

EFP06



# Ethanol as a Fuel for Road Transportation

Main Report

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May 2009

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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## 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-wheel, including economical, environmental and social aspects. It is however not the aim of this report to assess every single one of these aspects. The present report aims at addressing the technical potentials and problems, but also 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 gasses, a potential which is a result of the production method. This, along with a potential for substituting fossil oil (and being renewable), are the main reasons why ethanol is considered and implemented. Therefore focus must be at these potentials and the central questions to ask are how much CO<sub>2</sub> can be mitigated and how much fossil fuel replaced? A number of life cycle assessments have been made in order to provide estimates. These assessments have generally shown that bioethanol has a very good potential and can mitigate CO<sub>2</sub> emissions very effectively, but... It has also been shown that both fossil fuel replacement and CO<sub>2</sub> mitigation potentials are totally dependent on the production method of the fuel. Bioethanol can be made from a wide range of biomass resources, not all equally effective regarding the before mentioned potentials. 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 USA, China, India and EU has since then increased their production remarkably.

Overall, bioethanol is the largest alternative transportation fuel and is projected to increase significantly and remain so. As transportation fuel is a very big sector globally, a shift towards more bioethanol usage will potentially have great consequences in many areas of life. Therefore the need for more comprehensive evaluation methods and regulations has been emphasized. Among those are the principles of sustainable development, particularly the need for the definition of indicators, regulations and criteria, for example resembling, those implemented in the forestry sector.

The most apparent problems related to producing the biomass and then processing it to bioethanol, are mainly pollution of and usage of water, use of fossil fuels in the production, soil degradation and land use conflicts. At layman's level the perhaps most intensely discussed has, at the time of writing, been the 'food versus fuel' problem. Clearly it should not be of interest, to deprive people from food in order to produce transportation fuels. As has been stated by 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. Besides that it has been discussed whether any real potential for greenhouse gas mitigation potential exists in the current form of production, especially outside Brazil, since another greenhouse gas, nitrous oxide (N<sub>2</sub>O), seems to be emitted when growing the feedstock crops. This gas is a very powerful greenhouse gas, about 300 times stronger than CO<sub>2</sub>. There has been investigations showing a negative potential, i.e. 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 carbon dioxide into the atmosphere, than the biofuel would be able to mitigate, even seen over a long time horizon.

At the time of writing much effort is being put in to solving the problems of the so called second generation ethanol technology, the way of producing bioethanol from cellulosic biomass. There is wide agreement about the advantages of this technology. One of them is the use of much cheaper feedstock, since 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, i.e. high yield per area of land used. Lately there has even been talked about using algae as feedstock, thereby avoiding land use conflicts. There are still issues to be solved before this technology can be used on a wider scale though, mostly the improvement of the cost efficiency as well as the process efficiency.

Ethanol has been shown to suit different kinds of integrated production scenarios. In Brazil the processes of producing ethanol and power has now been integrated at many locations with success. Previously the excess biomass, i.e. bagasse was burned under open air as oppose to being converted to power. This has a significant effect on the overall efficiency of the fuel. In the US, the 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, first generation and second generation bioethanol. The solid carbon, which remains from the ethanol production, is burned in the very efficient power plant which then supplies the ethanol process with cheap low grade steam.

The fuel properties of ethanol differ from gasoline. Depending on the application, i.e. what kind of blend is used or if it is used neat, the vehicle needs special specifications for some parts to function properly. Firstly, ethanol is hygroscopic and it takes an effort to avoid water contamination and the problems that follow. Moreover, the production methods favor a content of water, as water can only be removed to a certain degree by normal distillation (up to about 95% purity), where after 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 mixing with either diesel or gasoline, if the ethanol contain more than a very small amount of water. Phase separation occurs and can in worst case make the fuel inapplicable, or in other cases causing all kinds of fuel system and engine problems. This all depend on ambient temperatures and the blending ratios of ethanol, gasoline and water, and these aspects are therefore deciding the choice of technology for a particular region or country. Worst are the blending problems when using low percentage ethanol blends containing water especially when used in cold climates. Mid and high percentage blends can contain much more water posing much less problems and in Brazil, ethanol containing 7% water is used widely. The strategy behind this Brazilian watery ethanol fuel is to minimize production costs, since less effort/energy is needed for removing water from the ethanol.

Another issue related to the cold climate markets, is cold starting, or more precisely engine start problems and excessive startup 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, which makes gasoline a relatively good fuel at cold ambient temperatures. The evaporative and flammability properties also contribute to this problem. There are solutions to these problems though. 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 measures can prevent these dangers. The evaporative properties and the chemical properties can in many cases cause worse evaporative emissions from the fuel system compared to gasoline application and likely much worse for diesel vehicles. It is important to state though, that this problem is worse for low percentage ethanol blends and it seems that high percentage ethanol blends and neat ethanol, offer improvement compared to gasoline (but likely not diesel).

Looking at the engine technical possibilities, it is so that almost all ethanol is used in gasoline vehicles. This is due to the fact that gasoline blends well with ethanol as opposed to diesel. In Brazil ethanol application is mandatory in gasoline vehicles, with the use of E25 and E100. In Sweden E85 is fairly widespread and in several other countries the use of E5 and E10 is mandatory. The further increase of ethanol application is somewhat limited by the unfortunate properties of ethanol when used in regular gasoline vehicles. The general limit for these vehicles is set at about 5-10% ethanol in gasoline. In the US and Sweden Flex Fuel Vehicles (FFVs) are currently on road being compatible with blends ranging from 0 to 85% ethanol content. These vehicles have demonstrated the technical feasibility of running on ethanol fuels with a high renewable content, while not having a higher cost. There are surely fuel compatibility issues, especially related to the older part of the vehicle fleet. Corrosion and different kinds of damages can occur in the fuels system, ultimately resulting in engine failure. It is therefore not recommended to fuel vehicles made before 1986 with ethanol fuels.

Many experimental studies have confirmed that ethanol in gasoline engines increases the engine (energy) efficiency, torque and power compared to baseline gasoline tests. This is mostly due to 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, where the mileage was improved compared to running on gasoline. There is little doubt that ethanol can improve the overall energy efficiency of the vehicle fleet, especially when using high percentage ethanol fuels or neat ethanol.

Looking at the current trends for engine development, ethanol looks like 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 (HCCI and CAI) are all compatible with ethanol.

Tailpipe emissions from vehicles running on ethanol fuels are generally cleaner compared to gasoline. However, focus is also on evaporative emissions which generally seems worse using ethanol fuels, as mentioned namely for low percentage blends. Investigations and models have shown that ethanol application does improve the overall health impact regarding so called air toxics, i.e. carcinogenic compounds such as benzene and butadiene.

Looking at diesel vehicles, ethanol can be applied with some limitations. Generally 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 (FAME), ethanol has been shown to blend quite well with diesel, and thus representing a fuel with a potential for a high degree of renewability, easily up to 30%. 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 a lot. The questions remain though, how ethanol impacts the size of the particulates and emission reduction systems. Many types of application techniques have been tried with relatively high degree of success, making it very possible to apply ethanol in diesel vehicles. Again ethanol seems to suit the engine development trends. Ethanol promotes a higher tolerance for EGR ratios which reduces NOx emissions, the lower emissions of particulate matter makes it possible to reduce NOx further, and ethanol can also be used in future HCCI engines.

When discussing the advantages and drawbacks of ethanol, it is important to notice the type of application. Generalization is not possible, since ethanol can be used in many forms. Furthermore a large range of ethanol/ gasoline blends have not been investigated sufficiently yet. What type of application is more favorable seems very much decided by infrastructural factors, especially the vehicle fleet configuration.

From a technical point of view, the 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, i.e. the more the better. Both the engine efficiencies and emissions improve with more ethanol in the fuel. Wet ethanol constitutes an even cleaner fuel both in the production and application phases. Summing up, ethanol application has many possibilities but with each type of application comes a set of challenges. There are technical solutions available for each challenge though.

## Abbreviations

<b>Abbreviations</b>	<b>Meaning</b>
AEBIOM	The European Biomass Association
AFR	Air/ Fuel Ratio
ANFAVEA	the Brazilian Automotive Industry Association's Energy & Environment Commission
ASTM	American Society for Testing and Materials
BE-diesel	Biodiesel/ Ethanol/ Diesel Blend
Btu	British Thermal Unit
CAI	Controlled Auto-Ignition
CCS	Combined Combustion System
CCS	Carbon Capture and Storage
CERC	Combustion Engine Research Center, Chalmers University
CH4	Methane
CHP	Combined Heat and Power
CI	Compression Ignition
CO	Carbon Monoxide
CO2	Carbon Dioxide
CO2eq	Carbon Dioxide Equivalent
CONCAWE	European Oil Company Organisation for Environment, Health and Safety
DDGS	Dried Distillers Grains with Solubles
DI	Direct Fuel Injection
E4D	Ethanol for Diesel
EBS	Ethanol Boosting System
ECU	Engine Control Unit
EDI	Ethanol Direct Injection
E-diesel	Specific Ethanol Diesel Blend
EEER (US)	Office of Energy Efficiency and Renewable Energy
EGR	Exhaust Gas Recirculation
EJ	Exa Joule (10 <sup>18</sup> )
EMPA	Swiss Federal Laboratories for Materials Testing and Research
ETBE	Ethyl Tertiary Butyl Ether
EU	European Union
EUCAR	The European Council for Automotive R & D
FAME	Fatty Acid Methyl Esters
FFV	Flex Fuel Vehicles
GDI	Gasoline Direct Injection
GHG	greenhouse gasses
GREET	The Greenhouse gases, Regulated Emissions and Energy use in Transportation model
HC	Hydro carbon
HCCI	Homogenous Charge Compression Ignition
IBUS	Integrated Biomass Utilization System

IEA	the 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	Kilo Watt Hour
LCA	Life Cycle Assessment
LEV	Low Emission Vehicle
LFL	Lower Flammability Limit
MBT	Maximum Brake Torque Ignition Timing
MTBE	Methyl Tertiary Butyl Ether
N <sub>2</sub> O	nitrous oxide
NEV	Net Energy Value
NO <sub>x</sub>	Nitrogen Oxides
NREL	(US) National Renewable Energy Laboratory
O <sub>2</sub> -diesel	Brand of Ethanol Diesel Blend
OBDS	On-Board Distillation System
OECD	Organisation for Economic Co-operation and Development
PAH	Poly Aromatic Hydro Carbons
PCCI	Partial Premixed Controlled Combustion
PFI	Port Fuel Injection
pHCCI	Partial Homogenous Charge Compression Ignition
PM	Particulate Matter
PZEV	Partial Zero-Emissions Vehicle
RFG	Reformulated Gasoline
RON	Research Octane Number
RVP	Reid Vapor Pressure
SADE	Spark Assisted Diesel Engine
SI	Spark Ignited
SUV	Sport Utility Vehicle
UFL	Upper Flammability Limit
UN	United Nations
UN FAO	United Nations' Food and Agriculture Organization
US	The United States (of America)
US DOE	United States Department Of Energy
US EPA	US Environmental Protection Agency
USDA-ARS	US Department of Agriculture, Agricultural Research Service
VOC	Volatile Organic Fractions
VVT	Variable Valve Timing
WTW	Well-to-Wheels (assessment)

## Introduction

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 both to environmental concerns over global warming and promising oil-importing countries a greater independence from oil-exporting ones.

Seeing that the 'hydrogen society' has yet to materialize, bioethanol seems, until then, to be a possible way of dealing with the rise in both oil prices and CO<sub>2</sub>-emissions. The subject of bioethanol, has been the subject of much discussion, research and development the recent years and the literature is abundant. There are several other reports and reviews of ethanol studies seen from various perspectives, and the view of these are incorporated where it is found appropriate. This report is based on scientific articles and literature on the subject, using sources such as the UN, the United States Department Of Energy (US DOE) and the International Energy Agency (IEA), as well as technical papers published by the Society of Automotive Engineers. This leaves the risk of obtaining a 'main stream' perspective but to counter that, the views of many debate forums and conference presentations, have been considered as well. Generally discussions on the topic of ethanol seems subject to a lot of 'half truths' and it is the hope of the authors of this report, to provide a report based on technically sound argumentation and differentiation on which proper decisions can be made.

Ethanol from biomass can provide substantial benefits to local, regional and global societies, provided the methods of 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, in table 1.

Table 1: Potential benefits and costs of biofuels. Source: <sup>(1)</sup>.

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

Most of the items in table 1 and others are discussed in more detail in the following.

## ***Security of Fuel Supply***

The fossil oil reserves are predicted to be limited and will be fading at some point in time, if not already. Recently we have experienced dramatic fluctuations in the oil price, indicating 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 social impacts on all levels of society. This means that we will reach a point where it makes much less economical sense to fuel our cars with fuels produced from fossil oil, since it will be cheaper to produce fuel otherwise, either from coal, gas, biomass or other sources such as 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***

CO<sub>2</sub> is a so called greenhouse gas (GHG), which means that 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 the changes we make regarding the ecosystem and atmospheric system in this regard. The IPCC (Intergovernmental Panel on Climate Change) has stated in the Climate Change Synthesis Report 2007 <sup>(2)</sup>, 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 greenhouse gas (GHG) emissions. It is therefore important to find ways to minimize the introduction of more GHG in to the atmosphere, a large part being caused by combustion of fossil fuels. The transportation sector is a large GHG contributor with about 13% (2004 numbers) of all anthropogenic GHG emissions <sup>(2)</sup>. 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 having numerous alternatives for producing electricity, e.g. wind and water energy, nuclear power, solar energy and more.

When considering the GHG issue related to ethanol it is important not to focus entirely on one aspect, as for example the application. It is more appropriate to view the situation as a whole and include all aspects of the fuel life cycle. Recently, some researchers have claimed that little to no GHG benefit is present using bioethanol for transportation in its current form, when looking at the production of the fuel <sup>(3)</sup>. It is recommendable to include considerations about the perspectives of using biomass not for ethanol and transportation, but for other possible CO<sub>2</sub> 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. It has been made apparent that the biomass is utilized significantly more efficiently this way, compared to ethanol usage as a biofuel <sup>(4)</sup>, but as earlier mentioned the alternatives for the transportation sector are realistically relatively few.

## Bioethanol as Energy Carrier – General Issues

This section is made to draw attention on some of the most important of many issues related to large scale ethanol production. It is not in the scope of this report to go into depth with ethanol production, but looking through the literature, it seems important to address the issues discussed here.

### *Distribution*

There are several issues concerning distribution of ethanol, especially for gasoline/ ethanol blends. Looking through the literature it seems mainly to be problems with using the existing gasoline pipelines due to the corrosive and watery nature of ethanol. Furthermore there are issues regarding the fuel stations, mostly concerning safety and storing issues. That being mentioned, it has been proven through years of practical experience, that ethanol can be distributed without major problems, using another set of procedures compared to gasoline. Ethanol is usually distributed in a system specifically designed for ethanol so that blending issues, e.g. 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 still only covers a relatively small fraction of the total fuel demand globally. It can be observed that the main suppliers of ethanol are the USA and Brazil.

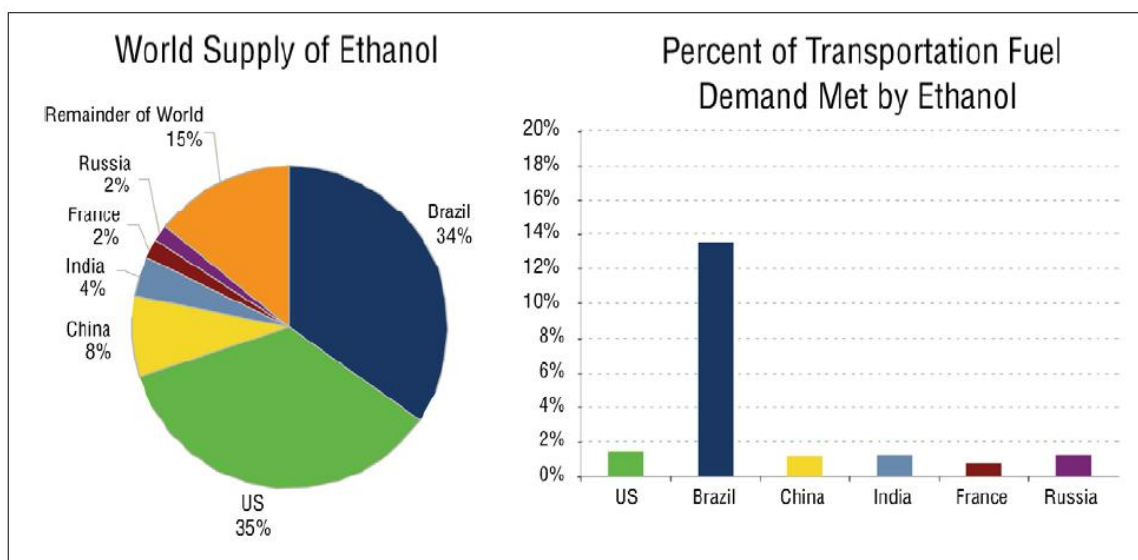


Figure 1: World supply and demand met figures. Source: <sup>(5)</sup> Energy Information Administration, 2003 and Renewable Fuels Association, 2005

The production of ethanol is increasing dramatically these years and it therefore seems important to discuss how ethanol is used most rationally. Figure 2 shows how ethanol production, which is mainly used for fuel purposes, has risen since year 2000.

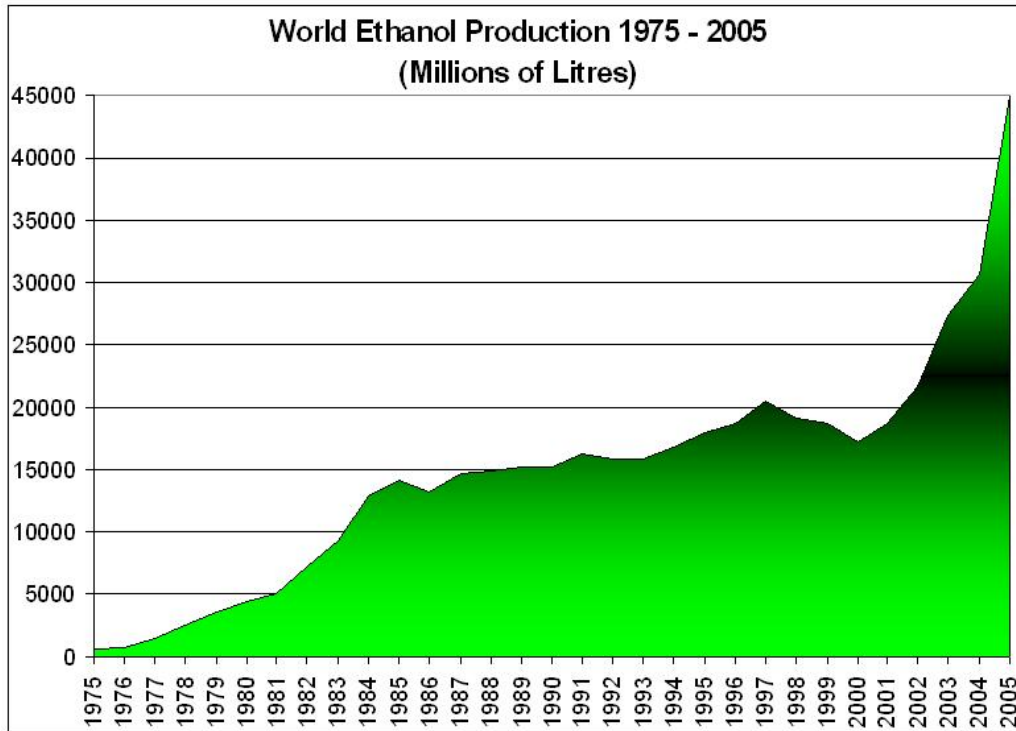


Figure 1: World ethanol production, Source: <sup>(6)</sup>.

If the world is going to experience a continued massive increase in ethanol production and usage, it will have tremendous effects on the people, economy and ecosystems of the planet. The IEA projects an average annual growth rate of 6.3% for consumption of liquid biofuels from 2005 to 2030, most of that being ethanol <sup>(15)</sup>. Secondly there will be an increasing dependency on the fuel which will demand reliable production. It is therefore of utmost importance that crop growing of the feedstock used for ethanol production is done in a sustainable way. Sustainability, according to what was found at the Rio Conference 1992, includes economical, social and ecological concerns and it seems very necessary to include all three 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' <sup>(8)</sup>.

Economics strongly influence which technical solutions a community or region will choose and thus influence the environment in different ways. At present it makes more economical sense to keep producing ethanol using first generation technology, even though the actual greenhouse gas mitigation and emission benefits in some cases seem rather limited <sup>(9)</sup>. 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. Looking at ecosystems, discussions concern topics such as the need to preserve valuable ecosystems, as for example the Amazon rainforests of Brazil, and ensuring good local soil and water quality.

## Feedstock

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

- Sugar rich biomass - Mainly sugar beet and sugar cane.
- Starch rich biomass - Grain (e.g. barley, wheat, corn, rice), potatoes, sorghum, cassava.
- 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 sugar canes but also beets. The majority of the remaining ethanol is produced from starch crops mainly grains such as corn and wheat <sup>(15)</sup>. Practically no ethanol is produced from cellulose rich biomass commercially, but commercial plants are planned <sup>(10)</sup>.

Not surprisingly the most efficient way to produce ethanol today (in terms of cost and CO<sub>2</sub> mitigation), is via the Brazilian sugar cane production. The feedstock, which is the major contributor to the cost, grows very fast there and the production methods have been refined through some years now. Furthermore it is relatively easy to make ethanol from sugar crops, since the fermentable sugars are more readily accessible compared to other feedstocks <sup>(15)</sup>.

Cellulosic ethanol production is now at a stage where trials of different feedstock are being conducted. The aim is to find crops which increase the biomass output as well as reduce negative environmental impacts. It has also been of interest to investigate the types of land (quality) the feedstock can grow on, this due to land use issues. Agricultural fertilizers are causing significant impact on the environment such as marine eutrophication, global warming, resource depletion, groundwater contamination, and stratospheric ozone destruction <sup>(11)</sup>. Thus since the motivation for use of ethanol is partly to reduce global warming, it should be of general interest to reduce the use of synthetic fertilizers in the production of feedstock for ethanol.

Some crops can naturally fixate nitrogen from the air, as for example peas, and thus reduce the need for fertilizers. Growing these crops alongside other crops is called intercropping and this method has been found to reduce the need for both fertilizers and pesticides in the case of a wheat and peas combination <sup>(7)</sup>. 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 crops for second generation ethanol production, because of its high yield, low fertilizer requirements and other desirable qualities such as soil restoring properties, good disease and pest resistance and low cost of production <sup>(12, 13)</sup>. A joint USDA-ARS (US Department of Agriculture, Agricultural Research Service) and Institute of Agriculture and Natural Resources (US) study <sup>(12)</sup> has found, that cellulosic ethanol production from switchgrass could reduce the greenhouse gas emissions up to 94% compared to gasoline. The switchgrass is intended for growing on marginal lands and the researchers estimated an ethanol yield of 85% of what is currently achieved on class 1 farm land with corn ethanol in the USA. 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.

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

## Production Methods

As will be discussed later, the production method is the key factor deciding 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 way of producing 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, where dry processing in some cases can save up to nearly 50% of the total energy used to produce the ethanol <sup>(15)</sup>.
2. Cooking and liquefaction where 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 aid of yeast to form CO<sub>2</sub> and watery ethanol (about 10% pure).
5. Distillation of the wet ethanol in order to concentrate the ethanol up to 95%.
6. Dehydration to the remaining 5% water is removed to make fuel grade ethanol.
7. Denaturing usually with gasoline to make the ethanol undrinkable.

The main inputs are: Feedstock, enzymes, yeast, energy, water and denaturant. Main outputs are ethanol, CO<sub>2</sub> and co-products which are mainly used as animal feed called distillers' grain (DDGS). The produced CO<sub>2</sub> is often captured and purified to be sold to other industries <sup>(14)</sup>.

In some cases in Brazil and other places, the energy input in the ethanol production comes from the crop used as feedstock. To provide heat for the boiling and distillation processes, the leftover biomass (bagasse) from the sugar canes is combusted. In many other cases the energy comes from fossil sources typically natural gas or coal. It thus has a big impact on the effective CO<sub>2</sub> mitigation benefit of the fuel 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 <sup>(14)</sup>. From an energy-economical view point, it therefore seems appropriate, to use waste heat from other processes such as for example electricity generation instead of high 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 of those. These methods can result in production of undesirable toxins which inhibit the following fermentation process. Once decomposed, the biomass requires a fermentation process where both hemicellulose (C5) and cellulose (C6) sugars must be processed.

A state-of-the-art report <sup>(15)</sup> has identified important research tasks for second generation ethanol production:

- Pre-treatment and decomposition processes which creates a minimum of toxic fermentation 'inhibitors' and uses less 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.
- Recovery of lignin waste products for use in for example power production.

At the time of writing practically all ethanol is produced by the so-called first generation technology. Second generation technology is currently at a stage where a lot of research is being done. Pilot and demonstration plants are running but commercial plants are still not in operation, though several are in the planning phase. Commercialization status of cellulosic ethanol (by 2007), excerpt from Ref. <sup>(10)</sup>:

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

The big 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 doesn't conflict, in the same way as first generation ethanol, with production of human food. Unfortunately the economics of cellulosic ethanol are presently at a stage where the low cost of feedstock does not outweigh the high cost of production.

The advantages of second generation technology compared to first generation are mainly:

- Much higher utilization of the individual plant, providing higher production efficiency and yield per hectare.
- No or less 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.
- Very high CO<sub>2</sub> mitigation, up to 94%.

Widespread usage of second generation technology has been projected by the IEA to be a reality after the year 2020 <sup>(16)</sup>.

## Integrated Approaches

Ultimately ethanol production can be combined with a range of other productions and might include process integration of the production of chemicals, power, heat, food, animal food and fuel<sup>(17)</sup>. It could also include usage of various resources such as household waste and agricultural waste, and include gasification and then use gas-to-liquid fuel process in production of ethanol and other fuels<sup>(18)</sup>. Another option would be to integrate the production of biodiesel and ethanol to minimize the transportation of biomass. As will be discussed later, biodiesel has shown promising blending properties for blends of ethanol and diesel. If the biodiesel is made from for example palm oil only the palm fruit is used. The integrated biofuel production could include cellulosic ethanol production from the left over biomass from the palm tree thus utilizing more of the palm, or it might be co-producing electric power using mostly waste heat for fuel production.

Seen on a global basis, electricity production from thermal power plants generally loses 55-65% of the fuel energy as relatively low temperature waste heat, though there are cases where 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 CO<sub>2</sub> emissions simply because the low temperature 'waste' heat principally does not cause much extra CO<sub>2</sub> 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 has the aim of reusing or re-circulating 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 furthermore beneficial to the overall energy balance and economy<sup>(19)</sup>. The 'philosophy' behind is that the 'waste' or co-product 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 left-over from the ethanol process. By integrating these two processes, there is furthermore a reduction in investments, because no power/ steam unit is needed for the ethanol plant<sup>(20)</sup>. Both the IBUS and Maxifuel concepts claim to have solved all major bottlenecks and barriers for cellulosic ethanol production, the only challenge remaining being the upscaling of the process into a cost effective industrial production.

One could even imagine a future scenario where a Carbon Capture and Storage (CCS) system was removing CO<sub>2</sub> emissions completely from the integrated processes, i.e. power plant and ethanol plant, making the GHG emissions so low that CO<sub>2</sub> is in fact removed from the atmosphere, seen 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). The general idea is to divide the life cycle of the fuel into all the phases of its 'life'; e.g. production, usage and disposal. As will later be shown, the main benefit of ethanol is due to the production.

### **Net Energy Value and Greenhouse Gasses**

One of the main reasons for using biofuels, including ethanol, is to reduce emissions of green house gasses (GHG). As mentioned earlier, greenhouse gasses are gasses which impair the earth's ability to radiate thermal energy to space. The amount of GHGs in the atmosphere is naturally mainly depending on the circulation of carbon, i.e. a balance where the amount of carbon is relatively constant. Important GHGs are CO<sub>2</sub>, methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O) and water vapor. In order to assess GHG potentials, the term or measure CO<sub>2</sub> equivalent (CO<sub>2</sub>eq) is used to express the amount of global warming potential as an equal amount of CO<sub>2</sub> <sup>(21)</sup>. The CO<sub>2</sub>eq for methane and nitrous oxide are 23 and 296 respectively, meaning methane has a 23 times stronger greenhouse potential than CO<sub>2</sub> <sup>(3)</sup>. The term CO<sub>2</sub> neutral is sometimes used to describe ethanol, but the term is misleading, as will be discussed in the following, since production of ethanol at the moment cannot be done without introducing fossil based CO<sub>2</sub> or other GHG into the atmosphere.

At this point in time there is a lot of debate on whether usage of ethanol in the transportation sector really causes reduced outlet of GHG. In order to asses this, the predominant tool used is the Life Cycle Assessment, or in fuel terms called a Well-to-Wheels assessment (WTW). In this case WTW assessments most often aim at estimating the net outlet of GHG and fossil fuel usage for the complete life cycle of a given fuel, by accounting various inputs and outputs associated with the entire life cycle of the fuel. There are international standards (ISO 14000 series) dictating how to make this kind of assessments, but there are also critics <sup>(22)</sup> that claim that using the standards can lead to using too narrow perspectives as will be discussed later in this section.

One often used, but also criticized term to evaluate ethanol, is the Net Energy Value (NEV). NEV is defined as the difference in energy content in the fuel product (output) and the energy used to produce it (input) <sup>(23)</sup>. 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.)

In the following some LCA studies and reviews of LCA studies on ethanol, are discussed. Figure 3 shows results from a number of major LCA studies.

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)

Figure 2: Summary of major LCA studies, source: <sup>(3)</sup>.

There seems to be an ongoing debate, whether production of ethanol has a positive NEV, i.e. less energy is used to produce the ethanol than the actual energy content in the ethanol, but the figure clearly shows that most of the major studies find a positive NEV. Work by Dr. Wang and Eric Larsson have reviewed a range of LCA studies and established that with current production and vehicle technologies, ethanol offers at least minor CO<sub>2</sub> (or CO<sub>2</sub>eq) emission reduction potential and has potential to reduce fossil energy usage compared to using gasoline. These investigations should be seen as 'worst case' scenario analyses since they consider first generation technologies using traditional crop growing and as such are not representative of cutting edge/ future scenarios. Studies on second generation production shows (as earlier mentioned) very significant improvements of both GHG emissions and fossil fuel usage.

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

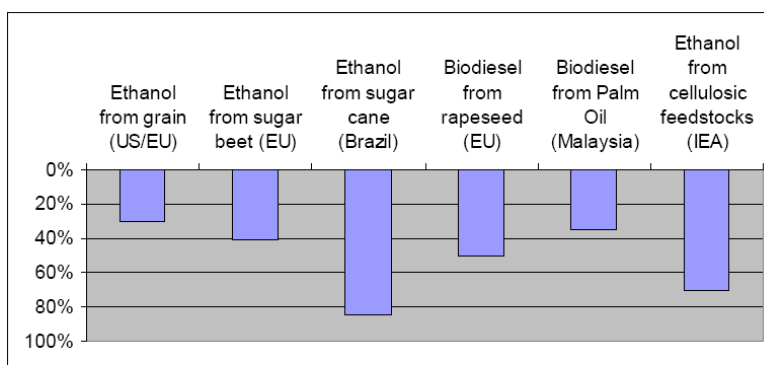
- Turning to second generation technologies.
- Process integration of power and ethanol production.
- Process heat used in ethanol production coming from biomass power co-production.
- General production efficiency improvements.

LCA studies <sup>(9)</sup> show, that GHG emission reduction for different gasoline/ ethanol blends made by corn, on first generation technologies are: 18 to 26%, and 21 to 29% for E10 and E85 respectively <sup>i</sup>. For cellulosic based ethanol it is estimated that GHG emissions reduction will reach about 85% for E10 and E85. The

<sup>i</sup> E10 is the common designation for gasoline containing 10% ethanol by volume. E85 is gasoline containing 70 to 85% ethanol.

numbers are based on displacement of gasoline, on energy equivalent basis using the <sup>ii</sup>GREET model. Similar results have been found by Ref. <sup>(22)</sup>, who has reviewed LCA studies and has come to the conclusion, that ethanol made from corn reduces GHG emissions by 10-50% while ethanol from grass (cellulose) reduces GHG emissions by 40-100%.

There are significant differences in GHG reduction with different feedstocks; corn, sugar cane or sugar beets. An OECD study <sup>(24)</sup>, based on figures from IEA and EMPA (Swiss Federal Laboratories for Materials Testing and Research), has found that CO<sub>2</sub>-equivalent Well-To-Wheel GHG emission reduction per driven kilometer, varies from about 30% for grain ethanol in the EU and USA, to 40% and 93% for sugar beet in EU and sugar cane in Brazil respectively. See figure 4. 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 CO<sub>2</sub>-equivalent GHG emissions per kilometre.

Figure 4: GHG WTW CO<sub>2</sub> equivalent reductions, source: <sup>(24)</sup>.

Wang et al. at the Argonne National Laboratory (US) 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 roughly half of the energy in the coals, is lost as heat (if not used as district heating). Wang et al. instead focuses on the fossil energy input. Figure 5 shows the so called Fossil Energy Ratio, which is the ratio between energy in an energy end product and the fossil energy input. It can be seen that first generation ethanol is doing quite well compared to existing energy products and second generation ethanol has a very great potential also in this regard.

<sup>ii</sup> 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, Argonne National Laboratory's Center for Transportation Research, with support from the U.S. Department of Energy's (DOE's) Office of Energy Efficiency and Renewable Energy (EERE).

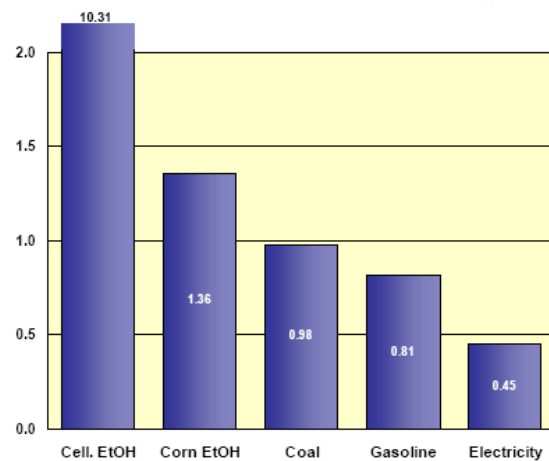


Figure 5: Energy output compared to fossil input, source: <sup>(25)</sup>.

## Discussion on LCA Studies and Results

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

1) Feedstock, e.g. corn, wheat, sugar canes, switch grass and more, 2) Allocation of co-products, i.e. how they are accounted for. Ethanol production leads to by-products which can be accounted for differently, as for example no allocation, allocation by energy content in certain co-products or allocation by share of process energy consumed to make co-product. The most important co-product in US corn based ethanol production, is called distillers dry grain and solubles (DDGS), which is 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 <sup>(24)</sup>. 3) Accountancy of nitrous oxides which will be discussed in a later paragraph. 4) Accountancy of 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 (CO<sub>2</sub>) emissions to the atmosphere, even though the biofuel is produced efficiently. Not all LCA studies include this issue <sup>(22, 26)</sup>. Considering these variables, it is not surprising that WTW assessments made around the globe have come to different results.

Related to crop production, is the emission of N<sub>2</sub>O which is a powerful GHG, about 300 times stronger than CO<sub>2</sub>. N<sub>2</sub>O emission from farming depends on a range of conditions such as soil condition, climate and crop and farming practice. Uncertainties in relation to predicting N<sub>2</sub>O emission are relatively large at this point in time, maybe so large that they can affect the outcome of a LCA decisively, if included in the LCA inventory <sup>(27)</sup>. Ref. <sup>(28)</sup> states that N<sub>2</sub>O originating from nitrogen fertilizer can account for up to 25% of the total GHG emissions from US corn ethanol.

A recent study <sup>(29)</sup> led by the Nobel prize-winning chemist Paul Crutzen, claims that commonly used biofuel crops may in fact lead to increased GHG emission due to N<sub>2</sub>O. Corn based ethanol was found to cause 0.9-1.5 times GHG emissions, as compared to what is saved in CO<sub>2</sub> emissions. Sugar cane ethanol was found to be a viable option with a factor of 0.5-0.9. The study has been received with criticism concerning basic

assumptions and numbers for crop-to-ethanol conversion, but a report <sup>(24)</sup> from OECD supports Crutzen’s skepticism.

Many researchers have pointed out that there exists a need for more comprehensive and holistic approaches, compared to the standard LCA methods. Replacing fossil fuel with biofuel has, as has been discussed here, many consequences on different levels on local and global scale.

Accordingly it can be concluded that ethanol has great potential as being part of the near future plans to mitigate greenhouse gasses but pitfalls do exist. It seems that recommending ethanol on a larger scale can only be done with good conscience, if exact knowledge of the effects are well documented and effective reductions of GHGs outputs and fossil fuel inputs are ensured in the production.

## Hydrous Ethanol

As will be presented in more detail later in this report, ethanol can be used as a fuel while containing water. The motivation for doing this 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 been proven by operation on a daily basis in Brazil and Sweden. Looking from an environmental perspective, maintaining water in ethanol minimizes the energy consumption in the production phase. Figure 6 shows the net energy balance of ethanol from US corn.

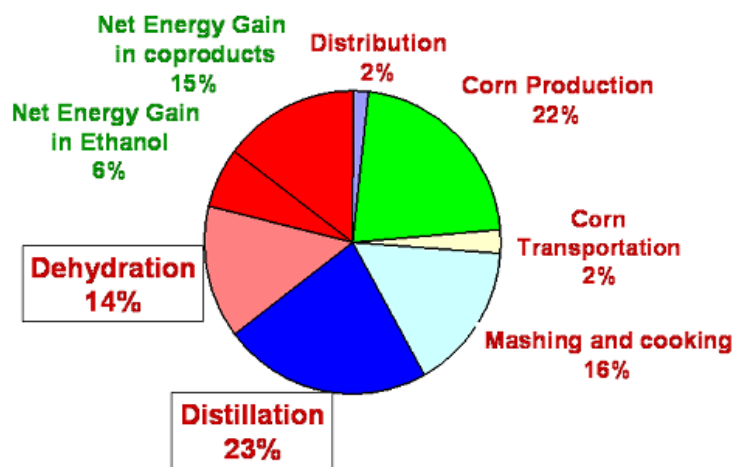


Figure 6: Net energy balance of US ethanol produced from corn. Source: <sup>(30)</sup>.

The circle in figure 6 represents all the energy of ethanol and co-products. It can be seen that (US corn based) anhydrous ethanol has a net energy gain of just 21% including the co-products of the production, while hydrous ethanol, with about 5% water content, would gain another 14%.

An effective way of using wet ethanol in internal combustion engines, is in the so called HCCI (homogenous charge compression ignition) engines and a few studies show that it might be possible to use ethanol containing up to 70% water in ethanol <sup>(31, 32)</sup>. According to Ref. <sup>(32)</sup> 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, in for example a hybrid vehicle with batteries, electric motor and a combustion engine. Ref. <sup>(32)</sup> states that distillation energy, when using ethanol with 65% water, would be reduced from 23% to only 3%, i.e. providing a net energy gain of 55% instead of 21% with anhydrous ethanol. Other investigations of ethanol production may find other numbers than these, but energy savings will in any case be significant using wet ethanol.

Combustion engines in general, suffer from a relatively low efficiency, i.e. utilization of the fuel energy. Even though the combustion engine has undergone many years of optimization and development, the CI engine (Compression Ignition, i.e. diesel engine), representing the most efficient application, still utilizes only roughly 25-35% 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. The important point of the before mentioned example, is that waste heat from the engine is used to compensate for the high water contents of the fuel instead of being wasted. In that way, waste energy from the vehicle replaces energy of relatively high quality or usefulness, that be coal, natural gas or biomass. See figure 7.

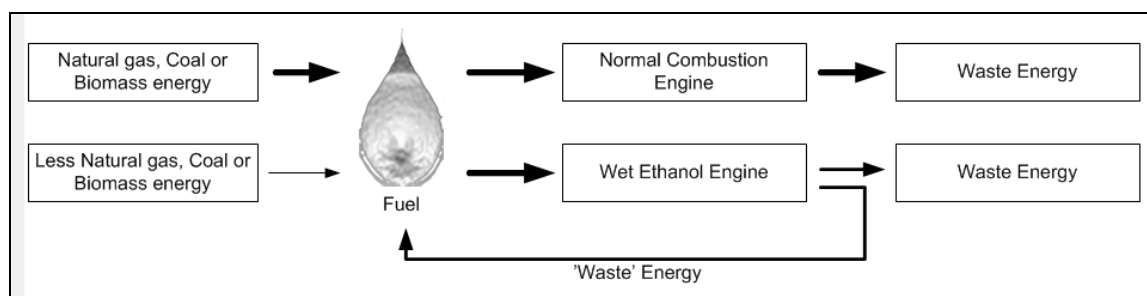


Figure 7: Schematic overview of energy flow using the 'wet ethanol engine' concept

While it does require relatively radical new-thinking to implement this kind of solution on a large scale, the potential for energy savings (and CO<sub>2</sub> mitigation) seen on a global, regional or national perspective will most probably make 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%) is used on a large scale with huge energy savings (not to mention economical savings). In the later sections in this report, the technical aspects of using wet ethanol will be discussed, but the utilization of wet ethanol generally requires dedicated technical solutions, i.e. solutions alternative to the current vehicle market.

## ***Sustainability***

Since one of the main purposes of bioethanol is to mitigate environmental impacts, especially greenhouse gasses, it is important to ensure certainty about the actual effects of the ethanol production. Furthermore, as ethanol usage increases on a global level, there will be an increasing pressure on the ecosystems and thus a need for principles of sustainable agricultural production, as 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 oriented social, environmental and economical impacts of a relatively sudden and very significantly growing industrial/ agricultural sector. Citing one report: '...there is no point in replacing one unsustainable system with another' <sup>(33)</sup>.

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. It is therefore not possible to directly compare the two fuels in this regard and any comparison will have to be a (subjective) weighing of different environmental effects. The Swiss Institute, EMPA <sup>(24)</sup> 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 8.

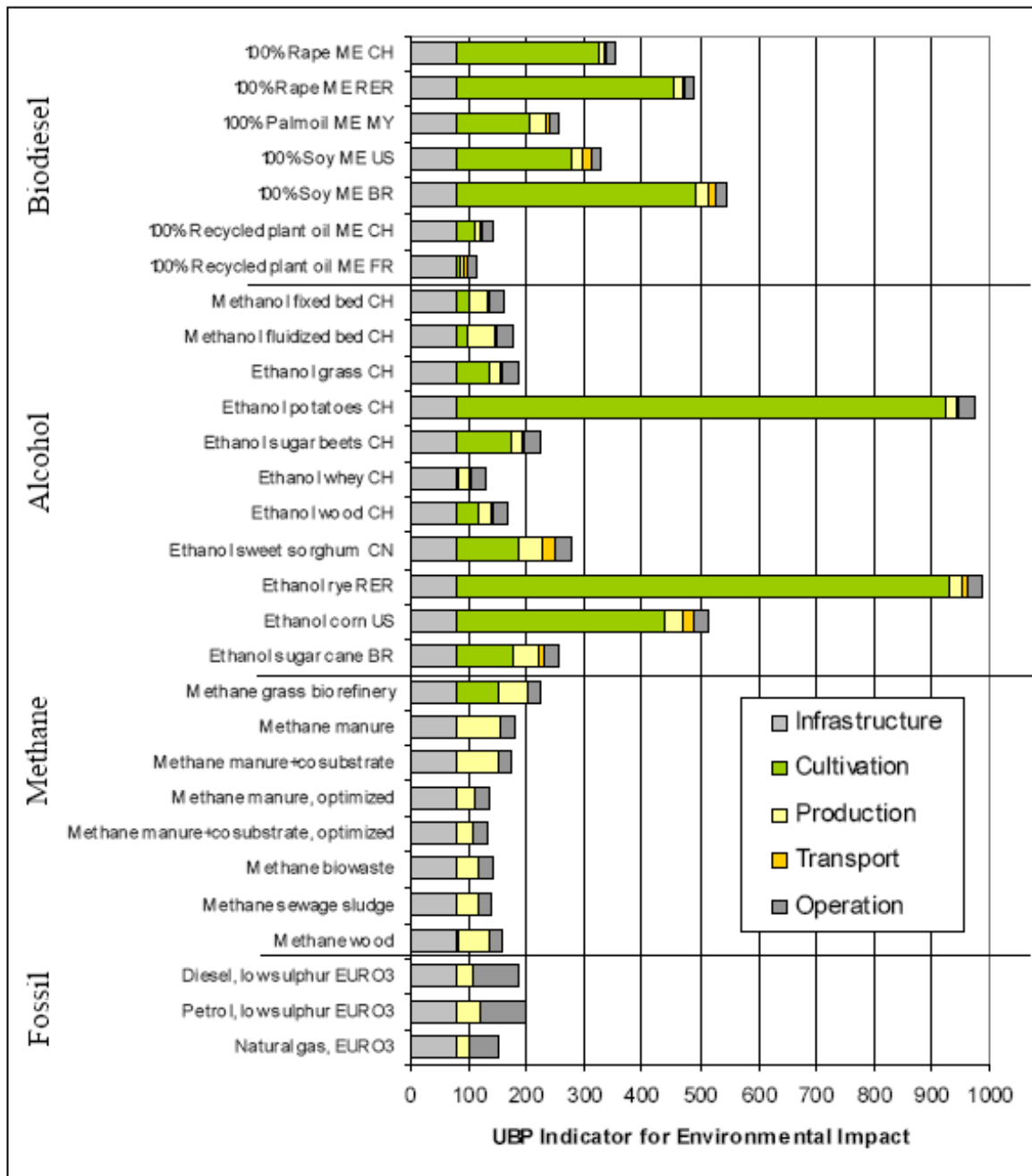


Figure 8: Environmental impact for ethanol and other fuel options, Source: <sup>(24)</sup>.

Note: CH = China, RER = European Union, MY = Malaysia, US = the United States, BR = Brazil, FR = France and CN = Canada.

Figure 8 shows that the impact from cultivation activities are very significant in the life cycle of ethanol (and biodiesel) made from different crops. The figure also shows that it would be a mistake only to consider the vehicle operation emissions.

The Roundtable on Sustainable Biofuels, consisting of non-governmental organizations, companies, governments, inter-governmental organizations, experts and others, are developing four criteria to form a tool to ensure a degree of sustainability in the production and use of biofuels. The criteria are concerning life cycle greenhouse gas efficiency, environmental impacts namely biodiversity, soil issues and water resources, social impacts (mainly food supply security) and implementation. There are currently many activities in the area of finding ways to ensure sustainability on the highest levels of influence, e.g. national governments, the European Commission, and the IEA. One example is work commissioned by the Dutch government, which suggests that criteria of sustainability should be satisfied in order to justify subsidies<sup>(24)</sup>. Another suggested approach is to learn from experiences gained with certification of forest products.

The European Biomass Association (AEBIOM)<sup>(34)</sup> is supporting the idea of sustainability, but expresses the importance of making all agricultural production sustainable, not only biofuels. As there already are policies to ensure some degree of sustainability in Europe, including biofuel crop growing, AEBIOM state that certification should target imported biofuels.

Reviewing a part of the literature on sustainability of ethanol production, the following general concerns have been summarized (not in prioritized order):

- Greenhouse gas emissions, seen over the entire fuel life cycle, must be significantly lower than for fossil fuels.
- It is considered of major importance that nutrients from the biomass are 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 when starting new biomass production.
- Soil erosion and degradation, as well as water resources and quality, are major concerns.
- The food security and prices locally and globally must be considered.
- As biofuels are an international commodity, international sustainability certification and labeling standards should be developed to ensure a minimum level sustainability.

## Land Use Issues

An important concern related to ethanol production, is that we on planet earth only have 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 another. For ethanol examples have already been outlined; as animal feed usually is a co-product of the ethanol production, it can in fact produce opportunities for at least the live stock industry<sup>(33)</sup>. Other examples are co-production of food and fuel with use of second generation technologies, and improvement of biodiversity with inter-cropping.

## Global Biofuel Potential

It is a very difficult task to assess the global energy potential for fuel biomass production accurately. One thing is what is technically possible, another thing the reality and 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 which will increase by over 50% by 2030, if the current annual growth rate remains unchanged<sup>(35)</sup>. With the recent increases in the crude oil price and the very likely decrease in oil production<sup>(36)</sup>, the growth might be slowed down though. Rapid growth in world consumption of transport fuels, will require the production of biofuels to grow much more rapidly, in order for the net CO<sub>2</sub> emissions from the transport sector to decrease or just stabilize. In recent years, this has indeed been the case, biofuel production doubling between 2000 and 2007, while crude oil production increased by 7.7%<sup>(16)</sup>. A quadrupling of worldwide biofuel production by 2020 (a plausible scenario), would correspond to the displacement of roughly 7% of fossil fuels for road transportation worldwide. Beyond 2020, the potential of second generation ethanol opens up for 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 more distant future (2050).

Doornbosch 2007<sup>(24)</sup>, using conservative figures, estimates the potential for displacement of fossil transport fuels to roughly 23% in 2050. Hoogwijk 2003<sup>(37)</sup> has charted four different future scenarios with different estimates of the energy production potential from biomass compared to from fossil fuels. In terms of fossil transportation fuel displacement, the scenarios range from values of 20% to approximately 50% displacement. Also, the IEA has made a forecast<sup>(16)</sup> for 2050 which indicates, that a fossil transportation fuel displacement of 100% 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.

As opposed 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 present potentials, understood as goals which can be reached only by actively pursuing them. 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.

It should be noted that the above scenarios only consider land-based biomass. Considering that 70% of the Earth's surface is ocean, the potential for sea-based biomass is clearly enormous. Some researchers and companies are at present working in this field, but the technologies and infrastructure needed for any large-scale marine biomass production are still in the development stage.

Though fraught with uncertainties and contingencies, the described future scenarios all show that ethanol and other biofuels have a large potential, but also that they are by no means an easy and effective solution for a sustainable transportation sector. It is incontrovertible that 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

The following is used as an example of important aspects in the ethanol discussion. A recent study <sup>(4)</sup> made at The Technical University of Denmark assessed a number of environmental impact categories such as GHG emissions, waste generation, ozone formation and acidification, related to ethanol production. The production technology of ethanol (called 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 is 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 general 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, i.e. using it in CHP production. Based on a life cycle analysis of the scenario, it is concluded that nutrients with production of ethanol are to some degree kept in the agricultural system due to the main co-product animal feed. Reversely burning biomass in the power plant makes it harder to recycle nutrients to keep the soil sustainable for future crop growing and minimization of fertilizer usage.

The report compares CHP with ethanol production and this is substance for a relevant debate. As for land use, it is surely highly relevant that the global usage of limited biomass is optimal and it is irrelevant how GHG reductions are obtained. Regarding fossil fuel scarcity the report concludes, that higher displacement is achieved with CHP. It is questionable though 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 point in 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 CO<sub>2</sub> storage at coal fired power plants. The report suggests electric cars as a solution in combination with CHP as the optimal utilization of biomass.

CHP is not an option in many countries since there is simply no need or economical viability for district heating, as for example in tropical countries. Thus CHP is surely by far the most ideal usage of biomass and it 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 as oppose to moving applications. Even with highly efficient electric motors the moving application will always 'lose' 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% energy conversion efficiency.

Considering the quality (or usefulness) of the energy, low temperature heat energy is categorized as lower quality than liquid fuels, thus the comparison is again not 'fair'. As has been discussed previously, integration of productions, technologies and processes seem a better overall solution. This LCA is an example among many that does not consider all aspects of the energy situation, as the report itself also recognizes. This is of course very understandable, but not entirely satisfactory and as suggested by Eric Larson and others, studies including all aspects of the biofuel and energy situation seem relevant and needed at this point.

## Biomass for Food or Biofuels

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

The UN Foundation report, Biofuels FAQ (2007) <sup>(38)</sup>, states that according to the United Nations' Food and Agriculture Organization (UN FAO), increased food production will be able to keep up with a growing population. Furthermore it is stated that the malnutrition on global scale is not caused by lack of food. Instead it seems the world could easily produce more food, if there was a demand, i.e. if the poor could pay for the food and create the demand. As most of the poorest people live of 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) for biofuel crop production. Biofuels seem (according to the Biofuels FAQ report) to potentially be a lifting pole 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 and 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.

A report from the European Biomass Association <sup>(34)</sup> 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. Firstly, the organization claim that there is land enough to grow both food and fuel crops and secondly, that there is an overproduction of food in the EU. AEBIOM furthermore points out that surplus food production is 'dumped' in developing countries, which results in local markets not being able to compete. Furthermore AEBIOM finds that crop prices have little influence on the final product prize. Wheat, for example, represents less than 10% of the bread price. AEBIOM therefore recommends that EU should not limit biofuels due to land use concerns or food prices, while recognizing that there might be local impacts on short term for countries depending on food imports. However, it should be noted that AEBIOM is an organization with a vested interest in this matter.

In an article December, 2007 <sup>(39)</sup> Simon Johnson, economic counselor and director of the IMF's (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 USA and worldwide from 2005-2007 and there has been rapeseed price increases too. A significant part of the price increases for food is due to biofuels policies according to IMF staff's assessment. Importantly, the effect is moderate for people in the rich countries, as food only represents about 10-15% of the consumption and the raw material represents a relatively small part of the actual food price. In less rich countries, food represents from 30-50% of the 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, he states that biofuels are not produced 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 to develop through 'freer' trade of biofuels.

It can thus be suspected from the above, that currently there is room for crop growing of biomass for fuel but it will not be without unfortunate consequences. In the literature it is repeatedly stated that cellulosic

ethanol is a solution to the food vs. 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, but the situation could turn into a competition for productive arable land using for example grasses for fuel production instead of food production. It will therefore probably be required to interfere with 'free' market forces and take a common step to prevent major fuel vs. food conflicts or tragedies. Seen in this perspective it seems important to work on a radical reduction of fuel usage (i.e. more efficient cars or less cars) since unfortunate consequences of massive biofuel production seem nearly unavoidable.

## Fuel Properties

This section deals with the chemical and physical properties of ethanol, especially those relevant for use in automotive vehicles. The more engine specific properties such as energy density, octane rating and others can be found 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 2 for relevant properties of ethanol, gasoline and diesel).

Ethanol is somewhat special in its electrochemistry, the molecule being polar at one end and non-polar at the other. The polarity of a molecule refers to the distribution of electric load in the molecule, and is a factor of significant importance for the physical and chemical behavior of substances. The presence of a hydroxyl group in the ethanol molecule, makes it able 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 non-polar end, makes ethanol soluble in both polar and non-polar substances. The polar end makes ethanol miscible with water (and other polar substances) and the non-polar end makes it miscible with many non-polar organic substances such as gasoline and, to a lesser extent, diesel fuel.

The hydrogen bonding occurring 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, though 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.

Both due to the production method, improper storage and accidental contamination, ethanol often contains a small amount of water. Water contamination of pure ethanol can occur very easily because ethanol is hygroscopic, meaning that 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 below 1%, or 'hydrous', generally referring to a water content between 5 and 10%. Anhydrous ethanol is also called pure, dry or absolute alcohol. Ethanol purities above 95.6% by mass (designated the azeotrope concentration) cannot be produced by traditional distillation methods, but requires separate dehydration equipment, a fact which makes anhydrous ethanol approximately 20-25 % more energy-demanding to produce than the ethanol/water azeotrope (calculated from <sup>(40)</sup>).

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

Table 2 summarizes the most significant fuel properties of ethanol compared to gasoline and diesel. The significance of engine-related properties such as heat of combustion, Reid vapor pressure and octane numbers will be addressed in the chapters on ethanol's usage in transportation.

Table 2: Properties for ethanol, gasoline and diesel

Property	Ethanol	Gasoline	Diesel
Chemical Formula	C <sub>2</sub> H <sub>5</sub> OH	C <sub>4</sub> to C <sub>12</sub>	C <sub>3</sub> to C <sub>25</sub>
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 (20°C)	0.4–0.9 (16°C)	2–6 (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–	42800–
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 <sub>2</sub> Emission [MJ fuel energy/kg CO <sub>2</sub> 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 Center. Ref. <sup>(41)</sup> ([http://www.eere.energy.gov/afdc/altfuel/fuel\\_properties.html](http://www.eere.energy.gov/afdc/altfuel/fuel_properties.html))  
(a) = calculated

## ***Ethanol Fuel Types***

Ethanol as a motor fuel is found in various forms around the world, in blends together with gasoline, diesel containing different amounts of water. Fuel producers design fuel blend specifications to suit local legislation, vehicles, weather, consumer habits and other conditions on 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% 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 CO<sub>2</sub> emissions. Firstly, the high octane rating of ethanol, will by adding ethanol to gasoline raise 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. Secondly, the fact that ethanol contains oxygen will make ethanol-containing gasoline burn cleaner and reduce the amount of harmful emissions of carbon monoxide (CO), particulates and unburned gasoline components (see section on Emissions). Other oxygen containing compound can be added with the same effect.

The ethanol used as additives 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 Brazil <sup>iii</sup>: 'Gasohol', containing roughly 20% anhydrous ethanol in gasoline, and 'E100' - hydrous ethanol without gasoline, and with a water content of roughly 7% by volume. E100 has the advantage of a lower cost of production energy and consequently monetary cost compared to 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: the 'E85' type, containing between 71 and 85% anhydrous ethanol, with gasoline constituting the rest of the blend. This is primarily used in Flex Fuel Vehicles in USA and Sweden. At the low temperatures experienced in these countries, the ethanol used in blends together with gasoline is required to be almost anhydrous in order to avoid phase separation (see section on water and blending issues).

Finally, recent years have seen an increase in the use of "diesohol" blends of diesel fuel and ethanol, for use in diesel engines. One such patented blend is the E-diesel blend, consisting of ca. 15% anhydrous ethanol sometimes including additives and about 85% diesel fuel. Another trademark blend, O<sub>2</sub>-diesel , consists of 7.7% anhydrous ethanol in diesel fuel, and is in use with success in more than 5000 busses in the Indian state of Karnataka <sup>(42)</sup>. Diesel/ethanol blends have the great advantage of reducing the particle emissions normally associated with diesel engines.

Another blend for compression ignition engines, the 'E95' type, contains no diesel fuel, but 95% hydrous ethanol and 5% additive, and has been used with success by the manufacturer Scania for busses and trucks in Sweden. Other ethanol fuel types exist and have been studied, but the ones mentioned above comprise the vast majority of the worldwide ethanol fuel consumption.

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<sup>iii</sup> Pure gasoline without ethanol is not available at Brazilian filling stations.

## **Water and Blending Issues**

The formulation of specific ethanol blends will almost always be limited by the need to avoid phase separation, meaning de-mixing of the fuel components. Though gasoline and ethanol are fully miscible, the presence of too much water in the blend can still cause phase separation, causing an upper gasoline-rich liquid layer and a bottom water-rich liquid layer. Since hydrous ethanol is less expensive and more carbon dioxide friendly to produce compared to anhydrous ethanol, there are as earlier mentioned economic and environmental incentives for allowing water in the fuel blends. Also, since ethanol is hygroscopic (meaning that it will tend to absorb water vapor from the atmosphere), intentionally or not there might be a substantial water content in an ethanol fuel blend, possibly leading to phase separation. Such instability problems become worse at low temperatures, and are very 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 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 <sup>(44)</sup>. The cases of ethanol/gasoline and ethanol/diesel blends will be examined separately below.

### **Ethanol/Gasoline/Water Miscibility**

Due to the molecular dissimilarity of water and gasoline (polar and non-polar molecules respectively) water is almost insoluble in gasoline and the two will form separate, liquid phases when mixed, water collecting at the bottom of the fuel tank due to its higher density. Since 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 engine, 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 will generally consist of a lower ethanol/water layer and an upper gasoline layer with a small content of ethanol <sup>(45)</sup>. Consequently, in the case of fuel tank phase separation, the separated ethanol/water layer will be delivered to the engine, with the gasoline fraction remaining in the tank. Even though this hydrous blend will have 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.

Since 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 plus 10 to minus 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 has been carried 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 <sup>(46, 47)</sup> has revealed some general tendencies:

- 1) Gasoline/water miscibility is proportional with the ethanol content in the blend, meaning that 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.
- 2) Gasoline/water miscibility increases with the temperature of the blend, though not in a strictly proportional way.

Even though these tendencies are universal (and very well known), the exact water tolerances recorded will depend on the exact composition of the gasoline used, and 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 is plotted in a ternary phase diagram as shown below:

### Phase Separation Curves

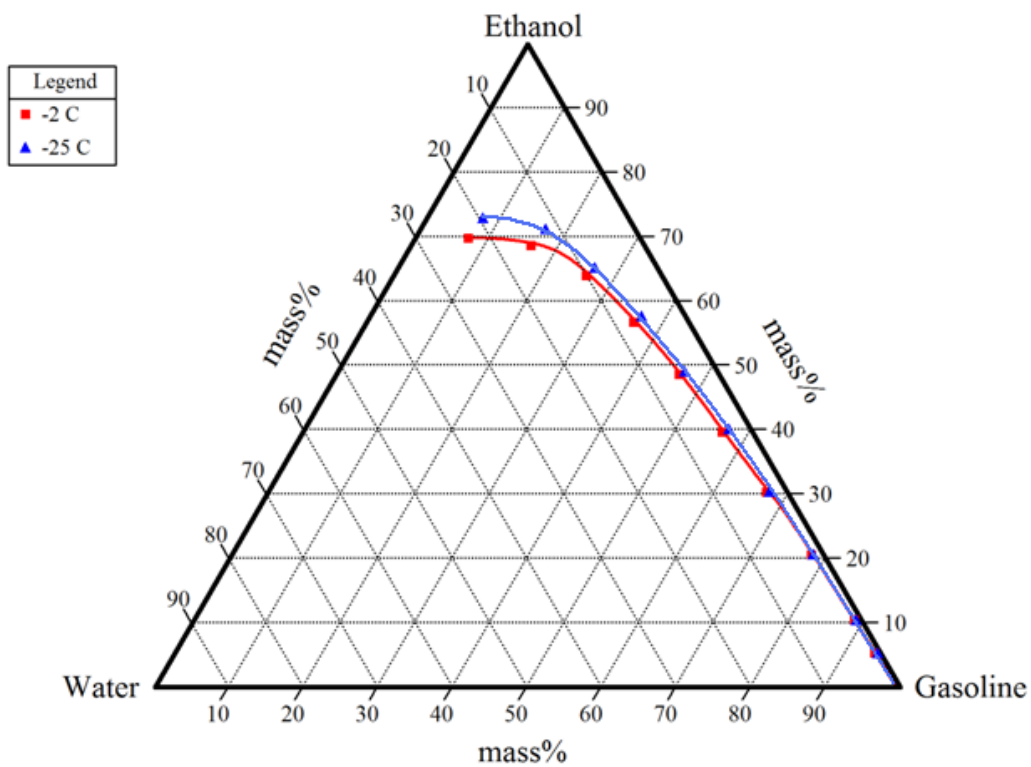


Figure 9: Ternary Phase Diagram

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  $-25^{\circ}\text{C}$  than at  $-2^{\circ}\text{C}$ , though 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:

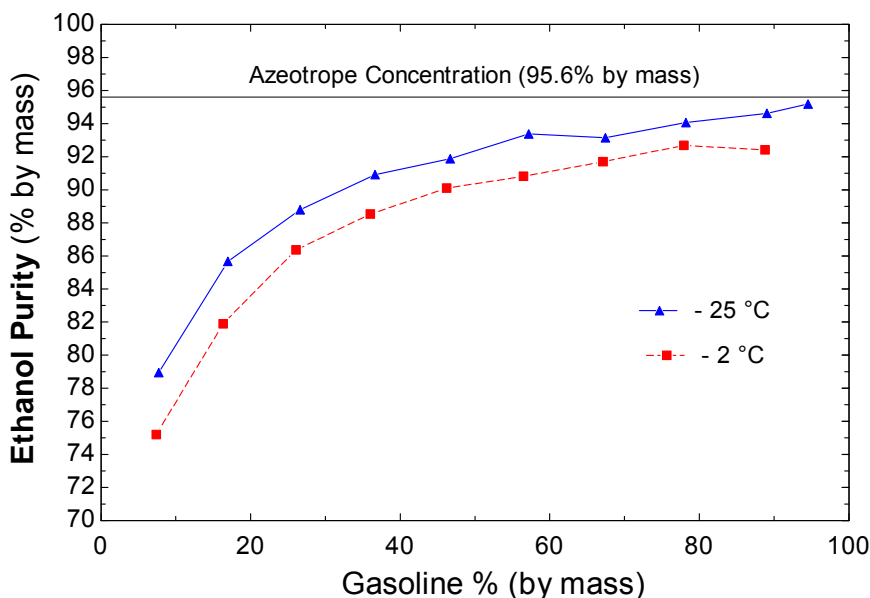


Figure 10: Ethanol purity requirement

Figure 10 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 very high gasoline content ( $>95\%$ ), but the data at hand clearly show that ethanol below the azeotrope concentration can be used in blends with gasoline contents below approximately 95%, at least as low as  $-25^{\circ}\text{C}$ .

It complicates the water tolerance issue somewhat when ethanol/gasoline/water blends are used in Flex Fuel Vehicles (FFV). The basic concept of the 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 be problematic having 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 9) 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 will not intersect the phase separation curves (see the figure below), making these blends acceptable for Flex Fuel use at  $-25^{\circ}\text{C}$ .

## Phase Separation Curves

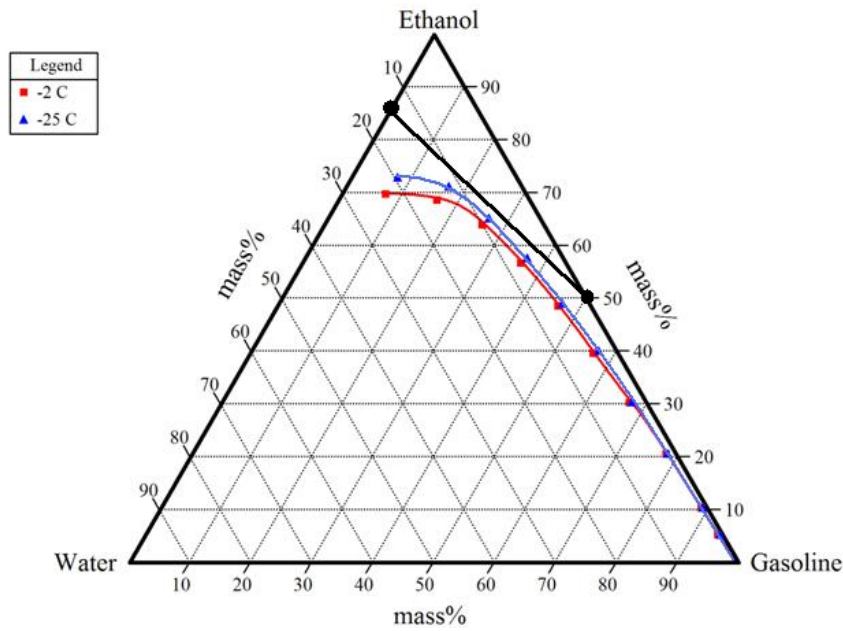


Figure 11: Phase Separation of Ternary Blends

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 presented results pre-suppose that the ethanol-rich flex fuel blend contains 20% gasoline by mass<sup>iv</sup> (as is often the case in the 'E85' type ethanol blends). Table 3 shows how the allowable water content increases with the content of ethanol.

Table 3: 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

<sup>iv</sup> When the ethanol-rich flex fuel blend is gasoline-free hydrous ethanol, the purity requirements are approximately one percentage point lower (ibid).

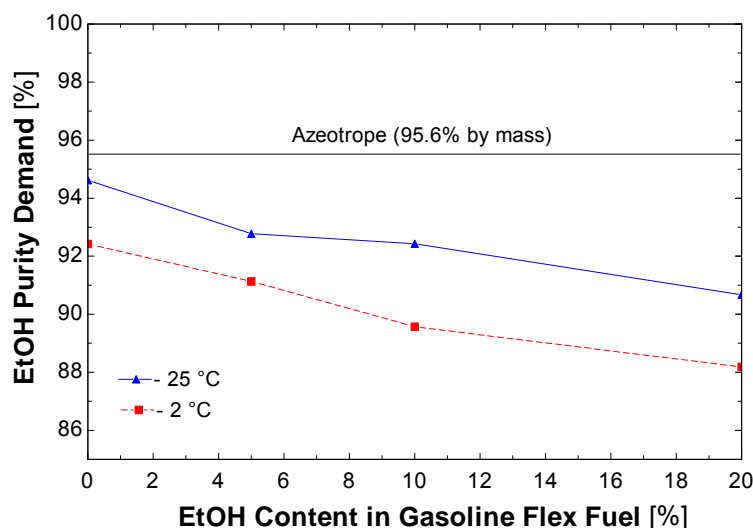


Figure 12: Purity requirement for Ethanol/ Gasoline Blends

The results obtained contradict the conventional wisdom of ethanol/gasoline fuel blends, demonstrating that hydrous blends at 95% purity would be acceptable for blending with present-day gasoline, even at low temperatures, down to -25 °C, in every conceivable mixture which 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 to the ethanol-rich flex fuel blend will be. 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 will phase separate into separate liquid phases; one consisting primarily of diesel, and the other primarily of ethanol<sup>(44)</sup>. It should be noted, however, that diesel fuel can experience phase separation problems even by itself at low temperatures. At sufficiently low temperatures, the paraffin components of the fuel will begin to freeze, giving the fuel a wax-like texture which will lead to engine failure. In normal diesel terminology, the temperature where the fuel turns into an unclear substance, is called the 'cloud point'. This point indicates the start of wax formation<sup>(48)</sup> whereas 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 (like is the case with milk). Even though emulsions generally have a better ethanol/diesel miscibility and recent research has focused more on ethanol diesel *solutions* (brand names such as E-diesel and O2-diesel)<sup>(49)</sup>. Solutions have the advantage that they can be produced by 'splash blending' 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 the use of an additive, a co-solvent, to ensure phase stability which is depending 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%) phase separation can occur<sup>(50)</sup>. An important advantage of using solutions is that the blend can be used immediately in diesel engines or with only minor engine adjustments. A major disadvantage to solutions is that they tend to absorb water and separate during storage, thus having limited storage capability, but similar problems are known with regular diesel exposed to water<sup>(51)</sup>. The percentages of ethanol most commonly blended into diesel are less than 20%<sup>(52, 53)</sup>. Newer techniques utilizes dispenser custom blending where 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 thus 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. Like 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 below.

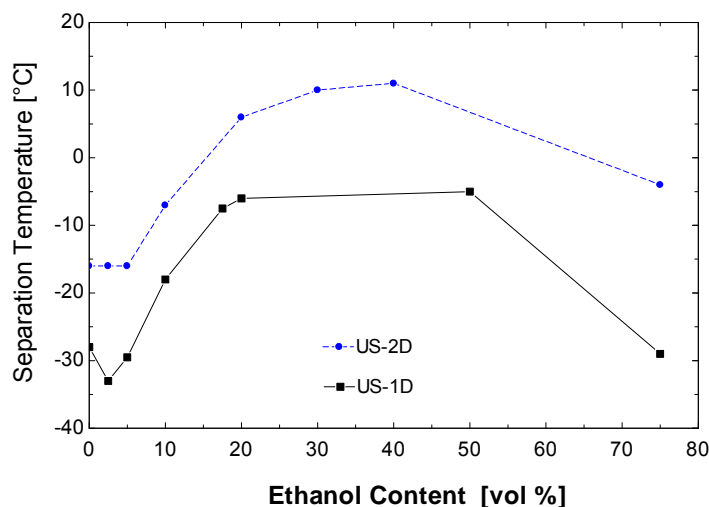


Figure 13: Phase separation temperatures of ethanol/diesel blends. Source: <sup>(44)</sup>.

*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.*

Several features of the data presented in figure 13 must be addressed. Firstly, phase separation is less likely to occur in solutions with either very high or very low ethanol content (solutions below the line will separate). For ethanol contents below 5%, the presence of ethanol does not lead to a lower separation temperature than the cloud point temperature of pure diesel, meaning that blends with an ethanol content below 5 vol% are just as tolerant to cold temperatures as pure diesel. The same seems to be true with

blends with an ethanol content above 75 vol%. In between these limits, however, serious de-mixing problems could occur.

Advances in the use of co-solvents have been shown to improve miscibility to the extent that the previously mentioned E-Diesel blend (15% anhydrous ethanol in diesel) has been made suitable for winter use, without risk of de-mixing<sup>(49)</sup>. The other patented ethanol/diesel solution, O<sub>2</sub>diesel, uses only approximately one percent of co-solvent to stabilize 7.7% 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% 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<sup>(52, 53)</sup>. Diesel/ ethanol blends are usually of the so called micro-emulsion type (meaning the droplets are very small) due to a high stability<sup>(54)</sup>. Diesel/ ethanol emulsions can contain up to 40% ethanol depending on the type of diesel<sup>(52)</sup>. Additives in considerable amounts can be necessary for high level ethanol emulsions and the cost of additives could be a major drawback to this approach. Biodiesel have been shown to enhance the solubility of ethanol in diesel and will be discussed in a later section<sup>(54)</sup>. The low temperature stability of emulsions can in some cases be even better than regular diesel fuels due to the additives<sup>(55)</sup>. It has been shown that, with the use of an emulsifying agent, blends with a high proportion of hydrous (5%) ethanol and diesel can be stable down to minus 15.5 °C.

Summing up, the use of ethanol as an additive, i.e. an ethanol content below 15% in diesel solutions, is technically feasible, even at winter temperatures. The data shown in figure 13 indicate that diesel blends with higher ethanol contents would probably encounter phase stability problems, unless the ethanol content is above 75%. The feasibility of this kind of ethanol rich blends has not been the cause of much, if any, published research so 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 etc. If blended with gasoline, diesel or a denaturing agent, the toxicity will increase.

Safety issues concerning fuels generally concern the dangers of fires 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 Limit (LFL/UFL), which mark the flammable temperature range. The flammable temperature ranges for ethanol fuel blends in closed containers can be seen below

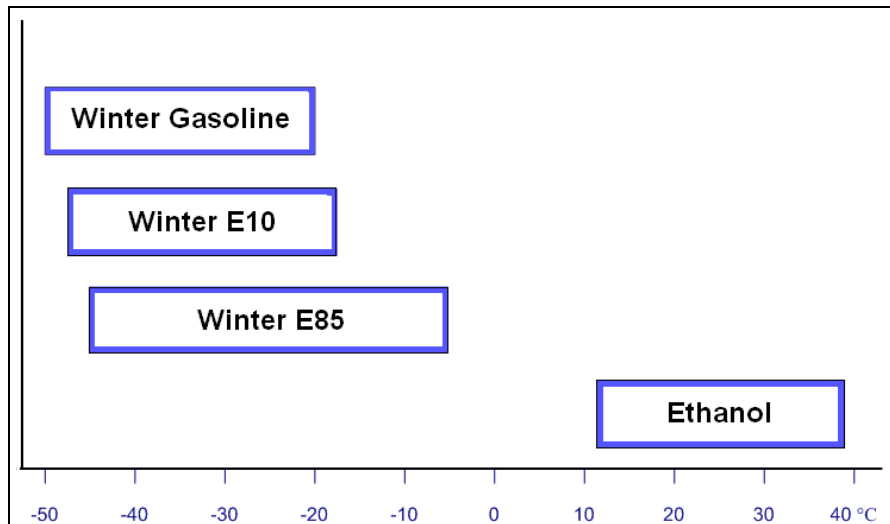


Figure 14: Flammability temperature ranges for gasoline. Source: <sup>(56)</sup>.

These flammability ranges apply to closed vessel conditions only, such as in fuel tank headspaces. Compared to gasoline, the flammability ranges of E85 and ethanol extend into more common ambient temperature, meaning that these blends will theoretically have a greater risk of fuel tank headspace fires, though the risk is still very small <sup>(56)</sup>. Only approximately a hundred cases of such fires (with all types of fuel) have been reported globally <sup>(57)</sup>. The primary risk of a fuel tank fire occurs during refueling <sup>(56)</sup> due to the possibility of discharges of static electricity between the filler neck and the fuel hose nozzle. Overall though, the fire hazard problem of pure ethanol or ethanol/gasoline blends seems manageable.

The perhaps 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 fuel tanks there will in many cases be a void (especially when partially full) where fuel vapors will mix with the air forming an ignitable mixture.

Ethanol/ diesel blends have been shown to have roughly the same flammability properties as neat ethanol making e-diesel belong in the safety class of gasoline fuel, not diesel fuels <sup>(49)</sup>. Even relatively small amounts of ethanol in diesel will dramatically lower the flashpoint and there is not a linear relation between ethanol percentage and flash point. In practice this means that for e-diesel blends which most commonly contains about 5-15% ethanol, the flash point is about the same as ethanol <sup>(58)</sup>. Furthermore the flammability limits are most unfortunate for ethanol fuels compared to both diesel and gasoline. For gasoline the vapors will be too concentrated above -20°C and for diesel the vapors will be too lean below 64°C <sup>(59)</sup>.

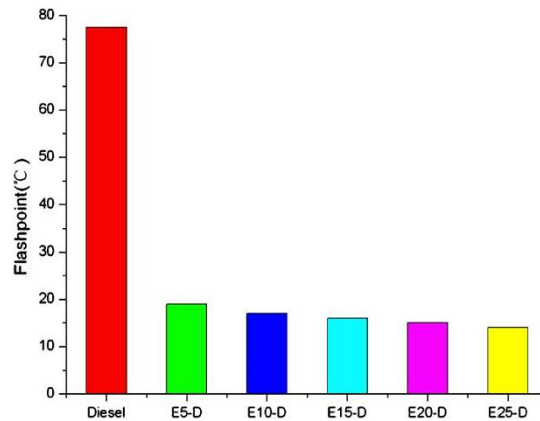


Figure 15: Flashpoint of ethanol diesel fuels, source <sup>(58)</sup>.

Figure 15 illustrates that even 5% ethanol in diesel will lower the flash to level close to that of neat ethanol.

The unfortunate flammability limits combined with the low flashpoint makes it necessary to take measures in order to store, distribute, handle and use 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 Ref. <sup>(59)</sup>:

- Fuel tanks in diesel vehicles would 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, i.e. from production to end-use.
- Electrical ground connections should be established when fuelling at stations and tank level detectors might also need redesign.

The necessary safety technology for ethanol/diesel blends is well-known and can be transferred directly from the solutions applied to gasoline, but it will incur some expenses to upgrade diesel fuel dispensers and vehicles to meet the demands posed by such blends.

It can be concluded that diesel-ethanol fuels should not be stored, distributed, handled or used without special consideration and precautions. On the other hand it does not require unknown and unproven technology to be able to utilize and gain the benefits from ethanol fuels. According to US NREL, Ref. <sup>(60)</sup>, the main technical barriers to commercialization of e-diesel, related to flammability, are:

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

## Ethanol Usage in Transportation

The global ethanol markets are expanding rapidly. The main markets can be seen in figure 16.

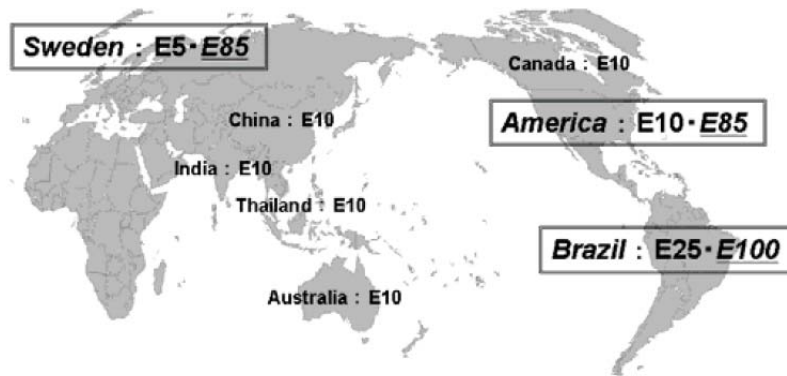


Figure 16: Overview of the global ethanol markets, source: <sup>(61)</sup>.

The figure shows that, apart from the Brazilian market, which is a special case, ethanol fuels are either low level blends such as E5, E10 or the high level blend E85, which is substituted by E70 in the winter time. 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). Besides the markets seen in the figure, ethanol fuels for the diesel market do exist, but on a much smaller scale and can be characterized as niche markets so far.

### ***Application in SI Engines***

The following section describes the possibilities and difficulties associated with the application of ethanol in gasoline passenger cars. Some important fuel properties will be discussed as well as the compatibility and potential of ethanol fuels in spark ignited engines.

### **Fuel Compatibility**

E5 and E10 are already on the market all around the world and have generally shown compatibility with existing SI engines <sup>(62)</sup>. 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 customers experience no apparent problems with their older vehicles, it is likely that increased fuel emissions by evaporation through the fuel system will occur.

A study <sup>(63)</sup> which included experimental work, made by Orbital, focused on the potential effects of using E20 in the Australian gasoline vehicle fleet. The concluded 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 catalysts, greater levels of wear and engine deposits.

In 2007 Orbital Australia <sup>(187)</sup> 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 selected test vehicles comprised vehicles which were 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 adverse impacts on driveability. 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 manufacturer's warranty. E5 or E10 usage is not always recommended by the manufacturers though. Potentially all future gasoline vehicles could be made compatible with all blends from E0 to E85, as is done with many vehicles in The US market, with no extra cost on the vehicle <sup>(62)</sup>. Furthermore all the major car manufacturers are likely capable of making vehicles compatible, even with hydrated ethanol (E100), since they all produce cars for the Brazilian market.

## Materials and Corrosion

One of the major concerns, regarding the use of ethanol as a transportation fuel, is the corrosive and degrading effect it can have on fuel systems and fuel storage facilities. The most notable compatibility problems identified in fleet tests are:

- 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 and/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 <sup>(64)</sup>.
- Fuel line clogging due to ethanol "stripping off" fuel system deposits. This has been observed in vehicles switching from pure gasoline operation to ethanol blends between 10 and 20 vol% ethanol <sup>(65)</sup>. However, this phenomenon has not been reported as problematic during the recent upsurge in use of E10 blends in the USA.

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 <sup>(63)</sup>. It was reported that fuel system degradation and corrosion started at approximately 14% ethanol in the blend <sup>(65)</sup>. 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 <sup>(66)</sup>.

A more recent test performed by the Minnesota Centre for Automotive Research directly compared anhydrous ethanol (water content was less than 1%) in E10 and E20 blends <sup>(67)</sup>, finding that both fuels showed similar, and serious, degradation of many plastic materials commonly used in non-FFV fuel systems, while neither of the two 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 it presented any concern.

As a conclusion; whereas anhydrous E10 could possibly cause perishing of plastics in many existing vehicles, hydrous ethanol blends seem likely to corrode or damage both the metal, rubber and plastic parts used in many current vehicles' fuel systems - damage which 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 will void the warranty of the vehicle. For all new non-FFVs produced in the USA this limit is 10%, whereas some Asian and European car manufacturers have specified a limit for new cars of only 5%, notably Fiat, Renault, Daewoo, Alfa Romeo and some Suzuki and Mazda models<sup>(68)</sup>. 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 list of ethanol compatibility for different gasoline vehicle models are available online<sup>(68, 69)</sup>.

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. From the findings of the Minnesota Centre for Automotive Research (cited above), however, it seems a feasible task to upgrade current vehicles to the use of blends with (at least) up to 20% anhydrous ethanol, since only certain plastic fuel system parts would need to be replaced.

In ethanol-compatible non-FFVs and gasoline/ethanol Flex Fuel Vehicles (FFVs), the problem of corrosion and degradation has been countered by the use of ethanol-resistant materials in fuel systems, stainless steel substituting aluminum, magnesium, lead, brass among other metals. PVC and some rubber parts being replaced by materials such as high-density polyethylene, nylon and fluorinated plastics such as Teflon<sup>(70)</sup>. These measures have effectively solved the materials compatibility issue with ethanol - FFVs experiencing no extra engine or fuel system wear from the use of E85<sup>(71)</sup>. It has not been possible to find any direct scientific documentation of the engine and fuel system wear in Brazilian vehicles running on E100, but by all accounts, the experience acquired by the car manufacturer industry by 30 years of experience with hydrous ethanol fuel seems to have eliminated any major compatibility problems through the correct choice of materials<sup>(73)</sup>.

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<sup>(64)</sup>. 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 same considerations as for FFVs need to be taken, regarding the choice of materials for fuel system and engine parts. When using ethanol-resistant materials, blends of diesel and anhydrous ethanol have been shown in several over-the-road tests to give the same engine and fuel system durability as pure diesel, even with as much as 30% anhydrous ethanol in the blend<sup>(49)</sup>. Similar tests of hydrous ethanol/diesel blends have not been found reported, but would be assumed to 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 non-resistant fuel components, such as those made of aluminum, lead magnesium and PVC, among others.

## Energy Density

One way of reducing the CO<sub>2</sub> emissions from a vehicle is to make it more fuel efficient, i.e. make it use less energy. Ethanol has significantly lower energy density<sup>v</sup>, about 2/3 compared to gasoline, so about 50% more fuel (by volume) is needed per km, if a given engine is equally fuel efficient on either fuel. In cases where an engine is equipped to utilize ethanol properly, ethanol usage can increase the energy efficiency of the engine and thereby off-set the otherwise higher fuel consumption. Looking at CO<sub>2</sub> emissions the increased efficiency would lead to lower CO<sub>2</sub> emissions, even though more fuel is used. The lower energy density of ethanol will in many cases necessitate 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 which are able to run on E85, or blends of E85 and regular gasoline (or low ethanol blends), will typically not experience a performance decrease, since the vehicle is prepared for the properties of ethanol.

Figure 17 shows the energy content of typical ethanol fuels currently on the market.

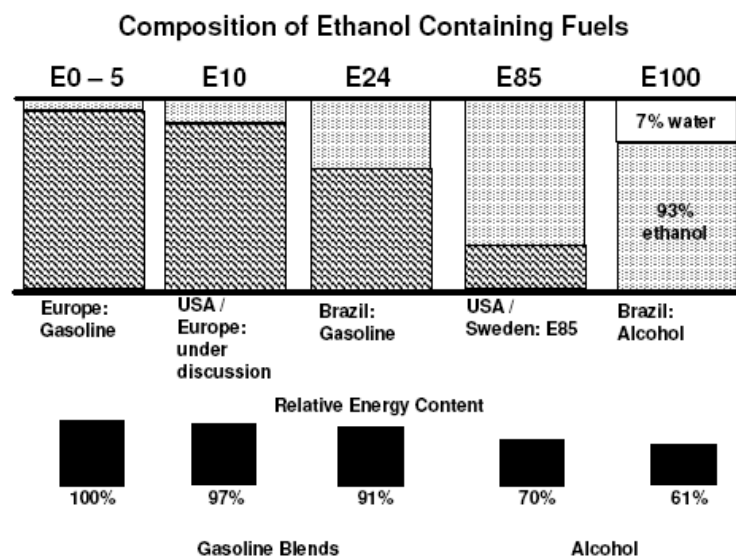


Figure 17: The relative energy content of ethanol fuels compared to gasoline. Source: <sup>(74)</sup>.

## Oxygen Content

It is widely recognized that so-called oxygenates, used as blending components in gasoline, are beneficial for both combustion efficiency and exhaust emissions especially CO emissions. Ethanol contains about 35% 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.

<sup>v</sup> Joule per liter

The oxygen content of ethanol gives cause to a lower stoichiometrical air/ fuel ratio (AFR) compared to gasoline, i.e. 9:1 and 14.7:1, for neat ethanol and gasoline respectively. This means that more fuel need to be injected per engine cycle. Considering the 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 why current gasoline engines do not need a fundamental re-design to run on ethanol and performs similarly with either fuel <sup>(75)</sup>.

Since the introduction of the three-way catalyst, passenger cars have been equipped with a so-called closed loop system to measure and ensure a stoichiometrical AFR, using the so-called 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 will not be able to adjust the AFR and will not run with a correct AFR. Incorrect AFR can cause problems such as too lean combustion possibly resulting in worse exhaust emissions, start problems, lack of power and/ or engine failures. Ethanol fuel usage is usually not recommended for these types of cars <sup>(68)</sup>.

## 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, i.e. 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 and 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 of increased compression ratio is, that NO<sub>x</sub> formation inside the engine increases with increasing compression ratio due to increased peak combustion temperatures <sup>(76)</sup>. Reversely, higher compression ratios with ethanol use seem to enable high EGR<sup>vi</sup> ratios which can reduce NO<sub>x</sub> significantly <sup>(77, 78)</sup>. The net outcome of these two mechanisms will depend on the configuration of the engine.

When a gas is compressed, its temperature will increase. If the temperature gets too high during the compression stroke in an SI engine, there is a possibility of premature auto-ignition of the fuel and shockwaves can form 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 will decrease. Furthermore, heavy knocking is very harmful to the engine. The two main parameters (in a well adjusted engine) deciding 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, i.e. a better fuel economy and relatively lower CO<sub>2</sub> emissions.

Currently, much work is being done by car manufacturers to develop engines which 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 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 engines, in practically all cases, are optimized for regular gasoline. Currently there are no vehicles on the market that can automatically change the compression

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<sup>vi</sup> EGR, Exhaust Gas Recirculation is a very common system that re-circulates a part of the exhaust gas back to the fresh air intake.

ratio according to the fuel, but some experimental concepts have been demonstrated, and many of the big car manufacturers are active in this area<sup>(79)</sup>. Unfortunately, variable compression ratio for optimal fuel efficiency in flex fuel vehicles is currently not economically feasible<sup>(80, 81)</sup>.

Other technologies can be used for getting a better utilization of high octane ethanol fuels, while maintaining tolerance for low octane fuels. Among those are Variable Valve Timing (VVT), turbo charging and ethanol boosting systems (EBS). Generally modern cars are moving towards more comprehensive and precise control of engine parameters (valve timing, ignition timing, AFR, injection timing, turbo and EGR) which do result in more flexibility to reach optimal combustion under all conditions, including different fuel octane numbers. These improvements give the industry much more freedom to make engines tolerant towards 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. Vaporization of the fuel in an SI engine absorbs energy from the engine surroundings thus lowering the temperature, in the intake manifold, combustion chamber 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 with ethanol fuels. 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 for especially DI (direct fuel injection) engines, but also for PFI (port fuel injection) engines, is the so-called charge cooling<sup>(82)</sup>. 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, will increase the air density thus enabling 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 will tend to increase engine efficiency due to lower internal heat losses, while also lowering exhaust gas heat losses, which is observed as lower exhaust gas temperatures using ethanol fuels. Work needed during the compression stroke has also been shown to decrease due to the high latent heat<sup>(77)</sup> 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 motivation for using ethanol containing water is mainly to eliminate the process of dehydration which is relatively energy consuming and costly. By running on hydrated ethanol, the overall life cycle energy cost is reduced significantly and hydrated ethanol is as such a more energy and CO<sub>2</sub> efficient fuel. As mentioned in an earlier chapter of this report, solutions of water, ethanol and gasoline are in some cases unstable, which is the main reason why hydrated ethanol usage has not been used in temperate climates. Hydrated ethanol is only used as either high level ethanol blends or neat ethanol<sup>(83)</sup> and only limited recent research is available on hydrated versus anhydrous ethanol in SI engines at this point. 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 of anhydrous ethanol. The latent heat of vaporization for hydrated ethanol is higher than anhydrous ethanol, increasing with water percentage. Water increases the octane number i.e. increases the knock limit but decreases the stoichiometrical AFR due to the lower energy content<sup>(83)</sup>.

The effects of water in SI engines has been investigated by using techniques such as injection of steam, direct and manifold injection of liquid water and water mixed into the fuel both direct and manifold injection. There are of course the Brazilian experiences which dates back as early as the seventies. A number of studies have shown that water addition has a very positive effect on reducing NO<sub>x</sub> (nitrogen oxides) emissions (up to 90%) but tends to increase HC (hydro carbon) emissions. (Most of the HC emissions are nowadays converted into water and CO<sub>2</sub> by the catalyst in modern cars.) The effect on engine efficiency is limited, i.e. anhydrous and hydrated ethanol with relatively high water content provide 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 this seems not to have been shown in the literature yet <sup>(83)</sup>.

A Dutch company called HE Blends has recently experimented with hydrous ethanol blends with 15% and 20% azeotropic ethanol (ca. 4% water) <sup>(84)</sup>. They tested a VW Golf mark 5 FSI, running 32.000 km over one year in ambient conditions from minus 20°C to plus 35°C. Observations showed lower fuel consumption while emissions complied with the Euro4 standard, with no engine optimization done. No deterioration of gaskets, seals, fuel system or anything else was found. HE Blends are currently cooperating with the European BEST initiative (Bio-Ethanol for Sustainable Transport), performing limited market trials and are doing further testing in programs under the Dutch and German governments.

## Technical Potential of Ethanol in SI Engines

This chapter addresses the advantages which 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. As earlier described, ethanol contains only about 2/3 the energy of gasoline, a fact which is of course reflected in the mileage proportionally, though offset somewhat due to the fact that ethanol can increase the efficiency of SI engines. The ideal solution to this problem would be, if engines were able to utilize ethanol so efficiently, that there would be no mileage penalty. With an experimental high compression ratio engine, it has actually been shown that E30 can have better mileage per liter compared to gasoline <sup>(85)</sup>.

As discussed earlier, 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 to regular gasoline. In that case the most modern cars are able to regulate the ignition timing and advance the timing to a degree that will increase engine efficiency a few percent.

Perhaps the strongest trend in SI engine development at present is downsizing, which basically means decreasing the cylinder volumes of the engine, while maintaining the original power and torque output. Though the engine volumes in many new vehicles are reduced, the trend is that engine performance is increased. The main goal of downsizing is reduced engine energy losses, resulting in higher fuel efficiency. As the efficiency of the SI engine is varying with the speed and load, it is of interest to use the speed/load range where the engine is working most efficiently, as much as possible, to reduce overall fuel consumption and CO<sub>2</sub> emissions. Unfortunately the optimal fuel economical range is in many cases different from running conditions on the roads, but downsizing brings the fuel economical range and road loads closer <sup>(86)</sup>.

To make downsizing attractive, it seems important for manufacturers to display that the smaller engine can perform as a much bigger one, only with improved fuel economy. One key technology in making downsizing possible is super charging, i.e. to increase the pressure of the inlet air stream 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 turbo are used to better boost the full engine operation range. An important challenge for successful downsizing is the performance at lower engine speeds since small engines normally doesn't have sufficient torque at this range<sup>(86)</sup>. At lower speeds pressures in the engine are relatively low and there are therefore room for raising the pressure and thus raise the yield. At higher speeds and loads pressure increases and the phenomenon of knocking will more easily occur when using turbo-charging. Due to its high octane number, ethanol can accept a higher degree of turbo charging, making downsizing an especially beneficial approach for ethanol engines.

A key parameter, when trying to utilize ethanol to 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 where it is almost knocking. KL timing is a typical setting that will keep the engine at its most fuel efficient (or powerful) level, limited by the given physical and chemical conditions in the engine. MBT timing is the timing that will provide 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)<sup>(81, 87)</sup>. This means that while increasing the compression ratio and/ or adding turbo charging, the main goal is to obtain MBT or get as close as possible with KL timing, but always to avoid the condition of knocking.

One way of obtaining high efficiency has been shown by Lotus Engineering on a Toyota engine. The engine is configured with a compression ratio of 11.5:1, which is high for a port fuelled injection (PFI) gasoline engine, and turbo. The result is that the engine efficiency is 9% higher using E85 compared to gasoline (RON 95). The difference is obtained solely due to different fuel, turbo and ignition timing, E85 running with MBT and gasoline with KL timing<sup>(81)</sup>.

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

Yet another strategy has been shown by the US EPA (Environmental Protection Agency) 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 modern diesel engines, while maintaining the low production cost and low exhaust emissions of the gasoline engine. This has been achieved. In order to prevent knocking, EGR has been used extensively. These studies and others have shown that ethanol engines can operate with higher EGR ratios compared to gasoline engines, (which is also true for ethanol in diesel engines), benefiting the exhaust emissions significantly. E30 has approximately 8% less energy per liter which would result in 8% lower mileage compared to running on gasoline, if engine efficiencies were equal on both fuels. The EPA studies have shown an increase in engine fuel efficiency of 10-12% making the vehicle able to actually run longer on a liter/gallon of E30 than gasoline<sup>(77)</sup>. Figure 18 shows data from measurements on the rebuilt VW TDI engine running on up to 100% ethanol compared to a regular US FFV.

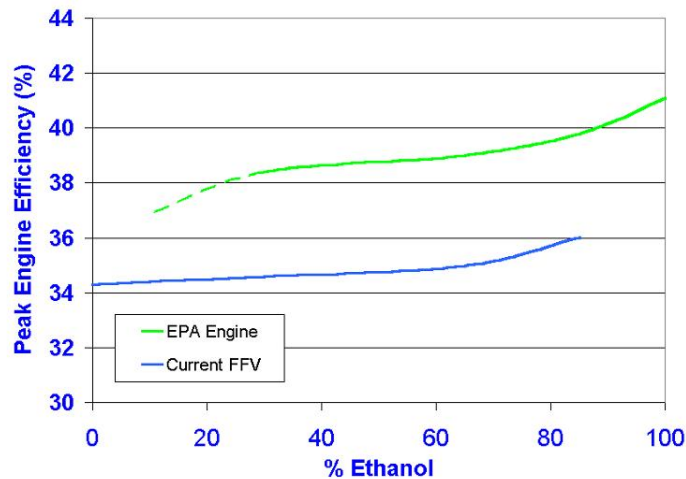


Figure 18: Peak engine efficiency running on different ethanol fuels, source: <sup>(88)</sup>.

The figure shows how engine efficiency increases with increasing ethanol content in the fuel. As can also be seen the current FFVs still have a great potential for increased fuel efficiency. The tests have shown not only very high peak efficiency, but also a broader operating range with high efficiency. US EPA presents this work as an alternative or bridging technology, which is cheaper, cleaner and more efficient than the original VW diesel engine <sup>(77)</sup>.

A study funded by US DOE <sup>(78)</sup> has been comparing current FFV against an FFV optimized for E85. Running on E85 before engine modifications, proved about 3% more efficient than regular gasoline. The compression ratio was raised and the engine now proved 10% more fuel efficient (in terms of energy) on E85 compared to gasoline. Finally a change in the gearing of the vehicle was made. Since the dedicated E85 vehicle now provided about 10% more torque, it was possible to make the engine run at lower speeds while maintaining the original performance. This method, called 'down-speeding', gained another 10% fuel economy increase. It is a general trend that ethanol makes engines 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 MIT professors has focused on gaining maximum engine efficiency with minimum ethanol usage. Seen in the light of ethanol being of limited supply, this concept seems very relevant. The concept is a so-called Ethanol Boosting System (EBS) and 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 depending on the load and speed of the engine. It is thus only at high loads and speeds ethanol injection is needed 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, turbo charging and downsizing. An increase of 30% efficiency compared to a conventional PFI gasoline engine is proposed <sup>(89)</sup>.

Trying to quantify the general potential of ethanol in SI engines compared to regular gasoline, the following reservations should be mentioned: A) Different engine designs react differently on factors such as; increased amounts of ethanol in the fuel, turbo charging, increased compression ratio etc. B) The potential efficiency increase must be seen over the full range of the engine, i.e. from idling to full power, or better even, the range that will typically be used on the road.

Looking through the literature in this area, 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 wherein the engine is more efficient with ethanol fuels is generally broader, compared to gasoline. In figure 19 examples from the literature is plotted into a diagram showing engine peak efficiency versus engine technology or fuel.

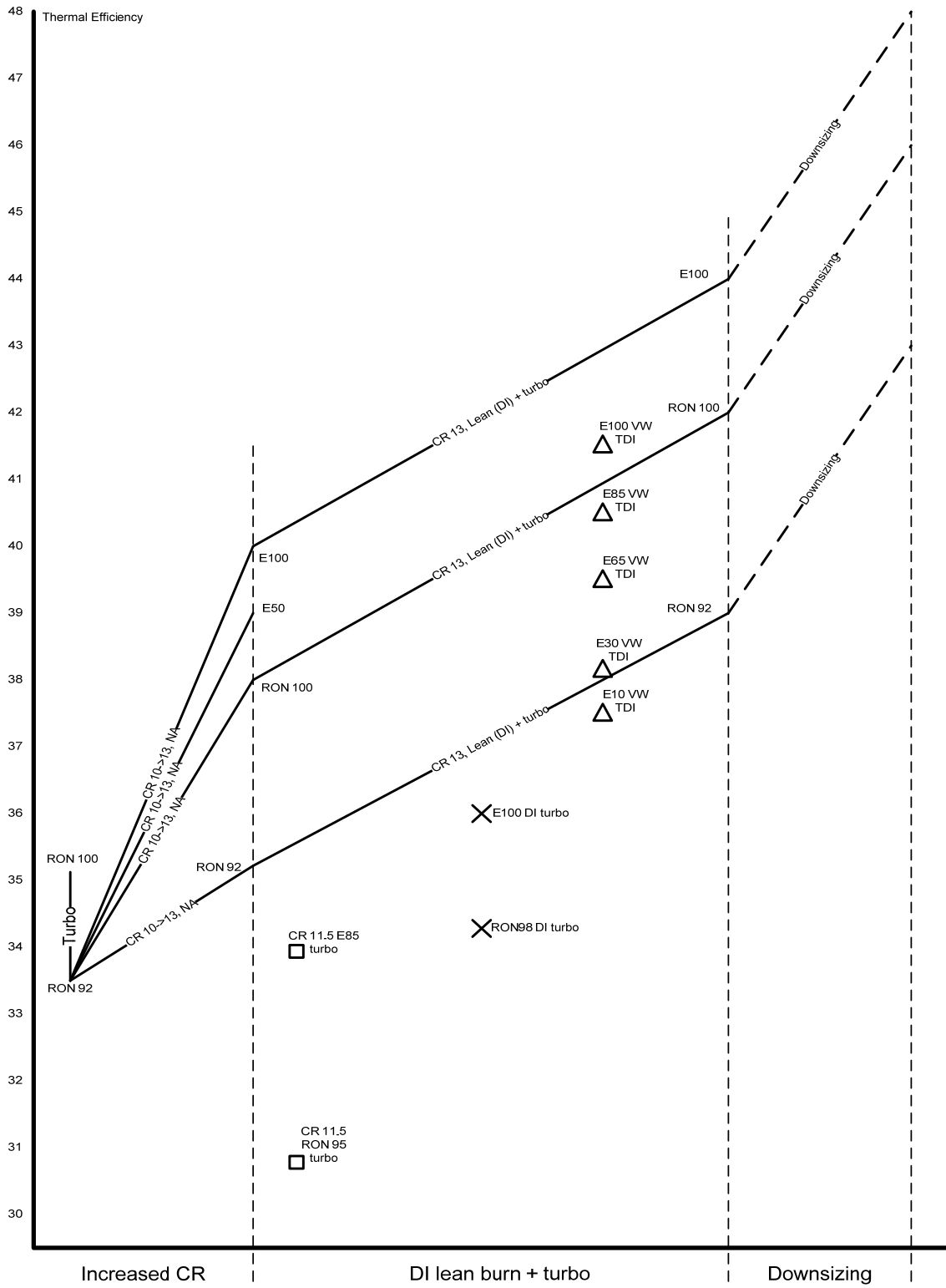


Figure 19: Efficiency potential of engines operating on ethanol.

Figure 19 shows the potential for ethanol application in gasoline engines. The lines represents one study, the squares, crosses and triangles other studies respectively. Sources: <sup>(90, 77, 75, 81, 91)</sup>.

It can be seen how peak engine efficiency is increased by applying various technologies and fuels. The data points are extracted from recent engine tests. The first part, reading from the left towards 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. Generally, the use of fuels with higher octane rating (RON) increases the potential gain of this technology (as previously described). One data set on the left shows the mere effect of applying turbo charging and a higher octane rating, using the same compression ratio.

The next part shows the potential when applying a range of technologies; turbo charging, lean combustion, and direct injection (DI). It is apparent that 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 section of the graph, a few other figures has been added to compliment the trends shown. At the lower end, the squares illustrates the effect of changing fuel from RON 95 to E85, i.e. an increase from about 30.7% to 33.8% only due to the fuel change. The crosses shows a similar trend in another study. The triangles is a special case where a diesel engine (earlier described) was adapted to run on gasoline/ethanol blends of various kinds. The crosses illustrate what can be achieved merely by changing the fuel and engine management, i.e. a significant engine efficiency increase from about 37.5% to 41.5%.

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% relatively <sup>(86)</sup>, but this is an estimate which may vary with the specific engine designs.

From the figure it is seen that engine efficiencies comparable to those of diesel engines has been obtained with the use of the mentioned (common) technologies and with the use of ethanol.

Looking at emerging gasoline engine technologies, ethanol shows promising qualities as well. CAI (Controlled Auto-Ignition) is an advanced gasoline combustion technique closely related to HCCI (Homogenous Charge Compression Ignition) combustion. As the name applies ignition of the fuel is obtained by auto-ignition, i.e. compression ignition. Mercedes Benz is one of the car manufacturers which are introducing this principle, under the name DiesOtto. They claim 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<sub>x</sub> 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 <sup>(92, 93)</sup>. Research done 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. This is mainly due to ethanol's tolerance of much higher EGR ratios <sup>(94)</sup>.

GM has developed an HCCI engine able to run on gasoline and E85. According to GM an increased fuel efficiency of 15% and low NO<sub>x</sub> emissions can be credited to the HCCI combustion mode, which (like in the DiesOtto concept) only happens 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) <sup>(95)</sup>. VW has also unveiled plans of a pHCCI engine <sup>(96)</sup>. As modern cars get more and more sophisticated in the computerized control of combustion parameters (ignition timing, super charge pressure, EGR rate, fuel injection), it would seem likely that advanced combustion modes such as CAI and HCCI will become commercially available soon, and that 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

There are two main potential problems related to cold engine start when using ethanol in SI engines: Reliable engine startup (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. Generally, the start up of the engine is not a problem in FFV vehicles as long as certain measures are taken. Cold start is generally not a problem when using low level blends such as E5 or E10 (other than those normally experienced with the use of gasoline fuel). An investigation of E10 made by CONCAWE and GFC<sup>(97)</sup> has shown that ethanol itself does not cause cold start problems, as much as the low volatility caused by ethanol blending. It is in other words possible to adjust and maintain a volatility level which is complying 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. Generally, where ethanol constitutes the larger part of the blend, cold start problems are more likely to arise<sup>(98)</sup>, but knowledge about cold start with ethanol fuels having ethanol percentages between 10-70% seems not well investigated.

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, will be too lean to successfully initiate and sustain combustion. Compared to gasoline, neat ethanol needs a higher gaseous concentration in air to be flammable, i.e. 3.3% by volume compared to roughly 1.0% for gasoline, see table 2. At the same time, being a pure substance, ethanol does not, like gasoline, contain any highly volatile components. It is the contents of volatile species, such as pentane and hexane, that allow gasoline fuelled engines to start at very low temperatures<sup>(70)</sup>. Due to the combination of these two factors, neat ethanol will have 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 to boost the vaporization of the fuel.

Considering a system used to overcome cold start problems, criteria such as efficiency, cost of technology, convenience of use and start-up emissions have to be evaluated according to the 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, primarily used in Brazil.
- Lowering the ethanol content of E85 to approximately 70%, in combination with a 'block heater' - an approach currently used in on-the-road FFVs in the northern hemisphere in the winter time.

## ***Dual Fuel***

Dual fuel systems incorporate two separate fuel systems, including a small auxiliary fuel tank which 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 <sup>(72)</sup>. The dual fuel concept is very effective in facilitating cold starts, but requires the car owner to monitor and refill two fuel tanks. It has been claimed that this would 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% ethanol, gasoline constituting the rest <sup>(99)</sup>. Even though this strategy is effective in starting the engine, it will invariably lead to very high emissions of unburned and partly burned fuel components during the cold start and warm-up phases of driving <sup>(70)</sup>, mainly because a major part of the injected fuel condenses on the cold cylinder walls, later to exit the engine unburned <sup>(100)</sup>. 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 simply consists of a heating element in the engine coolant which, 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 in the vehicle to the power grid, and secondly 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. Though 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, there are also advantages to the block heater. First of all the devices needed are inexpensive and efficient in facilitating cold starts. Secondly, it reduces 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**

As discussed earlier, significant measures are currently being taken to avoid cold start problems. The current trends of the 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 direct gasoline injection (GDI), variable valve timing (VVT) and, in general, a very 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. While 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 concerning the ethanol direct injection engine (EDI), but scientific documentation of these efforts is limited.

A study by Toyota<sup>(61)</sup> on a PFI engine has shown how cold start problems can be related to fuel injection amounts, see figure 20. The figure shows the required amount of fuel in the initial injection for three different fuels. It is shown that 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 since ethanol acts as a conductor and this can cause misfires as opposed to gasoline which acts as an insulator<sup>(101)</sup>. The increased amount of fuel is injected to provide enough flammable mixture, or to increase the amount of highly volatile compounds. This will under normal conditions result in worsened tailpipe emissions.

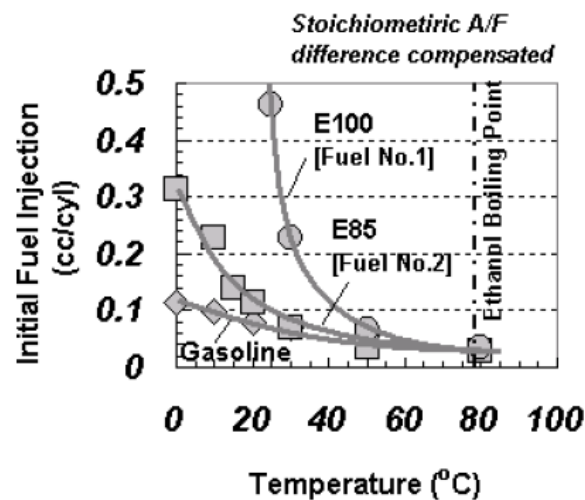


Figure 20: Source: <sup>(61)</sup>, showing the increased amount of fuel needed for successful engine start.

Trying to inject more fuel during cold condition 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 will therefore not start. The time duration of fuel injection in DI engines is limited compared to PFI engines due to the risk of injecting fuel directly into the exhaust pipes. A study<sup>(102)</sup> made by GM has 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 improving vaporization too. The high pressure is provided by delaying the start by about one second leaving the fuel pump time to build up pressure. It was noted in the study that the requirement for the extra amount of fuel at cold temperatures decreased by a

factor 10 with DI compared to PFI systems. Despite the lesser amount of fuel required, the maximum fuel flow still constituted a limit for low temperature start up.

A study made by AVL <sup>(74)</sup> has investigated the spray inside the combustion chamber during engine start up. During start up, DI engines have the possibility to significantly reduce the excessive amounts of fuel, due to 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. Effective reduction has in this case been found to depend not only on high pressure injections but, perhaps more importantly, 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 shown its potential for cold starting with high level ethanol fuels <sup>(61)</sup>. 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. The result was that the lower limit in terms of temperature for successful cold start was moved downwards. See figure 21.

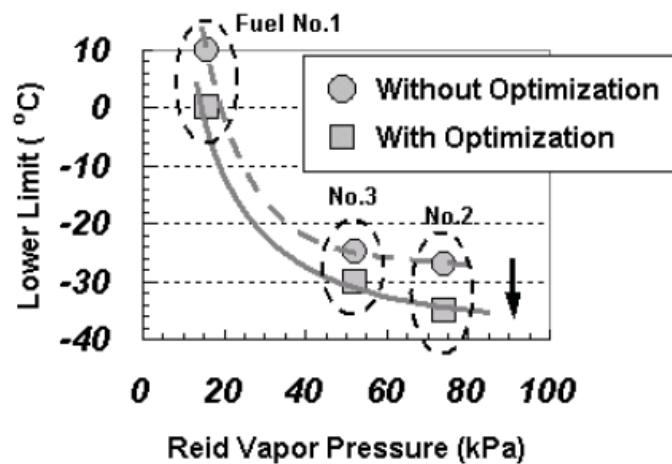


Figure 21: Source: <sup>(61)</sup>, Lower limit for cold start is improved with VVT.

Figure 21 shows that in this case VVT is not a complete solution to the problem of cold start as Fuel No.1 (hydrous E100) still has a lower limit of 0°C. Another way of increasing the peak compression temperature has been described in Ref. <sup>(77)</sup> and the technique is simply to increase the start up cranking speed of the engine. This also helps to improve air-fuel mixing.

## ***Fuel Additives***

The much lower limit obtained by Fuel No.2 and 3 (E85) in figure 21 is due to an increased vapor pressure through the chemical formulation of the fuel. It can be seen that 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<sup>(61)</sup>. 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 investigation<sup>(103)</sup> has focused on MTBE (methyl tertiary butyl ether), 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 minus six degrees Celsius, i.e. more than good enough for the Brazilian market.

Additives could very well be an important part of the cold start problem solution, but further tests, including environmental assessments, should be made. However, it seems clear that 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 1998-2000 Ethanol Challenges – a competition where American universities were to convert a specific gasoline car to run on anhydrous E85. Very thorough design reports have been published<sup>(70, 104)</sup> and in 2000, a patent was issued for the system. (Patent 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 two seconds at minus 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 two minutes of cold starts, the volatile fuel is delivered to the engine, after which period the engine block and intake manifold have been 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 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 300 US\$. 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 60 US\$ 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 presently in existence, 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 it was to be used in mass-production vehicles.

A preliminary investigation at The Technical University of Denmark <sup>(105)</sup> 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 need more studying. Furthermore safety risk might be associated with the highly volatile fuel.

In relation to the Ethanol Challenges, a study <sup>(101)</sup> from Kettering University have suggested a relatively simply 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 has been shown to improve cold start up and initial idling at least to some degree.

The US NREL <sup>vii</sup> has provided a patented catalytic converter technology, not specifically designed for ethanol, which 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 <sup>(107)</sup>.

## **Emissions**

Looking at 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 haven't 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, E10 <sup>188)</sup>.

## **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 tumour growth, blood flow problems and air-way related diseases especially asthma and reduced lung function <sup>(107)</sup>. Besides the personal tragedies, disabilities and discomforts related to these illnesses there are substantial economic costs for the society, related to air pollution from road vehicles.

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<sup>vii</sup> National Renewable Energy Laboratory (under the US Department of Energy)

Particulate or soot emissions are generally not associated with the same concern in gasoline vehicles as with diesel vehicles. Since combustion in the SI engine is homogeneous, the mass of the particle emissions are much less compared to diesel engines. Research indicates however, that it is not as 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 have a relatively bigger surface area which enables a larger transport of carcinogenic PAH (Poly Aromatic Hydro Carbons) molecules into the lungs. Furthermore, smaller particles are more damaging because of their ability to penetrate deeper into the lungs. In the reviewed literature the trend is that ethanol blends provide PM (Particulate Matter) emission reductions of up to 50% compared to regular gasoline <sup>(108)</sup>. In 2005, the Australian Biofuels Taskforce report reviewed available literature and found that earlier assumptions of ethanol having no significant impact on PM emissions must be revised, as they found PM emissions to be 40% lower with E10 <sup>(109)</sup>. In 2008 an Australian study <sup>(188)</sup> investigated PM emissions from E5 and E10 use. The study utilised two real-time particle analysers, the EEPS (Engine Exhaust Particle Sizer) and the ELPE (Electrical Low Pressure Impactor). Both techniques impact a charge and 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% decrease with E5 use, and an average 33% PM decrease with E10 use. Investigations have shown that aromatic content in fuel is linked to PM emissions <sup>(110)</sup>. Aromatics in gasoline helps raise the octane rating as do ethanol, so by using ethanol there is a potential of decreasing the aromatic content, thus decreasing PM emissions.

A well known phenomenon created by vehicles in urban areas is (photochemical) smog. Emissions of hydrocarbons, nitrous oxides and carbon monoxide will, driven by the energy of sunlight, react (by complex photochemical reactions) to form ozone among other substances. Ozone is poisonous and can cause, or worsen, respiratory diseases when near ground level. In order to reduce the amount of ground level ozone, a new kind of gasoline called Reformulated Gasoline (RFG) was introduced in the nineties, among other places in the USA and Europe. RFG gasoline contains <sup>viii</sup> oxygenates which reduces tailpipe emission of CO and HC due to a better combustion <sup>(111)</sup>. Experimental investigations have shown that ethanol and MTBE as oxygenates would provide a similar effect on ozone formation <sup>(110)</sup>. There are though, ongoing discussions on whether usage of ethanol in gasoline blends improves or worsens this situation. Furthermore, there are mixed opinions whether ethanol usage increases NOx emissions <sup>(110)</sup>. A 2008 Australian study <sup>(188)</sup> found that oxides of nitrogen and ozone production increased with E10 use. The E5 results were variable for NO<sub>2</sub> emissions and E10 led to an increase in NO<sub>2</sub>. A lot of investigations have found that serious incidents of smog in several US cities have been reduced since the introduction of E10 <sup>(112)</sup> and a review <sup>(113)</sup> of the Brazilian ethanol program ProAlcool, states that the general pollution in the metropolitan area of Sao Paulo is about 20% lower due to the use of ethanol (though specific details are not available). Furthermore, tests were carried out by the Brazilian Automotive Industry Association's Energy & Environment Commission (ANFAVEA) showing that raw engine out emissions of CO and HC was about 15% lower with Brazilian gasohol compared to regular gasoline. NOx increased by 4% using gasohol. Comparing gasoline with hydrous ethanol (E100) the investigation found emissions reduced to 51%, 53% and 86% for CO, HC and NOx respectively <sup>(114)</sup>.

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 US EPA to be about 70% of total air toxins emitted from gasoline vehicles <sup>(110)</sup>. 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 <sup>(115, 116)</sup>. Air toxins also contribute to the formation of ground level ozone.

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<sup>viii</sup> gasoline blending substance containing oxygen, most commonly MTBE, ETBE and ethanol

The reviewed literature showed general agreement, that usage of ethanol reduces emissions of benzene and 1,3-butadiene while formaldehyde increases moderately and acetaldehyde increases dramatically. The US EPA has attached each pollutant with a risk factor, so that an overall risk assessment is made possible, see table 4.

Table 4: Air toxins risk factors from the US EPA, source: <sup>(117)</sup>.

Compound	EPA Risk ( $\mu\text{g}/\text{m}^3$ )-1	EPA factor (normalized)
1,3-butadiene	$2.8 \times 10^{-4}$	1.000
Benzene	$8.3 \times 10^{-6}$	0.030
Formaldehyde	$1.3 \times 10^{-5}$	0.046
Acetaldehyde	$2.2 \times 10^{-6}$	0.008

Using these factors, a number of studies find that the reduction of 1,3-butadiene and benzene outweighs the increases of formaldehyde and acetaldehyde. The EPA <sup>ix</sup> Complex Model have found, that with the use of 10% ethanol in gasoline, the weighed risk of air toxins, is reduced by 21% <sup>(108, 110)</sup>. 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 <sup>(62)</sup>. The 2008 Australian study <sup>(188)</sup> found small increases in peak ozone concentrations from airshed modelled results for E5/E10 emission scenarios. This implies that the observed reduction in tailpipe emissions of volatile organic compounds (VOC) and carbon monoxide (CO) were not sufficient to cancel out increases in the evaporative VOC mass emissions associated with higher vapour pressure of ethanol blended fuel compared to gasoline. The study <sup>(188)</sup> found that over 97% of the estimated health savings were based on PM<sub>2.5</sub> impacts on mortality and morbidity (eg asthma, cardiovascular disease). The small remainder of impacts were associated with health savings as a result of overall air toxic reductions.

## Overall Findings

Comparing ethanol usage in general compared to gasoline gave the following results across all blending percentages, according to the reviewed literature. Sources: <sup>(108, 109, 118-132, 188)</sup>.

- HC reductions are generally reduced, up to 70%, while one study showed increases up to 20%.
- Almost all studies showed CO reductions, up to 60%, while a few showed increases up to 27%. The Australian study <sup>(188)</sup> found CO reductions of 95% for both E5 and E10.
- NOx emissions results are mixed. Some state reductions of about 60% while others stated increases of about 30%. FFVs and dedicated vehicles for high level ethanol blends or neat ethanol showed tolerance for higher EGR ratios reducing Nox.
- PM is generally not in focus for gasoline vehicles though some find 40-50% reductions.
- CO<sub>2</sub> emissions are found to be about 5% less per kilometer.
- Methane ranges from same amount of emission to 120% increase.
- Benzene is found to be reduced in all cases from 25 to 80%.
- 1,3-butadiene were in all cases reduced from 10 to 80%.
- Toluene was reduced by 30 to 80%.
- Xylene reduced up 80%.
- Formaldehyde increased up to 70%.
- Acetaldehyde increased dramatically up to 3500%.

<sup>ix</sup> US EPA modeling tool used to predict environmental changes due to fuel specifications.

## Evaporative Emissions

A common critique of ethanol fuels is, that while usage of ethanol fuels often improves tailpipe emissions, it increases evaporative emissions. However, this is not necessarily correct. Looking at emissions from the entire vehicle, evaporative emissions have been subject to increased research in recent years. The focus is on emissions of the so called volatile organic fractions (VOC), which are hydrocarbons that evaporate from the vehicle. The rate of evaporation is strongly related to the so called Reid Vapor Pressure (RVP) of the fuel. The vapor pressure of ethanol/ gasoline blends can be seen in figure 22.

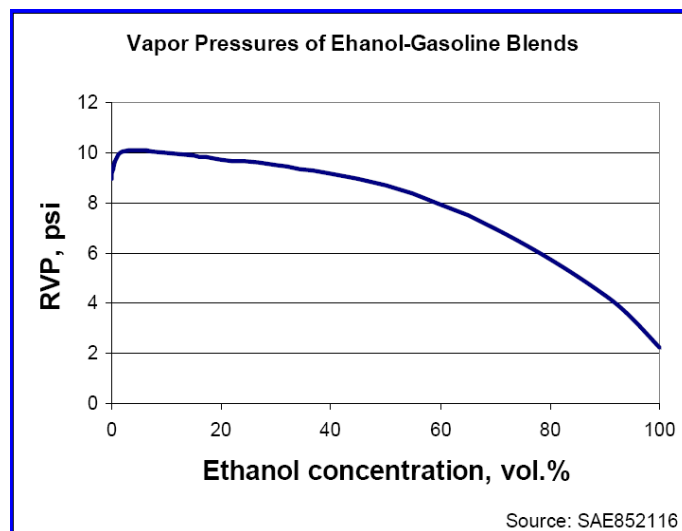


Figure 22: Vapor pressure of ethanol/ gasoline blends. Source: <sup>(133)</sup>.

The figure shows how low ethanol levels increases the RVP of ethanol/gasoline fuels, having a maximum at 5 to 10% 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 it could be expected that ethanol would 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 so called azeotropic phases with some of the hydrocarbons of the gasoline, resulting in very low boiling points for these phases <sup>(82)</sup>.

In practice, however, E10 type blends do not generally 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 <sup>(134)</sup>. 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 of emissions: Permeation of fuel components through fuel system components of vehicles, leaks of liquid, vapor and fuel tank venting canister losses <sup>(135)</sup>, and evaporative emissions associated with the re-fuelling of vehicles. Leaks are relatively easily dealt with by regular vehicle maintenance. Though 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. This depends on ethanol content <sup>(136)</sup>.

Increased permeation of hydrocarbons due to ethanol fuels, is an area not fully understood, but positive results with reducing these emissions have been obtained in for example LEV and PZEV vehicles <sup>(135)</sup>. The general trend in the literature, is that low percentage ethanol blends, 5-10%, tend to increase permeation while high percentage blends, mainly E85, seems to cause lower emissions compared to regular gasoline. It has not been possible to find literature about permeation data using middle percentage ethanol fuels (E20-E70) other than what is seen in figure 23.

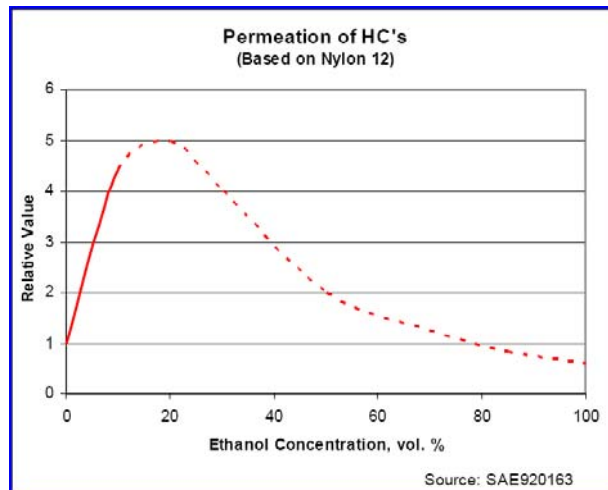


Figure 23: Permeation of hydrocarbons, source: <sup>(133)</sup>.

A part of the evaporative emissions are stopped by the so called carbon canister. Fuel vapors within the fuel system of vehicles are circulated through the canister containing activated carbon. It works by absorbing fuel vapors while the engine is not running and releasing these vapors into the engine when it is running, purging the filter. See figure 24.

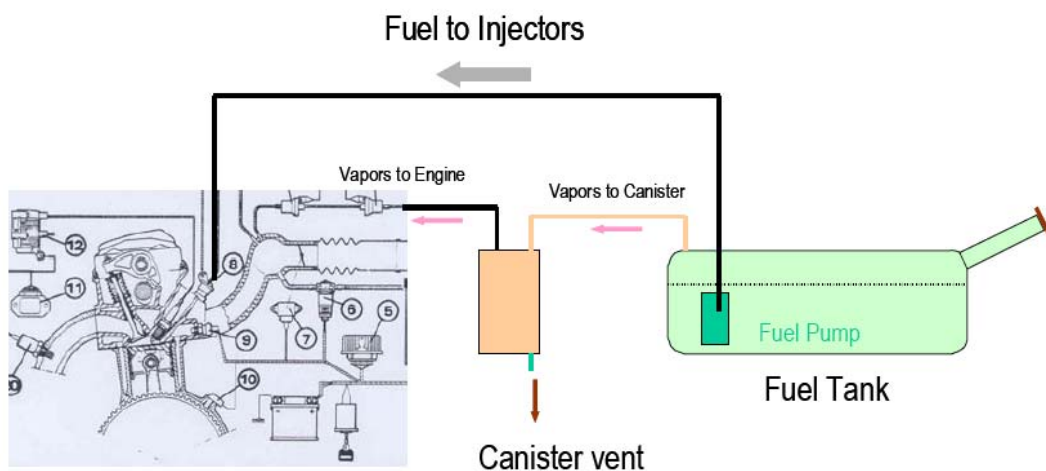


Figure 24: Evaporative emissions control system, source: <sup>(137)</sup>.

Unfortunately ethanol seems to be prone to accumulate in the canister, compromising the efficiency<sup>(137)</sup>. It has been found very difficult to remove the ethanol from the canister even when running on normal gasoline. It is not clear, on how long term, or to exactly which degree, the canister efficiency is reduced. It might depend on the individual model design and fuel type used. Due to this phenomenon ethanol usage indirectly results in increased VOC emissions longer than ethanol is actually used in the vehicle.

Evaporative emissions have been investigated in Sweden in 2006, and have been found to be as significant as up to one third of the total emission from all road traffic in Sweden<sup>(138)</sup>. Out of 50 cars tested, 20 exceeded the limit set by an EU directive. The cars were between six months and five years old and had driven 15.000-80.000 km. The limit was in some cases exceeded by 20 times the limit value.

A study<sup>(63)</sup> of the effects of using E20 in the Australian fleet showed that evaporative emissions would be equal or in some cases less, for E20 compared to using gasoline. The more recent 2008 Australian study<sup>(188)</sup> found that evaporative emissions of acid aldehydes such as acetaldehyde and formaldehyde increased with the use of E5 and E10 compared to gasoline (ULP). Total hydrocarbons (THC) 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 vapour canisters of the vehicles.

Another comprehensive study<sup>(139)</sup> of seven modern European vehicles was made for the European Commission by <sup>x</sup>CONCAWE/EUCAR/JRC. The tested fuels used were two splash blended E5 and E10 fuels, with unadjusted RVP values, and E5 and E10 that was 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<sup>(136)</sup> which indicates that the emissions were mainly due to canister losses and not permeation.

Ten US vehicles were tested<sup>(136)</sup>, both older and newer (model year 1978-2001). By using E6, permeation increased by 65% on average for all vehicles, compared to using gasoline. In the newer vehicles (post 1996) permeation increased by 157% with E6.

It seems there are still serious issues to be solved when using low percentage ethanol/ gasoline blends. Since emissions from vehicles are under increasingly stringent regulations, this issue might pose a hurdle for especially E5 and E10 blends. However, problems do seem solvable, especially when considering the Californian LEV and PZEV vehicles.

The Australian study on the health impacts of ethanol blend fuel<sup>(188)</sup> selected a representative sample of vehicles from the current Australian fleet and compared actual emissions (exhaust & evaporative) from E5, E10 and gasoline (ULP). Emissions data was used to model the Sydney urban airshed under different scenarios eg all vehicles using E10, and determine the potential health impacts on the population.

The results of this study include:

- Emissions from E5 and E10 show that the levels of some pollutants marginally increased, such as oxides of nitrogen and aldehydes, while other emissions such as PM, CO and benzene decreased;
- PM<sub>2.5</sub> emissions from tailpipe tests showed an average 19 % decrease with E5 use and an average 33% decrease with E10 use;

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<sup>x</sup> JRC = Joint Research Center, EUCAR = The European Council for Automotive R & D

- Increases in population exposure were seen for ozone for all E5/E10 scenarios and for nitrogen dioxide for the E10 scenarios;
- 97% of potential health cost savings were due to decreases in PM related mortality;
- Potential health cost savings would reduce over time as newer vehicles with advanced emission control systems replace 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. It can therefore be expected, that the same possibilities and problems are present for SI engines in two-wheelers as well as for cars. Manufacturers do not recommend the use of ethanol fuels in general, with a few exceptions for E5<sup>(140, 141, 68)</sup>.

The main concern in relation to two-wheelers is the exhaust emissions, especially for two-stroke engines. Research is relatively limited in this area, but by summarizing the available literature<sup>(142, 119, 143, 144, 145)</sup> the following can be concluded:

- HC and CO emissions are consistently reduced with the use of ethanol, even in small amounts. HC has shown increase in one case.
- The more ethanol in the fuel, the cleaner tailpipe emissions.
- One case has shown increased catalytic converter efficiency due to ethanol usage.
- Cases of additional wear and corrosion due to ethanol usage has been found.
- Fuel energy efficiency increases
- Volumetric fuel consumption (L/km) increase with increased ethanol usage
- 

### ***Ethanol Application in CI Engines***

The diesel or CI engine is considered the most fuel efficient engine for transportation for widespread usage, at this point in time, 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 the global CO<sub>2</sub> issue and local urban pollution issues. Furthermore, ethanol used in CI engines, compared to the use in SI engines, represents a more efficient way of utilizing the energy in ethanol simply due to the higher engine efficiency which is about 30% higher on average 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 the standard fuel specifications used today. 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 performing better than running on diesel. The following will highlight fuel properties which have been reported as problematic in the literature.

## Energy Content

Depending on its specific composition diesel oil has an energy content of about 36MJ/liter, where ethanol as mentioned earlier has 21. Consequently the engine will need injection of relatively larger volumes of fuel, compared to using diesel oil, in order to get the same power output. If for example the fuel injectors are not big enough to deliver the needed flow of fuel, the maximum power output of the engine will decrease. Thus typical differences in vehicle design when using ethanol in diesel engines are larger fuel injectors, fuel pump and fuel tank. The energy content of ethanol/diesel blends decreases by approximately 2% for each 5% ethanol added by volume, so adjustments or design changes will be more profound, with high ethanol percentage fuels or neat ethanol engines <sup>(49)</sup>. 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 due to 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, when speaking about 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 US ASTM D975 and EU EN590 standards, in the USA 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 <sup>(146)</sup>, but the cetane rating of neat ethanol is estimated to about 5 to 15, which means that the fuel will likely not auto-ignite under the conditions existing in standard diesel engines.

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

## 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 <sup>(148, 48)</sup>. Current commercial ethanol/diesel blends, containing less than 15% ethanol, have been shown to be well above the US ASTM standard limits for lubricity and viscosity of fuels used in diesel engines <sup>(49)</sup>. Experiments have shown that blends of winter-type diesel and ethanol (without additives) can contain roughly 45% ethanol without falling below the ASTM viscosity limit, whereas summer type diesel could only contain about 20% <sup>(49)</sup>.

Thus when using ethanol/ diesel blends and neat ethanol, lubrication additives have to be added, or other materials need to be used, in order to ensure prevention of this kind of problems. As will be discussed later, Scania busses are currently operating on a daily basis running on 95% ethanol and 5% additive with no more maintenance than Scania's regular diesel busses. It can therefore be concluded that lubrication problems can be overcome by 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. As diesel fuel pumps are designed for a fuel with a higher viscosity, pumping problems can occur<sup>(49)</sup>. Lubricating properties are affected negatively and also leakage problems might occur with ethanol fuels. During cold ambient conditions diesel fuels can begin to solidify but adding ethanol might actually improve this situation as will be discussed in a later section. Fuel spray characteristics are also changed due to lower viscosity of ethanol fuels though not much literature on this subject have been found.

## **Vapor Pressure**

Ethanol has a higher vapor pressure than diesel, meaning it will evaporate more readily. Using 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 will often need to be prevented<sup>(51)</sup>. As with SI engines the high vapor pressure of ethanol should be expected to cause higher evaporative emissions but not much literature has been found on this topic. Furthermore safety risks are associated with the high vapor pressure, as described in an earlier section.

## **Application Techniques**

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

- Ethanol and diesel oil blends - emulsions and solutions
- Neat ethanol - using<sup>xi</sup> spark ignition, glow plug or cetane improving additives
- Separate ethanol injection - dual fuel injection or fumigation

## **Ethanol/ Diesel Blends**

Three general types of blends have been studied in the literature: Pure solutions of ethanol and diesel, solutions with additives and emulsions. The literature mainly focuses on solutions with additives since this application is easier to adapt to the existing fuel/ vehicle fleet, and the production price has curbed interest in emulsions.

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<sup>xi</sup> This may rather be classified as an SI engine

Judging on the basis of the literature, there seems to be a definite potential for improving the efficiency of the CI engine by blending ethanol into the diesel fuel <sup>(77, 58, 150, 151, 152, 153, 154)</sup>. 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% point or 5-10% 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 <sup>(51, 153, 58, 152)</sup>.

A very typical performance issue is the increased fuel consumption (on litre basis). While engines might be more efficient in terms of energy, ethanol still carries significantly less energy per litre, 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 <sup>(155)</sup>. Reviewing the literature, it is apparent that cases of both less and more power/ torque output, from running on ethanol diesel fuels compared to regular diesel, can be found.

A review of the existing literature about exhaust gas emissions of engines running on e-diesel blends, has been made by the Lubrizol Cooperation, published in 2003. The data consist of a range of different engine configurations, driving patterns and e-diesel blends. The main results of the review can be seen in table 5.

Table 5: Average exhaust emissions from e-diesel blends. Source: <sup>(156)</sup>.

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

Table 5 shows emissions from e-diesels both with and without cetane improving additives. ‘Equal Cetane Number Data’ represents the cases where fuels are containing additives. Negative values represent a reduction in emissions from e-diesel tests compared to conventional diesel. It can be concluded that e-diesels with cetane improving agents have a better performance, regarding the regulated emissions, compared to plain ethanol/diesel blends, especially HC, CO and PM. NOx emissions don’t seem to be affected by ethanol content in diesel oil. It can also be concluded that HC emissions increase or at best are equal when using e-diesel compared to regular diesel. CO and NOx emissions are similar using either e-diesel or conventional diesel looking at an average on a number of studies. PM emissions are reduced significantly with e-diesel and in at least one case up to 72% using an unmodified ethanol/diesel blend <sup>(156)</sup>. That being said, it is now discussed whether emissions of HC and CO from diesel vehicles are of significant importance as they are relatively easily reduced, with the use of oxidation catalysts.

More recent publications show similar trends where PM and smoke are significantly reduced in almost any case with the use of ethanol in diesel <sup>(150, 148, 153, 157, 158, 154, 159)</sup>. The results of the individual studies vary due to different conditions regarding engine loads, engine modifications and fuel additives among other things. Most studies have focussed on lower ethanol ratio blends, typically less than 20% while only a few have investigated up to 50% ethanol. It seems, however, to require a significant amount of additive to sustain

such blends. It can be concluded that e-diesel, and other ethanol diesel fuel blends, has 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 study <sup>(51)</sup> put it this way: '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 and smoke in CI engines has some positive side effects:

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

The so-called NOx/PM trade-off, is a well known phenomenon which very simply put is a situation, where NOx emissions will go up if the engine parameters are adjusted to obtain lesser PM emission and vice versa. By using ethanol this balance can be tipped much more in favour of lesser NOx with less PM penalty, see figure 25.

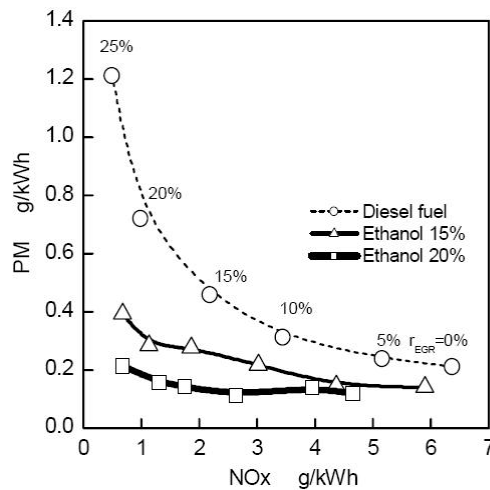


Figure 25: NOx/ PM trade-off, source: <sup>(160)</sup>.

Figure 25 shows how the NOx/ PM emissions are affected by using E15 and E20 compared to regular diesel while changing the EGR (Exhaust Gas Recirculation) ratio. NOx emissions are normally difficult to reduce, especially without costly emission control equipment, but as can be seen in the figure, NOx could be reduced from about 4.7 g/kWh to 1.3 practically without increasing PM emissions. This trend is a general potential for all diesel engines running on diesel/ ethanol fuels. With the use of diesel particulate filters this balance might be further exploited.

Evaporative emissions from vehicles were found to be a problem in an Australian study <sup>(161)</sup>. As well as ethanol causes increased vapour pressure in low level ethanol/gasoline blends, the same happens with ethanol/ diesel blends. Increased vapour pressure usually results in higher evaporative emissions, but as opposed to gasoline vehicles, diesel vehicles usually have no evaporative emission control measures since this is not a problem normally associated with this kind of vehicles. It hasn't been possible to find sources testing this matter properly.

## 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, among other effects, create 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<sup>(162)</sup>.

Biodiesel blended into ethanol and conventional diesel (sometimes called BE-diesel or EB-diesel) has shown to be a solution to many of the 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, e.g. to improve the solubility<sup>(163, 164)</sup>. Most commonly tested are blends with relatively little ethanol content, about 5-10%, 10-20% biodiesel and 70-80% conventional diesel, thus being fuels with 20-30% renewable contents, which is relatively high compared to the current technical and political expectations. The main advantages using biodiesel in e-diesel are potentially:

- Biodiesel has good lubricity, mitigating low lubricity of ethanol/ diesel blends.
- A high viscosity mitigating the low viscosity of ethanol/ diesel blends.
- The high cetane rating of biodiesel (compared to 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 emission increases with ethanol while biodiesel reduces those 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.

One of the major barriers for biodiesel use in cold climates is the low temperature properties, often described by the cloud point. Reversely ethanol blended into biodiesel/ diesel blends can potentially provide the following advantages:

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

Sources: <sup>(162, 165, 159, 166, 167, 168)</sup>

In a study<sup>(169)</sup>, tallow ester was blended with ethanol in the ratio of 65:35% to match the viscosity equal to US standard No.2 diesel. This blend was then mixed with conventional diesel and the properties investigated. As example a blend of 32.5% ester, 17.5% ethanol and 50% diesel oil had better cetane rating, similar viscosity and density as the specified No.2 diesel.

Biodiesel can also be used to prevent phase separation of E-diesel as according to Refs. <sup>(165, 166)</sup> who found BE-diesel to be stable well below 0°C. A commercial ethanol diesel, O<sub>2</sub>-diesel, is at the time of writing being tested in a fleet operating in Washington, USA. It has proven to perform satisfactorily with regard to cold flow properties and has a stability down to minus 26°C <sup>(170)</sup>.

In a few cases biodiesel has even been found to prevent lowering the flash point in ethanol/diesel blends <sup>(159, 166)</sup>. This represents huge possibilities, because it is in practice only the low flash point which is limiting the widespread use of low level ethanol fuels for diesel engines (see earlier section on safety). As mentioned earlier even 5-10% ethanol in diesel reduces the flash point almost to that of neat ethanol, i.e. 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% e-diesel with 1% biodiesel and 45°C for 10% e-diesel with 1% biodiesel <sup>(167)</sup>. The use of higher percentages of biodiesel did, in this study, not improve the flash point further while higher percentages of ethanol lowered the flashpoint significantly.

The most important perspective of this ethanol fuel, is probably the rate of fossil diesel replacement without any engine or vehicle alterations, still 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 6: – EB-diesel compared to conventional diesel, selected properties

Property	ASTM D975	EN 590	E-diesel (E15)	BE10-diesel
Density @ 15°C g/cm <sup>3</sup>	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 <sup>2</sup> /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

Sources: <sup>(171, 167, 172, 59)</sup>.

## 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 too long ignition delays. It also requires compatible fuel system materials and special engine calibration. Using an ignition improving agent will increase the cetane number and experiences with Scania busses in Sweden <sup>(173)</sup>, shows that with about 5% ignition improver, the engine requirements are met. There are several types and brands of ignition improvers on the market and therefore the properties, price and effects have to be considered.

The concept of the spark assisted diesel engine (SADE) bridges the two main engine types; the spark ignited and the compression ignited 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 might be somewhat disappearing. An example is the CAI system in Mercedes Benz's DiesOtto concept <sup>(92, 93)</sup> where

the engine switches automatically between spark ignition and compression ignition 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 done at Helsinki University of Technology showed the unique flexibility of this concept. By using spark plugs in a diesel engine it was made to run successfully on gasoline, diesel and neat ethanol <sup>(151)</sup>. The SADE concept showed superior efficiency and power compared to the baseline diesel engine and was operating with smoke free emissions.

Using a spark plug ignition system requires some degree of redesign of the CI engine, but has the advantage of not needing an ignition improver while achieving diesel like or better engine efficiencies <sup>(52, 77, 151)</sup>. Since the combustion chamber is originally optimized for diesel fuel combustion, the geometry is not necessarily particularly well suited for ethanol combustion though. 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 can with ethanol give cause to knocking <sup>(53)</sup>. Because the spark assisted diesel engine can run stoichiometrically, the use of a regular three-way catalyst for emission reduction purposes is possible. 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 hundreds degrees Celsius below normal ignition temperature <sup>(52)</sup>. Catalytic ignition can provide the advantage of a decreased ignition delay which is normally an issue for ethanol usage in CI engines <sup>(174)</sup>. A solution made by a company called Sonex Research is a special piston where 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 <sup>(175)</sup>.

Another alternative, but elegant solution for neat ethanol use, is to manufacture the cetane improving agent on-board the vehicle. CERC (Combustion Engine Research Center, Chalmers University), which is a center established by cooperation of the Swedish auto and fuel industry and Swedish authorities, has provided research showing how cetane enhancing ethers can be produced catalytically on-board from ethanol during vehicle operation <sup>(176)</sup>.

### ***Performance of Neat Ethanol Applications***

There are four main potential advantages of using neat ethanol compared to regular diesel in CI engines:

- Maximum fossil fuel replacement.
- Very low PM (or smoke) and NOx emissions.
- High energy efficiency.
- Use of wet ethanol and thus provide a high degree of CO<sub>2</sub> mitigation.

Compared to using ethanol fuel blends, it is given that using neat ethanol will provide maximum replacement of fossil fuel. Low NOx emissions have been the result in most studies of engines running on neat or high percentage ethanol fuels. This is due to a high latent heat and lower combustion temperatures, but in cases (where fuel properties are not properly accommodated by engine adjustments) low NOx can also be caused by a too late ignition of ethanol due to its lacking ability to self ignite. This late ignition will move the combustion later into the expansion stroke of the CI engine reducing pressures and temperatures in the cylinder causing lower engine efficiency <sup>(150)</sup>. So called smoke free operation can be

obtained with use of neat ethanol. In many cases of research on dedicated ethanol engines, increased efficiencies are consistently seen, compared to base line 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 done by letting ethanol be evaporated into the air stream 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 varied 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% ethanol (by energy) can be fumigated. An important advantage of fumigation is that hydrous ethanol can be used<sup>(55, 177)</sup>. Use of fumigation in turbo charged diesel engines, which now constitutes 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<sup>(53)</sup>. 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 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<sup>(177)</sup>. By using a pilot injection of diesel to help ignite a later injection of neat ethanol, up to 90% ethanol (by energy) can be used at high loads and 50-60% at low and medium loads<sup>(150, 53)</sup>. 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 which opens opportunities for controlling the combustion to a very high degree, for example much more effectively aiming at highest efficiency or lowest NOx and PM emissions<sup>(160)</sup>. This technique is a variant of what is called the partial premixed controlled combustion (PCCI).

Lubrication additives and/or improved materials might be needed for this technique. Main advantages are high engine efficiencies, high displacement of fossil diesel and low NOx and PM emissions<sup>(55)</sup>.

## Hydrated Ethanol in CI Engines

As described previously, the motivation for 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 incentive in Brazil.

An Indian Study <sup>(178)</sup> were carried out on 150-200<sup>o</sup> proof<sup>xii</sup> ethanol/ diesel blends from 10-20% ethanol. Firstly the tendency of phase separation was investigated and results showed that 150<sup>o</sup> and 160<sup>o</sup> ethanol was not suitable for blending even as low as 10%. 170<sup>o</sup> could be used with up to 15% ethanol in the blend. Density of the blends showed increase with increase of water content in the blends. Viscosity of the ethanol blends showed to be very similar to neat diesel. Power output (brake horse power) showed to be very similar from 25-100% loads with all types of blends. Fuel efficiency was measured to be higher with ethanol/ diesel blends than with neat diesel. This example shows that even with up to 15% 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 presented it should be noted 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 will likely not be similar in colder climates.

Though research in this area is limited, studies suggest that there are potential advantages, mainly low NOx emission and high engine efficiency. There are experiences in Sweden with busses running on 95% hydrated ethanol (5% water) with no additional problems compared to regular diesel busses, (see next section). Hydrated ethanol fuels, at this point in time, must be used in special applications, but as such has a great potential, not least for CO<sub>2</sub> mitigation. The ideal use of ethanol in transportation could very well be hydrated ethanol in CI engines, due to two important reasons: It is highly energy efficient on a life cycle basis in the production phase, and equally fuel efficient 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 USA, Australia, Sweden, Denmark, Ireland and not least India <sup>(62)</sup>. Millions of miles have been driven so far and fleet trials are still ongoing, most recently and on the greatest scale so far, in the state of Karnataka in India.

Karnataka, India should by the time of writing have the, until now, largest ethanol-diesel fleet in the world comprising about 5200 busses using O<sub>2</sub>diesel (Energiesel), which is diesel containing 7.7% ethanol and 0.5% biomass based additive <sup>(179)</sup>. The fleet will use about 120 million liters of e-diesel per year. The blend 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 <sup>(42)</sup>. Energenics, the O<sub>2</sub>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 to regular diesel. The benefits of running on O<sub>2</sub>diesel are in this case reduced smoke by 50% and slightly reduced fuel costs about 0.25 rupee (0.0045 Euro) per liter <sup>(179)</sup>.

Scania, as another example, have been producing heavy duty engines for busses running on ethanol since the mid-eighties, with serial production since 1990. More than 600 busses have been operating in the Swedish cities with a significantly better emission performance than regular diesel busses. The third generation busses are currently running on a blend of hydrous ethanol and 5% ignition improver (E95), a fuel which is utilized as efficiently as diesel fuel, with up to 44% thermal efficiency, and the engines now

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<sup>xii</sup> Proof is a US measure for how much water present in an ethanol/ water blend. Proof is accompanied by a number which is twice the percentage by volume of ethanol, for example 200<sup>o</sup> proof is pure ethanol and 160<sup>o</sup> proof is 80% ethanol in 20% water (Wikipedia, Oct 2007).

possess fully proven technology with no operational drawbacks. Busses are fitted with EGR and an oxidizing catalyst (suited to reduce acetaldehyde emissions) resulting in low NOx 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 <sup>(180)</sup>.

Fleet trials like these illustrate what may well be the most easily available potential use for relatively clean, highly efficient ethanol application in CI engines. Busses 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, as described earlier. At the same time hazardous emissions in the city areas could be reduced with ethanol fuels, although some research show that this benefit might be of minor importance compared to using modern diesel engine equipped with diesel particle filter <sup>(181)</sup>.

## Discussion

Each of the previously discussed application techniques has advantages and drawbacks which are summarized in table 7. Common advantages for all techniques are low particulate or smoke exhaust emissions and a potential for highly efficient combustion, comparable to or better than using regular diesel oil. General disadvantages are high volumetric fuel consumption, special handling of the fuel due to a low flashpoint, not full compliance with fuel standards and extra expenses for modification of fuel, engine or both. For some of the techniques, there would be no need for compliance with diesel standards, as for example when the vehicle is dedicated to ethanol usage.

Table 7: Overview of Ethanol/ Diesel Solutions

Method	Fossil Diesel Displacement	Potential Advantages	Possible Drawbacks
<b>Blends, solutions</b>	Up to 20%	Can be used in unmodified diesel engines.  Less expensive compared to emulsions.	Requires anhydrous ethanol if additive cost and dosage must be minimal.  Properties such as low energy content, low viscosity and lubricity.  Phase instability when stored.
<b>Blends, emulsions</b>	Up to 40%	Can be used in unmodified diesel engines.  Higher fossil fuel displacement compared to solutions.	As Blends, Solutions.  Cost.
<b>Blends of ethanol, biodiesel and conventional diesel</b>	Up to 100%	Very high displacement of fossil fuel.  Close to compliance with existing fuel standards.	Limited research done.  Requires anhydrous ethanol.
<b>Dual Injection</b>	Up to 90%	Anhydrous ethanol is no requirement.  Higher engine power output compared to diesel use.  Flexibility regarding fuel choice	Requires an extra separate fuel system for ethanol.  Requires a lubricant additive.  Extra effort for the end-user to fill two tanks is needed.
<b>Fumigation</b>	50-60%	Anhydrous ethanol is no requirement.	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.  Higher engine power output compared to diesel use.	Extra effort for the end-user to fill two tanks is needed.
<b>Neat Ethanol with Spark Ignition (SADE)</b>	100%	Anhydrous ethanol not required.  Maximum displacement of fossil fuel.  Potentially the cleanest of all alternatives.	Many modifications needed; Ignition system components.  Limited research done.  Not able to run on regular diesel.
<b>Neat Ethanol with Glow Plug</b>	100%	Maximum displacement of fossil fuel.  Only simple modification needed.	Limited research done.  Not able to run on regular diesel.
<b>Neat Ethanol with Ignition Improver</b>	95%	Has been proved to function well on a daily basis.  Maximum displacement of fossil fuel.	Extra cost of additive.  Not able to run on regular diesel.

The most accomplished commercial success among the discussed application techniques is E-diesel. O<sub>2</sub>diesel is perhaps the world's leading provider of e-diesel fuels. They have produced an additive that can be used for different fuel variants; a fuel with 7.7% ethanol and less than 1% additive and a newer formulation which consists of 20% biodiesel, 7.7% ethanol, 0.7% additive and conventional diesel. Other variants have also been tested. The latter version thus consists of 28% renewable non-fossil fuel. Several fleet tests have, as mentioned earlier, been or are currently being conducted around the world, and can be described as successful. O<sub>2</sub> e-diesel has recently (as of Oct. 2003) been recognized 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 the automaker industry representatives Volvo, Delphi, Renault and Petrobras.

Many of the described application techniques can 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 markets, the Brazilian seemingly being the only one. The applications must therefore in most cases be seen as suggestions for future development and might require some infrastructural additions. Some of the applications have not been developed to the maximum potential and some are still in a very early developing stage. It is clear that either political will, or perhaps rapid rising oil prices, is needed for these techniques to be applied on a larger scale. The societal and environmental benefits these techniques can potentially deliver seem very significant though. Any significant net energy gain, such as what could be obtained using hydrated ethanol compared to anhydrous ethanol, is very significant, looking at society as a whole.

Emission advantages do seem consistent looking through the literature, 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. It could be a problem, however, that the literature, with a few exceptions, report 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 has shown how ethanol reduced PM emission by mass, but alarmingly increased the number of particles, compared to regular diesel<sup>(181)</sup>. If this is a general trend, a revision of the health benefits of ethanol/diesel fuels is needed. Further studies are needed in this area. Acetaldehyde emissions from ethanol application in CI engines, is also an area not well studied. One study<sup>(147)</sup> has 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 apparently a number of unanswered questions, which 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.

The auto manufacturer industry seems not all to 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 <sup>(172, 182, 183)</sup>. It can therefore be concluded that ethanol diesel fuels needs to have 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. As mentioned, many studies suggest that ethanol fuels, even with low percentages of ethanol, used in diesel engines causes less smoke or PM, 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 will start smoking heavily when too much fuel is injected. With ethanol, and therefore less smoke, there is a potential for increased power and torque, since the smoke limit is changed significantly <sup>(184)</sup>.

Improving the efficiency of the CI engine, which is already the most efficient engine for commercial transportation, is outstanding. As earlier described, the potential of increased efficiency due to use of ethanol fuels in CI engines, is much smaller than for SI engines, i.e. only about maximum 5-10% increase. This potential is not enough to offset the lower energy content of ethanol and is therefore influencing the fuel consumption (L/km) negatively. The technical potential of the CI engine is therefore more focused on emission reductions, especially NO<sub>x</sub> and PM. Since particulate matter can be effectively filtered, (thus minimizing the advantage of ethanol fuels in this regard significantly), focusing on NO<sub>x</sub> emissions might be more efficient. Focus should also be on the size of the particles emitted from the exhaust, even though emissions regulations are yet not focused on this at the time of writing. One of the main NO<sub>x</sub> 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<sub>x</sub>. This approach could be pursued further.

Looking through the literature, the near future of the CI engine seems to be the HCCI (Homogenous Charge Compression Ignition) engine. The HCCI engine is seen as a combination of the best features of SI and CI engine principles, i.e. high fuel efficiency of the CI engine and clean emissions of the SI engine. Only there are major technical barriers for full commercialization of the HCCI engine at the moment, most importantly gaining satisfactory control of the combustion and operating range. This means that 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 rates of water in hydrated ethanol. A few examples of tendencies found in the literature for ethanol and HCCI combustion are: 1) Ethanol reduces emissions, as is the trend for CI engines. 2) High ethanol fractions reduce smoke and NO<sub>x</sub> emissions to a minimum <sup>(150)</sup>. 3) Very 'wet' ethanol, with up to 60-70% water, can be used in HCCI engines, constituting a very significant reduction in life-cycle energy use of ethanol <sup>(174, 185, 186)</sup>.

It can be concluded that ethanol, both anhydrous and hydrous, has many possibilities for successful application in compression ignition engines. On the other hand, it seems to be necessary with implementations, which are not compatible with the existing fuel system, in order to fully utilize the potential of ethanol in CI engines.

## Conclusions

The following provides a summary of the most important conclusions regarding engine technical aspects and other aspects.

### *Technical Aspects*

- 1) Ethanol has a number of unique properties which makes it a superior fuel for gasoline vehicles, but also a number of properties which are unfortunate looking at the 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) It has been shown repeatedly that the more ethanol added to the gasoline the better effect.
  - c) Ethanol fuels have been known to cause starting problems but there are technical solutions available.
  - d) It is an issue that especially smaller amounts of ethanol in gasoline contributes to increased evaporative emissions from the fuel system compared to regular gasoline usage.
  - e) Ethanol is more corrosive compared to gasoline.
- 2) Ethanol has a number of properties which are unfortunate for use as a fuel for diesel vehicles in the current form.
  - a) The very low cetane rating does not comply with current diesel specifications.
  - b) Regarding safety the flammability properties and flash point creates 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) It is expected that evaporative emission will also 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 the smoke and particulate matter emissions when diesel/ethanol blends are used compared to regular diesel. The effect of ethanol on particulate size need to be investigated further.
  - i) EGR ratios can be higher when using ethanol in diesel fuel thus help to reduce NOx emissions.
- 3) As a neat fuel or if the vehicle is designed for ethanol use, as for example the flex fuel vehicle, the mentioned problematic properties can be accommodated fully.
  - a) Flex fuel vehicles provide examples of a bridging technology with very few, if any, drawbacks.
  - b) Neat ethanol vehicles present the ultimate technical application for ethanol in many regards.
    - i) Both spark ignition and compression ignition type engines can be used.
    - ii) The engine can be fully optimized for ethanol providing maximum efficiency.
    - iii) Water contamination is not a problem.
    - iv) Hydrous ethanol can be used.
    - v) Exhaust emissions are cleaner as well as evaporative emissions.
- 4) The advantageous effects of ethanol increases with increasing ethanol percentage in both gasoline and diesel applications.
- 5) Without making changes in the existing vehicles the application of ethanol fuels is limited to low percentage gasoline/ ethanol blends with the exception of flex fuel vehicles.

- 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 since 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) Providing 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 contributes to cleaner exhaust emissions also 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) Especially transport over long distances is problematic since 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) Possibilities of problems such as poor engine performance or failure, excessive wear and corrosion and high evaporative emissions. Likely there will be no benefit of the ethanol.
- 13) There is a significant potential gain in CO<sub>2</sub> mitigation for application of hydrous ethanol. This is due to the production method.

### ***Other Aspects***

- 14) While the fossil fuel dependency is reduced due to application of ethanol in vehicles the greenhouse gas (GHG) mitigation is in some cases doubtful.
- 15) The greenhouse gas mitigation potential of ethanol depends strongly on the production method including the choice of crop for feedstock.
  - a) There is still a significant input of fossil based energy related to the ethanol production.
  - b) N<sub>2</sub>O emissions strongly reduce the GHG mitigation potential.
  - c) Carbon sequestration is a serious issue as well when clearing land for feedstock production.
- 16) Concerns have been voiced about important issues related to the sustainability of ethanol production.
  - a) Conflicts with other biomass consuming sectors, most importantly the food production.
  - b) Important issues such as the GHG mitigation potential are not accounted for.
  - c) Land use issues such as water usage and pollution, destruction of valuable natural habitats and more.
- 17) Second generation ethanol seems to be a solution to many of the above mentioned issues.
- 18) Ethanol can be an important contributor to the reduction of anthropogenic GHG emissions.
- 19) With the use of integrated production methods, as for example fuel, fodder and power co-production, significant 'symbiotic' benefits can be achieved.
- 20) Carbon capture and storage methods can be applied in the production of ethanol and ultimately reduce the atmospheric CO<sub>2</sub> content.

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