar end makes ethanol miscible with water (and other polar substances), and the nonpolar end makes it miscible with many nonpolar organic substances, such as gasoline and, to a lesser extent, diesel fuel.

The hydrogen bonding in ethanol also causes the substance to have a rather low volatility for a molecule of such relatively small molecular weight. Under atmospheric conditions ethanol is a liquid, although it will gradually evaporate if exposed to the atmosphere. It is colorless, has a distinct taste and smell, and is categorized as a mildly toxic substance.

Because of the production method, improper storage, and accidental contamination, ethanol often contains a small amount of water. Water contamination of pure ethanol can occur easily because ethanol is hygroscopic; that is, it will absorb water from the atmosphere if stored in an open container. Ethanol, as a fuel, is generally produced in either of two purities: anhydrous, meaning that the water content is less than 1 percent, or hydrous, generally referring to a water content between 5 and 10 percent. Anhydrous ethanol is also called pure, dry, or absolute alcohol. Ethanol purities above 95.6 percent by mass (designated the azeotrope concentration) cannot be produced by traditional distillation methods, but require separate dehydration equipment, a fact that makes

anhydrous ethanol approximately 20–25 percent more energy-demanding to produce than the ethanol/water azeotrope (calculated from Martinez-Frias et al.⁴⁰).

To avoid the heavy taxation levied on spirits for consumption, it is normally required that fuel ethanol be made undrinkable. To accomplish this, a measure of a foul-tasting or toxic substance (normally less than 10 percent) is added to ethanol after distillation, and it is then called denatured alcohol. The denaturant used is sometimes been methanol, propanol, or acetone, but with fuel ethanol an obvious choice is often gasoline.

Table 3 summarizes the most significant fuel properties of ethanol compared to those of gasoline and diesel. The significance of engine-related properties such as heat of combustion, Reid vapor pressure, and octane numbers is addressed in the sections on ethanol usage in transportation.

Table 3: Properties for Ethanol, Gasoline, and Diesel

Property	Ethanol	Gasoline	Diesel
Chemical Formula	C ₂ H ₅ OH	C ₄ to C ₁₂	C ₃ to C ₂₅
Molecular Weight [g/mol]	46,07	100–105	≈200
Carbon [mass%]	52,2	85–88	84–87
Hydrogen [mass%]	13,1	12–15	33–16
Oxygen [mass%]	34,7	0	0
Liquid Density, 20°C [kg/l]	0.792	0.72–0.78	0.81–0.88
Viscosity [cST]	1.52	0.4–0.9	2–6
	(20°C)	(16°C)	(37°C)
Boiling temperature, 1 atm [°C]	78.4	27–225	288–340
Reid vapor pressure, [kPa]	16	50–100	0.1–0.15
Flammability Limit, 20°C [vol%]	3.3–19	1.0–8.0	0.6–5.5
Stoichiometric Air/Fuel Ratio	9	14.5–14.7	14.6–15
Flash point temperature, closed cup, atmospheric conditions [°C]	12	-42	74
Autoignition temperature [°C]	423	257	≈315
Heat of Vaporization [kJ/kg]	910	330–400	225–600
Heat of Combustion (Lower Heating Value) [kJ/kg]	26900	42000–44000	42800–45300
Heat of Combustion (Lower Heating Value) [kJ/liter]	21300	≈32000	≈37200
Research octane no.	108	90–100	N/A
Motor octane no.	92	81–90	N/A
(R + M)/2	100	86–94	N/A
Cetane no.	--	5–20	40–55
Water Tolerance, volume %	Completely miscible	Negligible	Negligible
Carbon Dioxide Emission [kg/kg fuel]	1.91	3.18	3.20
Energy per CO ₂ Emission [MJ fuel energy/kg CO ₂ emitted] (a)	14.1	≈13.5	≈13.8

Sources: Sinor 1993 (Sinor et al.: Current and Potential Future Performance of Ethanol Fuels, SAE tech paper 930376) and U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Alternative Fuels Data Center⁴¹ (a) = calculated

Ethanol Fuel Types

As a motor fuel ethanol is found in various forms around the world, in blends together with gasoline and diesel containing different amounts of water. Fuel producers design fuel blend specifications to suit local legislation, vehicles, weather, consumer habits, and other conditions of the market in which they operate.

Somewhat more than half of the fuel ethanol used worldwide is used as an additive to gasoline, meaning that ethanol constitutes 5–10 percent of the overall fuel mass in the blend.

There are two major reasons for using ethanol as an additive to gasoline, apart from any reduction in CO₂ emissions. First, adding ethanol to gasoline raises the octane number of the fuel blend, thus guarding against engine knock (premature ignition), which can damage the engine. Ethanol is thus able to replace more costly octane-boosting components such as alkylate. Second, because ethanol contains oxygen, ethanol-containing gasoline burns more cleanly and reduces the amount of harmful emissions of carbon monoxide (CO), particulates and unburned gasoline components (see section on Emissions). Other oxygen-containing compounds can be added with the same effect.

The ethanol used as an additive is normally anhydrous, in order to prevent phase separation (de-mixing) of the water and gasoline in the blend (see section on Water and Blending Issues) Two other major types of ethanol blends, which are widely used in Brazilⁱⁱ, are gasohol, containing roughly 20 percent anhydrous ethanol in gasoline, and E100, hydrous ethanol without gasoline and with a water content of roughly 7 percent by volume. E100 has the advantage of a lower cost of production energy and consequently monetary cost compared to that for anhydrous ethanol, whereas gasohol has a better cold starting capability and a much higher energy content per liter. Additionally, a new type of ethanol blend has recently become more widespread, E85, containing between 71 and 85 percent anhydrous ethanol, with gasoline constituting the rest of the blend. This is primarily used in flex fuel vehicles (FFVs) in the United States and Sweden. At the low temperatures experienced in these countries, the ethanol used in blends with gasoline is required to be almost anhydrous in order to avoid phase separation (see section on Water and Blending Issues).

Finally, in recent years there has been an increase in the use of “diesohol” blends of diesel fuel and ethanol, for diesel engines. One such patented blend is the E-diesel blend, consisting of about 15 percent anhydrous ethanol, sometimes including additives, and about 85 percent diesel fuel. Another trademark blend, O₂-diesel, consisting of 7.7 percent anhydrous ethanol in diesel fuel, has been successfully used in more than 5,000 busses in the Indian state of Karnataka.⁴² The greatest advantage of diesel/ethanol blends is their reduction of the particle emissions normally associated with diesel engines.

ⁱⁱ Pure gasoline without ethanol is not available at Brazilian filling stations.

Another blend for compression ignition engines, E95, contains no diesel fuel, but 95 percent hydrous ethanol and 5 percent additive and has been used with success by the manufacturer Scania for busses and trucks in Sweden.⁴³ Other ethanol fuel types have been studied, but those mentioned here account for the vast majority of the worldwide ethanol fuel consumption.

Water and Blending Issues

The formulation of specific ethanol blends will almost always be limited by the need to avoid phase separation, that is, de-mixing of the fuel components. Although gasoline and ethanol are fully miscible, the presence of too much water in the blend can cause phase separation — an upper gasoline-rich liquid layer and a bottom water-rich liquid layer. Because hydrous ethanol is less expensive and more CO₂ friendly to produce compared to anhydrous ethanol, there are economic and environmental incentives for allowing water in the fuel blends. Also, because ethanol is hygroscopic (meaning that it tends to absorb water vapor from the atmosphere), intentionally or not there might be substantial water content in an ethanol fuel blend, possibly leading to phase separation. Such instability problems worsen at low temperatures and are likely to cause engine malfunctions and misfires. Additionally, a separate water-rich liquid phase in the fuel system can cause significant corrosion of many metals (see section on Materials and Corrosion).

Unlike ethanol and gasoline, ethanol and diesel fuel are not fully miscible. Not only do ethanol–diesel blends have even lower water tolerances than ethanol/gasoline blends, but also experimental studies have shown that even with anhydrous ethanol, phase separation can occur between ethanol and diesel at the winter temperatures encountered in temperate climates.⁴⁴ The cases of ethanol–gasoline and ethanol–diesel blends are examined separately below.

Ethanol/Gasoline/Water Miscibility

Because of the molecular dissimilarity of water and gasoline (polar and nonpolar molecules, respectively), water is almost insoluble in gasoline and the two form separate, liquid phases when mixed, water collecting at the bottom of the fuel tank due to its higher density. Because the fuel line inlet is located near the bottom of the fuel tanks both at filling stations and in vehicles, even a small amount of water in the blend can result in a large fraction of water in the fuel being delivered to vehicles or engines, respectively.

Because ethanol–water blends and ethanol–gasoline blends each are fully miscible, it is only in ternary (three-component) blends with both gasoline and water present that the mixture may suffer from phase separation. In this case, the resulting liquid layers generally consist of a lower ethanol–water layer and an upper gasoline layer with a

small content of ethanol.⁴⁵ Consequently, in the case of fuel tank phase separation, the separated ethanol–water layer is delivered to the engine, with the gasoline fraction remaining in the tank. Even though this hydrous blend has a significant heating value, it is still doubtful whether a vehicle could operate with this kind of uncertain fuel composition without misfire or other problems occurring. It has been assumed then that phase separation must always be avoided, and in order to do this, the exact miscibility limits of ethanol–gasoline–water blends must be examined.

Because the likelihood of phase separation becomes higher at low temperatures, it is more important to establish the water tolerances at the lower winter temperatures (i.e., from +10 to –40°C, depending on latitude and climate). However, the low-temperature miscibility limits of ternary ethanol–gasoline–water-blends have been the subject of surprisingly few publicly available research projects. For this report, an experimental investigation was out at the Technological Institute of Aarhus in Denmark, mapping the phase separation curves at –2°C and –25°C. These data, as well as other miscibility experiments performed at higher temperatures,^{46,47} have revealed some general tendencies:

- Gasoline–water miscibility is proportional to the ethanol content in the blend; that is, the larger the ethanol content in the ternary mixture, the larger the amount of water and gasoline that can coexist in the same liquid phase, the reason being the above-mentioned polarity characteristics of ethanol.
- Gasoline–water miscibility increases with the temperature of the blend, although not in a strictly proportional way.

Even though these tendencies are universal (and very well known), the exact water tolerances recorded depend on the exact composition of the gasoline used and on the measurement methods and criteria used to determine phase separation. In these experiments, Danish winter-grade gasoline (RON 95) was mixed with anhydrous ethanol and distilled water added in increments until the cloud point was reached, signifying the point at which two liquid phases co-exist. The data obtained are plotted in a ternary phase diagram in Figure 8.

Phase Separation Curves

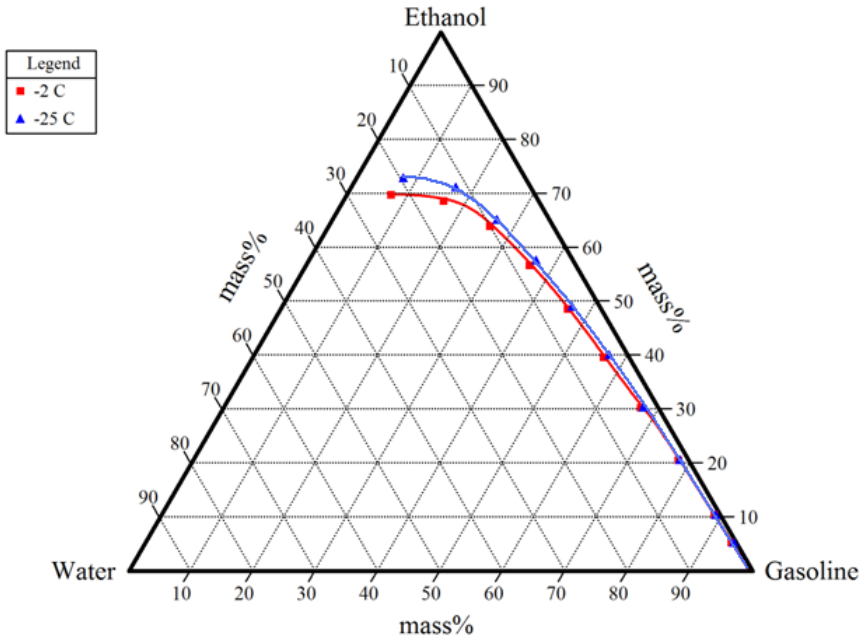


Figure 8: Ternary Phase Diagram

Blends above the curves are in one phase at the given temperature; blends below the curves are phase-separated. The water tolerances are somewhat worse at -25°C than at -2°C , although not much. The miscibility data can also be presented as the purity requirement of ethanol as a function of gasoline content in the blend, ethanol purity referring to the ethanol percentage of the combined water and ethanol content. See Figure 9.

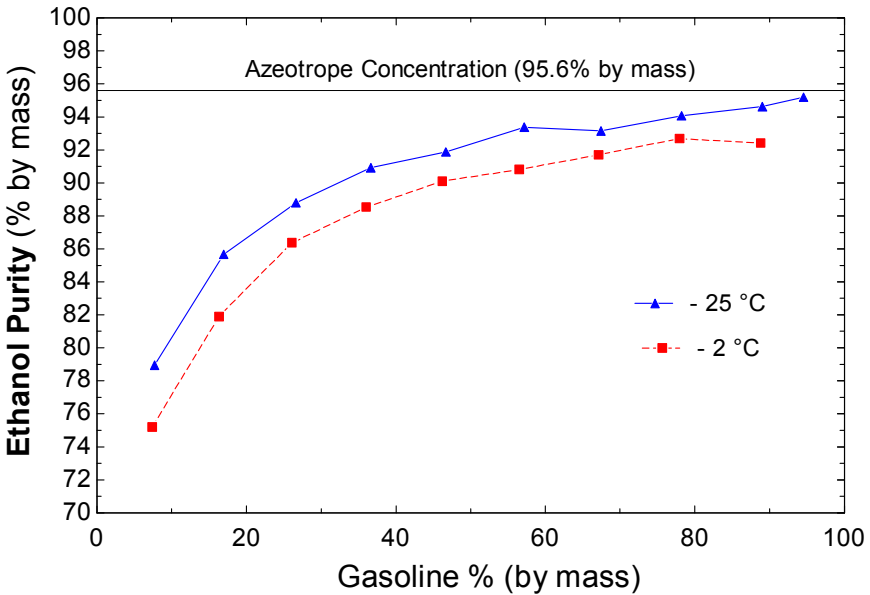


Figure 9: Ethanol Purity Requirement

Figure 9 shows how the ethanol purity requirement increases with the gasoline content of the blend, while decreasing with the temperature. Experimental uncertainties make it much harder to establish the exact water tolerances in blends with a high gasoline content (>95 percent), but the data at hand clearly show that ethanol below the azeotrope concentration can be used in blends with gasoline contents below approximately 95 percent, at least as low as -25°C .

It complicates the water tolerance issue somewhat when ethanol–gasoline–water blends are used in FFVs. The basic concept of flex fuel technology is that it allows the car owner to fill up with several different fuel types (for example, anhydrous E85 and pure gasoline are the two fuels used in the *northern* flex fuel concept). If phase separation is to be avoided, it is therefore crucial that the blend is also stable in any mixture of the two. The FFV concept has many advantages but also puts a greater limit on the water content in the blend. For example, it is problematic with half a tank of a stable, ethanol-rich blend if the act of filling up the tank with another of the vehicle’s specified flex fuels causes phase separation. The phase separation curves in the ternary phase diagram (Figure 8) can be used to find a compatible pair of flex fuels: Along a straight line connecting the coordinates of the two fuels lie all the possible blends resulting from mixing the two. Consequently, if this *tie line* is above the relevant phase separation curve, no phase separation will occur in any conceivable mixture of the two flex fuels. For example, it is apparent that a line connecting (a) an 85–15 ethanol–water blend and (b) a 50–50 gasoline–anhydrous ethanol blend does not intersect the phase separation curves (see Figure 10). making these blends acceptable for flex fuel use at -25°C .

Phase Separation Curves

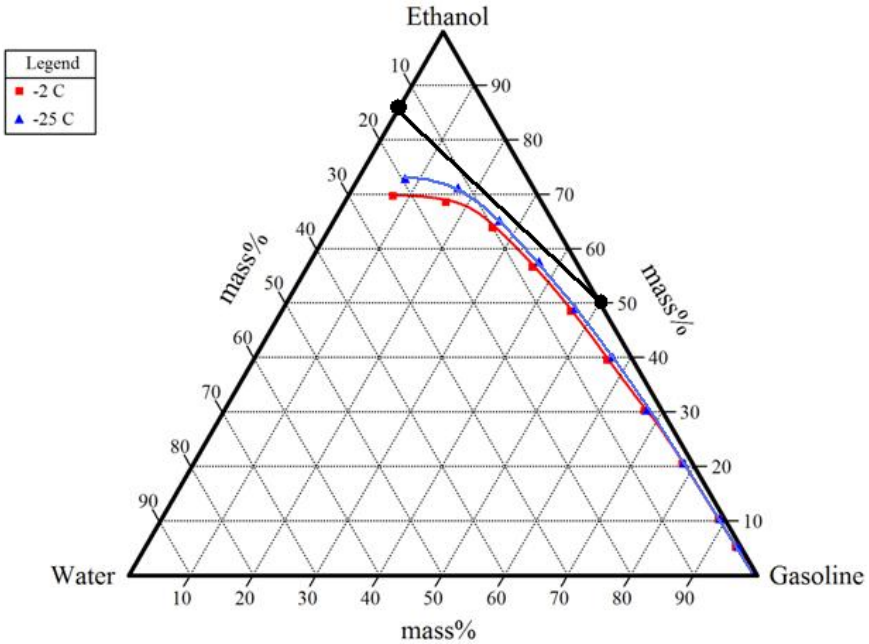


Figure 10: Phase Separation of Ternary Blends

The main point here is that the higher the ethanol content of the gasoline-rich flex fuel blend, the higher the allowable water content of the ethanol-rich flex fuel blend. Applying a set of equations to the experimental data, it is possible to calculate the approximate limits to the water content of ethanol-rich flex fuels, when coupled with different gasoline-rich flex fuels. The results assume that the ethanol-rich flex fuel blend contains 20 percent gasoline by mass (as is often the case in the E85-type ethanol blends). Table 4 shows how the allowable water content increases with the content of ethanol.

Table 4: Required Ethanol Purities of Ethanol-Rich Flex Fuel Blends

Gasoline-rich Flex Fuel blend	Minimum Ethanol Purity at -25°C (% by mass)	Minimum Ethanol Purity at -2°C (% by mass)
Pure Gasoline	94.7	92.5
E5 (5% anhydrous ethanol by mass)	92.8	91.2
E10 (10% anhydrous ethanol by mass)	92.5	89.6
E20 (20% anhydrous ethanol by mass)	90.7	88.2

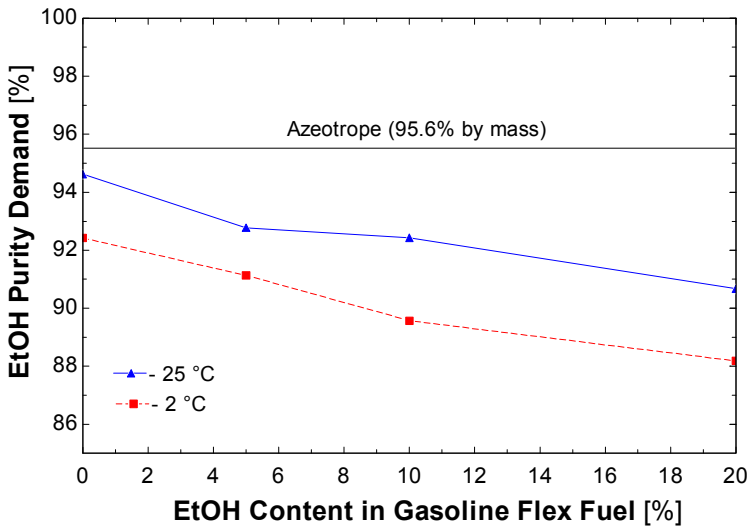


Figure 11: Purity requirement for Ethanol–Gasoline Blends

The results contradict the conventional wisdom of ethanol-gasoline fuel blends, demonstrating that hydrous blends at 95 percent purity would be acceptable for blending with present-day gasoline, even at low temperatures, down to -25°C , in every conceivable mixture that could occur in the fuel tank of an FFV. The higher the ethanol content of the gasoline flex fuel blend, the less restrictive the purity requirement for the ethanol-rich flex fuel blend. It has also been demonstrated that even when used as an additive to gasoline, ethanol is not required to be anhydrous. That being said, these findings would need to be verified in actual fuel system tests, in order to find any unforeseen effects on these miscibility limits. In vehicle application of hydrous blends, deposits and fuel residue in the fuel system and on the bottom of the tank would enter the fuel blend, which could lead to a change in the miscibility characteristics.

Ethanol and Diesel Miscibility

At low temperatures and certain mixing proportions, ethanol–diesel solutions separate into two liquid phases, one primarily consisting of diesel and the other primarily ethanol.⁴⁴ However, diesel fuel can experience phase separation problems even by itself at low temperatures. At sufficiently low temperatures, the paraffin components of the fuel begin to freeze, giving the fuel a wax-like texture that leads to engine failure. In normal diesel terminology, the temperature at which the fuel turns into an unclear substance is called the “cloud point,” indicates the start of wax formation.⁴⁸ The “pour point” designates the temperature at which the wax formation becomes so pronounced that the liquid is no longer pumpable.

There are two distinct forms of ethanol–diesel blends: solutions and emulsions. Solutions are homogeneous mixtures consisting of a single liquid phase; the diesel and ethanol molecules are completely mixed. In emulsions, two separate liquid phases coexist in the blend; it is a mixture of droplets (as is the case with milk). Even though emulsions generally have a better ethanol–diesel miscibility, recent research has focused more on ethanol diesel *solutions* (brand names such as E-diesel and O₂-diesel).⁴⁹ Solutions have the advantage that they can be produced by splash blending of the fuel components, whereas emulsions must be prepared by a more gradual heating and mixing process, making emulsions more costly to produce.

The stability of solutions of ethanol and diesel can be increased significantly with an additive, a co-solvent, to ensure phase stability which depends on the chemical composition of the diesel, the water content, and temperature. In the laboratory absolute ethanol can be dissolved in diesel in any ratio, but with just trace amounts of water (0.1–0.2 percent) phase separation can occur.⁵⁰ An important advantage of solutions is that the blend can be used immediately in diesel engines or with only minor engine adjustments. A major disadvantage of solutions is that they tend to absorb water and separate during storage, thus having limited storage capability, but similar problems are known to occur with regular diesel exposed to water.⁵¹ The percentages of ethanol most commonly blended into diesel are less than 20 percent.^{52,53} Newer techniques utilize dispenser custom blending in which the blending of ethanol, diesel oil, and solvents or other fuel additives is done as the fuel is poured into the vehicle fuel tank. If the fuel is utilized within a short period, problems with storage and phase separation can be avoided. The most common engine adjustment needed (if any) to accommodate E-diesel is injection timing and nozzle orifice size, depending on the percentage of ethanol in the blend.

Additives normally needed in ethanol–diesel blends are used to improve cetane rating, fuel lubrication, corrosion protection, and phase stability. As in ethanol-gasoline blends, the stability of ethanol–diesel blends and solutions increases with the temperature and decreases with the water content. The stability of emulsions increases as the droplet size decreases. The necessary percentage of stabilizing component rises as the temperature falls. Also, in the case of fuel blends, this stabilizing component must be combustible in itself. For simple ethanol–diesel solutions without a co-solvent, the phase separation temperatures are plotted in Figure 12.

Several features of the data presented in Figure 12 must be addressed. First, phase separation is less likely to occur in solutions with either very high or very low ethanol content (solutions below the line separate). For ethanol contents less than 5 percent, the presence of ethanol does not lead to a lower separation temperature than the cloud point temperature of pure diesel; that is, blends with an ethanol content less than 5 percent by volume are just as tolerant to cold temperatures as pure diesel. The same seems to be true for blends with an ethanol content more than 75 percent by volume. In between these limits, however, serious de-mixing problems could occur.

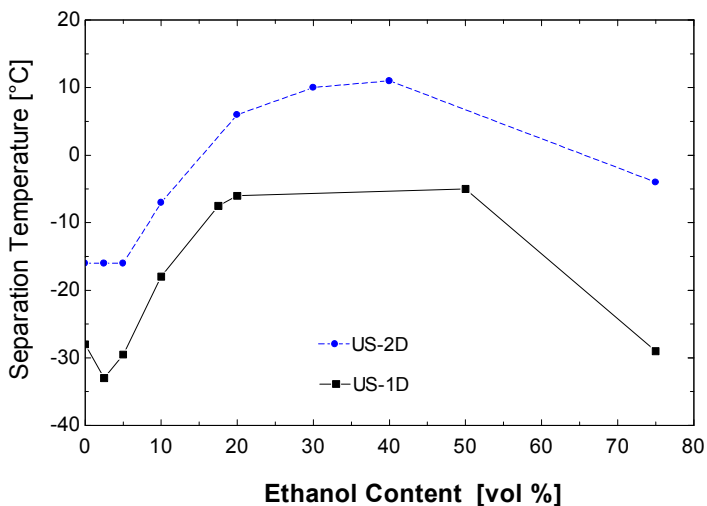


Figure 12: Phase Separation Temperatures of Ethanol/Diesel Blends (Source: Gerdes et al.⁴⁴). Note: US-2D and US-1D are the standard diesel types in the USA for summer and winter use, respectively, US-1D being characterized by a higher volatility and lower flash point and cloud point temperatures than US-2D.

Advances in the use of co-solvents have been shown to improve miscibility to the extent that the previously mentioned E-diesel blend (15 percent anhydrous ethanol in diesel) has been made suitable for winter use, without risk of de-mixing.⁴⁹ The other patented ethanol–diesel solution, O₂diesel, uses only approximately 1 percent of co-solvent to stabilize 7.7 percent ethanol in diesel.

Emulsions are mixtures of immiscible liquids, and ethanol and diesel are made into stable emulsions with the help of emulsifying agents. It is possible to make emulsions of both hydrous (5 percent water) and anhydrous ethanol with diesel. A major problem is keeping the emulsions stable, especially at low temperatures. Phase-separated emulsion inside the fuel system can, as mentioned in other cases, pose risks of misfiring or even engine damage,^{52,53} Dieselethanol blends are usually of the so-called micro-emulsion type (i.e., the droplets are very small) due to a high stability.⁵⁴ Diesel–ethanol emulsions can contain up to 40 percent ethanol depending on the type of diesel.⁵² Additives in considerable amounts can be necessary for high-level ethanol emulsions, and the cost of additives could be a major drawback. Biodiesel has been shown to enhance the solubility of ethanol in diesel and is discussed later.⁵⁴ The low-temperature stability of emulsions can in some cases be even better than that of regular diesel fuels due to the additives,⁵⁵ It has been shown that, with the use of an emulsifying agent, blends with a high proportion of hydrous (5 percent) ethanol and diesel can be stable down to -15.5°C .

In summary, the use of ethanol as an additive, that is, an ethanol content less than 15 percent in diesel solutions, is technically feasible, even at winter temperatures. The data in Figure 12 indicate that diesel blends with higher ethanol contents would probably encounter phase stability problems, unless the ethanol content is more than 75 percent. The feasibility of this kind of ethanol-rich blend has not been the focus of much, if any, published research thus far.

Toxicity and Safety

Compared to gasoline and diesel, ethanol is much less toxic to humans and the environment. Unlike diesel and gasoline fuels, it contains no carcinogenic components and is fully degradable if spilled due to leakages in storage tanks and the like. If blended with gasoline, diesel, or a denaturing agent, the toxicity increases.

Safety issues of fuels generally concern the dangers of fire and explosion of vapors in closed spaces. For fuel vapors to be flammable, the ratio between fuel vapor and air must be between two specific limits: the upper and lower flammability limits (LFL/UFL), which mark the flammable temperature range. The flammable temperature ranges for ethanol fuel blends in closed containers are shown in Figure 13.

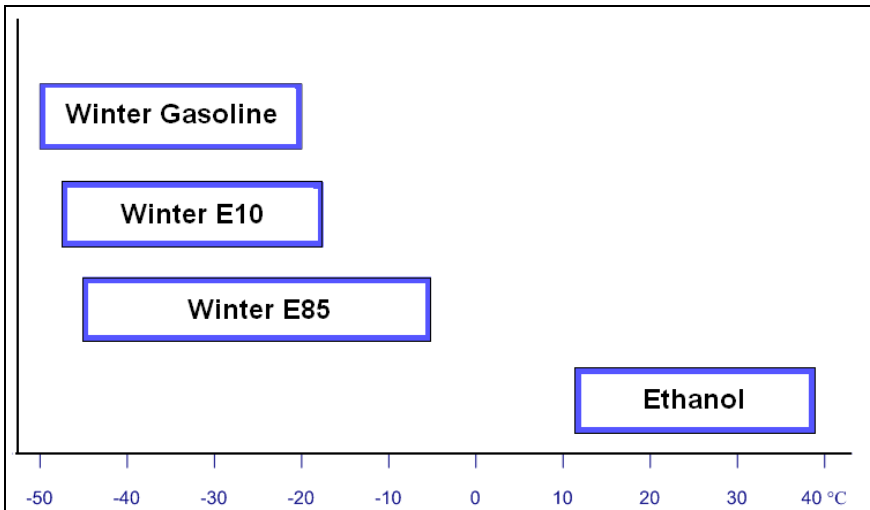


Figure 13: Flammability Temperature Ranges for Gasoline (Source: Valavds⁵⁶)

These flammability ranges apply to closed-vessel conditions only, such as in fuel tank headspaces. Compared to those for gasoline, the flammability ranges of E85 and ethanol extend into more common ambient temperatures; that is, these blends theoretically have a greater risk of fuel tank headspace fires, although the risk is still very small.⁵⁶ Only approximately 100 cases of such fires (with all types of fuel) have been reported globally.⁵⁷ The primary risk of a fuel tank fire occurs during refueling⁵⁶ due to the possibility of discharges of static electricity between the filler neck and the fuel hose nozzle. Overall, however, the fire hazard problem of pure ethanol or ethanol–gasoline blends seems manageable.

Perhaps the most serious concern about ethanol usage in CI engines is the low flash point of ethanol, which is about 13°C, compared to the 74°C specified in the US ASTM D-975 fuels standard for conventional diesel. The flash point is the lowest temperature at which a fuel can form an ignitable mixture with the air (Wikipedia). In many fuel tanks there is a void (especially when partially full) where fuel vapors mix with the air, forming an ignitable mixture.

Ethanol–diesel blends have been shown to have about the same flammability properties as neat ethanol, placing E-diesel in the safety class of gasoline fuel, not diesel fuels.⁴⁹ Even relatively small amounts of ethanol in diesel dramatically lower the flashpoint, and there is not a linear relation between ethanol percentage and flashpoint. In practice, this means that for E-diesel blends, which most commonly contain about 5–15 percent ethanol, the flashpoint is about the same as that for ethanol.⁵⁸ Furthermore, the flammability limits for ethanol fuels are most unfortunate compared to those for both diesel and gasoline. For gasoline the vapors are too concentrated above –20°C, and for diesel the vapors are too lean below 64°C.⁵⁹

Figure 14 illustrates that even 5 percent ethanol in diesel lowers the flashpoint to level close to that of neat ethanol.

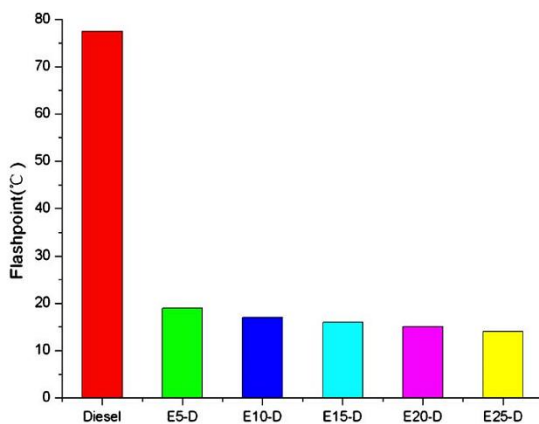


Figure 14: Flashpoint of Ethanol Diesel Fuels
(Source: Li et al.⁵⁸)

The unfortunate flammability limits combined with the low flashpoint make it necessary to take measures for storing, distributing, handling, and using ethanol and E-diesel. In order to mitigate the risk level to a level comparable to that of diesel and gasoline. The following measures are recommended by Waterland, Venkatesh, and Unnasch⁵⁹:

- Fuel tanks in diesel vehicles need to be upgraded to at least the safety standards of gasoline vehicles, including the installation of valves and possibly flame arrestors in the fuel-filling ports and tank vent in order to guard against accidental ignition of fuel tank headspace vapors.
- Vapor recovery system should be incorporated in all fuel transfer facilities, that is, from production to end use.
- Electrical ground connections should be established when fuelling at stations, and tank-level detectors might also need to be redesigned.

The safety technology necessary for ethanol–diesel blends is well-known and can be transferred directly from that for gasoline, but some expenses will be incurred in upgrading diesel fuel dispensers and vehicles to meet the demands posed by such blends.

Diesel–ethanol fuels should not be stored, distributed, handled, or used without special consideration and precautions. On the other hand, the technology for utilizing ethanol fuels and realizing their benefits is not unknown and unproven. According to the National Renewable Energy Laboratory (NREL),⁶⁰ the main technical barriers to commercialization of E-diesel, related to flammability, are as follows:

- The low flashpoint, which limits the use to fleets;
- OEM warranties, which do not accept e-diesels in the current fleet (U.S.); and
- Fuel specification, standardization, and approval.

Ethanol Usage in Transportation

Global ethanol markets are expanding rapidly; the main markets are shown in Figure 15.

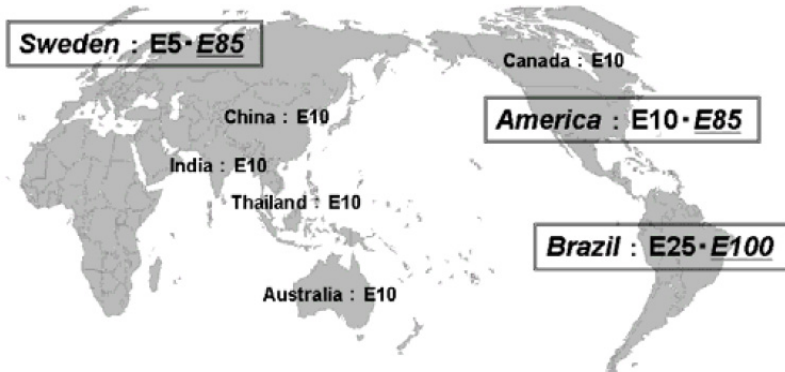


Figure 15: Overview of the Global Ethanol Markets (Source: Tsunooka⁶¹)

The figure shows that, apart from the Brazilian market, which is a special case, ethanol fuels are either low-level blends, such as E5 and E10, or the high-level blend E85, which is substituted by E70 in the wintertime. In the Brazilian market and markets with E85, fuel is blended in the fuel tank by the consumer, and the resulting ethanol percentage therefore varies considerably. Unfortunately there is not much literature on these blends (called commingled blends). In addition to the markets shown in the figure, ethanol fuels for the diesel market do exist but on a much smaller scale and can be characterized as niche markets.

Application in Spark-Ignited Engines

This section describes the possibilities and difficulties associated with the application of ethanol in gasoline passenger cars. Some important fuel properties, as well as the compatibility and potential of ethanol fuels in spark-ignited (SI) engines, are discussed.

Fuel Compatibility

E5 and E10 are already on the market all around the world and have generally shown compatibility with existing SI engines.⁶² The problems still observed are associated with older vehicles. These problems are mainly related to corrosion in fuel lines, swelling and cracking of rubber or plastic parts in the fuel line, and cold start of the engine. Even

though costumers experience no apparent problems with their older vehicles, it is likely that increased fuel emissions by evaporation through the fuel system occur.

An Orbital study,⁶³ which included experimental work, focused on the potential effects of using E20 in the Australian gasoline vehicle fleet. The study found that the potential effects of E20 were increased tailpipe emissions (regulated and unregulated), lower engine capacities in vehicles that are not able to adjust engine parameters for ethanol (older cars), deterioration of exhaust catalyts, and greater levels of wear and engine deposits.

In 2007 Orbital Australia¹⁸⁷ completed a study on the assessment of the operation of vehicles in the Australian fleet on ethanol blend fuels. The study examined 16 vehicles for operability and compatibility with E5 and E10 fuels. The test vehicles selected were those listed as *not* suitable for ethanol use by the Federal Chamber of Automotive Industries (FCAI). The test results showed that using E5 and E10 fuels in these vehicles resulted in corrosion or component distortion and had adverse impacts on drivability. The results of this study supported advice from vehicle manufacturers and importers as published by the FCAI for Australian-supplied vehicles.

All new vehicles can run on at least E5 without problems and usually under the manufacturer's warranty. E5 or E10 usage is not always recommended by manufacturers, however. Potentially all future gasoline vehicles could be made compatible with all blends, from E0 to E85, as is done with many vehicles in the U.S. market, with no extra cost on the vehicle.⁶² Furthermore, all the major car manufacturers are capable of making vehicles compatible, even with hydrated ethanol (E100), since they all produce cars for the Brazilian market.

Materials and Corrosion

A major concern regarding about the use of ethanol as a transportation fuel is its corrosive and degrading effect on fuel systems and fuel storage facilities. The most notable compatibility problems identified in fleet tests are as follows:

- *Degradation of some rubber and plastic materials.* This occurs because of the solvent-like nature of ethanol, ethanol molecules being absorbed into the material, causing them to soften and swell.
- *Degradation of metals due to the acidic or galvanic nature of ethanol.* Although anhydrous ethanol in itself is only slightly corrosive to metals, the hygroscopic nature of ethanol makes water contamination of anhydrous ethanol almost impossible to avoid. In the highly likely case that the ethanol contains water, either intentionally or through absorption from the air, the risk of metal corrosion increases significantly, relative to the water content, one of the main reasons

being corrosive contaminants in the water, such as sodium chloride and organic acids.⁶⁴

- *Fuel line clogging due to ethanol “stripping off” fuel system deposits.* This has been observed in vehicles switching from pure gasoline to ethanol blends between 10 and 20 percent by volume.⁶⁵ However, this phenomenon has not been reported as problematic during the recent upsurge in use of E10 blends in the United States.

The extent and seriousness of these effects have been examined in several large-scale tests. A fleet test funded by the Australian Government found that E20 ethanol blends would seriously degrade the fuel system of three different cars manufactured before 1990.⁶³ It was reported that fuel system degradation and corrosion started at blends of approximately 14 percent ethanol.⁶⁵ However, the water content of the ethanol used in these tests seems to have been so high that the ethanol would not qualify as anhydrous.⁶⁶

A more recent test performed by the Minnesota Center for Automotive Research directly compared anhydrous ethanol (water content less than 1 percent) in E10 and E20 blends,⁶⁷ finding that both fuels showed similar, and serious, degradation of many plastic materials commonly used in non-FFV fuel systems. Neither of the two blends had a corrosive effect on common fuel system metals, either aluminum, brass, copper, cast iron, or stainless steel. Additionally, neither E10 nor E20 caused degradation in elastomers (rubbers) to the extent that presented concerns.

Whereas anhydrous E10 could possibly cause perishing of plastics in many existing vehicles, hydrous ethanol blends seem likely to corrode or damage the metal, rubber, and plastic parts used in many current vehicles’ fuel systems — damage that could lead to fuel-metering imprecision, equipment failure, fuel leaks, and engine malfunction.

For non-FFVs, the potentially damaging effect of ethanol blends has prompted manufacturers to specify a maximum ethanol fuel content, transgression of which voids the warranty of the vehicle. For all new non-FFVs produced in the United States, this limit is 10 percent. Some Asian and European car manufacturers have specified a limit for new cars of only 5 percent, notably for Fiat, Renault, Daewoo, Alfa Romeo, and some Suzuki and Mazda models.⁶⁸ Older models in general tend to have lower ethanol content limits, whereas some old models, and even some new luxury cars, do not accept ethanol in the fuel at all. Two complementary and fairly comprehensive and updated lists of ethanol compatibility for different gasoline vehicle models are available online.^{68,69}

Overall, there seems to be a serious hindrance to the widespread use of hydrous ethanol blends in many current cars, at least in low-percentage-ethanol blends. Based on the findings of the Minnesota Center for Automotive Research,⁵⁷ however, upgrading current vehicles to the use of blends with (at least) up to 20 percent anhydrous ethanol seems feasible, since only certain plastic fuel system parts would need to be replaced.

In ethanol-compatible non-FFVs and gasoline–ethanol FFVs, the problems of corrosion and degradation have been countered by the use of ethanol-resistant materials in fuel systems, stainless steel substituting for aluminum, magnesium, lead, and brass among other metals. Polyvinyl chloride and some rubber parts are replaced by materials such as high-density polyethylene, nylon, and fluorinated plastics such as Teflon.⁷⁰ These measures have effectively solved the materials compatibility problem with ethanol, with FFVs experiencing no extra engine or fuel system wear due to the use of E85.⁷¹ There is no direct scientific documentation on the engine and fuel system wear in Brazilian vehicles running on E100, but by all accounts, the 30 years of experience of car-manufacturers with hydrous ethanol fuel seems to have eliminated any major compatibility problems through the correct choice of materials.⁷³

It has recently been documented that the use of E85 in some cases can lead to an increased amount of intake valve deposits compared to operation on pure gasoline.⁶⁴ However, the same research also documented that this issue can be effectively dealt with by the use of so-called deposit control additives in the fuel.

In the case of diesel-ethanol blends, the considerations are the same as those for FFVs regarding the choice of materials for fuel system and engine parts. When ethanol-resistant materials are used, blends of diesel and anhydrous ethanol have been shown in several over-the-road tests to provide the same engine and fuel system durability as pure diesel, even with as much as 30 percent anhydrous ethanol in the blend.⁴⁹ Similar tests of hydrous ethanol–diesel blends have not been reported, but we assume they would show increased corrosion and wear, especially because of the increased risk of phase separation of ethanol–water and diesel. Should such de-mixing occur in either ethanol–gasoline–water or ethanol–diesel blends, it is evident that ethanol or ethanol–water concentrations locally in the fuel system could become significantly higher than these limits, leading to damage of any nonresistant fuel components, such as those made of aluminum, lead magnesium, and PVC, among others.

Energy Density

One way of reducing CO₂ emissions from a vehicle is to make it more fuel efficient, that is, make it use less energy. Ethanol has a significantly lower energy density (Joule per liter), about two-thirds of that of gasoline, so about 50 percent more fuel (by volume) is needed per kilometer, if a given engine is equally efficient on either fuel. If an engine is equipped to utilize ethanol properly, ethanol usage can increase the energy efficiency of the engine and thereby offset the otherwise higher fuel consumption. The increased efficiency would lead to lower CO₂ emissions, even though more fuel is used. The lower energy density of ethanol in many cases necessitates a higher fuel tank capacity and fuel flow rate, if vehicle range and performance are to be maintained. The degree to which these measures are needed depend on the percentage of ethanol in the fuel. For low-ethanol blends (E5 and E10), which are used in unmodified cars, a slight decrease in performance is not unusual. Vehicles that can run on E85, or blends of E85 and regular

gasoline (or low-ethanol blends) typically do not experience a performance decrease, since the vehicle is prepared for the properties of ethanol.

Figure 16 shows the energy content of typical ethanol fuels currently on the market.

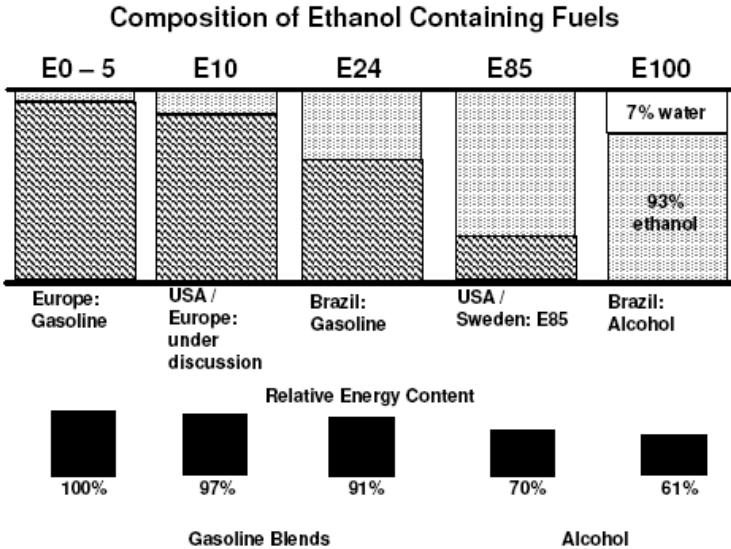


Figure 16: The Relative Energy Content of Ethanol Fuels Compared to Gasoline (Source: Kapus et al.⁷⁴)

Oxygen Content

When used as blending components in gasoline, oxygenates are beneficial for both combustion efficiency and exhaust emissions, especially CO emissions. Ethanol contains about 35 percent oxygen by weight and is therefore categorized as an oxygenate. Compared to other oxygenates such as MTBE, ETBE and FAME, ethanol is less toxic and therefore a good alternative.

Because of its oxygen content, ethanol has a lower stoichiometrical air-fuel ratio (AFR) than gasoline, that is, 9:1 and 14.7:1, for neat ethanol and gasoline, respectively. Thus more fuel must be injected per engine cycle. In terms of energy content, a given volume (that of the engine cylinders) of stoichiometrical air-fuel mixture contains about the same amount of energy with gasoline and ethanol. This is one of the main reasons current gasoline engines do not need a fundamental redesign to run on ethanol and perform similarly with either fuel.⁷⁵

Since the introduction of the three-way catalyst, passenger cars have been equipped with a closed-loop system to measure and ensure a stoichiometrical AFR, using the lambda probe (an oxygen sensor). Newer cars are therefore able to automatically adjust the AFR, at least when using low-ethanol blends (E5 and E10). Older cars without a closed-loop system or cars with a carburetor cannot adjust the AFR and will not run with a correct AFR. An incorrect AFR can cause such problems as too lean combustion, possibly resulting in worse exhaust emissions, start problems, lack of power, or engine failures. Ethanol fuel usage is usually not recommended for these types of cars.⁶⁸

Octane Number

Perhaps the greatest advantage of ethanol as a fuel in SI engines is its high octane number. The efficiency of an SI engine, that is, the ability to convert fuel energy to mechanical energy, mainly depends on the compression ratio. It is therefore advantageous to increase this as much as possible. The major restraint is the fuel octane number — high-octane fuels can be used with higher compression ratios, thus yielding higher energy efficiency.

A drawback is that NO_x formation inside the engine increases with increasing compression ratio due to increased peak combustion temperatures.⁷⁶ Conversely, higher compression ratios with ethanol use seem to enable high EGRⁱⁱⁱ ratios, which can reduce NO_x significantly.^{77,78} The net outcome of these two mechanisms depends on the configuration of the engine.

When a gas is compressed, its temperature increases. In an SI engine, if the temperature gets too high during the compression stroke,, there is the possibility of premature auto-ignition of the fuel and shockwaves forming inside the cylinder. This phenomenon is called knocking and is a design and operating parameter in gasoline and ethanol fuel engines. In SI engines, the fuel–air mixture is ignited at the start of the expansion stroke, and it is not desirable to have a premature ignition before that point because the efficiency of the engine decreases. Furthermore, heavy knocking is very harmful to the engine. The two main parameters (in a well-adjusted engine) determining whether an engine will knock or not is the compression ratio of the engine and the ability of the fuel to withstand auto-ignition. This fuel characteristic is called the anti-knock index, or the octane number. A fuel with a high octane number can thus be used in an SI engine with a high compression ratio, offering a higher overall efficiency, that is, a better fuel economy, and relatively lower CO₂ emissions.

Currently, much work is being done by car manufacturers to develop engines that can make optimal use of many different fuels. Operating a gasoline car on low-ethanol blends will likely take advantage of the higher octane number of ethanol to some

ⁱⁱⁱ EGR (exhaust gas recirculation) is a very common system that recirculates a part of the exhaust gas back to the fresh air intake.

degree. Raising the compression ratio and utilizing the higher octane rating can be problematic, if the vehicle has to be compatible with both neat gasoline and ethanol-blended fuels. The result is therefore that most engines are optimized for regular gasoline. Currently there are no vehicles on the market that can automatically change the compression ratio according to the fuel, but some experimental concepts have been demonstrated, and many of the major car manufacturers are active in this area.⁷⁹ At present, unfortunately, variable compression ratio for optimal fuel efficiency in FFVs is not economically feasible.^{80,81}

Other technologies can be used for achieving better utilization of high-octane ethanol fuels, while maintaining tolerance for low-octane fuels. Among those are variable valve timing (VVT), turbocharging, and ethanol-boosting systems (EBS). In general, modern cars are moving toward more comprehensive and precise control of engine parameters (valve timing, ignition timing, AFR, injection timing, turbo, and EGR), which results in more flexibility to reach optimal combustion under all conditions, including different fuel octane numbers. These improvements give the industry more freedom to make engines tolerant toward low-octane fuels, while designed for utilization of high-octane ethanol fuels.

Alternatively, ethanol in low-level blends can be used while maintaining a regular octane number. Adding ethanol can, instead of boosting octane number, remove the need for other more toxic or expensive octane-boosting gasoline components, such as alkylate or aromatic compounds.

Another important fuel property of ethanol is its rather high latent heat of vaporization, a measure of the amount of energy required to evaporate the fuel. In an SI engine, vaporization of the fuel absorbs energy from the engine surroundings, thus lowering the temperature in the intake manifold and combustion chamber of the materials and air, depending on the injection method. Since ethanol has a much higher heat of vaporization than gasoline, engine temperatures tend to be lower when ethanol fuels are used. This property complements the high octane number, because auto-ignition or knocking is less likely to occur with a cooler running engine. A benefit of the high latent heat, especially for direct fuel injection (DI) engines but also for port fuel injection (PFI) engines, is the charge cooling.⁸² A cooling of the intake air—fuel mixture, due to a relatively large amount of ethanol (due to the lower stoichiometrical AFR) and the high latent heat, increases the air density, thus allowing more air to enter the fixed volume of the engine cylinders. When more air is forced into the engine, more fuel can be injected and more power is created by the same engine size, resulting in increased efficiency. Furthermore, the lower operating temperatures tend to increase engine efficiency because of lower internal heat losses and also lower exhaust gas heat losses, which is observed as lower exhaust gas temperatures. The work needed during the compression stroke has also been shown to decrease due to the high latent heat,⁷⁷ thus contributing to improved engine efficiency. The high heat of vaporization has the major disadvantage of further worsening the engine cold start properties of ethanol fuels.

Water Content

The purpose of using ethanol containing water is mainly to eliminate the process of dehydration, which is relatively energy-consuming and costly. With hydrated ethanol, the overall life cycle energy cost is reduced significantly, and, as such, hydrated ethanol is a more energy- and CO₂-efficient fuel. Solutions of water, ethanol, and gasoline are in some cases unstable — the main reason hydrated ethanol has not been used in temperate climates. Hydrated ethanol is only used as either high-level ethanol blends or neat ethanol,⁸³ and only limited recent research is available on hydrated versus anhydrous ethanol in SI engines. The water in ethanol carries no energy, and relatively larger volumes of fuel must therefore be carried in the fuel tank and injected to the engine to obtain engine outputs and driving ranges similar to those for anhydrous ethanol. The latent heat of vaporization for hydrated ethanol is higher than that of anhydrous ethanol, increasing with water percentage. Water increases the octane number, that is, increases the knock limit but decreases the stoichiometrical AFR due to the lower energy content.⁸³

The effects of water in SI engines have been investigated by using techniques such as injection of steam, direct and manifold injection of liquid water, and water mixed into the fuel with both direct and manifold injection. There is of course the Brazilian experience, which dates back to the 1970s. A number of studies have shown that water addition has a very positive effect on reducing NO_x emissions (up to 90 percent) but tends to increase hydrocarbon (HC) emissions. (Most HC emissions are converted into water and CO₂ by the catalyst in modern cars.) The effect on engine efficiency is limited; that is, anhydrous and hydrated ethanol with relatively high water content provides similar efficiencies. Potentially, hydrated ethanol should be able to provide further increases in engine efficiency by running with even higher compression ratios than anhydrous ethanol, but research on this has not been reported in the literature yet.⁸³

A Dutch company called HE Blends recently experimented with hydrous ethanol blends with 15 percent and 20 percent zeotropic ethanol (approximately 4 percent water).⁸⁴ A VW Golf mark 5 FSI, running 32.000 km over 1 year in ambient conditions was tested from -20°C to +35°C. Observations showed lower fuel consumption while emissions complied with the Euro4 standard, without engine optimization. No deterioration of gaskets, seals, fuel system, or anything else was found. HE Blends is currently cooperating with the European BEST initiative (Bio-Ethanol for Sustainable Transport), performing limited market trials and performing further testing in programs under the Dutch and German governments.

Technical Potential of Ethanol in SI Engines

This section addresses the advantages that might realistically be achieved with ethanol, focusing especially on energy efficiency. One of the main hurdles for customer acceptance of ethanol could well be the lower mileage that comes with its use. Ethanol

contains only about two-thirds the energy of gasoline, a fact proportionally reflected in the mileage, although offset somewhat by increases in the efficiency of SI engines. Ideally, if engines were able to utilize ethanol so efficiently, there would be no mileage penalty. With an experimental high-compression-ratio engine, it has actually been shown that E30 can achieve better mileage per liter than gasoline.⁸⁵

Ethanol represents a superior fuel for the SI engine, with respect to the key properties — octane number and latent heat of vaporization. Basically ethanol has the ability to withstand high pressures and temperatures without igniting uncontrollably. In the case of low-ethanol blends (E5-10), it is possible to produce fuels with a slightly higher or similar octane number compared that for regular gasoline. In that case the most modern cars are able to regulate the ignition timing and advance the timing to a degree that increase engine efficiency by a few percentage points.

At present, perhaps the strongest trend in SI engine development is downsizing, that is, decreasing the cylinder volumes of the engine while maintaining the original power and torque output. Although engine volumes in many new vehicles are being reduced, engine performance is being increased. The main goal of downsizing is to reduce engine energy losses, resulting in higher fuel efficiency. Because the efficiency of the SI engine varies with the speed and load, it is of interest to use the speed-load range at which the engine works most efficiently as much as possible, to reduce overall fuel consumption and CO₂ emissions. Unfortunately the optimal fuel economical range is in many cases different from running conditions on the road, but downsizing brings the fuel economical range and road loads closer.⁸⁶

To make downsizing attractive, manufacturers must demonstrate that the smaller engine can perform as well as a much larger one, only with improved fuel economy. One key technology in making downsizing possible is supercharging, that is, increase the pressure of the inlet airstream to the engine. The pressure is provided by either a compressor, which is driven mechanically or electrically by the engine, or a turbocharger, which is driven by the exhaust gas from the engine. Sometimes both compressor and turbocharger are used to boost the full engine operation range. An important challenge for successful downsizing is the performance at lower engine speeds, since small engines normally do not have sufficient torque at this range.⁸⁶ At lower speeds, pressures in the engine are relatively low, so there is room for raising the pressure and thus the yield. At higher speeds and loads, pressure increases and the phenomenon of knocking can more easily occur with turbo-charging. Due to its high octane number, ethanol can accept a higher degree of turbocharging, making downsizing an especially beneficial approach for ethanol engines.

A key parameter, when trying to utilize ethanol at its maximum potential, is the ignition timing. Two important timings are knock-limited ignition timing (KL) and maximum brake torque ignition timing (MBT). In modern cars, ignition timing is controlled real time by the electronic control unit during operation, and KL timing is used to retard the ignition of the fuel to a point at which it is almost knocking. KL timing is a typical setting

that keeps the engine at its most fuel-efficient (or powerful) level, limited by the given physical and chemical conditions in the engine. MBT timing provides the highest efficiency if knocking is not an issue. Thus the SI engine at full load provides optimum efficiency when operating at highest knock-free compression ratio, stoichiometrical AFR, and optimum ignition timing (MBT).^{81,87} Thus, in trying to increase the compression ratio and/or add turbocharging, the main goal is to obtain MBT or get as close as possible with KL timing, but always avoid the condition of knocking.

One way of obtaining high efficiency has been developed by Lotus Engineering on a Toyota engine. The engine is configured with a compression ratio of 11.5:1, which is high for a PFI gasoline engine, and with a turbocharger. The result is that the engine efficiency using E85 is 9 percent higher than that using gasoline (RON 95). The difference is solely due to different fuel, turbocharging, and ignition timing, E85 running with MBT, and gasoline with KL timing.⁸¹

Another strategy has been to improve the knock sensor in order to more closely approach the knocking limit, thus gaining efficiency. For the Brazilian market, Ford has designed an engine optimized for E93 (7 percent water), which is still able to run efficiently on E25 (gasohol). In addition to increased compression ratio, Ford used a full-range knock sensor and an electronically controlled valve for better engine coolant temperature control. The higher precision in knock detection optimized ignition timing, and the valve ensured higher coolant temperatures when running on E93 in order to reduce heat losses and increase engine efficiency.⁷³

Brusstar et al. at the U.S. EPA used yet another strategy on a modified VW turbo diesel engine. The goal of a number of studies has been to provide an example of an ethanol (and methanol) engine with efficiencies comparable to those of modern diesel engines while maintaining the low production cost and low exhaust emissions of the gasoline engine; this was achieved. In order to prevent knocking, EGR was used extensively. This study and others showed that ethanol engines can operate with higher EGR ratios than gasoline engines (which is also true for ethanol in diesel engines), benefiting the exhaust emissions significantly. E30 has approximately 8 percent less energy per liter, which would result in 8 percent lower mileage compared to running on gasoline, if engine efficiencies were equal on both fuels. The EPA study showed an increase in engine fuel efficiency of 10–12 percent, allowing the vehicle to actually run longer on a liter/gallon of E30 than gasoline.⁷⁷ Figure 17 shows data from measurements on the rebuilt VW TDI engine running on up to 100 percent ethanol compared to a regular U.S. FFV.

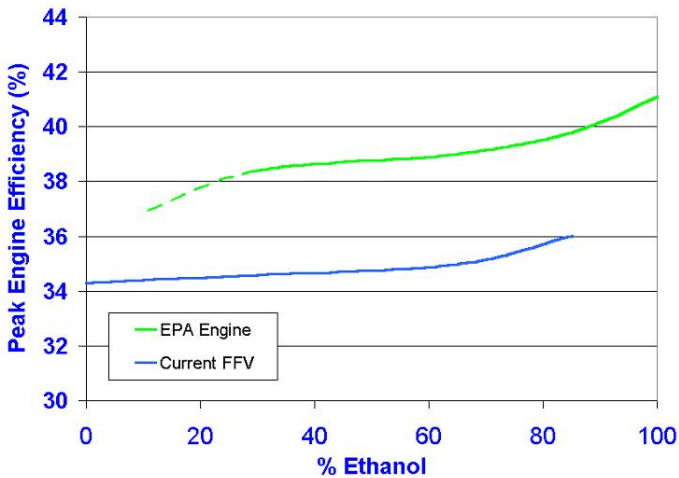


Figure 17: Peak Engine Efficiency Running on Different Ethanol Fuels (Source: Brusstar⁸⁸)

The figure shows how engine efficiency increases with increasing ethanol content in the fuel. Also, the current FFVs still have the potential for increased fuel efficiency. The tests showed not only very high peak efficiency but also a broader operating range with high efficiency. The U.S. EPA presents this work as an alternative or bridging technology, which is cheaper, cleaner, and more efficient than the original VW diesel engine.⁷⁷

A study funded by the U.S. DOE⁷⁸ compared a current FFV against an FFV optimized for E85. Running on E85 before engine modifications proved to be about 3 percent more efficient than running on regular gasoline. When the compression ratio was raised, the engine proved 10 percent more fuel efficient (in terms of energy) on E85 compared to gasoline. Finally, when the gearing of the vehicle was changed, the dedicated E85 vehicle provided about 10 percent more torque. Thus it was possible to make the engine run at lower speeds while maintaining the original performance. This method, called down-speeding, gained another 10 percent increase in fuel economy. In general, ethanol allows engines to provide more power and torque compared to running on gasoline (provided they can accommodate the fuel properties of ethanol), so down-speeding could be an alternative or complementary technique to downsizing.

A recent proposed concept from researchers at the Massachusetts Institute of Technology (MIT) focuses on gaining maximum engine efficiency with minimum ethanol usage. With the limited supply of ethanol, this concept seems very relevant. The concept, EBS, aims at optimum utilization of the properties of ethanol and gasoline by injecting ethanol via a separate fuel system. Pure ethanol or E85 is supplied on demand to avoid knocking according to the engine requirements and depending on the load and speed of the engine. Thus ethanol injection is needed only at high loads and speeds, and ethanol consumption is therefore calculated to be only 1/20 of the gasoline

consumption, while still maintaining very high efficiencies due to high compression ratio, turbocharging, and downsizing. An increase of 30 percent efficiency over that of a conventional PFI gasoline engine is proposed.⁸⁹

In general, the potential of ethanol in SI engines compared to regular gasoline presents the following caveats: (a) Different engine designs react differently based on factors such as increased amounts of ethanol in the fuel, turbocharging, increased compression ratio, and so on; and (b) the potential efficiency increase must be observed over the full range of the engine, that is, from idling to full power or, even better, the range that will typically be used on the road.

According to the literature, there is little doubt that ethanol, even in limited amounts, increases the efficiency of the modern SI engine, at both part and full load and across many different engine configurations. Also, the range over which the engine is more efficient with ethanol fuels is generally broader, compared to gasoline. In Figure 18 examples from the literature show engine peak efficiency versus engine technology or fuel.

Figure 18 shows the potential for ethanol application in gasoline engines. The lines represents one study, and the squares, x's, and triangles other studies, respectively.^{75,77,81,90,91} Peak engine efficiency is increased by applying various technologies and fuels. The data points are extracted from the results of recent engine tests. The first part, from left to right, shows the efficiency increase due to increased compression ratio, from 10:1 to 13:1. The efficiency increases at different ratios depending on the fuel used. In general, the use of fuels with a higher research octane rating (RON) increases the potential gain of this technology. The data set on the left shows the effect of applying turbocharging and a higher octane rating, using the same compression ratio.

The second part shows the potential for a range of technologies: turbocharging, lean combustion, and DI. The effect is similar for the three types of fuel — RON 92, RON 100, and E100 (neat ethanol). E100 shows a significant efficiency gain even though high efficiency is already obtained due to the high compression ratio of 13:1. In this part of the graph, a few other figures have been added to compliment the trends shown. At the lower end, the squares illustrate the effect of changing fuel from RON 95 to E85, that is, an increase from about 30.7 to 33.8 percent due only to the fuel change. The x's show a similar trend in another study. The triangles are a special case in which a diesel engine was adapted to run on gasoline–ethanol blends of various kinds. The x's illustrate what can be achieved merely by changing the fuel and engine management, that is, a significant engine efficiency increase from about 37.5 to 41.5 percent.

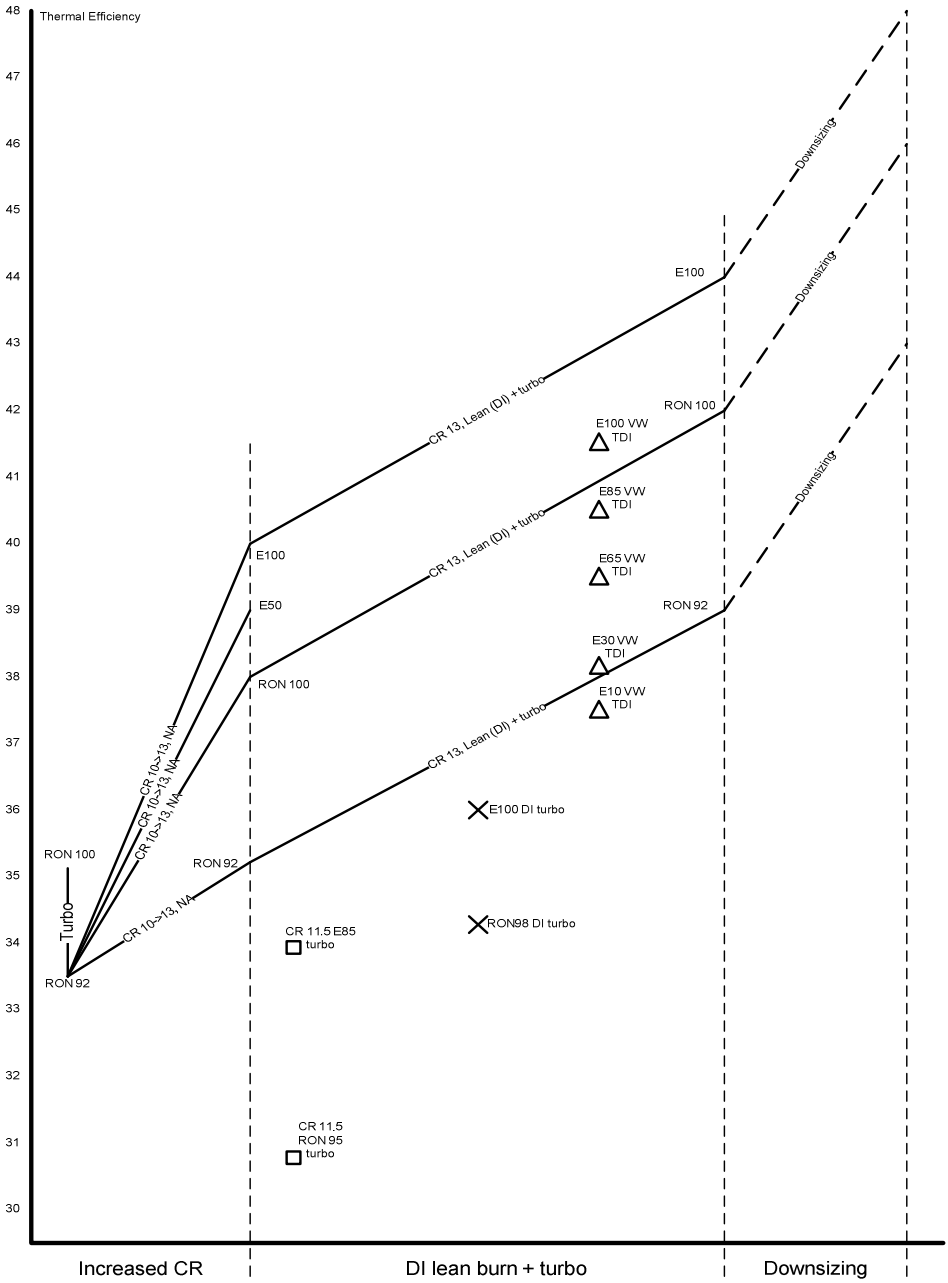


Figure 18: Efficiency Potential of Engines Operating on Ethanol

The last part of the figure shows the potential of downsizing the engines using RON 92, RON 100, and E100. Downsizing is assumed to provide an efficiency gain of 10 percent,⁸⁶ but this estimate may vary with the specific engine designs.

Figure 18 shows that engine efficiencies comparable to those of diesel engines have been obtained with the use of common technologies and ethanol.

Ethanol shows promising qualities for gasoline engine technologies as well. Controlled auto-ignition (CAI) is an advanced gasoline combustion technique closely related to HCCI combustion. As the name implies, ignition of the fuel is obtained by auto-ignition, that is, compression ignition. Mercedes Benz is one car manufacturer that is introducing this principle, under the name DiesOtto. The company claims that since ignition starts from many points simultaneously (instead of at one point as in the spark ignition engine), combustion is very even and happens at relatively low temperatures, resulting in low NO_x formation. CAI operation is used at partial loads (low and medium loads) and spark ignition at high loads, and the switch between the two modes can be made within one combustion cycle.^{92,93} Research by Ford Motor Company has shown that ethanol is well suited for CAI and can improve the load range at which CAI can be used, mainly because of ethanol's tolerance of much higher EGR ratios.⁹⁴

General Motors (GM) has developed an HCCI engine that can run on gasoline and E85. According to GM, an increased fuel efficiency of 15 percent and low NO_x emissions can be credited to the HCCI combustion mode, which (as in the DiesOtto concept) happens only when conditions inside the engine make it possible. A possible solution to the fundamental problems of the HCCI engine, namely, combustion control, seems to be using the combustion mode HCCI only partly (sometimes called pHCCI, or CCS, combined combustion system).⁹⁵ Volkswagen (VW) has also unveiled plans for a pHCCI engine.⁹⁶ As modern cars become more and more sophisticated in the computerized control of combustion parameters (ignition timing, supercharge pressure, EGR rate, fuel injection), advanced combustion modes such as CAI and HCCI will likely become commercially available soon, and ethanol fuels could be well utilized in these regimes. Wolfgang Steiger, VW's director of energy conversion, foresees that the differences between SI and CI engines will disappear, since the only real difference between diesel pHCCI and gasoline CAI is the fuel.

Cold Start Issues

When ethanol is used in SI engines, there are two main potential problems, related to cold engine start: reliable engine start-up (while avoiding excessive cranking) and cold-start emissions related to excessive amounts of fuel and a relatively slow heating (light off) of the three-way catalyst. Start-up of the engine generally is not a problem in FFV vehicles as long as certain measures are taken. Cold start is generally not a problem when low-level blends such as E5 or E10 are used (other than those problems normally experienced with gasoline fuel). An investigation of E10 by the European Oil Company

Organisation for Environment, Health and Safety (CONCAWE) and GFC⁹⁷ showed that ethanol itself does not cause cold-start problems, as much as the low volatility caused by ethanol blending. In other words, it is possible to adjust and maintain a volatility level that complies with the existing gasoline standards.

Even in a tropical climate, such as the Brazilian, measures do have to be taken to accommodate some unfortunate properties of ethanol related to engine start-up. In general, when ethanol constitutes the larger part of the blend, cold-start problems are more likely to arise,⁹⁸ but problems with fuels having ethanol percentages between 10 and 70 percent have not been investigated thoroughly.

In SI-engines, cold-start problems occur because the air–fuel mixture produced in the engine at low ambient temperatures, depending on the type of ethanol fuel, is too lean to successfully initiate and sustain combustion. Compared to gasoline, neat ethanol needs a higher gaseous concentration in air to be flammable, that is, 3.3 percent by volume compared to about 1.0 percent for gasoline; see Table 3. At the same time, being a pure substance, ethanol does not, like gasoline, contain any highly volatile components. It is the volatile species, such as pentane and hexane, that allow gasoline-fuelled engines to start at very low temperatures.⁷⁰ Due to the combination of these two factors, neat ethanol has a lower gaseous concentration than gasoline, at a given ambient temperature. At the same time, ethanol needs a higher gaseous concentration than gasoline to be combustible. The main focus for a solution is therefore boosting the vaporization of the fuel.

In considering a system for overcoming cold-start problems, criteria such as efficiency, cost of technology, convenience of use, and start-up emissions have to be evaluated for the particular geographical location and market situation.

Current Commercial Solutions

Current vehicles running on high-ethanol-content fuel blends use either of two separate cold-start solutions:

- Dual-fuel systems, primarily used in Brazil.
- Lowering the ethanol content of E85 to approximately 70 percent, in combination with a block heater — an approach currently used in on-the-road FFVs in the northern hemisphere in the wintertime.

Dual-Fuel Systems

Dual-fuel systems incorporate two separate fuel systems, including a small auxiliary fuel tank that contains a volatile fuel blend for cold starts. The concept has been used for many years in Brazil in dedicated ethanol vehicles, using gasohol as the auxiliary fuel,

and is still the cold start solution used in modern Brazilian FFVs.⁷² The dual-fuel concept is very effective in facilitating cold starts but requires the car owner to monitor and refill two fuel tanks. This type of system might be unacceptable to consumers in more affluent countries, where the demand for user-passive systems is stronger.

E85 with Block Heater

In cold climates, the blending of large amounts of gasoline into ethanol is generally used as the cold-start solution. According to the season and local climate, E85 contains between 70 and 85 percent ethanol, gasoline constituting the remainder.⁹⁹ Even though this strategy is effective in starting the engine, it invariably leads to very high emissions of unburned and partly burned fuel components during the cold-start and warm-up phases of driving,⁷⁰ mainly because a major part of the injected fuel condenses on the cold cylinder walls and later exits the engine unburned.¹⁰⁰ This tendency can be partly mitigated by the use of a block heater — currently implemented by Ford and Saab in their northern hemisphere FFVs. The block heater is a heating element in the engine coolant that, powered by an external cord connected to the power grid, heats the coolant to the optimal temperature of about 90°C.

The block heater solution has several serious shortcomings, however. Chief among them is the need to plug the vehicle into the power grid and the poor choice between either wasting energy in keeping the coolant always warm when not driving, or alternatively, having to wait a very long time for the engine to heat up sufficiently before starting the engine. Although the block heater solution avoids the need to monitor two fuel tanks, the system can arguably be less user passive than the dual-fuel technology. At the same time, the need for an external power source necessitates national infrastructures of electrical power connections in the public space.

However, the block heater also has advantages. First, the devices needed are inexpensive and efficient in facilitating cold starts. Second, they reduce cold-start emissions considerably, both by vaporizing a greater fraction of the fuel and by heating the cylinder walls enough to prevent the (highly emission-producing) condensation of fuel species on cold cylinder walls.

Current Engine Technology Trends and Other Potential Solutions

Significant measures are currently being taken to avoid cold-start problems with ethanol fuels. Current trends in engine technologies seem to suggest that less significant, or no measures at all, will be needed, other than what can be achieved with electronic engine calibration and management. Among the promising technologies are gasoline direct injection (GDI), variable valve timing (VVT), and, in general, a significant degree of engine management and control due to advances in sensor and ECU (engine control unit, i.e., the engine computer) technology.

Direct Injection

Direct in-cylinder fuel injection technology has recently been considered a solution to the cold-start difficulties with pure ethanol and E85. Although the direct injection technology in itself is fully developed and commercial, its adaptation for higher percentage ethanol blends and FFV is still being developed. A few concept vehicles have been manufactured for showcase purposes, and several automaker and research institutions are working on projects with the ethanol direct injection (EDI) engine, but scientific documentation of these efforts is limited.

A Toyota study⁶¹ on a PFI engine has shown how cold-start problems can be related to fuel injection amounts. Figure 19 shows the required amount of fuel in the initial injection for three different fuels. As the temperature decreases, the amount of fuel needed increases and most significantly so with E100 fuel (hydrated ethanol). The more fuel injected, the greater the risk of liquid deposits inside the cylinder. Complications can then arise due to liquid ethanol deposits on the spark plug, because ethanol acts as a conductor and this can cause misfires, in contrast to gasoline, which acts as an insulator.¹⁰¹ The increased amount of fuel is injected to provide enough flammable mixture or to increase the amount of highly volatile compounds; under normal conditions, this results in worse tailpipe emissions.

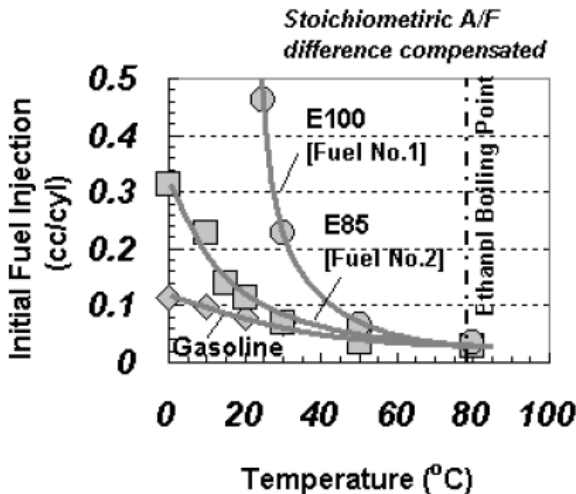


Figure 19: The Increased Amount of Fuel Needed for Successful Engine Start (Source: Tsunooka et al.⁶¹)

During cold conditions injection of more fuel with a DI fuel system can cause problems because the DI system is designed to operate on high pressures. During engine start-up there might not be sufficient pressure to provide the needed amount of fuel, in the time available for injection and the engine therefore does not start. The time duration of fuel injection in DI engines is limited, compared to that in PFI engines, due to the risk of injecting fuel directly into the exhaust pipes. A GM study¹⁰² investigated the possibility of high-pressure start to ensure the injection of a sufficient amount of fuel. The high-pressure option enables a much shorter injection time period and makes it possible to inject at the end of the compression stroke, where the compressed air is very hot, providing much improved fuel evaporation. High-pressure start also enables better fuel atomization, also improving vaporization. The high pressure is provided by delaying the start by about 1 second, leaving the fuel pump time to build up pressure. The study noted that the requirement for the extra amount of fuel at cold temperatures with DI decreased by a factor 10 compared to PFI systems. Despite the lesser amount of fuel required, the maximum fuel flow still constituted a limit for low-temperature start-up.

An AVL study⁷⁴ investigated the spray inside the combustion chamber during engine start-up. During start-up, DI engines can significantly reduce the excessive amounts of fuel because of the high pressure and precise control of the injection. Thereby DI can reduce unburned fuel emissions, which is important, because the catalyst is not yet hot enough to reduce these emissions. In this case, effective reduction depends not only on high-pressure injections but also, perhaps more importantly, on the use of multiple-injection strategies (fuel injection is split up into several smaller injections).

Variable Valve Timing

VVT enables the intake and exhaust valves to open and close at different times and lifting heights according to the conditions and needs of the engine. The technology is already widespread, and Toyota has demonstrated its potential for cold starting with high-level ethanol fuels.⁶¹ By limiting the amount of intake air with aid of VVT, the effective compression ratio is raised, and an increase in peak compression temperature (more than 100°C) was obtained. As a result, the lower limit in terms of temperature for successful cold start was moved downward; see Figure 20.

Figure 20 shows that in this case VVT is not a complete solution to the problem of cold start, because Fuel No.1 (hydrous E100) still has a lower limit of 0°C. Another way of increasing the peak compression temperature has been described by Brusstar.⁷⁷ The technique is simply to increase the start-up cranking speed of the engine; this also helps to improve air–fuel mixing.

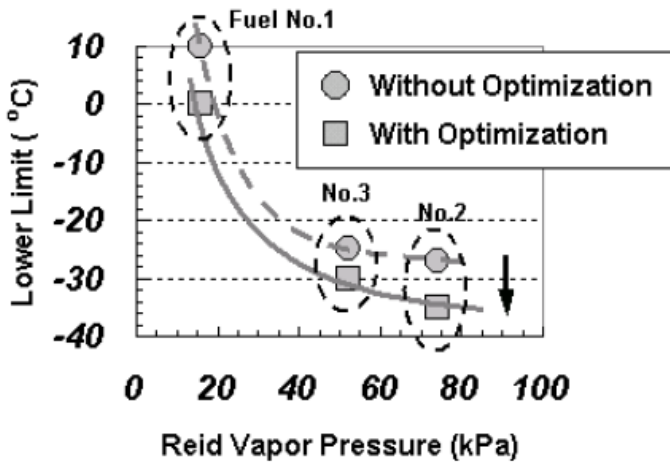


Figure 20: Lower Limit for Cold Start is Improved with VVT
 (Source: Tsunooka et al.⁶¹)

Fuel Additives

The much lower limit obtained by Fuels No. 2 and No. 3 (E85) in Figure 20 is due to an increased vapor pressure through the chemical formulation of the fuel. Reid vapor pressure (RVP) has a much larger effect than VVT. In this case, the higher RVP is obtained by adding butane to the ethanol along with gasoline, since butane was found to have a very significant impact on RVP, more so than regular gasoline constituents.⁶¹ The difference is so significant that hydrous E100 fuel containing a small amount of butane would have better cold-start properties than an E85 fuel containing regular gasoline.

A Brazilian market investigation¹⁰³ focused on MTBE as a possible solution to the cold-start problem (even though MTBE has been criticized for its unfortunate environmental properties). The results showed that using MTBE as an additive, successful engine start could be made with temperatures down to -6°C , more than good enough for the Brazilian market.

Additives could very well be an important solution to the cold-start problem, but further tests, including environmental assessments, should be conducted. However, the RVP of the gasoline used to blend with ethanol is very important.

On-Board Distillation System

An on-board distillation system (OBDS) was implemented and documented by students from the University of Texas at Austin, participating in the three 1998f–2000 Ethanol Challenges — a competition in which American universities were to convert a specific gasoline car to run on anhydrous E85. Very thorough design reports have been published,^{70,104} and in 2000, a patent was issued for the system. (The patent is currently owned by the University of Texas at Austin.)

OBDS showed superior results in the cold-start events of the Ethanol Challenge, having a starting time of less than 2 seconds at -18°C , a better result than even a stock gasoline version of the same car. Also, the emissions level of the team's car was among the lowest in the competition. In the same way as the dual-fuel technology, OBDS employs two separate fuel systems: a main system for normal operation and an auxiliary one for cold starts. The difference is that OBDS produces its own cold-start fuel by distillation. During normal warmed-up operation, the fuel returning to the tank from the fuel rail is run through a distillation column, thus extracting the most volatile fuel components and storing them in a separate cold-start fuel tank. When this 2-liter tank is full, the distillation column is automatically bypassed. During the first 2 minutes of cold starts, the volatile fuel is delivered to the engine; then the engine block and intake manifold are heated sufficiently for the normal E85 blend to be used without danger of misfires or large emissions.

The Ethanol Challenges demonstrated that the system can be made to fit inside the engine compartment of both an sport utility vehicle (SUV) and a sedan-type car, meaning that existing vehicles could potentially be retrofitted with OBDS. The cost of the system for retrofitting was estimated at US\$300. In the case of vehicles being produced with an incorporated OBDS, it was estimated that the extra cost of an OBDS-equipped car would be roughly US\$60 compared to a stock version.

In essence, OBDS provides the cold-start capability of the dual fuel system, by a user-passive and relatively inexpensive technology, which can be retrofitted for existing vehicles. Overall, the patent seems to be superior to other SI cold-start systems, when comparing price, convenience of use, start-up time, emissions, and potential for retrofitting. The distillate is more volatile than gasoline, giving better cold-start performance and lower cold-start and warm-up emissions than gasoline or bi-fuel vehicles. At the same time, the price of the system is fairly low, both when used as a conversion kit but especially if used in mass production vehicles.

A preliminary investigation at The Technical University of Denmark¹⁰⁵ indicated that OBDS could not be used with hydrous ethanol–gasoline blends without incurring a heightened risk of phase separation in the fuel tank. If hydrous fuel blends were to be combined with OBDS, this issue would require more study. Furthermore, the highly volatile fuel might present safety risks.

In relation to the Ethanol Challenges, a study¹⁰¹ at Kettering University suggested a relatively simple and cost-effective method to help ensure proper cold start in FFVs using E85, increased spark energy. Using a system that provides more spark energy and multiple sparks was shown to improve cold start-up and initial idling at least to some degree.

The U.S. NREL developed a patented catalytic converter technology, which, although not specifically designed for ethanol, in any case should reduce harmful ethanol cold-start emissions. The idea is to keep the converter warm and fully efficient as long as possible after a trip. A normal converter drops in temperature rather fast, but this solution keeps the converter warm enough to be fully effective more than 24 hours after the last trip.¹⁰⁶

Emissions

In the end use of ethanol fuels, there are two main concerns regarding fuel-related emissions; tailpipe emissions and evaporative emissions. Tailpipe emissions have been reduced over the years by increasingly strict regulations, while evaporative emissions have not had the same degree of focus. With the introduction of ethanol, evaporative emissions are in some cases at a level comparable to tailpipe emissions and must therefore be addressed.

In 2008 an Australian Government study measured both evaporative and exhaust emissions from vehicles using ethanol blend fuels E5 and E10.¹⁸⁸

Tailpipe Emissions

Tailpipe emissions from internal-combustion-driven vehicles are primarily problematic because they cause harm to human health, especially in densely populated areas, and they cause environmental damage locally, regionally, and globally. Of greatest immediate risk for humans are particles, gaseous irritants, and aromatic hydrocarbons. Examples of health problems related to these risks are lung cancer, accelerated tumor growth, blood flow problems, and air-way-related diseases, especially asthma and reduced lung function.¹⁰⁷ Besides the personal tragedies, disabilities, and discomforts related to these illnesses, there are substantial economic costs for society related to air pollution from road vehicles.

Particulate or soot emissions from gasoline vehicles generally do not present the same concerns as those from diesel vehicles. Because combustion in the SI engine is homogeneous, the mass of the particle emissions is much less compared to that for diesel engines. Research indicates, however, that it is not so much the mass of particles emitted as the size of individual particles that is important. The same particle mass divided on more but smaller particles has a relatively larger surface area, which enables

a larger transport of carcinogenic poly aromatic hydrocarbons) molecules into the lungs. Furthermore, smaller particles are more damaging because of their ability to penetrate deeper into the lungs. According to the literature, the trend is that ethanol blends provide particulate matter (PM) emission reductions of up to 50 percent, compared to regular gasoline.¹⁰⁸ In 2005, the Australian Biofuels Taskforce report reviewed the literature and found that earlier assumptions of ethanol having no significant impact on PM emissions must be revised, because they found PM emissions to be 40 percent lower with E10.¹⁰⁹

In 2008 an Australian study¹⁸⁸ investigated PM emissions from E5 and E10 use. The study utilized two real-time particle analyzers, the Engine Exhaust Particle Sizer (EEPS) and the Electrical Low Pressure Impactor (ELPI). Both techniques impact a charge, measure the particles, and count the number of particles within particular size bins. Plots of the number distribution as a function of particle diameter were determined. The ELPI classifies particles according to their dynamic mass. PM emissions from tailpipes of 2006+ vehicles showed an average 19 percent decrease with E5 use, and an average 33 percent PM decrease with E10 use. Investigations have shown that aromatic content in fuel is linked to PM emissions.¹¹⁰ Aromatics in gasoline helps raise the octane rating as does ethanol; thus by using ethanol there is the potential for decreasing the aromatic content, thus decreasing PM emissions.

A well-known phenomenon created by vehicles in urban areas is (photochemical) smog. Emissions of HC, N₂O, and CO driven by the energy of sunlight react (by complex photochemical reactions) to form ozone, among other substances. Ozone is poisonous and can cause or aggravate respiratory diseases when near ground level. To reduce the amount of ground-level ozone, a new kind of gasoline called reformulated gasoline (RFG) was introduced in the 1990s, among other places in the United States and Europe. RFG^{iv} contains oxygenates, which reduce tailpipe emission of CO and HC due to better combustion.¹¹¹ Experimental investigations have shown that ethanol and MTBE as oxygenates would provide a similar effect on ozone formation.¹¹⁰ However, discussions on whether usage of ethanol in gasoline blends improves or worsens this situation are continuing.

Furthermore, there are mixed opinions on whether ethanol usage increases NO_x emissions.¹¹⁰ A 2008 Australian study¹⁸⁸ found that production of NO_x and ozone increased with E10 use. The results for E5 were variable for nitrogen dioxide (NO₂) emissions and for E10 led to an increase in NO₂. Many investigations found that serious incidents of smog in several U.S. cities have been reduced since the introduction of E10,¹¹² and a review¹¹³ of the Brazilian ethanol program ProAlcool stated that the general pollution in the metropolitan area of Sao Paolo is about 20 percent lower due to the use of ethanol (although specific details are not available). Furthermore, tests by the Brazilian Automotive Industry Association Energy & Environment Commission (ANFAVEA) showed that raw engine out emissions of CO and HC were about 15 percent

^{iv} Gasoline blending substance containing oxygen, most commonly MTBE, ETBE, and ethanol.

lower with Brazilian gasohol compared to regular gasoline. NO_x emissions increased by 4 percent using gasohol. Comparing gasoline with hydrous ethanol (E100), the investigation found emissions for CO, HC, and NO_x reduced to 51 percent, 53 percent, and 86 percent, respectively.¹¹⁴

Many studies focus on air toxins emitted from vehicles, species such as benzene, 1,3-butadiene, acetaldehyde, and formaldehyde. Air toxins are substances that pose particular health risks to humans. Benzene is believed to be the most significant compound, calculated by the U.S. EPA to be about 70 percent of total air toxins emitted from gasoline vehicles.¹¹⁰ Some studies also include emissions of toluene and xylene. Benzene and 1,3-butadiene are considered carcinogenic, while acetaldehyde and formaldehyde are classified as probable carcinogens.^{115,116} Air toxins also contribute to the formation of ground-level ozone. Review of the literature showed general agreement, that usage of ethanol reduces emissions of benzene and 1,3-butadiene while formaldehyde emissions increase moderately and acetaldehyde emissions increase dramatically. The U.S. EPA has attached a risk factor to each pollutant to develop an overall risk assessment; see Table 5.

Table 5: Air Toxins Risk Factors from the U.S. EPA (Source: Hammel-Smith et al.¹¹⁷)

Compound	EPA Risk (µg/m ³)-1	EPA factor (normalized)
1,3-butadiene	2.8x10 ⁻⁴	1.000
Benzene	8.3x10 ⁻⁶	0.030
Formaldehyde	1.3x10 ⁻⁵	0.046
Acetaldehyde	2.2x10 ⁻⁶	0.008

Using these factors, a number of studies found that the reduction of 1,3-butadiene and benzene emissions outweighs the increases of formaldehyde and acetaldehyde emissions. The EPA^v Complex Model found that with the use of 10 percent ethanol in gasoline, the weighed risk of air toxins, is reduced by 21 percent.^{108,110} A Canadian investigation found that increased emissions of aldehydes are of low risk since the amounts are small and the substance can be efficiently removed by catalytic converters.⁶² The 2008 Australian study¹⁸⁸ found small increases in peak ozone concentrations from airshed modeled results for E5 and E10 emission scenarios. This finding implies that the observed reduction in tailpipe emissions of volatile organic compounds (VOC) and CO were not sufficient to cancel increases in the evaporative VOC mass emissions associated with higher vapor pressure of ethanol-blended fuel compared to gasoline. The study¹⁸⁸ found that more than 97 percent of the estimated health savings were based on PM_{2.5} impacts on mortality and morbidity (e.g., asthma, cardiovascular disease). The other small of impacts were associated with health savings as a result of overall air toxic reductions.

^v U.S. EPA modeling tool used to predict environmental changes due to fuel specifications.

Overall Findings

Comparison of ethanol usage in general to gasoline showed the following results across all blending percentages, according to the literature^{108,109,118-132,188}

- HC emissions are generally reduced, up to 70 percent, although one study showed increases up to 20 percent.
- Almost all studies showed CO reductions, up to 60 percent, while a few showed increases up to 27 percent. The Australian study¹⁸⁸ found CO reductions of 95 percent for both E5 and E10.
- NO_x emission results were mixed. Some stated reductions of about 60 percent, while others stated increases of about 30 percent. FFVs and dedicated vehicles for high-level ethanol blends or neat ethanol showed tolerance for higher EGR ratios, reducing NO_x.
- PM was generally not a focus for gasoline vehicles, although some found 40–50 percent reductions.
- CO₂ emissions were found to be about 5 percent less per kilometer.
- Methane ranged from same amount of emission to a 120 percent increase.
- Benzene was found to be reduced in all cases from 25 to 80 percent.
- Emissions of 1,3-butadiene were in all cases reduced from 10 to 80 percent.
- Toluene emissions were reduced by 30–80 percent.
- Xylene emissions were reduced up to 80 percent.
- Formaldehyde emissions increased up to 70 percent.
- Acetaldehyde emissions increased dramatically, up to 3500 percent.

Evaporative Emissions

A common critique of ethanol fuels is that although use of ethanol fuels often improves tailpipe emissions, it increases evaporative emissions. However, this is not necessarily correct. Evaporative emissions from the entire vehicle have been the subject of increased research in recent years. The focus is on emissions of VOC, which are hydrocarbons that evaporate from the vehicle. The rate of evaporation is strongly related to the RVP of the fuel. The vapor pressure of ethanol–gasoline blends is shown in Figure 21.

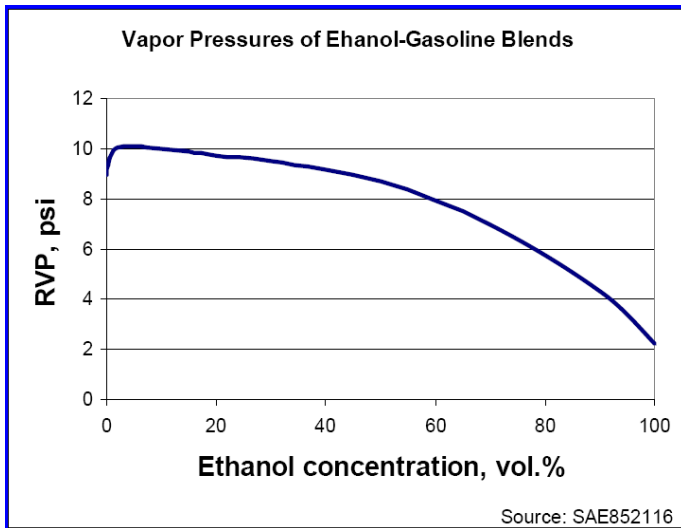


Figure 21: Vapor Pressure of Ethanol/Gasoline Blends (Source: Kassel¹³³)

The figure shows how low ethanol levels increase the RVP of ethanol–gasoline fuels having a maximum of 5 to 10 percent ethanol. The RVP can vary depending on the composition of the base gasoline fuel blend stock. Ethanol itself has a lower RVP than gasoline, so ethanol would be expected to always lower the RVP in a gasoline blend. The reason for the initial increase in RVP of low-level ethanol–gasoline blends is that ethanol forms azeotropic phases with some of the HC of the gasoline, resulting in very low boiling points for these phases.⁸²

In practice, however, E10-type blends generally do not have a higher vapor pressure than pure gasoline, because manufacturers deliberately avoid the problem by using less volatile gasoline for mixing with ethanol, in order to meet the specified limit for vapor pressure of fuels. However, when mixing E10 and pure gasoline, the act of filling up the fuel tank could conceivably lead to the formation of E5 blend with a vapor pressure above the specified limit.¹³⁴ To guard against this possibility, fuels must be formulated with a sufficient margin to the specified vapor pressure limits.

Evaporative emissions can be divided into four types: (1) permeation of fuel components through fuel system components of vehicles, (2) leaks of liquid, vapor, (3) fuel tank venting canister losses,¹³⁵ and (4) evaporative emissions associated with refueling of vehicles. Leaks are relatively easily to deal with by regular vehicle maintenance. Although the vapor pressure of ethanol fuels can be adjusted to levels of regular gasoline, studies suggests that this not the deciding factor in relation to permeation; it depends on ethanol content.¹³⁶

Increased HC permeation due to ethanol fuels is not fully understood, but positive results with reducing these emissions have been obtained in, for example, low-emission vehicles (LEVs) and partial zero-emissions vehicles (PZEVs).¹³⁵ As reported in the literature, low-percentage ethanol blends, 5–10 percent, tend to increase permeation, while high-percentage blends, mainly E85, seem to cause lower emissions compared to regular gasoline. Literature reports on permeation data using mid-percentage ethanol fuels (E20–E70) have not been found, other than what is shown in Figure 22.

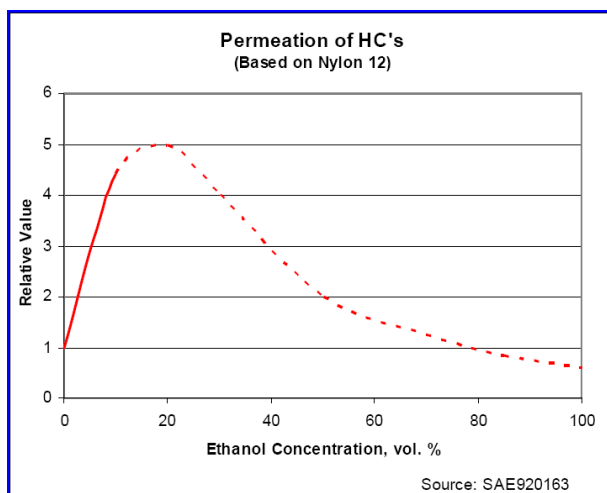


Figure 22: Permeation of Hydrocarbons
(Source: Kassel¹³³)

A part of the evaporative emissions are stopped by the carbon canister. Fuel vapors within the fuel system of vehicles are circulated through the canister containing activated carbon, which absorbs fuel vapors while the engine is not running and releases these vapors into the engine when it is running, purging the filter. See Figure 23.

Unfortunately ethanol seems to be prone to accumulate in the canister, compromising efficiency.¹³⁷ Studies have found that it is very difficult to remove the ethanol from the canister, even when running on normal gasoline. It is not clear how long term or to exactly what degree canister efficiency is reduced. It might depend on the individual model design and fuel type. Because of this phenomenon, ethanol usage indirectly results in increased VOC emissions longer than ethanol is actually used in the vehicle.

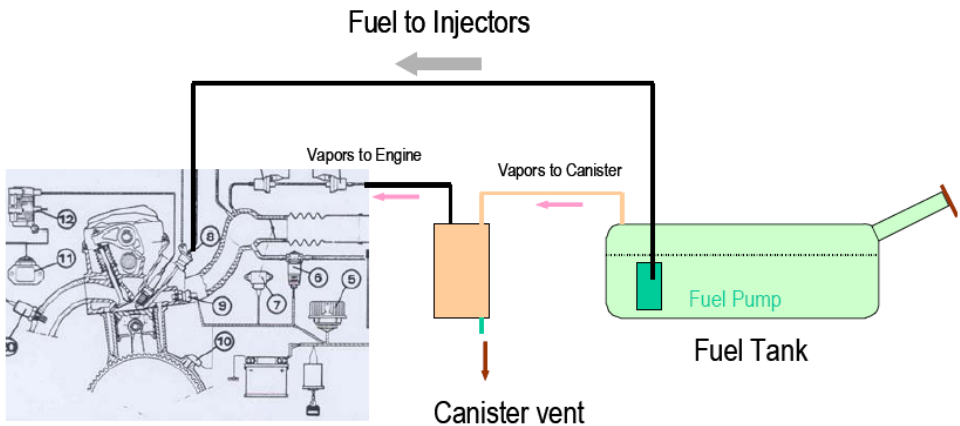


Figure 23: Evaporative Emissions Control System (Source: CONCAWE/EUCAR/JRC Joint Programme¹³⁷)

Evaporative emissions were investigated in Sweden in 2006 and found to be as significant as up to one-third of the total emissions from all road traffic in Sweden.¹³⁸ Out of 50 cars tested, 20 exceeded the limit set by an EU directive. The cars were between 6 months and 5 years old and had been driven 15,000–80,000 km. The limit was in some cases exceeded by 20 times the limit value.

A study⁶³ of the effects of using E20 in the Australian fleet showed that evaporative emissions for E20 would be equal to or in some cases less than those for gasoline. The more recent 2008 Australian study¹⁸⁸ found that evaporative emissions of acid aldehydes such as acetaldehyde and formaldehyde increased with the use of E5 and E10 compared to gasoline. Total hydrocarbons also increased with E5 and E10 blends. Evaporative emissions of alcohols were influenced by individual vehicle factors that are likely to depend on the design of vapor canisters of the vehicles.

Another comprehensive study¹³⁹ of seven modern European vehicles was made for the European Commission by CONCAWE/EUCAR/JRC. The fuels tested were splash-blended E5 and E10 fuels with unadjusted RVP values and E5 and E10 with RVP adjusted to meet standard values. Results showed that evaporative emissions from the vehicles depended strongly on the vapor pressure of the fuel. The tests did not show any specific connection between ethanol content and evaporative emissions at the same RVP. This lack of ethanol effect is supported by Soloman's findings.¹³⁶ which indicated that the emissions were mainly due to canister losses and not permeation.

Ten U.S. vehicles were tested,¹³⁶ both old and new (model year 1978–2001). By using E6, permeation increased by 65 percent on average for all vehicles, compared to using gasoline. In the newer vehicles (post-1996), permeation increased by 157 percent with E6.

Serious issues remain to be solved when using low-percentage ethanol–gasoline blends. Because emissions from vehicles are under increasingly stringent regulations, this issue might pose a hurdle for E5 and E10 blends especially. However, problems do seem solvable, particularly for the Californian LEV and PZEV vehicles.

The Australian study on the health impacts of ethanol blend fuel¹⁸⁸ selected a representative sample of vehicles from the current Australian fleet and compared actual emissions (exhaust and evaporative) from E5, E10, and gasoline (ULP). Emissions data were used to model the Sydney urban airshed under different scenarios, for example, all vehicles using E10, to determine the potential health impacts on the population.

The results of this study were as follows:

- Emissions from E5 and E10 showed that the levels of some pollutants such as NO_x and aldehydes, marginally increased, while other emissions, such as PM, CO, and benzene, decreased.
- PM_{2.5} emissions from tailpipe tests showed an average 19 percent decrease with E5 use and an average 33 percent decrease with E10 use.
- Increases in population exposure were seen for ozone for all E5 and E10 scenarios and for NO₂ for the E10 scenarios.
- A total of 97 percent of potential health cost savings were due to decreases in PM-related mortality.
- Potential health cost savings would be reduced over time as newer vehicles with advanced emission control systems replaced older vehicles.

Ethanol Usage in Two-wheelers

Small two-wheelers are usually powered by either two- or four-stroke engines, while larger motorcycles are powered mostly by four-stroke engines, all of the SI type. Therefore, the same possibilities and problems can be expected to be present for SI engines in two-wheelers as well as for cars. In general, manufacturers do not recommend the use of ethanol fuels, with a few exceptions for E5.^{140,141,68}

The main concern for two-wheelers is the exhaust emissions, especially for two-stroke engines. Research in this area is relatively limited, but the available literature^{119,142–145} can be summarized as follows:

- HC and CO emissions are consistently reduced with the use of ethanol, even in small amounts. HC showed increase in one case.
- The more ethanol in the fuel, the cleaner the tailpipe emissions.
- One case showed increased catalytic converter efficiency due to ethanol usage.

- Cases of additional wear and corrosion due to ethanol usage were found.
- Fuel energy efficiency increases.
- Volumetric fuel consumption (L/km) increases with increased ethanol usage.

Ethanol Application in CI Engines

The diesel or CI engine is currently considered the most fuel-efficient engine for transportation for widespread usage, but it has the major disadvantage of being a significant polluter and therefore a major health concern, especially in densely populated areas. Using ethanol fuels in the CI engine has been shown to reduce tailpipe emissions in many cases, and as such, ethanol can be part of a solution to both global CO₂ and local urban pollution issues. Furthermore, ethanol use in CI engines, compared to use in SI engines, represents a more efficient way of utilizing the energy in ethanol simply because of the higher engine efficiency, which on average is about 30% higher for CI engines.

Fuel Compatibility

Ethanol fuels have some fundamentally different properties compared to diesel oil, but most of these can be adjusted to meet today's standard fuel specifications. It is certain that CI engines can be adapted to run on ethanol fuels, in all kinds of ethanol–diesel blends and in many specific cases perform better than on diesel. The following sections highlight fuel properties that have been reported as problematic in the literature.

Energy Content

Depending on its specific composition, diesel oil has an energy content of about 36 MJ/liter, whereas that of ethanol is 21 MJ/liter. Consequently the engine needs injection of relatively larger volumes of fuel, compared to diesel oil, in order to have the same power output. If, for example, the fuel injectors are not large enough to deliver the needed flow of fuel, the maximum power output of the engine decreases. Thus typical differences in vehicle design for ethanol in diesel engines are larger fuel injectors, fuel pump, and fuel tank. The energy content of ethanol–diesel blends decreases by approximately 2 percent for each 5 percent ethanol added by volume, so adjustments or design changes are more profound, with high ethanol percentage fuels or neat ethanol engines.⁴⁹ For that reason the energy content could in practice present an upper limit for the ethanol percentage in standardized fuels, because the low energy content could compromise the functionality of vehicles because of inadequate power and torque. As a

result of the lower energy content, engines running on ethanol fuels have higher (volumetric) fuel consumption in almost all cases.

Cetane Rating

Ethanol's advantage of being a high-octane fuel for spark-ignited engines is one of the most fundamental disadvantages for usage in CI engines. A fuel's ability to auto-ignite, that is, diesel fuels, is designated by its cetane rating. Current diesel engines are designed to run on fuel that has cetane numbers of 40 and 51, according to U.S. ASTM D975 and EU EN590 standards, in the United States and the EU, respectively. The exact cetane number of ethanol has been contested, because the standard methods for measuring and estimating the rating cannot be applied properly,¹⁴⁶ but the cetane rating of neat ethanol is estimated to be about 5 to 15; that is, the fuel will likely not auto-ignite under the conditions existing in standard diesel engines.

Combustion characteristics change due to the lower cetane rating. In short, ignition starts later with ethanol fuels than with diesel, but the time at which the combustion ends is the same. This means that the combustion is more violent at times with ethanol compared to diesel.^{147,148} In blends of ethanol and diesel fuel, the cetane number decreases with increasing percentage of ethanol with linear proportionality.¹⁴⁹ In order to use ethanol fuels in standard diesel engines, it is therefore common practice to use additives, ignition improvers, to overcome ignition problems. Applying an ethanol fuel with too low a cetane number in CI engines can among other things result in poor cold-starting, rough idling,¹⁴⁷ and excessive NO_x emissions.⁵¹

Lubricating Properties

The fuel system of the diesel engine, mainly the fuel injectors and fuel pump, relies on the lubricating properties of the fuel in use. Ethanol is considered a low lubricity fluid, and problems with failing or significantly increased wear on fuel pumps and injectors have been observed, while other tests have shown no problem in this regard.^{148, 48} Current commercial ethanol–diesel blends, containing less than 15 percent ethanol, have been shown to be well above the U.S. ASTM standard limits for lubricity and viscosity of fuels used in diesel engines.⁴⁹ Experiments have shown that blends of winter-type diesel and ethanol (without additives) can contain approximately 45 percent ethanol without falling below the ASTM viscosity limit, whereas summer-type diesel could only contain about 20 percent.⁴⁹

Thus, when ethanol–diesel blends and neat ethanol are used, lubrication additives have to be added or other materials need to be used to ensure prevention of this kind of problem. Scania busses are currently operating on a daily basis on 95 percent ethanol and 5 percent additive with no more maintenance than Scania's regular diesel busses.

Therefore lubrication problems can be overcome by using additives and/ or improved materials.

Viscosity

The viscosity of ethanol is much lower than that of diesel and does not meet the requirements of diesel standards. Because diesel fuel pumps are designed for a fuel with a higher viscosity, pumping problems can occur.⁴⁹ Lubricating properties are affected negatively, and leakage problems might also occur with ethanol fuels. During cold ambient conditions, diesel fuels can begin to solidify, but adding ethanol might actually improve this situation. Fuel spray characteristics are also changed due to lower viscosity of ethanol fuels, although not much literature on this subject has been found.

Vapor Pressure

Ethanol has a higher vapor pressure than diesel; that is, it will evaporate more readily. With E-diesel, the high vapor pressure in combination with a low viscosity can cause vapor locks and cavitations inside the fuel system, resulting in too little fuel being delivered to the engine. If optimal performance is required, these problems need to be prevented.⁵¹ As with SI engines, the high vapor pressure of ethanol should be expected to cause higher evaporative emissions, but few reports on this topic have been found in the literature. Furthermore safety risks are associated with the high vapor pressure.

Application Techniques

Ethanol usage in diesel engines has been studied fairly thoroughly since the early 1980s, and the general techniques for utilization can be divided into three main categories:

- Ethanol and diesel oil blends, emulsions and solutions;
- Neat ethanol, using SI,^{vi} glow plug, or cetane-improving additives; and
- Separate ethanol injection, dual-fuel injection or fumigation.

Ethanol–Diesel Blends

According to the literature, three general types of blends have been studied: pure solutions of ethanol and diesel, solutions with additives, and emulsions. The reports mainly focus on solutions with additives, because these are easier to adapt to the existing fuel- vehicle fleet, and the production price has curbed interest in emulsions.

^{vi} This may rather be classified as an SI engine.

Based the literature, there seems to be a definite potential for improving the efficiency of the CI engine by blending ethanol into the diesel fuel.^{77,8,150–154} This potential is in itself significant, because the diesel engine running on diesel normally is considered the most effective power unit for transportation. The potential is on average about 2 to 4 percentage points, or 5–10 percent relative fuel energy efficiency improvement with low-percentage-ethanol diesel fuels, compared to neat diesel. The improved efficiency is more pronounced at medium and higher loads and increases somewhat with increased ethanol content in the blend. This potential might not be gained simply by changing fuel but might require modifications and adjustments.^{51,58,153,152}

A typical performance issue is the increased fuel consumption (on a liter basis). Although engines might be more efficient in terms of energy, ethanol still carries significantly less energy per liter, thus more fuel is needed for a given distance driven. Power and torque, on the other hand, has been seen to increase especially when the fuel system is modified to accommodate a higher fuel flow.¹⁵⁵ Review of the literature shows cases of both less and more power and torque output from ethanol diesel fuels compared to regular diesel.

In 2003, the Lubrizol Corporation published a review of the existing literature on exhaust gas emissions of engines running on E-diesel blends. The data cover a range of different engine configurations, driving patterns, and E-diesel blends. The main results of the review are presented in Table 6.

Table 6: Average Exhaust Emissions from E-diesel Blends
(Source: Corkwell, Jackson, and Daly¹⁵⁶)

	HC	CO	NOx	PM
All Data				
Average	41%	16%	1%	-13%
Minimum	-16%	-30%	-20%	-72%
Maximum	164%	93%	25%	65%
Equal Cetane Number Data				
Average	6%	-9%	-2%	-25%
Minimum	-16%	-30%	-20%	-31%
Maximum	22%	5%	25%	-20%

Table 6 shows emissions from E-diesel fuels both with and without cetane-improving additives. “Equal cetane number data” represents the cases in which fuels contain additives. Negative values represent a reduction in emissions in E-diesel tests compared to conventional diesel. E-diesel fuels with cetane-improving agents have better performance for the regulated emissions, compared to plain ethanol–diesel blends, especially for HC, CO, and PM. NO_x emissions do not seem to be affected by ethanol content in diesel oil. Also, HC emissions increase or at best are equal for E-diesel compared to regular diesel. CO and NO_x emissions are similar using either E-diesel or

conventional diesel, based on the average in a number of studies. PM emissions are reduced significantly with E-diesel and in at least one case up to 72 percent using an unmodified ethanol–diesel blend.¹⁵⁶ That being said, the discussion focuses on whether emissions of HC and CO from diesel vehicles are of significant importance since they are relatively easily reduced with the use of oxidation catalysts.

Recent publications show similar trends, that is, PM emissions and smoke are significantly reduced in almost any case with the use of ethanol in diesel.^{148,150,153,154,157–159} The results of the individual studies vary due to different conditions of engine loads, engine modifications, and fuel additives, among other things. Most studies focused on lower ethanol ratio blends, typically less than 20 percent, while only a few investigated blends containing up to 50 percent ethanol. However, a significant amount of additive is required to sustain such blends. E-diesel and other ethanol diesel fuel blends have a substantial emission reduction potential, both in older and modern engines, provided the engine is adjusted or in other ways made ready for proper ethanol usage. One study⁵¹ stated, "A multitude of pitfalls exist with the use of ethanol in diesel solution. Fortunately, these pitfalls can be overcome with low or no incremental cost."

Reducing the amount of PM emissions and smoke in CI engines has some positive side effects:

- Possibility of moving the NO_x/PM trade-off balance in order to reduce NO_x emissions more efficiently; and Possibility of increasing power and torque output in smoke-limited engines.

The NO_x/PM trade-off is a well known phenomenon, a situation in which NO_x emissions increase if the engine parameters are adjusted to lower PM emissions and vice versa. By using ethanol, this balance can be tipped much more in favor of lower NO_x with less PM penalty, see Figure 24.

Figure 24 shows how the NO_x/PM emissions are affected by using E15 and E20 compared to regular diesel while changing the EGR ratio. NO_x emissions are normally difficult to reduce, especially without costly emission control equipment, but as shown in Figure 24, NO_x could be reduced from about 4.7 to 1.3 g/kWh, practically without any increase in PM emissions. This trend has potential for all diesel engines running on diesel–ethanol fuels. With the use of diesel particulate filters this balance might be further exploited.

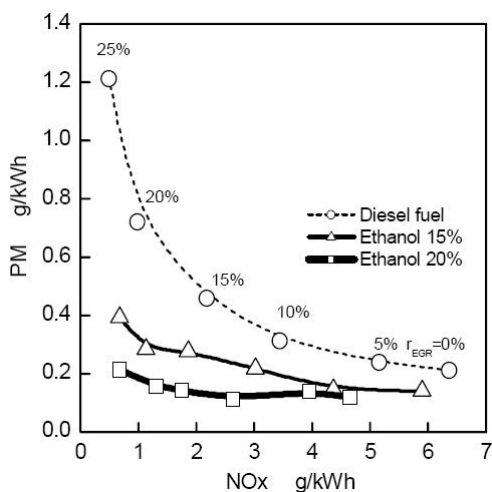


Figure 24: NO_x/PM Trade-Off (Source: Mohammadi¹⁶⁰)

Evaporative emissions from vehicles were found to be a problem in an Australian study.¹⁶¹ Ethanol causes increased vapor pressure in low-level ethanol–gasoline blends, and the same phenomenon occurs with ethanol–diesel blends. Increased vapor pressure usually results in higher evaporative emissions, but in contrast with gasoline vehicles, diesel vehicles usually have no evaporative emission control measures, because this problem is not normally associated with diesel vehicle. Studies that have investigated this matter properly are not available.

Biodiesel/Ethanol/Diesel Blends

While blending biodiesel into ethanol-diesel is relatively new, it has promising perspectives for both fuels. Biodiesel fuels are usually methyl esters, which are derived from vegetable or animal oils or fats that can be blended into regular diesel to a certain degree and used often without any engine or fuel system modifications. However, the use of neat biodiesel can create, among other effects, problems due the relatively high viscosity. In direct-injected CI engines, this can create fuel spray atomization problems and thus inefficient combustion, injector coking, and deposits.¹⁶²

Biodiesel blended into ethanol and conventional diesel (sometimes called BE-diesel or EB-diesel) has been shown to be a solution to many problems associated with the properties of ethanol–diesel blends. Biodiesel can be blended with ethanol at any ratio and can act as a renewable, phase-stabilizing additive for ethanol–diesel blends, for example, to improve the solubility.^{163,164} Most commonly tested are blends with relatively little ethanol content, that is, about 510 percent, 10–20 percent biodiesel, and 70–80 percent conventional diesel. Thus these are fuels with a 20–30 percent

renewable content, which is relatively high compared to current technical and political expectations. The main advantages of using biodiesel in E-diesel are potentially as follow:

- Biodiesel has good lubricity, mitigating the low lubricity of ethanol–diesel blends.
- Biodiesel has a high viscosity, mitigating the low viscosity of ethanol–diesel blends.
- The high cetane rating of biodiesel (compared to that of regular diesel), up to 66, is useful in ethanol–diesel blends to compensate for the low cetane rating of ethanol.
- Biodiesel can prevent phase separation of ethanol–diesel blends and could increase the renewable content of diesel fuels significantly.
- Formaldehyde and acetaldehyde emissions increase with ethanol, while biodiesel reduces these emissions.
- BE-diesel offers a fuel with an energy content similar to that of fossil diesel.
- Perhaps most importantly, biodiesel seems to somewhat increase the flashpoint of E-diesel fuel.

A major barrier for biodiesel use in cold climates is the low-temperature properties, often described by the cloud point. Conversely, ethanol blended into biodiesel–diesel blends can potentially provide the following advantages^{159,162,165–168}:

- Better cold weather properties, that is, lower cloud and pour points;
- Lower viscosity, providing improved fuel spray characteristics and thus possibly improved combustion efficiency;
- Low smoke and NO_x emissions; and
- Improvement of problems with deposits and carbon build-ups in the engine.

In a study¹⁶⁹ tallow ester was blended with ethanol in the ratio of 65:35 percent to match the viscosity equal to U.S. standard No.2 diesel. This blend was then mixed with conventional diesel, and the properties were investigated. As an example, a blend of 32.5 percent ester, 17.5 percent ethanol, and 50 percent diesel oil had a better cetane rating and similar viscosity and density as the specified No.2 diesel.

Biodiesel can also be used to prevent phase separation of E-diesel, according to He et al.¹⁶⁵ and Fernando et al.,¹⁶⁶ who found BE-diesel to be stable well below 0°C. A commercial ethanol diesel, O₂-diesel, is currently being tested in a fleet operating in Washington, D.C. It has been shown to perform satisfactorily with regard to cold flow properties and has a stability down to –26°C.¹⁷⁰

In a few cases biodiesel has even been found to prevent lowering the flash point in ethanol–diesel blends.^{159,166} This finding represents huge possibilities, because in practice it is only the low flash point that limits the widespread use of low-level ethanol fuels for diesel engines. Even 5–10 percent ethanol in diesel reduces the flash point almost to that of neat ethanol, that is, 13°C, whereas the flash point for pure diesel is up to about 75°C. Remarkably, biodiesel even in very small amounts has been shown to mitigate that trend. The flash point was 56°C for 5 percent E-diesel with 1 percent biodiesel and 45°C for 10 percent E-diesel with 1 percent biodiesel.¹⁶⁷ In this study, the use of higher percentages of biodiesel did not improve the flash point further, while higher percentages of ethanol lowered the flash point significantly.

The most important perspective of ethanol fuel is probably the rate of fossil diesel replacement without altering any engine or vehicle and maintaining the PM emission advantage of ethanol–diesel blends. With further research, or relatively few additives EB-diesel might well be able to comply with existing diesel fuel standards.

Table 7: EB-Diesel Compared to Conventional Diesel, Selected Properties (Sources: Waterland, Venkatesh, and Aunnasch⁵⁹; Jordanov et al.¹⁶⁷; AFDC¹⁷¹; Nyllund et al.¹⁷²)

Property	ASTM D975	EN 590	E-diesel (E15)	BE10-diesel
Density @ 15°C g/cm ³	0.803-0.887	0.820-0.845	0.851	0.833
Cetane No.	min. 40	min. 51	45	50
Flash Point °C	min. 52	min. 55	13	45
Heat of Combustion MJ/kg	43	-	40.4	43.1
Viscosity @ 40°C mm ² /s	1.9-4.1	2.0-4.5	2.25	2.21
Lubricity µm	<360	max. 460	-	<360
Cloud Point °C	-19	-	-5	-24

Neat Ethanol

Using neat ethanol in diesel engines requires either an ignition system with a spark plug, glow plug, an ignition improver agent added to the fuel, or another kind of ignition aid in order to ignite the fuel properly and/or avoid lengthy ignition delays. Neat ethanol also requires compatible fuel system materials and special engine calibration. Using an ignition improving agent increases the cetane number, and experiences with Scania busses in Sweden¹⁷³ show that with about 5 percent ignition improver, the engine requirements are met. Several types and brands of ignition improvers are on the market, and therefore the properties, prices, and effects have to be taken into consideration.

The concept of the spark-assisted diesel engine (SADE) bridges the two main engine types — the SI engine and the CI engine. The SADE concept can be based on either engine type and is possibly the engine concept of the near future, where the borders defining the SI and CI engines are disappearing. An example is the CAI system in Mercedes Benz's DiesOtto concept,^{92,93} in which the engine switches automatically between SI and CI modes during operation. The spark plug is a very efficient way to address ethanol's poor auto-ignition properties in CI engines, and even neat ethanol can then be used. Experimental work at the Helsinki University of Technology showed the unique flexibility of this concept. By using spark plugs, a diesel engine operated successfully on gasoline, diesel, and neat ethanol.¹⁵¹ The SADE concept showed superior efficiency and power compared to the baseline diesel engine and operated with smoke-free emissions.

Using an SI system requires some redesign of the CI engine but has the advantage of not needing an ignition improver while achieving diesel-like or better engine efficiencies.^{52,77,151} Since the combustion chamber is originally optimized for diesel fuel combustion, the geometry is not particularly well suited for ethanol combustion, however. An important feature of the diesel combustion chamber is its ability to swirl (create turbulence) the air-fuel mixture in order to enhance mixing and combustion. The high degree of turbulence with ethanol can cause knocking.⁵³ Because the spark-assisted diesel engine can run stoichiometrically, a regular three-way catalyst can be used to reduce emissions. Together with the potentially smokeless combustion, the catalyst makes this alternative way of ethanol usage perhaps the cleanest possible while also being the most efficient.

Another method for ignition assistance for ethanol in CI engines is the catalytic combustion that can be achieved with a glow plug coated with a catalytic material. The catalyst reduces the temperature at which the combustion can start, sometimes up to several hundred degrees Celsius below normal ignition temperatures.⁵² Catalytic ignition can provide the advantage of decreasing the ignition delay, which is normally an issue for ethanol usage in CI engines.¹⁷⁴ A solution developed by a company called Sonex Research is a special piston in which small cavities are part of the design. The cavities actively enhance pre-ignition chemical reactions and thus act as a cetane-improving technology in a neat ethanol engine.¹⁷⁵

Another alternative but elegant solution for neat ethanol use is to manufacture the cetane-improving agent on-board the vehicle. The Combustion Engine Research Center at Chalmers University, a center established by the Swedish auto and fuel industry in cooperation with Swedish authorities, has conducted research showing how cetane-enhancing ethers can be produced catalytically on-board from ethanol during vehicle operation.¹⁷⁶

Performance of Neat Ethanol Applications

There are four main potential advantages of using neat ethanol, rather than regular diesel, in CI engines:

- Maximum fossil fuel replacement;
- Very low PM (or smoke) and NO_x emissions;
- High energy efficiency; and
- Use of wet ethanol, thus providing a high degree of CO₂ mitigation.

Compared to ethanol fuel blends, neat ethanol provides maximum replacement of fossil fuel. In most studies of engines running on neat or high-percentage ethanol fuels, low NO_x emissions have been reported due to a high latent heat and lower combustion temperatures. However, in cases in which fuel properties are not properly accommodated by engine adjustments, low NO_x can also be caused by a too late ignition of ethanol because it lacks the ability to self-ignite. This late ignition moves the combustion later into the expansion stroke of the CI engine, reducing pressures and temperatures in the cylinder and causing lower engine efficiency.¹⁵⁰ So-called smoke-free operation can be obtained with neat ethanol. In many cases research on dedicated ethanol engines has consistently shown increased efficiencies, compared to baseline diesel fuel configurations.

Dual Systems

Although the concept of having two systems handling two different fuels can seem unrealistic for widespread commercial use, it still offers advantages over less complicated solutions. The one major disadvantage for the end user is the need to fill two separate fuel tanks. However, a relatively lower fuel price on ethanol could probably motivate car users to use it anyway, especially if the result is also increased fuel efficiency.

Fumigation of ethanol into diesel engines is accomplished by letting ethanol be evaporated into the airstream in the intake manifold of the engine. An extra fuel system for ethanol including fuel tank, lines, controls, and a carburetor or fuel injection nozzle is needed for this kind of operation. The amount of ethanol used at different loads and speeds is modified to optimize performance. At low loads no or very little ethanol is supplied in order to prevent flame quenching and misfiring. At high loads the amount of ethanol is also relatively small to prevent pre-ignition and knocking. At medium range loads up to 50–60 percent ethanol (by energy) can be fumigated. An important advantage of fumigation is that hydrous ethanol can be used.^{55,177} Use of fumigation in turbocharged diesel engines, which now constitute practically all diesel engines, has been shown to be problematic in some cases. Mechanical damage has been observed due to impingement of liquid spray on the turbo compressor.⁵³ Advantages of this technique are increased engine efficiency in some cases, relatively large replacement of

diesel fuel, relatively easy retrofitting of the system, and the fact that the engine is flexible enough to run on regular diesel if needed.

Dual injection, or pilot injection, is a combination of two individual fuel systems, one for ethanol injection and one for diesel injection. Dual injection refers to the direct injection of two fuels into the combustion chamber.¹⁷⁷ By using a pilot injection of diesel to help ignite a later injection of neat ethanol, up to 90 percent ethanol (by energy) can be used at high loads and 50–60 percent at low and medium loads.^{53,150} This technique offers great engine flexibility, because a range of ethanol percentages can be used as well as neat diesel if necessary. The flexibility extends to the engine parameters, and this creates opportunities for controlling the combustion to a very high degree, for example, more effectively aiming at the highest efficiency or the lowest NO_x and PM emissions.¹⁶⁰ This technique is a variant of what is called partial premixed controlled combustion (PCCI).

Lubrication additives and/or improved materials might be needed for this technique. The main advantages are high engine efficiencies, high displacement of fossil diesel, and low NO_x and PM emissions.⁵⁵

Hydrated Ethanol in CI Engines

The purpose of using hydrous or wet ethanol primarily lies in the production stage and not as much in the application. Hydrous ethanol is, however, a more affordable fuel compared to anhydrous ethanol, and this is used as an incentive in Brazil.

An Indian study¹⁷⁸ was carried out on 150–200° proof^{vii} ethanol–diesel blends from 10 to 20 percent ethanol. First, the tendency of phase separation was investigated, and the results showed that 150° and 160° ethanol was not suitable for blending even as low as 10 percent; 170° could be used with up to 15 percent ethanol in the blend. Density of the blends increased with increased water content in the blends. Viscosity of the ethanol blends was shown to be very similar to that of neat diesel. Power output (brake horsepower) was shown to be very similar, from 25 to 100 percent loads with all types of blends. Fuel efficiency was found to be higher with ethanol–diesel blends than with neat diesel. This example shows that even with up to 15 percent water in ethanol–diesel blends, issues such as power output, viscosity, and phase separation did not present problems, while the efficiency of the engine even increased. Regarding the phase stability, note that the study does not indicate at which temperature the fuel is stable. Assuming that Indian standards are used, temperatures could be relatively high and the results likely would not be similar in colder climates.

^{vii} Proof is a U.S. measure for how much water is present in an ethanol–water blend. Proof is accompanied by a number that is twice the percentage by volume of ethanol; for example, 200° proof is pure ethanol and 160° proof is 80 percent ethanol in 20 percent water (Wikipedia, Oct 2007).

Although research in this area is limited, studies suggest that there are potential advantages, mainly low NO_x emissions and high engine efficiency. Experience in Sweden with buses running on 95 percent hydrated ethanol (5 percent water) showed no additional problems compared to regular diesel buses. At present, hydrated ethanol fuels must be used in special applications but as such have a great potential, especially for CO₂ mitigation. The ideal use of ethanol in transportation could very well be hydrated ethanol in CI engines for two important reasons: It is highly energy efficient on a life cycle basis in the production phase and it is equally as fuel efficient as or better than diesel in the application phase.

Fleet Trials

Comprehensive fleet trials have been conducted with ethanol in diesel engines, in different climates around the world; various states in the United States, Australia, Sweden, Denmark, Ireland, and not least India.⁶² Millions of miles have been driven so far, and fleet trials are ongoing, most recently and on the greatest scale so far, in the state of Karnataka in India.

Karnataka, India, should by now have the largest ethanol–diesel fleet in the world, comprising about 5,200 buses using O₂-diesel (Energiesel), which is diesel containing 7.7 percent ethanol and 0.5 percent biomass-based additive.¹⁷⁹ The fleet uses about 120 million liters of E-diesel per year. The components are blended at the dispensing pump by an automated computerized injection-blending unit that can also dispense regular diesel. This method has several advantages, including protection from contaminants, independence from fuel-blending companies, and use of regular fuel infrastructure.⁴² Energenics, the O₂-diesel producers, claim that the blending method is compatible with all base diesel fuels and that Energiesel can be used in diesel engines without any modifications, while maintaining engine power output and fuel economy, comparable that of regular diesel. The benefits of running on O₂-diesel are in this case smoke reductions of 50 percent and slight fuel cost reductions of about 0.25 rupee (0.0045 Euro) per liter.¹⁷⁹

Scania, as another example, has been producing heavy-duty engines for buses running on ethanol since the mid-1980s, with serial production since 1990. More than 600 buses have been operating in Swedish cities with significantly better emission performance than regular diesel buses. The third-generation buses are currently running on a blend of hydrous ethanol and 5 percent ignition improver (E95), a fuel that is utilized as efficiently as diesel fuel, with up to 44 percent thermal efficiency, and the engines now possess fully proven technology with no operational drawbacks. Buses are fitted with EGR and an oxidizing catalyst (suited to reduce acetaldehyde emissions), resulting in low NO_x emissions and very low levels of HC and CO. To accommodate the fuel properties of ethanol and reduce the amount of ignition-improving additive, the engines have a significantly increased compression ratio, ethanol-resistant materials in the fuel system, and a larger fuel tank.¹⁸⁰

Fleet trials like these illustrate what may well be the most easily available potential use for relatively clean, highly efficient ethanol applications in CI engines. Buses are in many cases fuelled from central facilities, where it would be relatively easy, compared to widespread commercial use, to install the necessary safety precautions. At the same time, hazardous emissions in urban areas could be reduced with ethanol fuels, although some research shows that this benefit might be of minor importance compared to using modern diesel engine equipped with diesel particle filters.¹⁸¹

Discussion

Each of the application techniques discussed in this report has advantages and drawbacks, which are summarized in Table 8. Common advantages for all techniques are low PM or smoke exhaust emissions and a potential for highly efficient combustion, comparable to or better than regular diesel oil. General disadvantages are high volumetric fuel consumption, special handling of the fuel due to a low flash point, less-than-full compliance with fuel standards, and extra expenses for modification of fuel, engine, or both. For some of these techniques, there would be no need for compliance with diesel standards, as, for example, when the vehicle is dedicated to ethanol usage.

The most accomplished commercial success among these application techniques is E-diesel. O2Diesel Corporation is perhaps the world's leading provider of E-diesel fuels. The company has produced an additive that can be used for different fuel variants; a fuel with 7.7 percent ethanol and less than 1 percent additive; and a newer formulation that consists of 20 percent biodiesel, 7.7 percent ethanol, 0.7 percent additive, and conventional diesel. Other variants have also been tested. The newer formulation thus consists of 28 percent renewable nonfossil fuel. Several fleet tests that have been or are currently being conducted around the world can be described as successful. O2Diesel Corporation's E-diesel has been recognized (as of October 2003) by the strict California Air Resources Board as an environmentally friendly alternative fuel. Furthermore, the company is cooperating with the IFP (French Petroleum Institute) in the E4D consortium (Ethanol for Diesel), which includes automaker industry representatives Volvo, Delphi, Renault and Petrobras.

Many of these application techniques may seem unrealistic with regard to the existing infrastructure of the fuel market and vehicles. Neat ethanol is not marketed as a transportation fuel in many places; Brazil seems to be the only one. The applications must therefore in most cases be seen as suggestions for future development and might require some infrastructure additions. Some of the applications have not been developed to their maximum potential, and some are still in the early development stage. Either political will or perhaps rapid rising oil prices are needed for these techniques to be applied on a larger scale. However, the potential societal and environmental benefits of these techniques can seem very significant. Any significant net energy gain, such as what could be obtained using hydrated ethanol compared to anhydrous ethanol, is very significant, for society as a whole.

Table 8: Overview of Ethanol–Diesel Solutions

Method	Fossil Diesel Displacement	Potential Advantages	Possible Drawbacks
Blends, solutions	Up to 20%	Can be used in unmodified diesel engines.	Require anhydrous ethanol if additive cost and dosage must be minimal.
		Less expensive compared to emulsions.	Properties such as low energy content, low viscosity, and lubricity.
			Phase instability when stored.
Blends, emulsions	Up to 40%	Can be used in unmodified diesel engines.	As blends, solutions.
		Higher fossil fuel displacement compared to solutions.	Cost.
Blends of ethanol, biodiesel, and conventional diesel	Up to 100%	Very high displacement of fossil fuel.	Limited research done.
		Close to compliance with existing fuel standards.	Requires anhydrous ethanol.
Dual injection	Up to 90%	Anhydrous ethanol is not required.	Requires an extra separate fuel system for ethanol.
		Higher engine power output compared to diesel use.	Requires a lubricant additive.
		Flexibility regarding fuel choice.	Extra effort for the end user to fill two tanks is needed.
Fumigation	50–60%	Anhydrous ethanol is not a required.	Additional weight and complexity due to extra fuel system and tank for ethanol.
		Only minor modifications needed to use ethanol, and easy to convert back to neat diesel use.	Extra effort for the end user to fill two tanks is needed.
		Higher engine power output compared to diesel use.	
Neat ethanol with spark ignition (SADE)	100%	Anhydrous ethanol not required.	Many modifications needed; Ignition system components.
		Maximum displacement of fossil fuel.	Limited research done.
		Potentially the cleanest of all alternatives.	Not able to run on regular diesel.
Neat ethanol with glow plug	100%	Maximum displacement of fossil fuel.	Limited research done.
		Only simple modification needed.	Not able to run on regular diesel.
Neat ethanol with ignition improver	95%	Has been proven to function well on a daily basis.	Extra cost of additive.
		Maximum displacement of fossil fuel.	Not able to run on regular diesel.

Review of the literature appears to show consistent emission advantages, but some emission factors deserve further discussion. PM emissions, which are considered the most harmful emissions to human health in urban areas, are reduced with the use of ethanol in CI engines. However, the literature, with a few exceptions, reports PM emission reductions with regard to mass emissions (g/km or g/kWh), since ultra-fine particles, which weigh less, are the most hazardous. A Swedish study showed how ethanol reduced PM emissions by mass, but alarmingly increased the number of particles, compared to regular diesel.¹⁸¹ If this is a general trend, the health benefits of ethanol–diesel fuels need to be re-examined; further studies are needed in this area. Acetaldehyde emissions from ethanol application in CI engines is also an area not well studied. One study¹⁴⁷ found that higher emissions, when compared to gasoline engines, are due to the lack of three-way catalysts on CI vehicles. This trend might well be general and thus pose requirements for oxidation catalysts. There are a number of unanswered questions that might be due to the limited usage of ethanol in diesel engines. Nonetheless, ethanol in diesel engines could represent a huge market for ethanol in the future.

Not all auto manufacturers approve of E-diesel, mainly because the fuel does not comply with current standards. Issues such as long-term durability, risks of water contamination in the fuel system, and risks of fire or explosion are major concerns.^{172,182,183} It can therefore be concluded that ethanol–diesel fuels require a separate set of fuel specifications.

Technical Potential of Ethanol in the CI Engines

As is the case with SI engines, ethanol can be used in downsized CI engines. The results of many studies suggest that ethanol fuels, even with low percentages of ethanol, used in diesel engines cause less smoke or PM emissions, compared to running on neat diesel, especially at high loads. In some cases, when using diesel oil, the amount of fuel that can be injected into the engine has to be limited, since the engine starts smoking heavily when too much fuel is injected. With ethanol and therefore with less smoke, there is a potential for increased power and torque, since the smoke limit is changed significantly.¹⁸⁴

The efficiency of the CI engine, already the most efficient engine for commercial transportation, is already outstanding, so . The potential of increased efficiency due to use of ethanol fuels is much smaller than that for SI engines, that is, a maximum increase of only about 5–10 percent. This potential is not enough to offset the lower energy content of ethanol and therefore influences the fuel consumption (L/km) negatively. The technical potential of ethanol for the CI engine therefore focuses more on reducing emissions, especially NO_x and PM. Since particulate matter can be effectively filtered (thus minimizing the advantage of ethanol fuels in this regard significantly), focusing on NO_x emissions might be more efficient. Focus should also be on the size of the particles emitted from the exhaust, even though emissions regulations

do not yet deal with this. One of the major NO_x -reducing devices on light-duty diesel vehicles is the EGR system. Ethanol fuels (even low-percentage blends) have shown significant potential for increasing the EGR ratios, thus reducing NO_x emissions. This approach could be pursued further.

Reviewing the literature, we think the near future of the CI engine is the HCCI engine, which is a combination of the best features of SI and CI engine principles, that is, the high fuel efficiency of the CI engine and the clean emissions of the SI engine. At present, there are major technical barriers for full commercialization of the HCCI engine, most importantly gaining satisfactory control of the combustion and operating range. Thus, HCCI engines currently are best suited for stationary applications. HCCI engines fuelled by ethanol fuels have been investigated using ethanol–diesel blends in all percentages, anhydrous ethanol, and different water content in hydrated ethanol. A few examples of conclusions in the literature for ethanol and HCCI combustion are as follows:

- Ethanol reduces emissions, as is the trend for CI engines.
- High ethanol fractions reduce smoke and NO_x emissions to a minimum.¹⁵⁰
- Very "wet" ethanol, with up to 60–70 percent water, can be used in HCCI engines, constituting a very significant reduction in life-cycle energy use of ethanol.^{174,185,186}

Ethanol, both anhydrous and hydrous, has many possibilities for successful application in CI engines. On the other hand, implementation of many of these applications, that take full advantage of the potential of ethanol in CI engines is not compatible with existing fuel systems.

Conclusions

Technical Aspects

- (1) Ethanol has a number of unique properties that make it a superior fuel for gasoline vehicles, but it also has a number of properties that are have disadvantages for existing car fleets.
 - (a) The high octane rating and oxygen content can provide high energy efficiency and cleaner exhaust emissions compared to regular gasoline.
 - (b) The more ethanol added to the gasoline, the better the effects.
 - (c) Ethanol fuels can cause starting problems, but technical solutions are available.
 - (d) Especially in smaller amounts, ethanol in gasoline contributes to increased evaporative emissions from the fuel system compared to regular gasoline usage.
 - (e) Ethanol is more corrosive than gasoline.
- (2) Ethanol has a number of properties that are disadvantageous for use as a fuel for diesel vehicles in their current form.
 - (a) The very low cetane rating does not comply with current diesel specifications.
 - (b) The flammability properties and flash point create a need for additional safety precautions compared to regular diesel application.
 - (c) Ethanol has a relatively low energy content, in some cases making it incompatible with current engines.
 - (d) Water pollution is also a general problem with diesel–ethanol blends.
 - (e) Ethanol provides poor lubrication for the fuel system and can in some cases harm the system.
 - (f) Evaporative emission also is expected to pose a problem when ethanol is used in diesel vehicles.
 - (g) Most of the shortcomings of ethanol usage in diesel applications can be mitigated with additives, one exception until now being the flash point.
 - (h) Ethanol helps reduce smoke and PM emissions when diesel–ethanol blends are used compared to regular diesel. The effects of ethanol on particulate size need to be investigated further.
 - (i) EGR ratios can be higher when ethanol is used in diesel fuel, thus helping to reduce NO_x emissions.
- (3) As a neat fuel or if the vehicle is designed for ethanol use, as for example the FFV, the problematic fuel properties seems to be much less of a problem, if any.
 - (a) FFVs are examples of a bridging technology with very few, if any, drawbacks.
 - (b) Neat ethanol vehicles present the ultimate technical application for ethanol in many instances.
 - (i) Both SI and CI engines can be used.
 - (ii) The engine can be fully optimized so that ethanol provides maximum efficiency.

- (iii) Water contamination is not a problem.
 - (iv) Hydrous ethanol can be used.
 - (v) Exhaust emissions, as well as evaporative emissions, are cleaner.
- (4) The advantageous effects of ethanol increase with increasing ethanol percentage in both gasoline and diesel applications.
 - (5) Without changes in existing vehicles, the application of ethanol fuels is limited to low-percentage gasoline–ethanol blends with the exception of FFVs.
 - (6) Diesel–ethanol blends are currently being applied with success in fleet tests in several countries.
 - (a) Application in this form in fleet tests is particularly suitable because the fuels do not need to comply with market standards but can still be used with minor vehicular modifications.
 - (7) Biodiesel (FAME) has been shown to be beneficial in combination diesel–ethanol fuels.
 - (a) Biodiesel improves the phase stability of these blends.
 - (b) Biodiesel increases the cetane number and therefore mitigates the decreasing effect of ethanol.
 - (c) The renewable content is relatively high for biodiesel–diesel–ethanol-blended fuels.
 - (d) Fuel lubrication properties improve with use of biodiesel.
 - (e) Biodiesel–diesel–ethanol-blended fuels are close to complying with existing diesel fuel specifications.
 - (8) Ethanol can be useful in biodiesel fuels.
 - (a) Ethanol provides better low-temperature fluid properties so it can be used in cold climates.
 - (b) Ethanol decreases the viscosity, which in some cases is a problem for biodiesel.
 - (c) Ethanol also contributes to cleaner exhaust emissions in this kind of application.
 - (9) Ethanol can be used to substitute more harmful gasoline components such as MTBE, ETBE, and aromatics.
 - (10) Ethanol is compatible with current engine development trends as well as advanced combustion techniques.
 - (11) The storage, distribution, and handling differ from both diesel and gasoline, and special procedures are therefore necessary.
 - (a) In particular, transport over long distances is problematic because fuels containing ethanol cannot be pumped through existing pipelines.
 - (12) If ethanol is to be used other than in low-percentage blends, older vehicles will not be compatible.
 - (a) Because of possible problems such as poor engine performance or failure, excessive wear and corrosion, and high evaporative emissions, it is likely there will be no benefit to ethanol usage in older vehicles.
 - (13) There is a significant potential gain in CO₂ mitigation for application of hydrous ethanol, because of the production method.

Other Aspects

- (1) While the fossil fuel dependency is reduced due to application of ethanol in vehicles, mitigation of GHG emissions is in some cases doubtful.
- (2) Ethanol's potential for GHG mitigation ethanol depends heavily on the production method, including the choice of crop for feedstock.
 - (a) There is still a significant input of fossil-based energy related to ethanol production.
 - (b) N₂O emissions strongly reduce the potential for GHG mitigation.
 - (c) Carbon sequestration is a serious issue as well when land is cleared for feedstock production.
- (3) Concerns have been raised about the sustainability of ethanol production.
 - (a) There is the potential for conflicts with other biomass-consuming sectors, most importantly, food production.
 - (b) Important issues such as the potential for GHG mitigation are not accounted for.
 - (c) There are land use issues such as water usage and pollution, destruction of valuable natural habitats, and more.
- (4) Second-generation ethanol seems to be a solution to many of these issues.
- (5) Ethanol can be an important contributor to the reduction of anthropogenic GHG emissions.
- (6) With the use of integrated production methods, as for example fuel, fodder, and power coproduction, significant *symbiotic* benefits can be achieved.
- (7) Carbon capture and storage methods can be applied in the production of ethanol and could ultimately reduce atmospheric CO₂ content.

References

1. IEA (International Energy Agency), "Biofuels for Transport—An International Perspective," 2004., <http://www.iea.org/textbase/nppdf/free/2004/biofuels2004.pdf>.
2. IPCC (Intergovernmental Panel on Climate Change). "Climate Change 2007: Synthesis Report—Summary for Policymakers," 2007. http://www.ipcc.ch/pdf/assessment-report/ar4/syr/ar4_syr.pdf.
3. Durante, D., and Miltenberger, M. "Issue brief: Net Energy Balance of Ethanol Production," 2004. www.ethanolacrossamerica.net/04CFDC-003_IssueBrief.pdf.
4. Jensen, K.H., and Thyø, K.A., "2nd generation bioethanol for transport: The IBUS concept," 2007. [www.man.dtu.dk/upload/institutter/ipl/publ/2.gen%20bioethanol for transport report.pdf](http://www.man.dtu.dk/upload/institutter/ipl/publ/2.gen%20bioethanol%20for%20transport%20report.pdf).
5. Fichera, J., and Kueter, J., "Considering Brazil's Energy Independence," 2006. www.marshall.org/pdf/materials/455.pdf.
6. RISE (Research Institute for Sustainable Energy). <http://www.rise.org.au/info/Res/biomass/ethanol002.JPG>.
7. Thomsen M.H., Nielsen, H., et al. "Sustainable bioethanol production combining biorefinery principles and intercropping strategies," 2007. http://www.risoe.dk/rispubl/reports/ris-r-1608_94-105.pdf.
8. ARIC Atmosphere, Climate & Environment Information Programme Web site. http://www.ace.mmu.ac.uk/eae/Sustainability/Older/Brundtland_Report.html.
9. Wang, M. "The Debate on Energy and Greenhouse gas Emission Impacts of Fuel Ethanol," 2005. www.transportation.anl.gov/pdfs/TA/347.pdf.
10. Reed, D.D., "Michigan Tech's Wood to Wheels Initiative," 2007. www.brdisolutions.com/Site%20Docs/TAC%20Meeting%20September%202010-11,%202007/W2W%208-30-2007.pdf
11. Crews, T.E., and Peoples, M.B., Legume versus fertilizer sources of nitrogen: ecological tradeoffs and human needs. *Agr. Ecosyst. Environ.*, 2004. <http://linkinghub.elsevier.com/retrieve/pii/S0167880903003402>.
12. University of Nebraska–Lincoln, "Biofuel: Major Net Energy Gain From Switchgrass-based Ethanol," *ScienceDaily*, Jan. 14, 2008. <http://www.sciencedaily.com/releases/2008/01/080109110629.htm>.

13. Samson, R.A., and Omielan, J.A., "Switchgrass a Potential Biomass Energy Crop for Ethanol Production," n.d.
14. Chiasson, A., Geo-Heat Center, "Geothermal Energy Utilization in Ethanol Production," 2007.
15. Larsen, H., and Petersen, L.S., "Risoe Energy Report 6," 2007.
16. IEA, "IEA Bioenergy: Potential Contribution of Bioenergy to the World's Future Energy Demand," September 2007.
17. Personal interview with Professor Birgitte Ahring, The Technical University of Denmark, 2007.
18. Personal interview with Professor Claus Feldby, Danish Royal Veterinary and Agricultural University, 2007.
19. BioGasol ApS—Technical University of Denmark, August 11, 2008. <http://www.biogasol.dk/2me2.htm>.
20. Kristensen, J.B., "Ignocellulosic bioethanol—close to commercial reality," n.d. www.siliconvalley.um.dk/.../A61D6D1C-67E2-4226-8CD0-C5E28A15237B/0/JanBachKristensen_013007_BiofuelTech.pdf.
21. Article on United Nations International Panel on Climate Changes, Wikipedia, November 2007. www.wikipedia.com.
22. Larson, E.D., Presentation "Lifecycle Analyses of GHG Impacts of Biofuels for Transport," March 7, 2006.
23. Math Pro Inc., "The Net Energy Value of Corn Ethanol: Is It Positive or Negative?" November 2005. http://www.mathproinc.com/pdf/2.1.6_Ethanol_NEV_Comparison.pdf.
24. Doornbosch, R., and Steenblik, R., "Biofuels: Is the Cure Worse than the Disease?" September 2007.
25. Wang, M., "Energy and Greenhouse Gas Emissions Impacts of Fuel Ethanol," 2005. www.anl.gov/Media_Center/News/2005/NCGA_Ethanol_Meeting_050823.ppt.
26. Bolcar, K., "Expanding the Life Cycle Analysis Boundaries for Corn-based Ethanol to Include Land-Use Change: Implications for Greenhouse Gas Emissions," 2007.

27. Edwards, R., et al., "Well-to-Wheels Analysis of Future Automotive Fuels and Powertrains in the European Context," 2006.
28. Wang, M., "An Update of Energy and Greenhouse Emission Impacts of Fuel Ethanol," 2005. <http://www.ethanol-gec.org/netenergy/UpdateEnergyGreenhouse.pdf>.
29. Corbyn, Z., "Biofuels could boost global warming, finds study," *Chemistry World*, 2007. <http://www.rsc.org/chemistryworld/News/2007/September/21090701.asp>.
30. U.S. DOE (Department of Energy), approved by Stephen Goguen, "Progress Report for Fuels Technologies," 2005. http://www1.eere.energy.gov/vehiclesandfuels/pdfs/program/2005_fuels_technologies.pdf.
31. Flowers, D.L., Martinez-Frias, J., Espinosa-Loza, F., Dibble, R., Kristic, M., Bining, A., and Killingsworth, N., "Development and Testing of a 6-Cylinder HCCI Engine for Distributed Generation," 2005. <http://www.osti.gov/bridge/servlets/purl/878600-WSanYt/878600.PDF>.
32. Flowers, D.L., and Aceves, S.M., Lawrence Livermore National Laboratory; Martinez Frias, J., University of California, Merced, "Improving Ethanol Life Cycle Energy Efficiency by Direct Utilization of Wet Ethanol in HCCI Engines," SAE (Society of Automotive Engineers) 2007-01-1867, 2007.
33. Rural Industries Research and Development Corporation, 2007, "Biofuels in Australia—An overview of issues and prospects." www.rirdc.gov.au/fullreports/index.html.
34. European Biomass Association, "AEBIOM answers to Commission's consultation on transportation biofuels," 2007.
35. Outlook for Biofuels, Advanced Motor Fuels and New Vehicles, IEA Advanced Motor Fuels, 2007.
36. The Oil Drum, "Peak Oil Update—October 2006: Production Forecasts and EIA Oil Production Numbers." <http://www.theoil drum.com/story/2006/10/3/104458/751>.
37. Hoogwijk, M., "The Potential of Biomass Energy under Four Land-Use Scenarios Part B: Exploration of Regional and Global Cost-Supply Curves," 2004. www.bioenergytrade.org/t40reportspapers/otherreportspublications/potentialofbiomassbymhoogwijk032004.
38. Detchon, R. United Nations Foundation, "Biofuels FAQ," 2007.

39. Johnson, S., "The (Food) Price of Success," International Monetary Fund, *Finance and Development*, Vol. 44, no.4, 2007. <http://www.imf.org/external/pubs/ft/fandd/2007/12/straight.htm>.
40. Martinez-Frias, J., et al., "Improving Ethanol Life Cycle Energy Efficiency by Direct Utilization of Wet Ethanol in HCCI Engines," ASME (American Society of Mechanical Engineers), 2007.
41. U.S. DOE, Web page for EERE (Office of Energy Efficiency and Renewable Energy). http://www.eere.energy.gov/afdc/altfuel/fuel_properties.html.
42. Rae, A., CEO O2Diesel, "Kanataka Bus Fleet Switching to Ethanol-Diesel Blend," Web site of Green Car Congress, Jan. 2007.
43. Scania Web site, "World premiere for Scania's first ethanol-powered trucks—rapid transition to sustainable urban transport," 2008. http://www.scania.com/news/press_releases/2008/q2/n08013en.asp.
44. Gerdes et al., "Miscibility of Ethanol in Diesel Fuels," *Ind. Eng. Chem. Res.*, 2001.
45. de Doz, "Liquid-liquid equilibria of water + ethanol + reformat," *Fluid Phase Equilibria*, 2005.
46. Letcher, "Ternary phase diagrams for gasoline-water-alcohol mixtures," *Fuel*, vol.65, 1986.
47. Castro et al., "Flexible Ethanol Otto Engine Management System," SAE tech paper no.942400, 1994.
48. Owen, "Automotive Fuels Handbook," p.419, SAE, 1995.
49. Hansen, "Ethanol-diesel fuel blends—a review," *Bio resource Technology*, 2005.
50. Zhang et al., "Preparation and emission characteristics of ethanol-diesel fuel blends," 2004. <http://www.ncbi.nlm.nih.gov/pubmed/15559814>.
51. Suppes, G.J., "Past Mistakes and Future Opportunities of Ethanol in Diesel," 2000(?).
52. Nagarajan, G., Rao, T.N., Jagadeesan. T.R., and Renganarayanan, S., Institute for Energy Studies, Anna University—Chennai, "Review of Ethanol in Compression Ignition Engine," 1997(?). <http://saeindia.org/saeconference/ethanolreview.htm>.
53. Ecklund, E.E., Bechtold, R.L., Timbario, T.J., and McCallum, P.W., "State-of-the-Art Report on the Use of Alcohols in Diesel Engines," SAE 840118, 1984.

54. McCormick, R., "Advanced Petroleum Based Fuels Program and Renewable Diesel Program," 2001.
55. Chiamonti, D., and Tondi, G., "Stationary Applications of Liquid Biofuels," 2003.
56. Vaivads, R.H., "Flammability Tests of Alcohol/Gasoline Vapors," SAE 950401, 1995.
57. Kroes, N., "Tax exemptions on biofuels for transport," letter, European Commission, 2006. http://ec.europa.eu/comm/competition/state_aid/register/ii/doc/N-652-2006-WLWL-en%2022.03.2006.pdf.
58. Li, D., Zhen, H., Xingcai, L., Wu-gao, Z., and Jian-guang, Y., "Physico-chemical properties of ethanol–diesel blend fuel and its effect on performance and emissions of diesel engines," 2004.
59. Waterland, L.R., Venkatesh, S., and Unnasch, S., NREL (National Renewable Energy Laboratory), "Safety and Performance Assessment of Ethanol/Diesel Blends (E-Diesel)," 2003.
60. McCormick, R.L., and Parish, R., NREL, "Milestone Report: Technical Barriers to the Use of Ethanol in Diesel Fuel," 2001.
61. Tsunooka, T., Hosokawa, Y., Utsumi, S., Kawai, T., and Sonoda, Y., Toyota Motor Corp., "High Concentration Ethanol Effect on SI Engine Cold Startability," SAE 2007-01-2036, 2007.
62. Fulton, L., and Howes, T., IEA, "Biofuels for Transport," 2004.
63. Orbital Engine Company, "Market Barriers to the Uptake of Biofuels Study: Testing Gasoline Containing 20% Ethanol (E20)," 2004.
64. Dumont, 2007, "Controlling Induction System Deposits in Flexible Fuel Vehicles (FFV) Operating on E85," SAE tech paper 2007-01-4071, 2007.
65. Orbital Engine Company, "A Literature Review Based Assessment on the Impacts of a 20% Ethanol Gasoline Fuel Blend on the Australian Vehicle Fleet," Report to Environment Australia, 2002.
66. Jones, B., Mead, G., Steevens, P., and Timanus, M., "The Effects of E20 on Metals Used in Automotive Fuel System Components," 2008.
67. State of Minnesota and the Renewable Fuels Association, "E20: The Feasibility of 20 Percent Ethanol Blends by Volume as a Motor Fuel," n.d.

68. Australian Federal Chamber of Automotive Industries (FCAI), Web site, 2008. <http://www.fcai.com.au>, 2008.
69. ADAC, Web site, 2008. <http://www.adac.de>.
70. Kane. E.L., et al., "Refinement of a Dedicated E85 1999 Silverado With Emphasis on Cold Start and Cold Drivability," SAE 2001-01-0679, 2001.
71. Chandler et al., "Final Results From the State of Ohio Ethanol-Fueled, Light-Duty Fleet Deployment Project," SAE technical paper 982531, 1998.
72. Vicentini, "Rating the Performance of Brazilian Flex Fuel Vehicles," SAE tech paper 2005-01-2206, 2005.
73. Giroldo et al., "Development of 1.6L Flex Fuel Engine for the Brazilian Market," SAE tech paper 2005-01-4130.
74. Kapus, P.E., Fuerhapter, A., Fuchs, H., and Fraidl, G.K., AVL LIST GmbH, "Ethanol Direct Injection on Turbocharged SI Engines—Potential and Challenges," SAE 2007-01-1408, 2007.
75. Brewster. S., Orbital Corp. Ltd., "Initial Development of a Turbo-charged Direct Injection E100 Combustion System," SAE 2007-01-3625, 2007.
76. Giroldo, M.B., Makant, W., Werninghaus, E., and Coelho, E.P.D., Ford Motor Company Brazil Ltda., "Development of 1.6L Flex Fuel Engine for Brazilian Market," SAE 2005-01-4130, 2005.
77. Brusstar, M.J., U.S. EPA (Environmental Protection Agency), et al., "High Efficiency and Low Emissions From a Port-Injected Engine With Neat Alcohol Fuels," SAE 2002-01-2743, 2002.
78. Gardiner, D.P., Nexum Research Corp., et al., "Improving the Fuel Efficiency of Light-Duty Ethanol Vehicles—An Engine Dynamometer Study of Dedicated Engine Strategies," SAE 1999-01-3568, 1999.
79. Green Car Congress, "Figuring Out How to Absorb 36B Gallons of Biofuel," 2008. <http://www.greencarcongress.com/2008/02/figuring-out-ho.html>.
80. Baeta. J.G.C., Universidade Federal de Minas Gerais, UFMG, et al., "Optimization Performance of Multi-Fuel Spark Ignition Engine Using a Turbocharging System," SAE 2006-01-2641, 2006.
81. Turner. JW.G., Lotus Engineering, et al., "Alcohol-Based Fuels in High Performance Engines," SAE 2007-01-0056, 2007.

82. Jeuland, N., "Potentiality of Ethanol as a Fuel for Dedicated Engine," *Oil and Gas Science and Technology*, vol.59, 2004.
83. Brewster. S., Orbital Corporation Ltd., et al., "The Effect of E100 Water Content on High-Load Performance of a Spray Guide Direct Injection Boosted Engine," SAE 2007-01-2648, 2007.
84. HE-Blends, Web site. <http://www.heblends.com/>, 2008-09-22.
85. Brusstar, M.J., "High Efficiency with Future Alcohol Fuels in a Stoichiometric Medium Duty Spark Ignition Engine," SAE 2007-01-3993, 2007.
86. Shahed. S.M., Honeywell/Garrett Engine Boosting Systems, "Gasoline Engine Downsizing and Boosting for CO₂ Emission Reduction," n.d.
87. Magnusson, J., "An investigation of Maximum Brake Torque Timing based on Ionization Current Feedback," master's thesis performed in vehicular systems, Department of Electrical Engineering at Linköping University, 2007. www.diva-portal.org/diva/getDocument?urn=nbn:se:liu:diva-9506-1_fulltext.pdf.
88. Brusstar, M.J., "Ethanol-Gasoline Blends: Fuel Economy and Emissions Benefits," presentation, 2003.
89. Bromberg, L., et al., MIT, "Calculations of Knock Suppression in Highly Turbocharged Gasoline/Ethanol Engines Using Direct Ethanol Injection," 2006.
90. Nakata, K., Toyota Motor Corp., et al., "The Impact of RON on SI Engine Thermal Efficiency," 2007, SAE 2007-01-2007.
91. Brusstar, M., and Bakenhus, M., "Economical, High-Efficiency Engine Technologies for Alcohol Fuels," n.d.
92. Green Car Congress, "Mercedes-Benz Introduces the Mixed-Mode DiesOtto Engine in the F 700 Research Car," 2007. <http://www.greencarcongress.com/2007/09/mercedes-benz-i.html>.
93. Green Car Congress, "Mercedes-Benz Presents the Combined SI-CAI 'DiesOtto' Concept Engine," 2007. <http://www.greencarcongress.com/2007/07/mercedes-benz-p.html>.
94. Man, K., Zhao, H., Ma, T., and Oakley, A.J., "Effect of Fuel Properties on Cai/Hcci Combustion and Emission in a 4-Stroke Gasoline Engine," 2004.

95. World Car Fan, "GM Develops New HCCI Combustion Technology," 2007. <http://www.worldcarfans.com/9070827.006/gm-develops-new-hcci-combustion-technology>.
96. Glunt, J., "VW unveils plans for HCCI-like combustion system," *Diesel Fuel News*, June 23, 2003. http://findarticles.com/p/articles/mi_m0CYH/is_11_7/ai_104634561.
97. Mcarragher, S., Shell Global Solutions (U.K.), et al., "Concawe/Gfc Study on Gasoline Volatility and Ethanol Effects on Hot and Cold Weather Driveability of Modern European Vehicles," SAE 2004-01-2002, 2004.
98. Markel, NREL, "Modelling and Cold Start in Alcohol-Fuelled Engines," 1998.
99. CRC (Coordinating Research Council), "Summary of the Study of E85 Fuel in the USA 2006," Report no. E-79, 2006.
100. Stanglmaier et al., "Condensation of Fuel on Combustion Chamber Surfaces as a Mechanism for Increased HC Emissions from SI Engines During Cold Start," SAE Technical Paper 972884, 1997.
101. Davis, G.W., Kettering University, et al., "The Effect of a Multiple Spark Discharge Ignition System and Spark Plug Electrode Configuration on Cold Starting of a Dedicated E85-Fueled Vehicle," SAE 1999-01-2664, 1999.
102. Marriott. C.D., GM Powertrain, et al., "Development of a Naturally Aspirated Spark Ignition Direct Injected Flex-Fuel Engine," SAE 2008-01-0319, 2008.
103. Silva, N.R., Fiat Automoveis SA, and Sodr , J.R., Pontificia University Catolica MG, "Using Additive to Improve Cold Start in Ethanol-Fuelled Vehicles," SAE 2000-01-1217, 2000.
104. Ku, J., et al., "Conversion of a 1999 Silverado to Dedicated E85 With Emphasis on Cold Start and Cold Driveability," SAE 2000-01-0590, 2000.
105. Johansen, T., "A Strategy for the Use of High Ethanol Content Fuel Blends in Denmark and Similar Climates," unpublished thesis, The Technical University of Denmark, 2008.
106. Benson, D., Burch, S., and Biel, J., "Keeping the Heat on Cold-Start Emissions," Technology Brief, n.d. <http://www.nrel.gov/vehiclesandfuels/energystorage/pdfs/techbr.pdf>.
107. Kearney, R., The University of Sydney, "Health Impacts of Traffic Pollution: A Case of Mandating Ethanol," 2006.

108. Clean Fuels Development Coalition, "The Ethanol Fact Book: A Compilation of Information About Fuel Ethanol," 2007.
109. Biofuels Taskforce, "Report of the Biofuels Taskforce to the Prime Minister," 2005.
110. Whitten, G.A., and Reyes, S., "Air Quality and Ethanol in Gasoline," 2004.
111. U.S. EPA, "Reformulated Gas," 2008. <http://www.epa.gov/OMSWWW/rfg.htm>.
112. Husley, B., and Coleman, B., "Clearing the air with ethanol: A review of the real world impact from fuels blended with ethanol," 2006.
113. Rosillo-Calle, F., and Cortez, I.A.B., "Towards ProAlcool II: A review of the Brazilian Bioethanol Programme," 1998.
114. Coelho, T., et al., "Brazilian Sugarcane Ethanol: Lessons Learned," 2005.
115. Winebrake, J., He, D., and Wang, M., "Fuel-Cycle Emissions for Conventional and Alternative Fuel Vehicles: An Assessment of Air Toxics," 2000.
116. "Report on the Health Effects of Aldehydes in Ambient Air," report prepared for COMEAP (Department of Health Committee on the Medical Effects of Air Pollutants), n.d.
117. Hammel-Smith, C., Fang, J., Powders, M., and Aabakken, J., "Issues Associated with the Use of Higher Ethanol Blends (E17-E24)," 2002.
118. Kelly, K., Eudy, L., and Coburn, T., "Light-Duty Alternative Fuel Vehicles: Federal Test Procedure Emissions Results," 1999. <http://www.nrel.gov/docs/fy99osti/25818.pdf>.
119. Maheshwari, M., Indian Oil Corporation Ltd., et al., "Indian Experience With the Use of Ethanol-Gasoline Blends on Two Wheelers and Passenger Cars," SAE 2004-28-0086, 2004.
120. Orbital Engine Company, "A Literature Review Based Assessment on the Impacts of a 20% Ethanol Gasoline Fuel Blend on the Australian Vehicle Fleet," 2002.
121. Sandquist, H., Karlsson, M., and Denbratt, I., Chalmers University of Technology, "Influence of Ethanol Content in Gasoline on Speciated Emissions from a Direct-Injection Stratified Charge SI Engine," SAE 2001-01-1206, 2001.
122. Cullen, K., GMPT Engineering, "Fuel Economy & Emissions: Ethanol Blends vs Gasoline," 2007.

123. Pikūnas, A., et al., Influence of Composition of Gasoline–Ethanol Blends on Parameters of Internal Combustion Engines,” 2003
124. Fuels and Lubricants Committee, Japan Automobile Manufacturers Association, “METI’s Conformity Test for Ethanol Blend Gasoline,” 2006.
125. Kelly, K., et al., “Light-Duty Vehicle Program Emissions Results (Interim Results from Alternative Fuel OEM Vehicles),” n.d.
126. Apace Research Ltd., “Intensive Field Trial of Ethanol/Petrol Blend in Vehicles,” 1998.
127. Jacobson, M.Z., “Effects of Ethanol (E85) Versus Gasoline Vehicles on Cancer and Mortality in the United States,” 2007.
128. Prakash, C., “Use of Higher than 10 volume percent Ethanol/Gasoline Blends In Gasoline Powered Vehicles,” 1998.
129. Prieur-Vernat, A., et al., “Biofuels and their Environmental Performance,” Panaroma, 2007.
130. Durbin. T.D., et al., “Effects of Ethanol and Volatility Parameters on Exhaust Emissions,” 2006.
131. Boulton, J.W., et al., “Modelling the Effects of E10 Fuels in Canada,” n.d.
132. Karman, D., “Ethanol fuelled motor vehicle emissions: A literature review,” 2003.
133. Kassel, R., “An Environmental Perspective: EPA’s RFS Proposal,” 2006.
134. French, R., “Phase equilibria of ethanol fuel blends,” *Fluid phase equilibria* 228, 27–40, Elsevier Science, 2005.
135. Haskew, H.M., et al., “Fuel Permeation from Automotive Systems: E0, E6, E10, E20 and E85,” CRC E-65-3, 2006.
136. Solomon, M., NESCAUM, “Evaporative Emission Impacts of Ethanol in Gasoline,” 2006.
137. CONCAWE/EUCAR/JRC Joint Programme, “Effect of ethanol on evaporative emissions,” n.d.
138. Swedish Road Administration, “Evaporative emissions related to blending ethanol into petrol,” Vägverket, 2006-04-03, 2006.

139. Martini, G., et al., "Effects of gasoline vapour pressure and ethanol content on evaporative emissions from modern cars," 2007.
140. Herman & Associates, "2003 Motorcycle Manufacturer Fuel Recommendations." <http://www.ethanolrfa.org/objects/pdf/2003motorcycles.pdf>.
141. Kansas Ethanol, "E10 unleaded with 10% ethanol," brochure, n.d. http://www.ksgrains.com/ethanol/E-10_SmEngines.pdf
142. Jaroonsithian, S., PTT Public Company Limited (Thailand), et al., "Investigation of 2-Wheeler Performance, Emissions, Driveability and Durability: Effect of Ethanol-Blended Gasoline," SAE 2007-01-2034, 2007.
143. Schramm, J., et al., "Emissions from Moped Fuelled by Gasoline/Ethanol Mixtures," n.d.
144. Varde, K.S., "Control of Exhaust Emissions from Small Engines Using E-10 and E-85 Fuels," 2002.
145. Li, L., Shanghai Jiao Tong University, et al., "Combustion and Emissions of Ethanol Fuel (E100) in a Small SI Engine," SAE 2003-01-3262. 2003.
146. Simonsen, H., and Chomiak, J., Chalmers University of Technology, "Testing and Evaluation of Ignition Improvers for Ethanol in a Di Diesel Engine," SAE 952512, 1995.
147. He, B., Tsing Hua University, et al., "Study on Combustion and Emission Characteristics of Diesel Engines Using Ethanol-Blended Diesel Fuels," SAE 2003-01-0762, 2003.
148. Mohammadi, A., Kyoto University, et al., "Fuel Injection Strategy for Clean Diesel Engine Using Ethanol Blended Diesel Fuel," SAE 2005-01-1725, 2005.
149. Chiaramonti, D., and Tondi, G., "Stationary Applications of Liquid Biofuels," 2003.
150. He, B., Wang, J., Yan, X., Tsing Hua University, "Homogeneous Charge Combustion and Emissions of Ethanol Ignited By Pilot Diesel on Diesel Engines," SAE 2004-01-0094, 2004.
151. Ubong, E.U., Helsinki University of Technology, "Development of an Ethanol Di Spark Assisted Diesel Engine (Sade)," SAE 901567, 1990.
152. Ajav, E.A., Singh, B., and Bhattacharya, T.K., "Thermal balance of a single cylinder diesel engine operating on alternative fuels," 2000.

153. Xing-cai, L., Jian-guang, Y., Wu-gao, Z., and Zhen, H., "Effect of cetane number improver on heat release rate and emissions of high speed diesel engine fueled with ethanol–diesel blend fuel," 2004.
154. Rakopoulos , C.D., Antonopoulos, K.A., and Rakopoulos, D.C., "Experimental heat release analysis and emissions of a HSDI diesel engine fueled with ethanol–diesel fuel blends," 2007.
155. Ashok, M.P., and Saravanan, C.G., "The performance and emission characteristics of emulsified fuel in a direct injection diesel engine," 2006.
156. Corkwell, K.C., Jackson, M.M., and Daly, D.T., The Lubrizol Corp., "Review of Exhaust Emissions of Compression Ignition Engines Operating on E Diesel Fuel Blends," SAE 2003-01-3283, 2003.
157. Can, O., Celikten, I., and Usta, N., "Effects of ethanol addition on performance and emissions of a turbocharged indirect injection Diesel engine running at different injection pressures," 2004.
158. Kim, H., Choi, B., Park, S., and Kim, Y., "Engine Performance and Emission Characteristics of CRDI Diesel Engine Equipped with WCC and DOC Using Ethanol Blended Diesel Fuel," n.d.
159. Chen , H., Shuai, S., and Wang, J., "Study on combustion characteristics and PM emission of diesel engines using ester–ethanol–diesel blended fuels," 2007.
160. Mohammadi, A., Kyoto University, et al., "Implementation of Ethanol Diesel Blend Fuels in PCCI Combustion," SAE 2005-01-3712, 2005.
161. Department of the Environment, Water, Heritage and the Arts, Australian Government, Web site. <http://www.environment.gov.au/settlements/transport/comparison/pubs/2ch7.pdf>.
162. Aakko, P., and Nylund, N., "Technical View on Biofuels for Transportation—Focus on Ethanol End-Use Aspects," 2004.
163. Fernando, S., "Phase Behavior of the Ethanol-Biodiesel-Diesel MIC," 2005.
164. Luengnaruemitchai, A., et al., "Solubility of a diesel–biodiesel–ethanol blend, its fuel properties, and its emission characteristics from diesel engine," 2007.
165. He, H., et al., "Emission reduction potential of using ethanol–biodiesel–diesel fuel blend on a heavy-duty diesel engine," 2006.

166. Fernando. S., et al., "Development of a Novel Biofuel Blend Using Ethanol-Biodiesel-Diesel Microemulsions: EB-Diesel," 2004.
167. Jordanov, D.I., et al., "Study on the performance characteristics of mixtures of biodiesel, conventional diesel and ethanol," 2007.
168. Fujibe, A., Kitami Institute of Technology. et al., "The Cold Flow Performance and the Combustion Characteristics with Ethanol Blended Biodiesel Fuel," SAE 2005-01-3707, 2005.
169. Ali, Y., and Hanna, M.A., "Physical Properties of Tallow Ester and Diesel Fuel Blends," 1994.
170. O₂-diesel, E-mission, Web site, "Largest O₂Diesel fleet set to roll in India," 2007. www.o2diesel.com.
171. U.S. DOE, EERE, AFDC (Alternative Fuels and Advanced Vehicles Data Center), Web site. <http://www.eere.energy.gov>.
172. Nylund, N., and Aakko, P., TEC; Niemi, S., and Paanu, T., Turku Polytechnic; Berg, R., Befri Konsult, IEA Advanced Motor Fuels, "Alcohols/Ethers as Oxygenates in Diesel Fuel: Properties of Blended Fuels and Evaluation of Practical Experiences," 2005.
173. Scania, Web site. www.scania.com.
174. Beyerlein, S., et al., "Homogeneous Charge Combustion of Aqueous Ethanol," 2001. <http://ntl.bts.gov/lib/11000/11000/11056/KLK316.pdf>.
175. Lu, J., and Pouring, A.A., Sonex Research, Inc., "Development of a New Concept Piston for Alcohol Fuel Use in a Ci Engine," SAE 961078, 1996.
176. Combustion Engine Research Center, Chalmers University of Technology, "Annual Report 1998," 1998.
177. Kumar, P., "Use of Ethanol in Compression Ignition Engine," n.d.
178. Bhattacharya, T.K., and Mishra, T.N. "Studies on Feasibility of using Lower Proof Ethanol-diesel Blends as Fuel for Compression Ignition Engines," October 2007. <http://www.ieindia.org/publish/ag/1203/dec03ag6.pdf>.
179. ENVIS (Environmental Information System), MoEF (Ministry of Environment and Forests), Government of India, Web site, "Pollution control technology." <http://www.terienviis.nic.in>, accessed 2007.

180. Scania, "Royal message: Scania ethanol buses to be tested in Brazil," 2007. http://www.scania.com/news/Press_releases/2007/Q3/N07053EN.asp.
181. Nord, K., Luleå University of Technology, et al., "Particulate Emissions from an Ethanol-Fueled, Heavy-Duty Diesel Engine Equipped with Egr, Catalyst and Dpf," SAE 2004-01-1987, 2004.
182. Rodríguez, J.C., and Zobel, A., "Life Cycle Assessment of Wood-Based Ethanol-Diesel Blends (E-Diesel)," 2003.
183. Bortolussi, J., Chief Technical Officer, Cummins, "Diesohol—Comments to Discussion Paper May 2004," 2004.
184. Abu-Qudais, M., Haddad, O., and Qudaisat, M. "The effect of alcohol fumigation on diesel engine performance and emissions," 2000.
185. Flowers, D.L., Martinez-Frias, J., Espinosa-Loza, F., Dibble, R., Kristic, M., Bining, A., and Killingsworth, N., Lawrence Livermore National Laboratory, "Development and Testing of a 6-Cylinder HCCI Engine for Distributed Generation," 2005. <http://www.osti.gov/bridge/servlets/purl/878600-WSanYt/878600.PDF>
186. Flowers, D.L., Aceves, S.M., and Frias, J.M., "Improving Ethanol Life Cycle Energy Efficiency by Direct Utilization of Wet Ethanol in HCCI Engines," SAE 2007-01-1867, 2007.
187. Orbital Australia, "Assessment of the Operation of Vehicles in the Australian Fleet on Ethanol Blend Fuels," Report to the Department of the Environment and Water Resources, Australian Government, February 2007. <http://www.environment.gov.au/atmosphere/fuelquality/standards/ethanol/index.html>.
188. "Evaluating the Health Impacts of Ethanol Blend Petrol," Report to the Department of the Environment, Water, Heritage and the Arts, Australian Government, June 2008. <http://www.environment.gov.au/atmosphere/fuelquality/publications/ethanol-health-impacts.html>.

