TECHNICAL VIEW ON BIOFUELS FOR TRANSPORTATION – FOCUS ON ETHANOL END-USE ASPECTS

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Summary

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ABSTRACT

Finland has proposed a joint project with Japan, USA and Sweden on ethanol as fuel for transportation. This review is targeted to benefit this possible new project, and also to collect information on ethanol for national discussions on liquid biofuels in Finland. The European Union has given target values for the use of both biofuels and alternative fuels in the transport sector. Reactions from Member States are expected on these indicative targets.

The most potential short-term options for liquid biofuels are biodiesel and ethanol. Biodiesel is mainly used as a blending component in diesel, but some engines are approved for operation also on neat biodiesel. Even operation on neat biodiesel requires no or only minor engine modifications. Ethanol can be used as a component in gasoline, and is sometimes also added to diesel. At high concentrations ethanol requires special engine technology. Today some synthetic fuel components are made from coal and natural gas. The amounts of biofuels and also the range of products could be increased if synthetic fuels were produced from biomass.

When considering the production potential of liquid biofuels in Finland, it is clear that all possible feedstocks and fuel options should be taken into account. Agriculture based biofuels from set-aside lands could, using current production technology, cover less than 2% of the consumption of transportation fuels in Finland. Wood-based and waste-based fuels would offer a significant reserve of raw material for liquid biofuels, if cost-effective production processes existed (limitations by competitive use).

Alcohols are liquid fuels, which mean good energy density, easy re-fuelling and storage. Basically the same kind of distribution system as for conventional fuels can be used. However, in the case of gasoline/ethanol blends the distribution system needs special attention to avoid problems caused by water, as blends are very sensitive to moisture. Fuel properties of ethanol are in many respects similar to gasoline. Ethanol up to some 10% can be blended with gasoline and used without modifications in ordinary spark-ignition engines. There is not much experience on the concentrations exceeding 10% with normal cars. The cars running on high-concentration blends (25%) in Brazil are, if not modified, at least recalibrated.

Special cars, Fuel Flexible Vehicles (FFV), have been developed for high concentration alcohol blends (up to 85%, the balance being gasoline). Gasoline improves the cold-startability, which is poor for ethanol due to low vapor pressure and high heat of evaporation. Gasoline also improves safety as the flame becomes visible. The reduction in emissions depends on how well the engine and the emission control system are designed and "tuned" for ethanol, but there should be a potential for emission reductions substituting gasoline for high-concentration ethanol blends.

Also heavy-duty diesel engines can use ethanol with certain limitations. The properties of ethanol are similar to gasoline, thus engine modifications (e.g. glow-plugs or pilot injection) or additives in fuel are needed, if ethanol is to be used in compression ignition

engines. One option to use ethanol in diesel engines is a low concentration ethanol/diesel blend (or emulsion). The main concerns with this E-diesel are the safety issues and the general suitability for diesel engines (low cetane, low lubricity, stability).

Biodiesel is suitable for current diesel engines, nontoxic and biodegradable, and thus an excellent fuel for use in sensitive environments. As a consequence, biodiesel is used e.g. in forest harvesting machinery. Many manufacturers, especially for non-road engines, allow the use of biodiesel within normal warranty conditions.

Many reviews have been conducted to assess reasonable policies for the introduction of biofuels. One of the reviews, published by Concawe, gave a critical view on the appropriateness of the EU targets for biofuels in transportation. Some other studies have given optimistic views on the production potentials of liquid biofuels. It remains to be seen how the targets can be met, and if met, at what costs.

CONTENTS

ABBREVIATIONS

CHP	combined heat and power
CNG	compressed natural gas
CO	carbon monoxide in exhaust gases
CO2	carbon dioxide
CRT	combination of an oxidation catalyst and a particulate trap (Continuously Regenerating Trap)
CVS	constant volume sampler
DI	direct injection
E85	a blend of 85% ethanol and 15% gasoline
E-diesel	diesel/ethanol blend
EGR	Exhaust Gas Recirculation
ETBE	ethyl tertiary butyl ether
FAME	fatty acid methyl ester
FFV	Flexible Fuel Vehicle (multipoint injection)
G-DI	gasoline direct injection
HC	total hydrocarbons in exhaust gases
HD	heavy-duty
IDI	indirect injection
LCA	life cycle analysis
LD	light-duty
LPG	liquefied petroleum gas
MPI	multipoint injection (conventional gasoline)
MTBE	methyl tertiary butyl ether
NOx	nitrogen oxides in exhaust gases
N2O	nitrous oxide, dinitrogen oxide, laughing gas
PAH	polyaromatic hydrocarbons
RFD	Swedish Environmental Class 1 diesel fuel
RME	rape seed oil methyl ester
RVP	Raid Vapour Pressure
SME	soy bean oil methyl ester
TDI	turbocharged direct injection diesel
TCDD	dioxin receptor binding affinity
UVOME	used vegetable oil methyl ester
VOE	vegetable oil ester

1 BACKGROUND

Alternative and renewable fuels have been a hot topic in several periods. In the 70's, the need for fuel substitutes arose due to the oil crises, later on, the potential for exhaust emission reductions gained interest. Lately, the focus has changed to the greenhouse gas discussion. For biofuels, one essential aspect to be taken into account is the policy related to agriculture.

The European Union has promoted biofuels since the White Paper for Renewable Energy Recources was launched in 1997. Today, there are important guidelines e.g. to promote alternative fuels for transport by setting step-by-step target values for renewables, and also an action plan that outlines an ambitious target of 20% substitution of on-road fossil fuels by alternative fuels by 2020. Each European country, also Finland, should decide how to react on the indicated guidelines and targets. Regarding biofuels for transportation, the production potentials, cost-effectiveness, security of supply, usability and LCA emissions and energy use is a complex equation. Careful consideration of all biofuel options is needed before the best solutions for national needs can be found.

There has been continuous research work on biofuels world-wide. However, in Finland the programs have concentrated rather on production than on end-use. The engine and emission control technologies develop continuously. Especially the last ten years have introduced a wide variety of different engine/aftertreatment technologies. The latest technology with complex control systems may increase fuel flexibility to some extent, but on the other hand, the requirements on engine cleanliness and component durability tend to increase.

Finland has proposed a joint project with Japan, USA and Sweden on ethanol as a fuel for transportation. This review is targeted to benefit the preparation phase of this possible new project, and is intended to be a part of the state-of-the-art review of the oncoming project. Also a glance on the other biofuels than ethanol is included in this review, but the focus is on ethanol.

It should be noted that at the time of finishing this report, extensive summary reports on biofuels are published [EC 2003, TÜV 2004 and IEA/EET 2004]. These reports give summaries and different point of views on e.g. policies, production potentials and life cycle analyses.

2 POLICY

2.1 WORLD-WIDE

Alternative and renewable fuels gain attention for many reasons. At first, oil crises of the 70's were the driving force for searching fuel substitutes. Later on the focus moved to pollution, and lately on the climate change. Today the main focus is on reduction of greenhouse gas emissions. However, when implementing alternative fuels typically also benefits regarding health risks associated with pollution are gained, as well as other environmental benefits of non-toxic and biodegradable fuels. It is predicted that the crude oil reserves will last only a few decades, and therefore searching substitutes for fossil fuels has high priority in current politics for alternatives and renewables (Figure 1). Renewables also decrease dependence on foreign fossil fuel supplies.

The policy for biofuels is often linked to agricultural and labour policy, e.g. the questions of how set-aside land should be used, need for subsidies, what are the effects on employment, which are the drawbacks, and competitive use of biomass feedstocks. Also ethical questions may arise, e.g. growing oil plants in certain areas may destroy rain forests, and the treatment of the labour force might be questionable in some countries.

Life cycle analyses (LCA) for renewables have shown a wide variation in the results. LCA takes into account energy and emissions of the total chain from production, distribution and end-use, and typically also include aspects like costs, tax policies and agricultural subsidies. Thus LCA is difficult to make, it is case-specific, and easily influenced by the pressure from groups of interest. Even the definition of LCA varies. Results are very dependent on the base data and the target country evaluated, e.g. use of fertilizers and formation of N_2O when growing crops. For example, a recent LCA from Cornell University concluded that corn-based ethanol in gasoline is environmentally harmful and economically inefficient [Cornell News 2003]. One must be extremely careful when applying the results from LCAs in different countries.

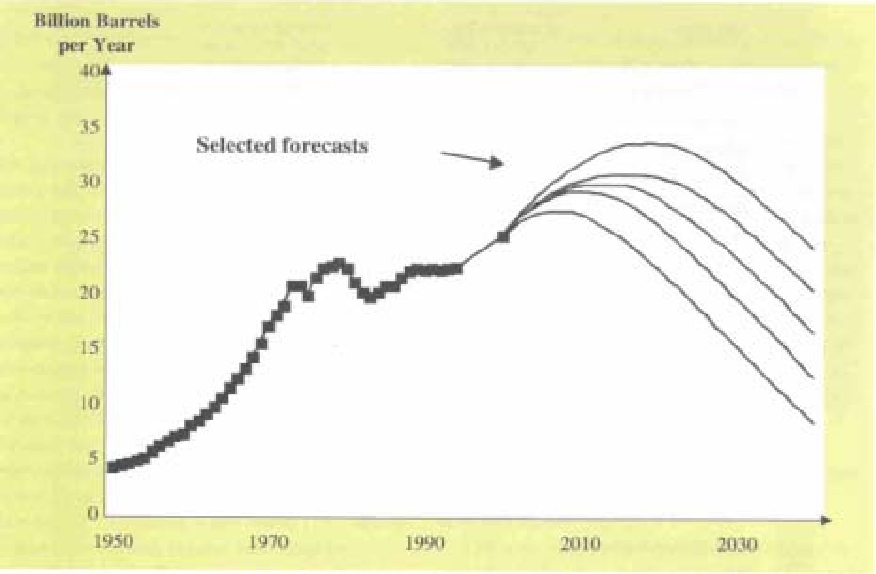

Figure 1. The world's total oil reserves and forecasts for future, IPCC 1997 [Månsson 1998].

There are not many potential biofuels available, even though, at least in theory, various pathways to produce a wide range of fuels exist. The most potential short-term options are biodiesel, which can be used neat or as a blend, and ethanol, which can be used as a component in gasoline, or even in diesel with some limitations[1]. At high concentrations, ethanol requires special engine technology. Used oils, animal fats and tall oil have also been considered as biodiesel feedstocks. The production costs might be lower using these raw materials, but the quality of end-products might be questionable.

The number of potential liquid biofuels would increase, if synthetic compounds currently made from coal and natural gas were produced from biomass. These options include gas-to-liquid diesel (e.g. Fischer-Tropsch), ethers (MTBE, ETBE) and dimethylether (DME). MTBE, and to a lesser extent ETBE, are used as gasoline components due to their excellent performance as motor fuel. All of these could be partly renewables, if biomass-based methanol would be available. In addition, if isobutene (C_4) would originate from gas fields, also the hydrocarbon feedstock part of ETBE or bio-MTBE could be classified as alternative [Mikkonen 2002]. DME is a questionable fuel option, as it requires new refuelling infrastructure, modified engines and also more processing than natural gas. Gaseous fuels in general need remarkable investments in both refuelling infrastructure and new or modified vehicles.

Biogas originating from e.g. wastewater treatment plants or landfills can be cleaned up and be used as a replacement for natural gas (methane) also in vehicle applications. As more and more biogas will be collected for energy use instead of just simply flaring the gas, this opens up interesting perspectives for then use of biogas in transportation.

Policies for biofuels vary from country to country. Some countries favour ethanol, whereas others favour biodiesel. Some countries use biofuels as blends with fossil fuels, whereas others prefer neat biofuels. In some areas the main objective is to improve local air quality, which is often best done using neat biofuels. When the focus is on the greenhouse effect, the same benefit for a given amount of biofuel is obtained using the fuel neat or as a blending component. When biofuels are used as blending components (fuel components), many technical benefits are obtained:

- fuel properties close to respective fossil fuels
- technical drawbacks of biofuels diminish
- no changes required for distribution chain or logistics
- no modifications needed in the engines or vehicles

Low concentration biofuels are used e.g. in France, where diesel may contain vegetable oil esters up to 5% without markings on the fuel pump. High concentrations, 10, 20 or even 30% of vegetable oil ester are used in some countries, but typically for limited target groups like local transport companies. Ethanol is already on the market in many

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[1] E-diesel, a blend of ethanol and diesel, arise many problems (Chapter 4.1.6).

countries, as low-concentration blends (5% in Europe), intermediate blends (25% in Brazil and 10% in U.S.) and high-concentration (E85) blends with gasoline. Also in Japan, there is an interest in using ethanol in gasoline. There is also some interest in ethanol/diesel blends, but these activities are limited to field tests and demonstrations, e.g. in U.S., Brazil, Sweden and Denmark.

A number of international organizations promoting specific biofuels exist. One of these is the "*International Ethanol Coalition"* promoting production and use of ethanol. Today the Coalition has members from five countries: USA, Brazil, Sweden, Mexico and Canada. All member countries hold regular conferences and meetings at conventions, conferences or annual events [International Ethanol Coalition 2000].

European Union

The European Union has promoted biofuels since the launch of the White Paper[2] for Renewable Energy Resources in 1997. This White Paper deals with renewables as energy sources in general, whereas the new guidelines, the Green Paper[3] on the security of energy supply, the White Paper[4] on transport policy, and the EC Directive on biofuels[5], promote alternative fuels for transport. The Green Paper (2000) and the White Paper (2001) set a target for 20% substitution of on-road fossil fuels by alternative fuels by 2020.

The EC Directive on biofuels outlines indicative, but ambitious, step-by-step target values for renewables in transportation, e.g. 2% by the end of 2005 and 5.75% by the end of 2010 (energy basis). Three options are considered to have the potential to achieve individually more than 5% of total transport fuel consumption over the next 20 years: biofuels available today, natural gas in the medium term and hydrogen and fuel cells in the long term. However, the EC Directive does not give preference to any specific alternative, nor does it exclude any options. Another EC Directive[6] allows tax incentives for biofuels.

European Union policy promoting renewable fuels has led to an increase in biofuel production. 0.78 million t/a of biodiesel was produced in 2001 in Europe, mainly in Germany (46%), France (40%), Italy (10%) and Austria (4%). Also production of bioethanol has been growing. In 2001, 0.2 million tonnes of ethanol was produced in Europe, mainly in France (42%), Spain (37%) and Sweden (21%) [ESRU].

The gasoline specification for EU[7] and also the regulations in some other countries limit oxygen content of gasoline to maximum 2.7 mass-%. This means maximum 7.8 vol-% ethanol, but the Directive, which contains maximum limit values for individual components, sets a maximum limit of 5 vol-% for ethanol. In general 10% ethanol is

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[2] White Paper, COM (97) 599
[3] Green Paper, COM (2000) 769
[4] White Paper, COM (2001) 370
[5] Directive 2003/30/EC, 8 May 2003
[6] Directive 2003/96/EC, 27 October 2003
[7] Directive 98/70/EC

believed to be applicable for all spark-ignition cars without problems. In Europe Sweden has been forerunner in using ethanol, with around 400 ethanol busses, and about 4000 Ford FFVs running on E85 plus about 600 000 cars running on gasoline containing 5% ethanol.

The following list gives some examples on policies for renewable fuels in different countries.

Brazil has a long history in using ethanol for transportation, and is the largest user and producer of fuel ethanol in the world. Ethanol consumption in 2001 was 10.6 million tonnes. The gasoline market in Brazil is very unique with ethanol blended in all gasoline. Brazil has a mandatory 25% anhydrous ethanol content in gasoline (24% before 2002, 22% before 1998), whereas gasohol in U.S. contains 10% ethanol. All cars in Brazil are modified for the unique market with only gasohol being available for spark-ignition cars. By the 2nd oil crisis in the beginning of 80's, cars capable of using 100% ethanol were introduced in Brazil. Today the market share of these vehicles is around 40%. However, the sales of neat ethanol vehicles have varied a lot according to changes in agricultural policy, that means the market price of ethanol [Jeanroy 2002]. In the beginning, production of fuel ethanol was based on subsidies. However, today pump price of ethanol is 60-70% of gasoline price (energy content) without any subsidies, and this is a result of reduced production costs with increased production volumes. "Brazilian alcohol program is now a paradigm to be followed" [Goldemberg 2004]. The ethanol production in Brazil will increase due to anticipated increase in exports [Jeanroy 2002].

In **USA** there is a policy for promotion of renewable fuels, but the actions are not harmonized in the different States. It is expected that the tax incentives and the Renewable Diesel program will increase the use of biofuels in USA [NBB News 2003]. The major renewables favoured so far in USA have been ethanol and soy bean esters (biodiesel). Biodiesel production in 2001 was only 0.065 million t/a. Ethanol production in 2002 was 6.7 million t/a. US EPA limits the ethanol content of gasoline to maximum of 10%, and the product must meet gasoline specification ASTM D 4814. In addition to gasohol, E85 for Fuel Flexible Cars is used (Chapter 4.1.5). Ethanol blended fuels accounted for 18% of all automotive fuels sold in U.S. in 2000. About half of the ethanol is used as gasohol (10%) and the other half as oxy-fuel or reformulated gasoline. The ban of MTBE in California from 2004 onwards is expected to increase ethanol consumption (5.7-7.7% ethanol) [RFA 2000, Jeanroy 2002].

In **Canada** ethanol-blended gasoline is promoted strongly, targeting an increase in production from some 0.2 million t/a in 2001 to some 5 million t/a in 2005. 'FleetWise' is a federal initiative involving a gradual increase in use of alternative fuels, such as ethanol, and alternative fuel vehicles. In Canada e.g. tax incentives, support to research, procurement policies and other political efforts has been used as tools to promote ethanol as alternative fuel [CRFA, IEA/EET 2004]. In 2003, the Canadian government was considering a law which would force oil companies to use 10% ethanol in gasoline [IEA/AMF AFIS 2003].

Japan is launching gasoline with 3% of ethanol in 2004 [IEA/EET 2004]. Japan is also starting up a trial of ethanol/gasoline blend, and plans to introduce a mandatory ethanol content of 10% in gasoline by 2008. The gasoline consumption in Japan is 55 - 60 million t/a. The ethanol needed will be imported, e.g. from Brazil [News Weekly 2003].

In **Australia**, there are blends containing up to 17% ethanol/gasoline on market (mostly 10% ethanol). In Australia, a vivid discussion on the appropriate ethanol content in gasoline is going on [Environment Australia 2002, Gordon 2002]. The current fuel ethanol production in Australia is about 0.04 million t/a, and target is 0.3 million t/a by 2010 [IEA/EET 2004]. The target is to cover 1% of the gasoline consumption with ethanol [Jeanroy 2002].

Austria has been a forerunner on bioenergy, starting one of the first biodiesel plants in the world in 1991. In 2000 the Austrian Government decided that diesel fuel shall contain 2% biodiesel (0.07 million t/a biodiesel). This was promoted also through the fuel excise tax system. Today Austria produces around 0.03 million t/a biodiesel [ESRU].

Actions taken in **France** have led to a dispute on subsidies for biofuels. The European Court first denied but later on approved the French request for biofuels subsidies. France is currently using 70% of its non-food set-aside land (410 000 hectares) for biofuel production – both biodiesel and bioethanol. France produced 0.3 million tonnes of biodiesel and 0.1 million tonnes of bioethanol in 2001, thereby making France large biofuel producer in the EU [ESRU]. Excise duty exemption for biodiesel is 0.35€/l. Generally RME is blended with diesel (5% biodiesel fuel). The use of a 30% biodiesel blend is limited to some 20 cities. Ethanol production in France represents 0.7% of gasoline consumption [Jeanroy 2002].

Germany is the main biodiesel producer in Europe: about 0.5 million tonnes in 2001, with a target of around 1 million t/a. However, the EU legislation limits the production of non-food crops in Europe, and Germany has to take this into account when considering its 1 million t/a biodiesel target. There is no excise tax for biodiesel in Germany, either blended or neat [ESRU, Jeanroy 2002].

Italy conducted a trial for the use of biodiesel with an exemption from excise duty for three years until 2004, for a maximum amount of 125 000 t/a. However, biodiesel is mainly used for heating purposes [ESRU, Jeanroy 2002].

Spain has invested heavily in the development of its bioethanol industry and is now producing around 0.4 million tonnes ethanol, all of which is used for ETBE production [ESRU]. In Spain, there is a program for Promotion of Renewable Energy from 1999 to 2010. The production targets for biodiesel and bioethanol by 2010 are 0.1 and 0.4 million t/a, respectively. The exemption of excise duties for all biofuels is in force until the end of 2012 [IEA AFIS, May 2003].

Sweden has been active in the field of biofuels for transportation. Sweden has significant forest reserves, like Canada and Finland, and thus production of ethanol from this source is an interesting option. Ethanol programs in Sweden have focused on problems related to hydrolysis of wood and fermentation of free sugars. As a result, there is production of ethanol from woodchips in Sweden. Sweden also co-operates with US DoE and e.g. IEA on ethanol issues. The target in Sweden is to cover some 3% of gasoline consumption with ethanol. Sweden is also interested on methanol produced by gasification of biomass, especially in combination with production of dimethyl ether (DME). A study in 1999 indicated that biomass-based methanol could cost less than what is expected for ethanol price over the next 5 to 10 years [Rehnlund]. However, ethanol production in Sweden is very modest, less than 0.1 million tonnes in 2001, and imported ethanol is needed to cover the consumption [Jeanroy 2002]. In Sweden, wood based ethanol could be produced in conjunction with pulp and paper mills, thus increasing total energy efficiency. A 50.000 t/a grain based ethanol factory exists in Norrköping. A new pilot plant factory for production of wood based ethanol has been built in Örnsköldsvik.

The market situation for fuel ethanol has been discussed as follows (applies also to the other biofuels to large extent): Increasing use of ethanol as fuel would influence ethanol and feedstock markets and distribution systems. Possibly, with financial assistance, fuel ethanol plants separate from traditional producers of industrial or beverage sector could emerge. E.g. in USA fuel ethanol producers dominate also the beverage and industrial markets. With an extensive use of fuel ethanol, an international market is needed to stabilise the regional production shortfalls, which are inevitable due to dependence of national supplies on e.g. weather. This means foreign farmers and industries benefit from the national subsidies. However, an international exchange is the only solution for large-scale fuel ethanol use. Anyway, fuel ethanol is not as dependent on a few countries, as the oil sector. Fuel ethanol, besides being environmentally friendly, is a support to farmers, who will profit and lobby for the production of fuel ethanol [Distillery Network].

As a summary, promotion on biofuels has resulted in increased production in many countries, even though there is no harmonization in e.g. fuel tax systems, not within US nor EU. Large differences exist in the "political will". Some very challenging indicative targets for the use of biofuels have been set, but the growth will depend on a number of factors. However, one of the ethanol studies states "outlook has never been brighter".

2.2 FINLAND[8]

The European policy on biofuels has to be taken into account in the Member States, even though no common solution for the whole of Europe is expected due to varying conditions in individual countries. Evaluation of policies and progress in individual countries within EU provide a baseline for discussions, as some countries are at least partly comparable with Finland from an economic and climatic point of view. Generally, it is clear that EU policies and promotion of renewable energies have already led to a significant increase in biofuels production over the last years.

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[8] Major part of the information in this Chapter was published Mäkinen 2003, Nylund 2004, Sipilä 2002.

The National Climate Change Policy in Finland has a target to reduce the greenhouse gas emissions to the emission level of the year 1990 by 2008-2012. Renewable energy sources (bioenergy), energy saving and additional nuclear power capacity are the key instruments. So far, liquid biofuels have had only a minor role in the national GHG policy, since transportation represents only some 20% of the CO_2 emissions in Finland. Heat and power production have been the key priorities due to the lower CO_2 abatement costs [Sipilä 2002].

The EU directive on liquid biofuels for transportation (2003/30/EC) sets step-to-step indicative targets for the use of biofuels in transportation. Even though these target values are recommendations, reactions and actions from Member States are expected. Currently there is no commercial production or consumption of biofuels for transportation in Finland.

The Ministry of Finance in Finland has the key role in the possible promotion of biofuels in Finland. Production costs of biocomponents can easily be 3-4 times higher than production costs of fossil fuels, and this can be compensated only with tax incentives. Unrealistic tax incentives or subsidies are not expected to be sustainable solution for biofuel use. Thus the key question is how to reduce costs to tolerable level. This is especially important in Finland where production costs in agriculture are higher than on average in Europe. Thus research work on biofuels in Finland is more focused on production than on end-use aspects. Conversion of wood- and waste-based raw materials to biofuels, including production of pyrolysis oil for boilers, gain the main attention [Sipilä 1997, 2002].

Several programs, some of them in Finland, have demonstrated that a variety of technical solutions to use biofuels exists. In the case of “conventional” biofuels (ethanol, biodiesel), the end-use properties are known to a large extent. If production levels are sufficient, and the price levels reasonable, the market exists.

In Finland the industry with an interest in biofuels for transportation is limited. The active companies have been the national oil company Fortum Oil and Gas (formerly Neste), Sisu Corporation (Valmet tractors and engines), the national alcohol company Primalco (formerly Alko Ltd) and producers of vegetable oils (e.g. Mildola and the Raisio Group). In addition, the pulping industry had some interest in tall oil based biodiesel [Nylund eeci].

There have been some activities to demonstrate the use of biofuels in transportation. Fortum Oil and Gas carried out a trial marketing 98-octane gasoline containing 5% ethanol in a limited area in southern Finland, with a 0.30 €/l tax incentive for the ethanol part. Generally, Fortum has expressed an interest in biocomponents in gasoline, diesel fuel and heating oils, and the company has participated in several research programs. The most recent activity is a new biocomponent, hydrated biodiesel with the trade name “NexBioDi” [Juva 2004]. The idea is to introduce the biocomponents into the feed stock of the refinery.

Certain Valmet (Sisu Diesel) engines have been approved for 100% biodiesel and vegetable oil based lubricants within normal warranty conditions. In the Finnish research institutes, a considerable knowledge regarding biofuels and alternative fuels is available [Nylund eeci].

It is interesting to compare policies of two neighbouring countries, Sweden and Finland. Sweden has put extensive efforts in renewable transportation fuels since early 90's, whereas Finland has been rather passive. One explanation for this difference might be that the transport sector is responsible of about 40% of CO_2 emissions in Sweden [Månsson 1998], but below 20% in Finland. Thus the transport sector has more significance regarding the greenhouse gases in Sweden than in Finland.

The indicative target values as set by the Biofuels Directive and the Green Paper (the latter with a target of 20% substitution of on-road fossil fuels by alternative fuels by 2020) are really challenging aims. As an expert in Finland pointed out, all possibilities for the use of alternative fuels should be taken into account in Finland, which is a country of long distances. For instance, natural gas, which today is limited to the southernmost part of Finland only, would need huge investments on distribution systems, and would in any case cover only part of the vehicle fleet. Liquid alternative fuels, blended in gasoline and diesel, are cost-effective [Mikkonen 2002]. However, the availability of raw-material limits the production capacity of many components. Thus many options of liquid biofuels are probably needed in parallel, and there is a need for bio/alternative components both for gasoline and diesel.

As mentioned before, there is no production or use of liquid biofuels for transportation in Finland, with the exception of certain trials. It is, however, possible to evaluate the theoretical production potentials of biofuels for transportation. Table 1 shows the current use of motor fuels in Finland [IEA Bioenergy Country report] and Table 2 an estimated potential of the production of ethanol and RME in Finland from set-aside land [Mäkinen, Sipilä]. The area of set-aside land in Finland was 200 000 ha in 1996, whereas in 1994 before joining EU the area was still 505 000 ha. Increased grain prices lead to decrease of set-aside fields. In Finland, evaluations of the possible non-food use of set-aside land have been carried out in e.g. 1993, 1995 and 1997. All studies so far have shown that it is not economically feasible to start production of ethanol or biodiesel for transportation in Finland. The production costs are far too high in Finland due to climatic conditions.

In the case of Finland the indicative target values of the Biofuels Directive are extremely challenging. This in demonstrated in Table 2, which shows the estimated potential of biofuel production in Finland. Only agricultural biofuels, biodiesel or ethanol, could be produced with commercially available technology. However, production potential of these fuels from set-aside land represents less than 2% of the consumption of transportation fuels in Finland.

Wood-based, and to a lesser extent, waste-based fuels would offer a significant reserve of raw material for liquid biofuels, on condition that cost-effective production processes existed, and there were no limitations set by competitive use. Apparently, all possibilities for renewable and alternative fuels should be taken into account in Finland when considering significant and sustainable use of liquid biofuels in Finland.

Table 1. The use of transportation fuels (road transport) in Finland in 2002 (Finnish Oil and Gas Association) [Nylund 2004].

Gasoline (Mt)	Diesel (Mt)	Light fuel oil (Mt)	Natural gas **) (MNm^3)	LPG ***) (Mt)
1.84	1.86	total 2.28, motor fuel appr. 0.75 *)	3.6	0.0

*) estimated use in farm tractors, work machinery etc.
**) value for 2003, source Gasum
***) very limited use

Table 2. <u>Estimated potential</u> of biofuel production in Finland [Mäkinen 2003, Sipilä 2002].

	tonnes/a	**% of motor fuel consumption in Finland**
RME or ethanol from set-aside lands	60 000	1.6
Wood-based fuels		
Ethanol from wood*)	>250 000	>6.8
Byproducts from pulp mills**)	*<80 000*	*<2.2*
Waste-based fuels		
Biogas	>10 000	>0.3
Solid recovered fuels for syngas	>50 000	>1.4

**) also other fuels, e.g. methanol, could be processed from wood*
***) soap-based diesel, methanol*

Biodiesel

Neat rape seed is cheaper than the respective methyl ester, but not suitable to be used as motor fuel in transportation (possibly usable for heating). The production potential of rape seed methyl ester from set-aside land in Finland is max. 60 000 t/a.

Bio-ethanol

Production potential of grain-based ethanol from set-aside land in Finland is around 60 000 t/a. However, this estimated potential is not in addition to but an option for production of biodiesel for set-aside land. Grain-based ethanol is expensive, and energy efficiency is poor. The side products can be used as animal feed-stuff.

In the future, production of bio-ethanol from cellulosic raw materials might become economically feasible. Additional wood resources, mainly forest residues, but also other biomass raw materials, might increase the ethanol production potential even up to 1 million t/a. Also other fuels, e.g. methanol, could be processed from wood/biomass. However, increasing industrial and municipal CHP production (combined heat and power) is expected to consume the major part of the additional production of wood-based energy.

Byproducts from pulp mills

Soap-based products, tall oil methyl ester or hydrated tall oil, could theoretically be suitable for diesel engines. However, there are some technical problems associated with this type of fuels. One obstacle is sulphur content, which is high when compared to current and future limit values. Methanol is another by-product from sulphate pulp mills. Anyway, limited production volumes in general and competitive use (e.g. paints) are estimated to prohibit using this soap-based diesel for transportation.

3 PRODUCTION

3.1 ETHANOL

The ethanol produced today is usually biomass-based. New efficient and cost-effective, methods of producing ethanol from variety of feedstocks e.g. agricultural crops, forestry raw materials and municipal waste are studied intensively [Månsson 1998].

Raw-materials/processes for ethanol production could be classified as follows:

- Production of ethanol from corn, sugar beat or cane or other **sugar rich crops by fermentation** using yeast followed by distillation is a well-known and simple process. This is suitable method in countries with sub-tropic climate keeping the costs of raw-material low enough for fuel-grade ethanol. However, raw material is too expensive in climates such as in Scandinavia.

- Production of ethanol from **starch** containing raw-materials like potatoes and grain, requires a mild **hydrolysis of starch into sugar before fermentation**. This is well-known and widely used process e.g. in Scandinavia, but too expensive for fuel grade ethanol.

- Production of ethanol from **cellulose and hemicellulose-containing raw materials** like straw, softwood, hardwood[9], waste paper and municipal refuse are cheap raw materials. The production of ethanol from these cellulosic materials is more complex and expensive than hydrolysis from starch. **Enzymatic and acid based hydrolyses** are the most studied processes for ethanol production from these materials (Figures 2 and 3). Also modified yeasts

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[9] Wood contains lignocellulose, which is a mixture of cellulose, hemicellulose and lignine. Lignocelluloce can be treated e.g. with base or acid to separate celluloce and hemicelluloce. Cellulose is molecular chain of glucose (6 carbon atoms) and different sugars can be separated with enzyme for fermentation with traditional yeast. Hemicellulose contains mainly non-glucose sugars, like pentoses (5 carbon atoms) xylose, galactoce, mannoce. Hemicelluloce contains about 40% pentoses, which cannot be treated by traditional yeast. Lignine is a polyaromatic material.

and drying by molecular-membranes are intensively studied. In theory, all kind of cellulose and hemicellulose can be converted into sugar [Månsson 1998].

- **Synthetic ethanol** can be produced e.g. from syngas via acetic acid or ethylen. There has also been research on the fermentation process of **synthesis gas** into usable products. Synthesis gas contains hydrogen (~50%), carbon monoxide (~25%), and carbon dioxide (~25%), and it can be produced from biomass by gasification or from natural gas. Traditionally syngas has been used for production of methanol, but also ethanol can be produced using inorganic heterogeneous catalysts or fermentation [Missisippi State University].

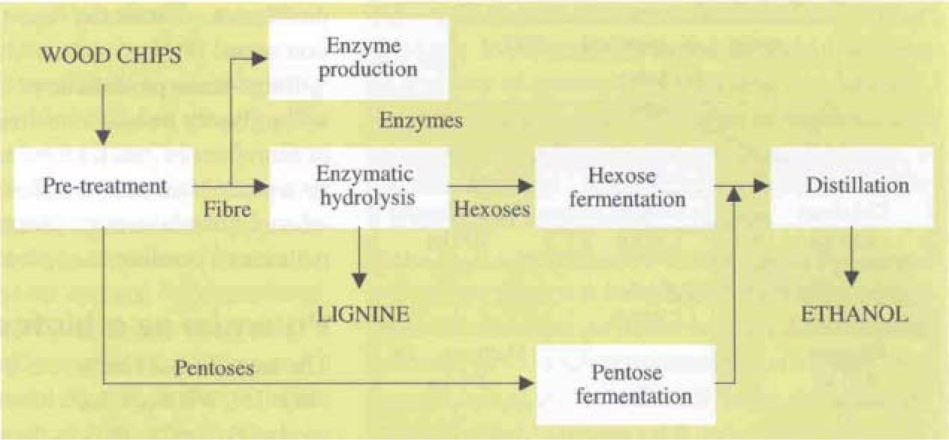

Figure 2. Schematic Figure on production of ethanol from lignocellulose based on enzymatic hydrolysis [Månsson 1998].

The world ethanol production in 2001 was estimated to reach 31.4 million t/a (Figure 4), which was still below the highest production ever, 33.0 million t/a in 1997. The amount of ethanol used as fuel was below 20 million tonnes in 2001. The use of ethanol as fuel is increasing world-wide. The announced projects indicate a growth of fuel ethanol production from some 20 million tonnes up to some 31 million tonnes by 2006. The share of fuel ethanol in 2005 could be almost 70% compared with around 63% in 2001 [Distillery Network].

The main producers of ethanol are Brazil and USA, but an increase in production has taken place also in other countries¨(Figures 4 and 5). New production centers could be Thailand, with a planned production of 0.65 million t/a, and China, with an announced production of 1.6 million t/a. The “Biofuel Directive” promotes biofuels, and an increase in production of ethanol can already be seen [Distillery Network].

In 1997 it was reported that 2.5 million t/a ethanol was produced for blending in gasoline in USA (corn based), in Brazil 8 million t/a and in France 0.4 million t/a. [Sipilä 1997]. In 2000 some 7.4 million t/a fuel grade ethanol was produced in U.S. [McCormick 2001]. In Brazil 4.9 million t/a hydrous ethanol was used in neat ethanol cars and 5.5 million t/a anhydrous ethanol in gasohol in 2002 [Winrock 2002].

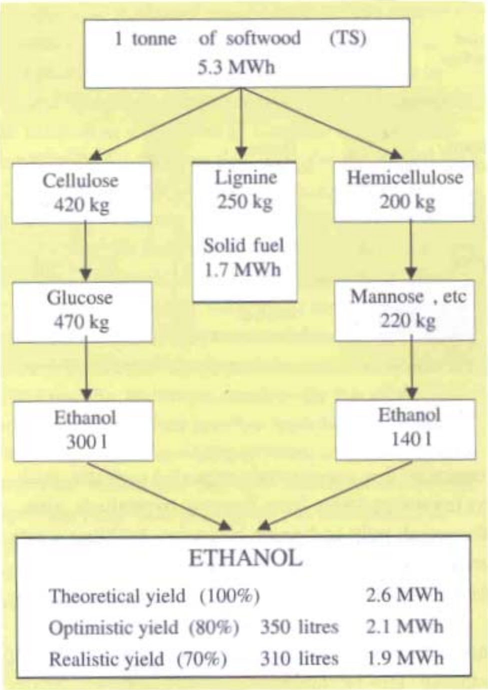

Figure 3. Theoretical ethanol yield [Månsson 1998]

America is the leading continent with 20.6 million t/a production of ethanol in 2001. This was around 2/3 of the world output. The world leader was Brazil, with 11.9 million t/a. However, USA may pass Brazil, if MTBE will be replaced by ethanol in California (MTBE ban from January 2004). The ethanol production in individual countries is shown in Appendix 1 [Distillery Network]

In Canada the production of ethanol is rising. The total amount of ethanol produced in Canada was 0.24 million tonnes in 2001 [Distillery Network]. This ethanol is based on wheat or corn, but some demonstrations using forestry raw materials are going on. One company (Iogen Corporation) is developing a process that will convert wood, hay, straw and other agricultural residues to ethanol. In 2002 Canada set a 1.3 million t/a target for ethanol use, which corresponds to a 35% market share of 10% ethanol containing gasoline [CRFA]. In 2003, the Canadian government is considering a law, which would force oil companies to blend 10% ethanol into gasoline [IEA/AMF AFIS 2003].

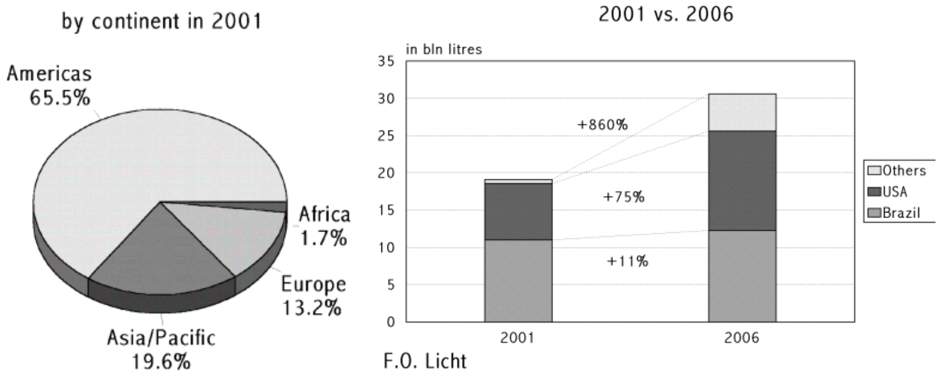

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Figure 4. World fuel ethanol production, total ethanol production in 2001 was 31.4 million tonnes [Distillery Network].

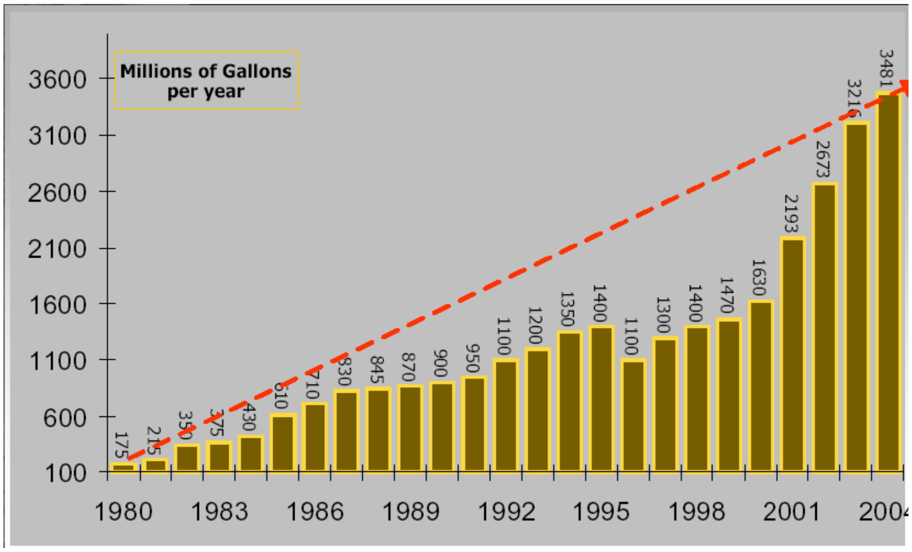


Figure 5. Ethanol production in USA, 1 US gallon ~ 3.79 liters [Williams 2002].

Unlike in US, Brazil or Canada, within EU there has not been such strong promotion of biofuels before the "Biofuel Directive", which is expected to increase the use of ethanol. In France in 2001, TotalFinaElf, the only producer of ETBE, manufactured 0.2 million tonnes of plant-based ethanol. France is using 70% of its non-food set-aside land (410 000 hectares) for biofuel production. Spain is expected to grow to become the largest bioethanol producer within the EU. A new plant in Salamanca has a capacity of 0.2 million t/a (the largest plant with biomass-based technology for ethanol world-wide). Production in Germany could increase slightly. In Italy, production is expected to fall, and production in central and eastern Europe is expected to grow only marginally. The Russian alcohol market is the largest in Europe. Official figures show total alcohol output of around 0.8 million tonnes in 2000, mainly beverage alcohol [Distillery Network].

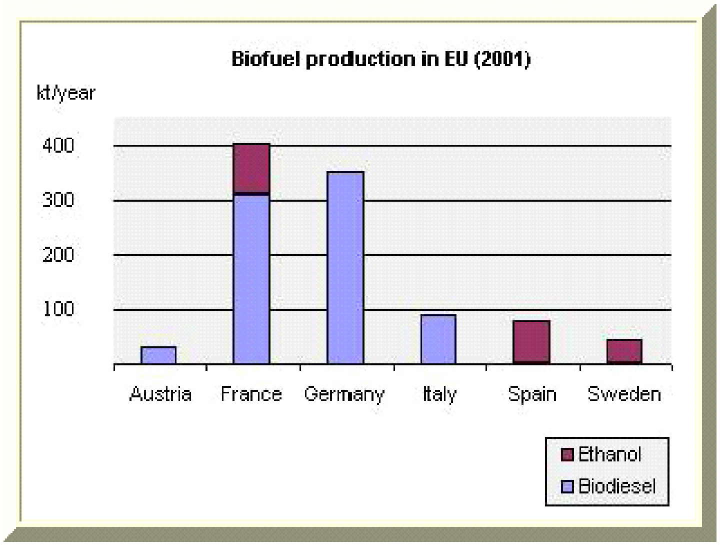


Figure 6. Biofuel production in EU [ESRU].

Sweden has carried out extensive programs on ethanol, focusing on new, cost-effective production technologies based on hydrolysis of woodchips and fermentation of free sugars, both hexoses and pentoses. Three techniques for hydrolysis have been priorized: dilute acid hydrolysis, and to a lesser extent strong acid hydrolysis and enzymatic hydrolysis. Also poisoning of yeast bacteria by compounds in the wood has gained interest. After lab-scale testing a pilot plant for production of ethanol from woodchips was built. The pilot plant in Örnsköldsvik uses hydrolysis technique with diluted acid. Later on large demonstration plants might be built. It is expected that this technique might be the base for production of approximately 100 000 t/a of ethanol in Sweden by 2005, and 150 000 t/a by year 2010. This production together with the already existing wheat-based ethanol production would correspond to more than 3% of gasoline consumption in Sweden [Rehnlund].

[Concawe 2002] has published a review on Biofuels in Europe. This report includes Table 3 showing potential production volumes of ethanol and/or RME in Europe. The scenarios shown are alternatives as land can be used only for one crop at the time. It seems that potential for ethanol would be higher than for RME, due to better yield of the sugar beet, which, however, can be grown only in certain areas. CONCAWE points out that if all the EU-15 set-aside land were used to produce RME that would represent only 2.3% of fuel demand, and using all the the set-aside land for ethanol 4.3% of total fuel consumption could be replaced. Energy is used also in the production process, and this reduces the potential net savings. When considering the Biofuels Directive with 5.75% biofuel target by 2010, it seems that a significant portion of the land currently used for food crops should be converted to biofuel production. Suitable land is also available in East-European countries, but the use of this land for biofuel production has not been agreed upon. CONCAWE mentions that EU currently has a surplus of gasoline and a deficit of diesel. Potential use of RME or ethanol would give CO_2 avoidance around 0.3% of the EU-15 emissions, but this benefit could even reduce if the N_2O emissions increase from crop production.

Japan is interested in blending ethanol into gasoline, as was described in the previous Chapter. With 10% ethanol in gasoline, the fuel ethanol consumption in Japan is estimated to be almost 6 million t/a. The ethanol should be imported as Japan does not have extra agricultural possibilities to increase production, and biomass based processes are not cost-efficient, yet [Carbohydrate Economy News].

In Africa the ethanol production is concentrated to South Africa (70%). The largest fuel company is SASOL, producing a variety of synthetic fuels using coal and gas as raw materials. The ethanol production capacity is around 0.22 million t/a. This synthetic ethanol is used for ethyl acetate, high purity ethanol and a small portion of it is used as fuel. In addition, South Africa produces increasing amounts of fermentation ethanol, with molasses being the major feedstock [Distillery Network].

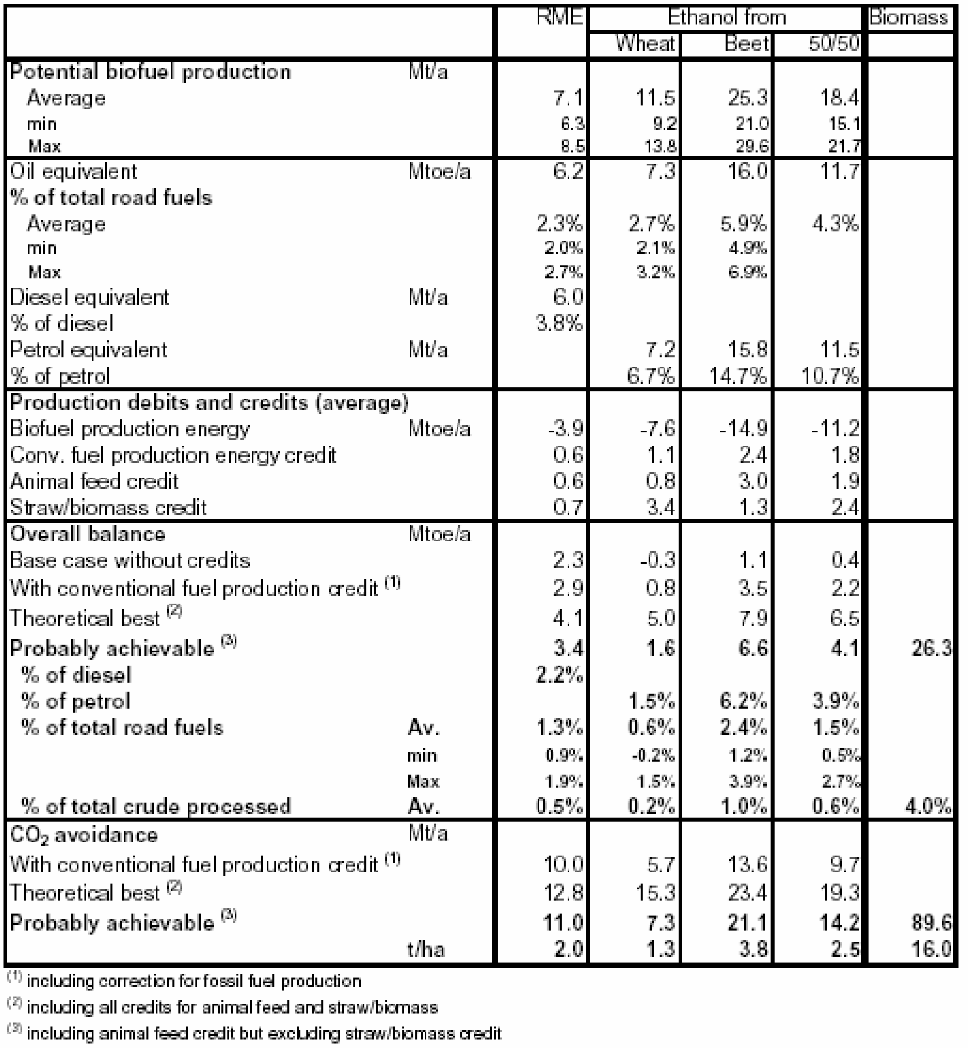
In Thailand the fuel ethanol program was started in 2000 to reduce oil imports and to make use of the country's agricultural products. So far, two oil companies distribute fuel ethanol blends. However, there are difficulties in finding sufficient quantities of feedstocks for ethanol production.

India has started to produce anhydrous fuel alcohol. Three pilot plants produce ethanol for gasoline blends with 5% alcohol. India's oil imports were around 75 million tonnes in 2001. The ethanol industry in India is suffering from oversupply, with a production capacity of 3.2 million t/a, and an actual production of around 1.8 million tonnes.

India’s alco-chemical industry fears that production of fuel ethanol could raise prices of molasses.

China is the latest country to announce a fuel ethanol program. Fuel ethanol production in China is estimated to be about 1.6 million t/a. At present, China consumes about 36 million t/a of gasoline [Distillery Network].

Table 3. Potential of biofuels in EU-15 [CONCAWE 2002].



		RME	Ethanol from			Biomass
			Wheat	Beet	50/50	
Potential biofuel production	Mt/a					
Average		7.1	11.5	25.3	18.4	
min		6.3	9.2	21.0	15.1	
Max		8.5	13.8	29.6	21.7	
Oil equivalent	Mtoe/a	6.2	7.3	16.0	11.7	
% of total road fuels						
Average		2.3%	2.7%	5.9%	4.3%	
min		2.0%	2.1%	4.9%		
Max		2.7%	3.2%	6.9%		
Diesel equivalent	Mt/a	6.0				
% of diesel		3.8%				
Petrol equivalent	Mt/a		7.2	15.8	11.5	
% of petrol			6.7%	14.7%	10.7%	
Production debits and credits (average)						
Biofuel production energy	Mtoe/a	-3.9	-7.6	-14.9	-11.2	
Conv. fuel production energy credit		0.6	1.1	2.4	1.8	
Animal feed credit		0.6	0.8	3.0	1.9	
Straw/biomass credit		0.7	3.4	1.3	2.4	
Overall balance	Mtoe/a					
Base case without credits		2.3	-0.3	1.1	0.4	
With conventional fuel production credit (1)		2.9	0.8	3.5	2.2	
Theoretical best (2)		4.1	5.0	7.9	6.5	
Probably achievable (3)		**3.4**	**1.6**	**6.6**	**4.1**	**26.3**
% of diesel		**2.2%**				
% of petrol			**1.5%**	**6.2%**	**3.9%**	
% of total road fuels	**Av.**	**1.3%**	**0.6%**	**2.4%**	**1.5%**	
	min	0.9%	-0.2%	1.2%	0.5%	
	Max	1.9%	1.5%	3.9%	2.7%	
% of total crude processed	**Av.**	**0.5%**	**0.2%**	**1.0%**	**0.6%**	**4.0%**
CO_2 avoidance	Mt/a					
With conventional fuel production credit (1)		10.0	5.7	13.6	9.7	
Theoretical best (2)		12.8	15.3	23.4	19.3	
Probably achievable (3)		**11.0**	**7.3**	**21.1**	**14.2**	**89.6**
	t/ha	**2.0**	**1.3**	**3.8**	**2.5**	**16.0**

(1) including correction for fossil fuel production

(2) including all credits for animal feed and straw/biomass

(3) including animal feed credit but excluding straw/biomass credit

3.2 ETBE

Ethanol can be a feedstock for the production of ethyl tertiary butyl ether (ETBE). Isobutylene, which is the other feedstock, is derived from natural gas condensates, or as a by-product of petroleum refining (Figure 7). ETBE is processed either in the units of oil refineries or in chemical plants. ETBE is similar to MTBE in respect of the end-use properties. Compared to ethanol, ETBE shows similar or better engine performance.

ETBE is produced mainly in Europe. France has been the leading producer with volumes of almost 0.2 million t/a (Figure 8). Production in France started already in 1993, and has increased up to 0.7% of the fuel consumption.

In Spain all bioethanol is converted to ETBE. At present, two bioethanol plants and three refineries produce a total of 180 000 t/a of ETBE, a figure close to the production in France. An additional production of 250 000 t/a is foreseen in the coming years [IEA AFIS May 2003].

At the moment US has no commercial ETBE production. The existing MTBE plants could easily be switched to produce ETBE. ETBE is likely to be used besides ethanol as replacement component of MTBE in California.

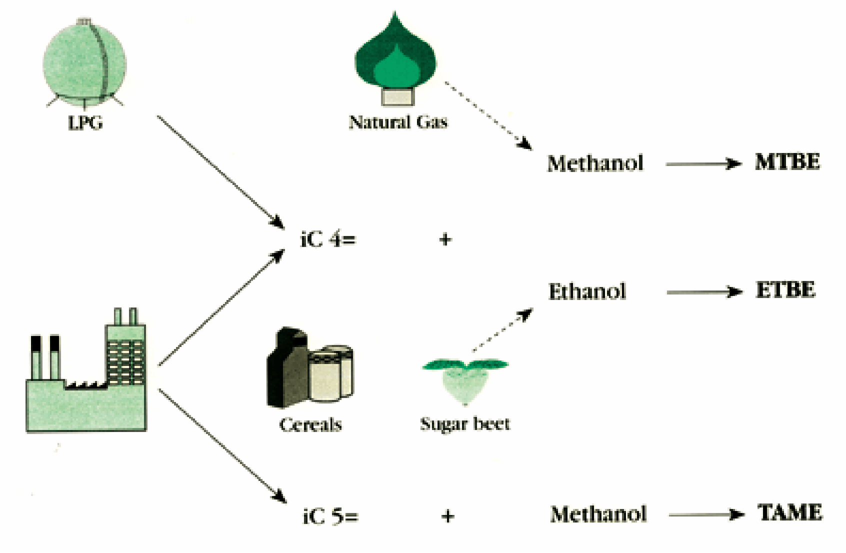
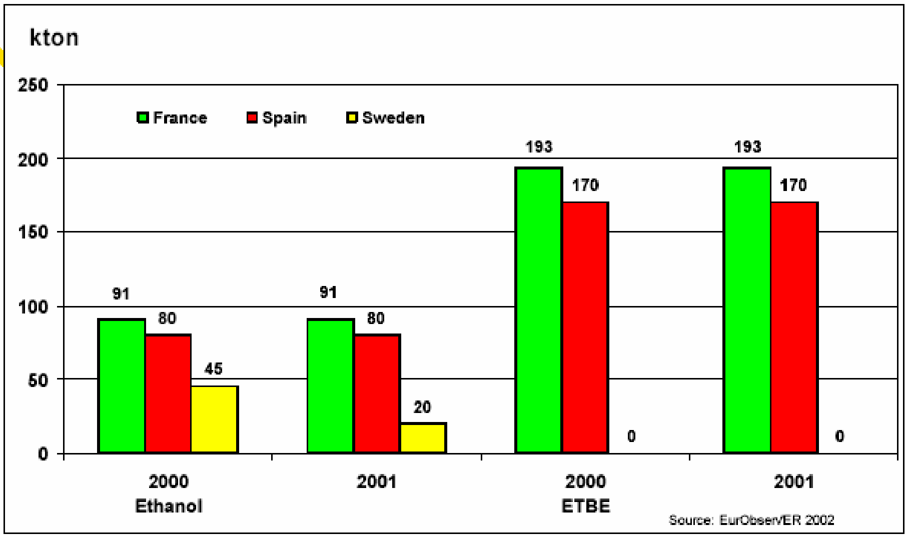


Figure 7. Schematic Figure of ETBE production [EFOA].



Source: EurObservER 2002

Figure 8. Production of ethanol and ETBE in Europe [VTT eubionet].

3.3 BIODIESEL

Traditionally biodiesel means fatty acid methyl esters (FAME). However, several feedstocks can be used in the transesterification. Vegetable oils and used vegetable oils are in principle similar, but the quality of used oils varies more. Animal fats are also an option as feedstock, offering lower costs than vegetable oils. However, additional cleaning may be required, and the quality of animal fat based biodiesel might be questionable (poor cold properties). Tall oil, a side-product from the pulp industry consisting of free fatty acids, has been also considered as feedstock, but the experience so far has not been too promising. Another tall oil product, hydrated tall oil, has shown better end-use performance.

Vegetable oils, animal fats, recycled cooking greases etc. can be transformed into biodiesel using transesterification. Oils and fats, which are triglycerides and/or free fatty acids react with alcohol to produce esters using catalyst (typically sodium or potassium hydroxide). The side-product is glycerol (glycerine). So far, only methanol is used as alcohol in current biodiesel plants, but ethanol could be used as well.

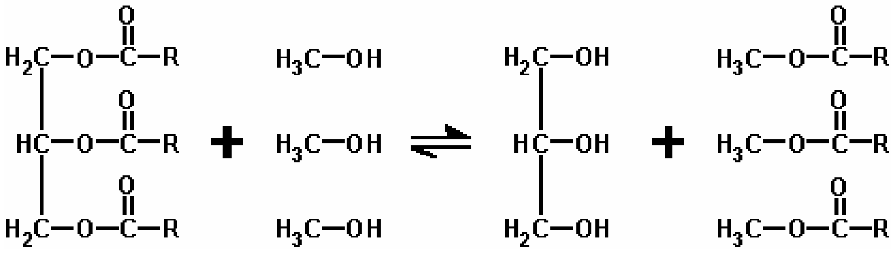
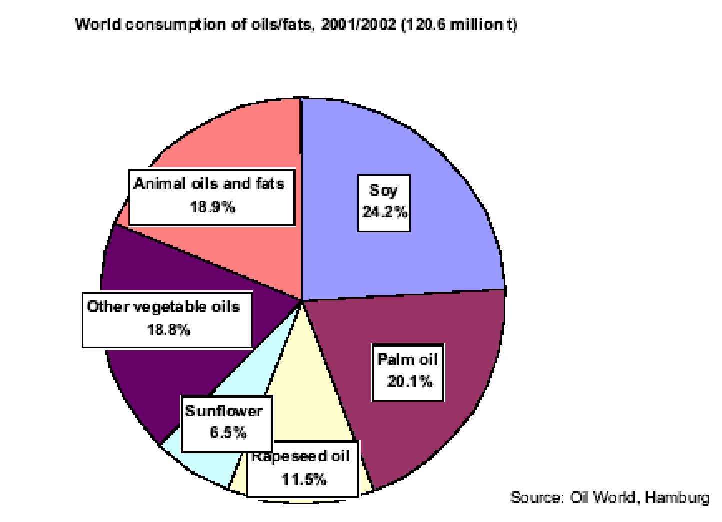


Figure 9. Schematic Figure of transesterification of rape seed oil to RME [Campa 2000].

U.S. biodiesel production is based largely on soybean oil and used cooking grease, whereas in Europe rape seed is the most popular feedstock. Japan is interested in used vegetable oil. Regardless of the process or feedstock the biodiesel must meet stringent specifications if used as a transportation fuel [Tyson 2001]. The chemical-grade fatty acid methyl esters used for e.g. detergents cannot be used as biodiesel [US DoE Biofuels].

The world consumption of oils and fats was about 120 million t/a in 2002. In Europe, the production of rape seed oil has been at the level of 3.5 million t/a, which is less than half of the production of soy bean oil in USA. The production of palm oil in Asia is growing rapidly, and estimated to be 18 million t/a in 2005. The world production of biodiesel was some 2.8 million t/a in 2003, and the major part (3/4) is produced in Europe [Bockey 2002]. Waste oils and animal fats are estimated to be 0.7-1 million t/a in EU, and around 3.2 million t/a in US.



Source: Oil World, Hamburg

Figure 10. World consumption of oils/fats [Bockey 2002].

Germany is the leading biodiesel producer in the world, with 0.5 million t/a production in 2001, large increase from 0.34 million t/a in 2000. Planned production capacity is almost 1 million t/a. In 2001, **France** produced about 0.3 million t/a of biodiesel (from colza and less from sunflower seeds). **Italy** produces 0.125 million t/a of biodiesel fuel (sunflower), basically for heating purposes. **Austria** produces roughly 25 000 t/a of biodiesel. The Czech Republic and Slovak Republic produce approximately 0.1 million t/a of biodiesel fuel. Belgium has halted all biodiesel production [Jeanroy 2002].

Biodiesel is produced also in countries outside Europe. Production in **US** was about 0.065 million t/a in 2001. **Brazil** has launched trials to convert used oil to biodiesel. Various Asian countries, including **Thailand**, are using palm oil and coconut oil [Jeanroy 2002].

4 TECHNICAL END-USE ASPECTS

4.1 ETHANOL

4.1.1 History

Ethanol has been known as an intoxicating drink since as early as 6000 – 4000 B.C., and distilled ethanol since around 800-500 B.C. In late 1800's, ethanol was used mainly as lamp fuel, the first large scale use took place in early 1900's due to shortage of petroleum supplies. 1826 Samuel Morey developed an atmospheric engine that ran on ethanol and turpentine. Henry Ford's Model T from 1908 and other early automobiles run on alcohol, gasoline or any combination of these. World War I increased the ethanol demand to around 0.2 million t/a. In 1920's gasoline became a major blending component in motor fuel. Also World War II increased ethanol demand, but after that ethanol use decreased until the oil crisis developed in the 1970's [EIA].

The use of ethanol as a motor fuel has increased since the late l970's due to gasoline shortages. In general ethanol reduces dependency of crude oil based fuels. Ethanol also improves the combustion properties of gasoline and reduces exhaust emissions. Lately the capability of ethanol to reduce greenhouse gas emissions and thus global warning has gained attention. For all these reasons ethanol as a motor fuel is receiving word-wide attention [EIA].

4.1.2 Fuel properties

The properties of ethanol are in many respects similar to gasoline. Thus it can be used in spark-ignition engines as a gasoline component, e.g. ethanol up to some 10% can be blended with gasoline and used without modifications in spark-ignition engine. The limit is set by the lean-out effect of ethanol (10 % ethanol corresponds to 3.7 % oxygen in the fuel). Special cars, so called Fuel Flexible Vehicles (FFV) have been developed for fuels containing up to 85% alcohol (Chapter 4.1.5). Also heavy-duty diesel engines can use ethanol with certain limitations (Chapter 4.1.6).

The alcohols that have been considered as transportation fuels are methanol and ethanol. Some heavier alcohols, like tert-butyl alcohol (TBA), would be technically suitable for spark-ignition engines, but economically not feasible. Methanol and ethanol resemble each other, and most properties apply to both fuels. Despite of the similarities, also some differences exist, e.g. methanol is toxic, corrosive and non-biodegradable. Actually, e.g. Fuel Flexible Vehicles (FFV) were firstly developed for methanol use, but were later on optimized for ethanol.

Alcohols are liquid fuels, which mean good **energy density, easy re-fuelling** and **storage**. Practically no changes are needed in current fuel distribution systems. However, in the case of gasoline/ethanol blends the distribution system needs special attention to avoid problems caused by water, as blends are very **sensitive to moisture**.

Oxygen content of ethanol (C_2H_5OH) is 35%. The oxygen content of a fuel influences the stoichiometric air to fuel ratio, which is 9 kg air/kg fuel for ethanol and 14.6 kg/kg for gasoline. With fixed fuel calibration the oxygen in the fuel leads to leaner and more effective combustion up to a certain limit. Cars with a closed-loop fuel control system can compensate the leaning effect at least up to some 3.5% oxygen content [Environment Australia 2002]

Density of ethanol is 0.79 kg/l. The **energy content** of ethanol is lower than for gasoline or diesel. The lower heating value of ethanol is 26.8 MJ/kg, whereas 42.5 MJ/kg of typical diesel fuel. The lower energy content is seen directly as higher volumetric **fuel consumption** with ethanol when compared to gasoline.

Octane numbers[10] of alcohols are high, and thus they can be used as octane boosters in gasoline. However, alcohols tend to increase Research Octane Number (RON) more than Motor Octane Number (MON), of which the latter is decisive for knocking under high-load conditions. The difference between RON and MON is called sensitivity. Sensitivity of gasoline is typically 8-10 units, whereas sensitivity of ethanol is 14 units. In addition especially methanol is prone to early ignition induced by hot surfaces.

Heat of vaporization (H_v) is significantly higher for alcohols than for gasoline components in general (Figure 11). If H_v is high, and especially if also the boiling point is high, this causes **problems to start up the engine and to run the cold engine**. Fuels with high H_v cool the air/fuel mixture. In a cold engine this leads to incomplete fuel vaporization, poor fuel/air mixing and poor combustion. This problem can be reduced by increasing fuel volatility, which is one basis for using 15% gasoline with alcohol in the FFV cars. H_v and boiling point combine so that the startability limit on 100 % alcohol is around +6 ^{o}C for methanol and +12 ^{o}C for ethanol [IEA AMF Annex II].

Blending **vapor pressures** for alcohols are significantly higher than their true vapor pressures. The higher the oxygen content of alcohol, the higher the non-ideality of blending vapor pressure [Piel 1990]. When ethanol is added to gasoline, one example showed that up to some 5-10% ethanol content RVP increased, but then gradually declined until at some 30-40% ethanol content RVP was at similar level as with gasoline [Environment Australia 2002]. Vapor pressure is controlled for reformulated gasolines. To obtain low vapor pressure with gasohol, the share of butanes and other typical gasoline compounds with low vapor pressure have to be reduced [Piel 1990]. This rules out the possibility of so-called splash-blending of ethanol if strict fuel specifications are to be met.

Flame temperatures for alcohols are lower than for e.g. aromatics. Thus NO_x emissions could be lower using alcohol fuels, and with neat methanol this is also the case. However, using oxygenates as low-level blends NO_x emissions tend to increase as a result of the enleanment effect that raises combustion temperature [Peal 1990].

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[10] Octane number is a measure of the resistance of fuel to the abnormal combustion known as “knock”. Research octane number, RON, relates to the low load operation. Motor Octane Number, MON, relates to heavy load operation.

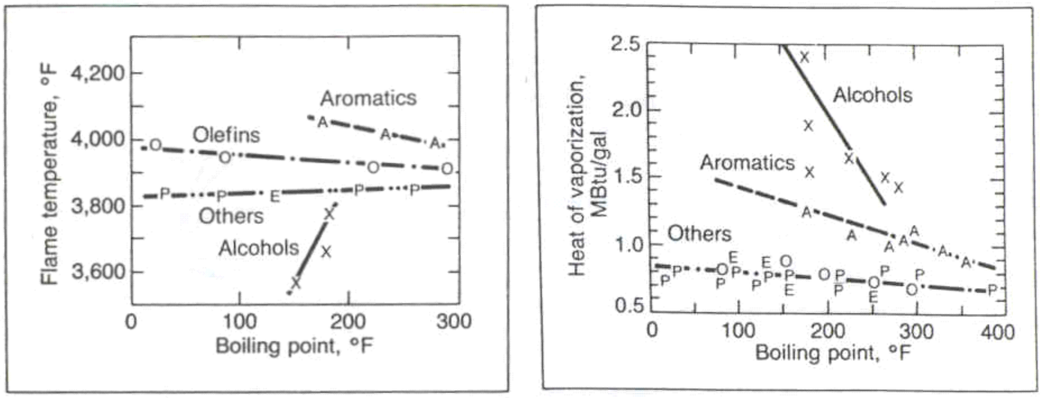


Figure 11. Flame temperature and heat of vaporisation with alcohols and other components of gasoline. X=alcohols, E=ethers, A=aromatics, P=paraffins, O=olefins [Piel 1990].

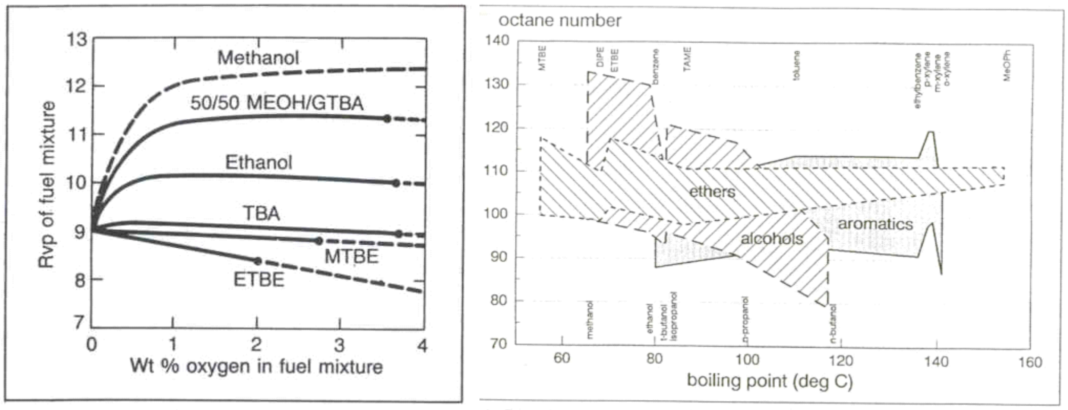
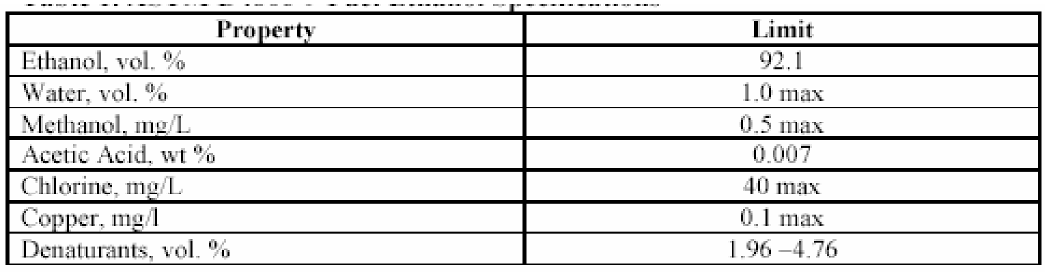


Figure 12. The effect of oxygenates on vapour pressure (left-hand side). Research octane number as a function of boiling point for oxygenates and aromatics (right-hand side) [Piel 1990, NN Oil Gas 1991].

Ethanol must be denatured when used as a fuel. In US the most common denaturant is gasoline. The minimum amount of denaturant is 2%, but as gasoline is cheaper than ethanol, it is typical to use 5% of denaturant. The ASTM D4706 **standard** gives requirements for ethanol used in gasoline, and in US, the same standard is used for ethanol in diesel (Table 4) [McCormick 2001]. *"Specifications, Definitions, and Regulations for the Composition of Industrial, Beverage and Fuel Alcohol Products in Various Countries"* are found at *"The Online Distillery Network for Distilleries & Fuel Ethanol Plants Worldwide"* [Distillery Network, specs].

Both hydrated and anhydrous ethanol grades are produced. Hydrated ethanol contains 95% ethanol and some 5% water after distillation. Dehydration produces an anhydrous grade with an ethanol content of 99.5%. Hydrated ethanol can be used for E85, whereas anhydrous ethanol is required for gasohol.

Table 4. ASTM D4706-9, fuel ethanol specifications [McCormick 2001].



Property	Limit
Ethanol, vol. %	92.1
Water, vol. %	1.0 max
Methanol, mg/L	0.5 max
Acetic Acid, wt %	0.007
Chlorine, mg/L	40 max
Copper, mg/l	0.1 max
Denaturants, vol. %	1.96 –4.76

4.1.3 Storage and handling

There is a lot of data on storage and stability of ethanol and ethanol blends. This section covers mainly the issues that relate to low-concentration ethanol blends with gasoline.

Alcohols are liquid fuels, which mean good energy density, easy re-fuelling and storage. Practically no changes are needed in current distribution systems. However, in the case of gasoline/ethanol blends the distribution system needs special attention to avoid problems caused by water, as blends are very sensitive to moisture. In practice, e.g. in U.S., the ethanol is blended into the gasoline at a product terminal just before it is delivered to retail or end-user due to water-solubility of ethanol. [Williams] has transported ethanol via pipelines, which is the cheapest method. However, they pointed out that e.g. the following actions should be taken: frequent dewatering of mainlines, closed floater storage tanks to prevent rainwater ingestion, commitment to dry storage tanks, inline corrosion monitoring, filtration system, ethanol quality oversight program, materials compatibility review, updated safety documentation & frequent dewatering of mainlines.

Anyway, it is technically difficult to transport ethanol in the pipelines. In addition to water-related problems, quantities large enough for transportation through pipelines are difficult to find (ethanol plants are too small). Railroads also face problems with unloading facilities [Distillery Network].

In the US, there are documented storage and handling procedures for low-concentration ethanol blends, e.g. for tanks, piping, fittings, pumps and dispensers. Some materials used in the storage systems may be unsuitable for ethanol, e.g. some single-walled fibreglass reinforced plastic tanks, some gaskets, sealants, adhesives and other materials. The unsuitable and suitable materials for high-concentration ethanol blends, such as E85, are discussed in [E85 Handbook]. E.g. aluminum, zinc, brass, lead, and lerne (lead-tin-alloy plated steel commonly used in fuel tanks), are incompatible with E85. Similarly, lists of compatible and incompatible nonmetallic materials for E85 are available.

Ethanol blends are sensitive to handling and storage practices due to the possibility of phase separation in the case of too high amount of water present. The amount of water that can be absorbed by low-concentration gasoline/ethanol blends without phase separation varies from 0.3 to 0.5%, depending on temperature, aromatics and ethanol content. The higher the ethanol content, the greater the amount of water absorbed by the fuel without phase separation. Ethanol is water-soluble and hygroscopic, and thus it carries moisture into the fuel system. In general it is important to ensure that water contamination does not occur in the distribution and storage with ethanol blends. In terms of storage and stability, more studies are needed.

Ethanol miscibility can be shown with a ternary phase diagram (Figure 13). The shaded region indicates the phase separated range. The mixture is in a single phase in all combinations of water and gasoline when the share of ethanol is over 70%. Point A indicates a mixture with 15% ethanol and 85% gasoline. If water is added, the composition changes as indicated by the arrow. Once the composition reaches that indicated by the end of the arrow, the single phase will split into two phases with the compositions indicated by points A’ and B’. For smaller fractions of ethanol, much smaller quantities of water are required to cause phase separation. For instance, ASTM D4806 states that with a water concentration of 0.5% E10 will separate [Powers 2001].

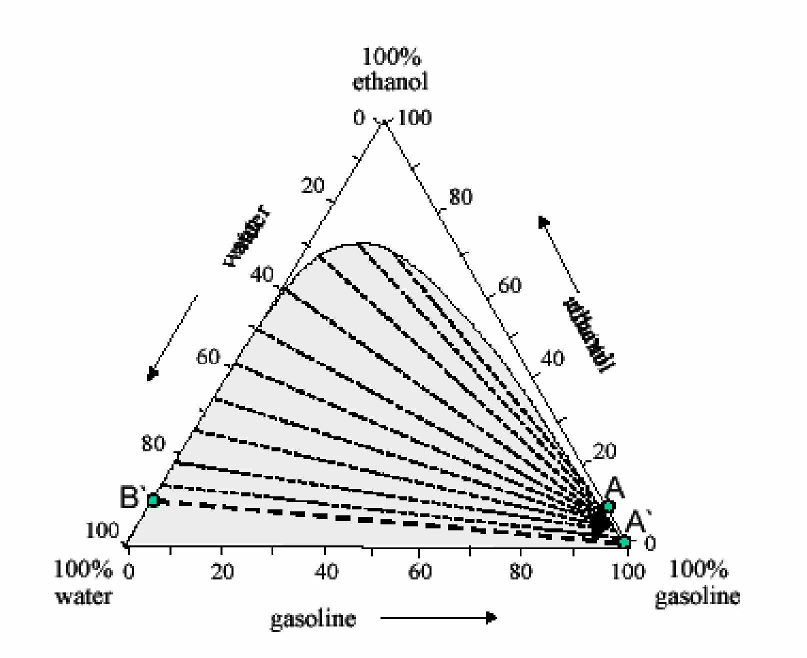


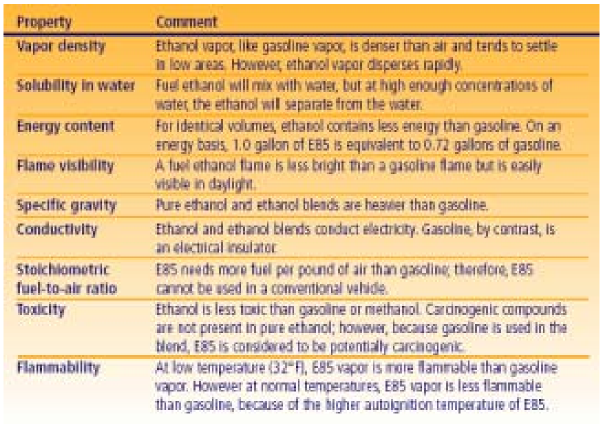
Figure 13. Ternary phase diagram for gasoline-ethanol-water system at 25 °C. Axes indicate percent of total mass. (Powers 2001, adapted from de Oliveira 1997).

The effects of water on an engine differ significantly depending on whether the water is in gasoline or in a separate phase. A small amount of water solution in a homogeneous ethanol/gasoline blend has no adverse effect. If phase separation occurs and ethanol/water phase is drawn into the engine it will stall. Phase separation can occur in a vehicle's tank if, for example, a quarter of a tank of ethanol blend is supplemented by three-quarters of a tank of petrol at refill, causing the concentration of ethanol in the blend to fall. In this situation, the presence of water normally contained within the ethanol blend may be sufficient to precipitate phase separation.

Methanol burns with an invisible **flame**, and ethanol with a slightly luminous flame. A small amount of gasoline in alcohol, like in E85, improves the visibility of flame, which is a safety factor in possible accidents.

There are a number of safety issues with ethanol, especially when E-diesel is concerned (Chapter 4.1.6.2). Tables 5 and 6 list some general properties and safety related issues for gasoline, diesel and ethanol. The **flash point**[11] of ethanol is 13°C. The flash point does not change linearly with blending ratio, and thus even a few percents of ethanol in diesel lowers the flash point close to 13°C. [McCormick 2001]. Storage and handling regulations for fuels are based on flash point, ethanol and ethanol blends fall into the same class as gasoline.

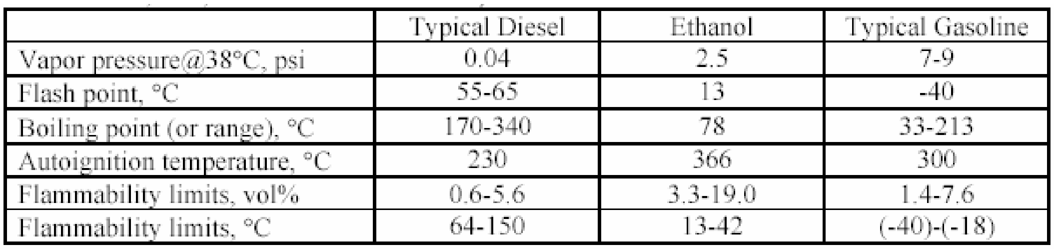
Table 5. E85 properties [E85 Handbook].



Property	Comment
Vapor density	Ethanol vapor, like gasoline vapor, is denser than air and tends to settle in low areas. However, ethanol vapor disperses rapidly.
Solubility in water	Fuel ethanol will mix with water, but at high enough concentrations of water, the ethanol will separate from the water.
Energy content	For identical volumes, ethanol contains less energy than gasoline. On an energy basis, 1.0 gallon of E85 is equivalent to 0.72 gallons of gasoline.
Flame visibility	A fuel ethanol flame is less bright than a gasoline flame but is easily visible in daylight.
Specific gravity	Pure ethanol and ethanol blends are heavier than gasoline.
Conductivity	Ethanol and ethanol blends conduct electricity. Gasoline, by contrast, is an electrical insulator.
Stoichiometric fuel-to-air ratio	E85 needs more fuel per pound of air than gasoline; therefore, E85 cannot be used in a conventional vehicle.
Toxicity	Ethanol is less toxic than gasoline or methanol. Carcinogenic compounds are not present in pure ethanol; however, because gasoline is used in the blend, E85 is considered to be potentially carcinogenic.
Flammability	At low temperature (32°F), E85 vapor is more flammable than gasoline vapor. However at normal temperatures, E85 vapor is less flammable than gasoline, because of the higher autoignition temperature of E85.

With ethanol, the vapor in the air space in the fuel tank is flammable in a wide temperature range. With gasoline the mixture is too rich and with diesel too lean to be ignitable in normal ambient temperature range. [Peckham 2003, McCormick 2001, Peckham 2001, Weyandt 2002]. On the other hand, the low evaporation speed of ethanol keeps the alcohol concentration so low that it is not explosive in accidents [IEA/AFIS 1999].

Table 6. Approximate combustion safety characteristics of neat fuels [McCormick 2001].



	Typical Diesel	Ethanol	Typical Gasoline
Vapor pressure@38°C, psi	0.04	2.5	7-9
Flash point, °C	55-65	13	-40
Boiling point (or range), °C	170-340	78	33-213
Autoignition temperature, °C	230	366	300
Flammability limits, vol%	0.6-5.6	3.3-19.0	1.4-7.6
Flammability limits, °C	64-150	13-42	(-40)-(-18)

One discussion item in conjunction with ethanol has been the risk of ground water contamination. It has been stated that the BTEX compounds in gasoline (benzene, toluene, ethylbenzene and xylene) could travel up to 2.5 times further in groundwater in

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[11] Flash point is the lowest temperature at which the vapour pressure of liquid is sufficient to produce a flammable mixture above the liquid, which ignite by a test flame in a vessel under specified conditions.

the presence of ethanol than in the absence of it due to the co-solvency effect. However, these statements of groundwater risks with ethanol have not been proven, and it has been stated that the traveling distance would not be as long as with MTBE [Environment Australia 2002].

A comprehensive review of the transport of ethanol and BTEX in the subsurface following a gasohol spill concluded the following: *"…co-solvent effects are expected to be minor at the ethanol concentrations expected from gasohol spills. Nevertheless, the inhibition of BTEX biodegradation and the possible decrease in sorption-related retardation suggests that ethanol is likely to increase BTEX plume lengths. The net effect of ethanol on natural attenuation of BTEX is likely to be system specific, depending largely on the release scenario and the assimilative capacity of the aquifer"* [Powers 2001b].

Special issues regarding safety, storage and handling of diesel/ethanol blends (E-diesel) are discussed in Chapter 4.1.6.2.

4.1.4 Spark-ignition cars, low-concentration blends

4.1.4.1 Suitability for cars

Low-concentration alcohol blends have been used for decades in some countries. A blend of alcohol in gasoline, called "gasohol", has been used in USA and Brazil since 70's. It is generally accepted that up to 10% ethanol can be blended into gasoline without problems or a need for modifications on the engine or in the car. However, this may apply to cars from 90's onwards, whereas older cars may encounter problems with fuel system materials [BAFF].

In Australia, blends containing up to 17% ethanol are on market. In 1999-2000 about 0.5 million t/a of E10 was sold in Australia. One distributor, Manilda Park Petroleum, has sold blends containing up to 20% ethanol content since 1992. In Australia, a vivid discussion on the appropriate ethanol content in gasoline has been going on. Ethanol producers and also some scientists are in favor of blends with ethanol content up to 20%, whereas the automotive companies are against blends with over 10% of ethanol warning that high ethanol levels make warranties void [Environment Australia 2002]. There have been claims of engine damages due to fuel containing 17% ethanol in Australia [Gordon 2002].

Environment Australia established "The Ethanol Task Force" to consider ethanol blends up to 20%. "The Ethanol Task Force" assisted in preparing a discussion document on this item, a document which summarizes the experience on the performance of low-concentration ethanol blends [Environment Australia 2002]: [12]

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[12] Australian Biofuels Association has pointed out that some details in the old studies, e.g. the quality of gasoline, was not as good as today, thus all problems found were not due to ethanol.

- E10 has been widely used for decades. In US, it was advised that certain parts of cars pre1980 should be replaced for E10 use (EGR valves, fuel inlet needle tips, fluoro elastomers in fuel lines evaporative control lines etc.). E10 cleans up fuel tanks and lines, which can plug the fuel filter.

- In Brazil, there is a long experience on 20% of ethanol in gasoline, but all cars are modified for this fuel (changes e.g. to the cylinder walls, cylinder heads, valves, valve seats, pistons, piston rings, intake manifolds, carburetors, electrical systems and nickel plating on steel lines). Some laboratory data showed damages with conventional paints (considerable when refueling).

- A car calibrated for E20 does not perform well with normal gasoline. The adjustments needed for proper AFR with E20, injectors may need to be changed to allow higher flow rates of fuel.

- There are not many field trials available with gasoline containing more than 10% ethanol with normal cars. An old study from 80's with 100 cars using hydrated and anhydrous E15 showed that some plastics and elastomers were not suitable for the blend. This study applies only to older cars, which are gradually disappearing from field.

- An increase in fuel consumption is directly related to lower energy content of ethanol. Increase up to 2.8% with E10 has been observed.

4.1.4.2 Exhaust emissions (tailpipe)

Greenhouse gases (tailpipe emissions)

The greenhouse gas, carbon dioxide released from ethanol production and use, is compensated to certain extent by the amount absorbed by the plants [Environment Australia 2002]. This is one of the main benefit with renewable fuels, and will be discussed later on. This Chapter focuses on the tailpipe emissions.

The tailpipe CO_2 emissions do not change much using low-concentration ethanol blends. One of the US EPA studies reported that tailpipe CO_2 was mostly unchanged with gasoline containing 10 - 40% ethanol for cars from 90's [Environment Australia 2002].

One study with cars from 80's and 70's showed that there was no significant difference in tailpipe nitrous oxide emission (N_2O, strong greenhouse gas) between base gasoline and a 10% ethanol blend [Environment Australia 2002]. This is a different issue than the possible increase of N_2O due to heavy fertilizer use in agricultural grain production [CRFA].

Methane is one of the important greenhouse gases. Only a few reports include methane emissions in conjunction with low-concentration ethanol blends. [Environment Australia 2002] refers to one study with an indication of similar or slightly reduced methane emission with E10 compared to gasoline.

Regulated and unregulated tailpipe emissions

Extensive research programs and field tests have been conducted with low concentration ethanol blends. The results on the environmental impacts have been partly contradictory. Regarding tailpipe emissions, in most cases reductions in CO, HC, PM, NO_x, CO_2, 1,3-butadiene and aromatics like benzene have been observed with low-concentration ethanol/gasoline blends, whereas aldehyde emissions tend to increase [Environment Australia 2002].

The results for regulated tailpipe emissions are slightly different with older cars compared to modern cars. With older cars, enleanment leads to decreased CO emission, but for modern cars with closed-loop systems and catalysts, benefits are gained only at cold start or heavy acceleration. For modern cars, a slight decrease in HC, but an increase in NO_x has been observed [Environment Australia 2002].

In a car with fixed fuel setting, oxygen in the fuel leans out the combustion and leads to lower exhaust emissions than with non-oxygenated gasoline. It has been claimed that the use of a 10% ethanol blend results in a 25-30% reduction in CO, and about 7% reduction in exhaust VOC's (HCs) when compared to gasoline. There is only a little difference in the NO_x emissions from ethanol-blended fuels in comparison to conventional fuels. Reports cite differences in the range of a 5% decrease to a 5% increase for low-level ethanol blends [CRFA].

A study with six cars from 1990's showed that there was a clear trend in reducing HC and CO emissions, but an increase in NO_x emission with increasing ethanol content (Figure 14). Below 12% ethanol content, the change in NO_x was insignificant. Above 17% ethanol content a strong increase in NO_x may indicate too lean mixture for the limits of the management system of closed loop control. Generally, for modern cars (closed-loop systems, TWC), the addition of ethanol up to 20% resulted in a reduction in CO, and a small reduction in HC, but if ethanol concentration exceeded 10% an increase in NO_x was seen [Environment Australia 2002].

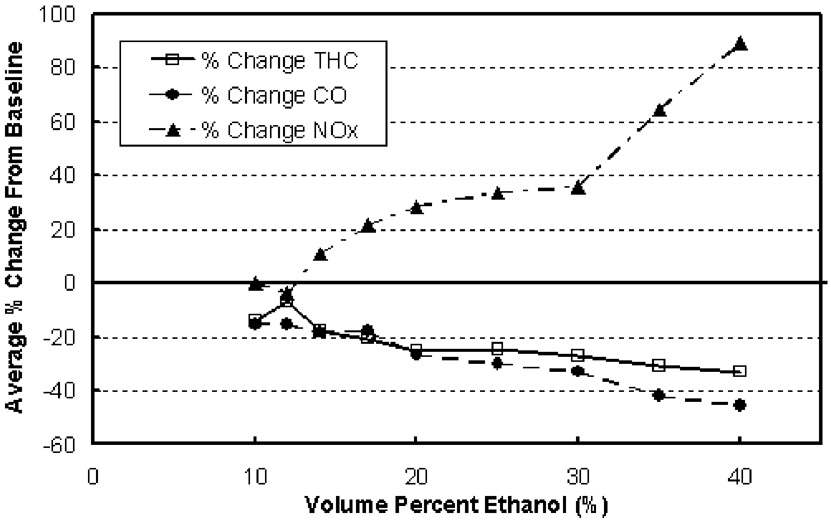

Figure 14. The effect of ethanol content on CO, HC and NO_x emissions with cars from 1990 or later [Environment Australia 2002].

Volatile organic compounds (VOC) are reactive, and significant sources of ground-level ozone[13] formation. VOCs are formed both as evaporative emissions and as tailpipe emissions (HCs). Ethanol blends reduce tailpipe VOC (HC) emissions when compared to gasoline [CRFA]. However, for evaporative emissions the situation is more complex. Up to 10 % ethanol blended into gasoline increases vapor pressure (RVP), but at higher concentrations the effect gradually declines. Evaporative emissions increase with increasing vapor pressure of the fuel, a phenomenon that can be avoided for ethanol blends by adjusting the composition of base gasoline.

In Canada, the volatility of ethanol blends must match to gasoline limits, but in U.S. higher volatility is allowed for ethanol blends. Thus there is an opposition in U.S. against ethanol by MTBE producers, refiners, and even environmentalists, claiming that using ethanol, the smog levels increase during hot summer days due to the possible increase in NO_x and VOC, the most important precursors for smog [Distillery Network].

[Environment Australia] referred to two studies showing lower diurnal, but higher hot soak evaporative emissions with a slight total increase of evaporative emissions for gasoline containing 10% of ethanol (RVP adjusted) compared to gasoline. Higher hot soak emissions were explained by distillation characteristics showing higher share of evaporated fuel at high temperatures with ethanol blend than with neat gasoline.

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[13] Ground-level ozone causes human respiratory problems and damages many plants but do not increase ozone in the stratosphere (protection from sun's UV). E.g. carbon monoxide, unburned hydrocarbons, benzene, and nitrogen oxides with sunlight form ground-level ozone, which form 'smog' with moisture and particulate matter.

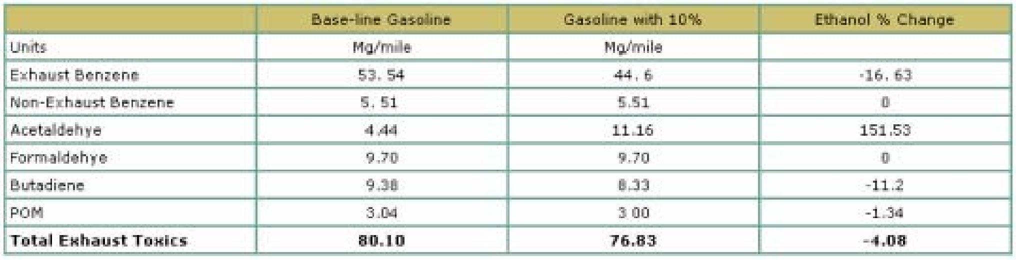
Aldehydes are associated with the health risks. All oxygenates, including ethanol, emit higher level of aldehydes than non-oxygenated gasoline. However, the Royal Society of Canada has determined that the risks associated with increased aldehyde emissions from ethanol-blended fuels are negligible, since the absolute emissions are small relative to other hazardous emissions, and efficiently removed by the catalyst [CRFA]. According to one of the US EPA studies with cars from 90's, acetaldehyde emissions increased as ethanol content increased, but formaldehyde stayed unchanged. Also [Environment Australia] states that this is the general trend in several studies, e.g. 200% increase in acetaldehyde has been reported. Furthermore, *"Acetaldehyde reacts with NO_x in the atmospheric photochemical system, and produces peroxyacetyl nitrate (PAN), which is a phytotoxicant and mutagen. This effect has been confirmed by measurements in Brazil, where increased levels of acetaldehyde and PAN have been recorded since ethanol and ethanol blends has been used as motor fuels".* Table 7 shows an US EPA estimation of the effect of 10% ethanol in gasoline on unregulated emissions. An increase of 151% in acetaldehyde emission is seen [Manitoba].

One of the US EPA "Air Toxics" is 1,3-butadiene. It has been stated that, in theory, the emission of 1,3-butadiene should be reduced when the ethanol content of gasoline increases. Substantial decrease has been shown in the some studies, but also negligible effects have been reported [Environment Australia 2002].

Ethanol, as an octane enhancer, can act as substitute for benzene and other aromatic hydrocarbons such as toluene and xylene. A reduction is seen also in emissions of benzene and 1,3-butadiene, both of which are carcinogenic [CRFA].

Neither sulfur dioxide nor particulate matter emissions are considered significant in the context of gasoline cars. Nevertheless, lower sulfur levels are beneficial for performance of aftertreatment devices. Ethanol contains no sulfur, and thus a dilution effect results in a lower sulfur content in gasoline [CRFA]. Particulate emissions with low-level ethanol blends seem to decrease when compared to gasoline [Manitoba].

Table 7. The results with the US EPA complex model for gasoline and a blend with 10% ethanol [Manitoba].



	Base-line Gasoline	Gasoline with 10%	Ethanol % Change
Units	Mg/mile	Mg/mile	
Exhaust Benzene	53. 54	44. 6	-16. 63
Non-Exhaust Benzene	5. 51	5.51	0
Acetaldehye	4.44	11.16	151.53
Formaldehye	9.70	9.70	0
Butadiene	9.38	8.33	-11.2
POM	3.04	3.00	-1.34
Total Exhaust Toxics	**80.10**	**76.83**	**-4.08**

4.1.4.3 Research in Finland

In Finland, there has been research work on alcohol fuels since late 70's, when gasoline containing 15% of methanol or ethanol was studied. The work included engine tests and also field tests with 13 passenger cars (carbureted engines). With an oxygen content of some 5-7% the carburetors had to be re-adjusted to obtain proper driveability. Some problems due to vapor lock formation were encountered. E15 did not cause any special problems or wear, but M15 was more troublesome regarding corrosion and risk of fuel phase separation at cold temperatures. The tests showed that M5 would require a co-solvent to prevent phase separation in cold climate, but M50 could be used just by recalibration and replacement of materials of fuel system [Nylund eeci].

Research in Finland on reformulated and oxygenated gasoline started around 1990 with a focus on ethers. In the beginning limited tests were carried out also with gasoline/ethanol blends. Corrosion problems were observed e.g. in storage tank materials, and water and stability problems were anticipated. Therefore the work on ethanol was discontinued at that time [Nylund eeci].

The latest activity on biofuels for transportation in Finland is a commercial trial marketing 98-octane gasoline containing 5% of ethanol by Fortum Oil and Gas. The ethanol is made from EU's surplus storage of wine. A fuel tax reduction of 0.30 €/liter is granted for the ethanol part for this demonstration.

Recently Fortum and VTT published results on ethanol and ETBE containing gasoline with various modern MPI and G-DI cars and also some older carburetted cars. No significant differences were observed for most of the emission components when ethanol containing fuels at 2% oxygen level were compared to reformulated gasoline. Acetaldehyde emission was higher for ETBE and ethanol containing fuels than for reformulated gasoline. Fuel quality did not affect particulate mass or PAH emissions. Some indication of lower mutagenicity of particulates with ETBE and ethanol containing fuels than with reformulated fuel was seen for some cars [Aakko 2002, Pentikäinen 2003].

4.1.5 High concentration alcohol blends for FFV cars

High concentration alcohol blends can be used in so called FFV Cars (Fuel Flexible Vehicles), which are built up to tolerate high concentration of ethanol. Lower heat value of alcohols is compensated automatically by increasing fuel injection volume.

Flexible Fuel Vehicles (FFV) went into productions in 1990's. The first prototypes were demonstrated already in the 1980’s. FFVs are versatile, and can operate on unleaded gasoline or any mixture of gasoline and ethanol up to 85% blend. FFVs are typically equipped with a fuel sensor determining the concentration of ethanol in the fuel. The fuel system automatically makes adjustments for best performance and emissions. Normally the basic fuelling strategy is set based on the signal from the fuel sensor, and the closed-loop fuel control takes care of the fine adjustment of air/fuel ratio. The fuel system must be designed for considerable variations in volumetric fuel flow. The Ford Taurus FFV car was introduced in 1996, and since then many other models from Ford, as well as FFVs from other manufactures have been introduced (e.g. Chrysler, General Motors, Isuzu and Mazda) [NICC].

Two pieces of US legislations, the Clean Air Act Amendments in 1990 and the Energy Policy Act in 1992 require that state, municipal, and private fleets must meet strict emission guidelines from 1998 onwards. These Acts promoted replacement of existing vehicles with newer technology, like FFVs. Auto manufacturers were required to meet the new standards, thus new cars were equipped with new technology like on-board diagnostic monitoring systems [NICC].

Typically a blend of 85% of ethanol and 15% of gasoline (E85) is used in the FFV cars. Gasoline improves the cold-startability of ethanol by increasing the vapor pressure (gasoline ~70-100 kPa Reid vs ~17 kPa Reid for ethanol)). A small portion of gasoline also improves safety in possible accidents: the flame becomes visible, whereas flame of neat ethanol is hardly visible.

According to [E85 Handbook] no additional additives are needed for E85, the additives included in the 15% gasoline portion are sufficient.

The E85 Handbook states that the reduction in emissions depends on how well the emissions control system and engine is designed and “tuned” for ethanol. The cars of today have been designed to meet stringent emissions regulations. When compared to gasoline cars, even to current low-emission cars, E85 cars can further reduce tailpipe and evaporative emissions. Compared to gasoline, most E85 cars produce lower CO and CO_2 emissions and the same or lower levels of HC emissions. NO_x emissions are about the same for ethanol and gasoline vehicles. Emissions resulting from fuel evaporation are lower for E85 than for gasoline [E85 Handbook]. [CRFA] estimates that the potential for NO_x reduction for E85 is some 20%, and the potential for exhaust VOC reduction some 30% or more, the latter due to a lower vapor pressure.

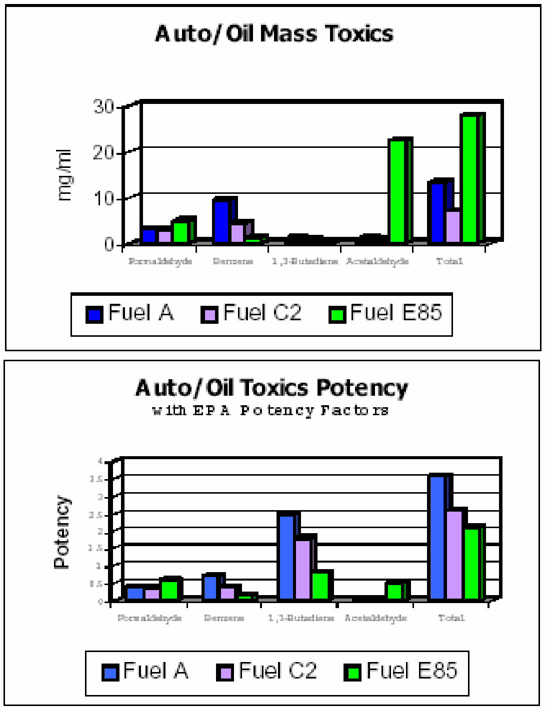


Figure 15. The effect of E85 to “Air Toxics” as mass emissions and with potency factors [Ethanol Express 2001]

Table 8. CARB and the U.S. EPA risk factors for "Air toxics" [Ethanol Express 2001]

Compound	CARB Risk $(\mu g/m^3)^{-1}$	CARB Normal-ized	EPA Risk $(\mu g/m^3)^{-1}$	EPA Normal-ized
1,3-Butadiene	1.7E-4	1.0	2.8E-4	1.0
Benzene	2.9E-5	0.17	8.3E-6	0.030
Fomalde-hyde	6.0E-6	0.035	1.3E-5	0.046
Acetalde-hyde	2.7E-6	0.016	2.2E-6	0.008

An example of a total assessment of toxic emissions with E85 and gasoline is given in Figure 15 using factors from Table 8 (CARB and the U.S. EPA risk factors) [Ethanol Express 2001].

There is a large increase in the acetaldehyde emissions with E85 when compared to gasoline. However, when "the toxicity potency" of the fuels is taken into account, it is noted that emissions from E85 are less harmful than from reference gasoline, since acetaldehyde is evaluated to be less toxic than e.g. 1,3 -butadiene and benzene [Ethanol Express 2001].

Optimisation of an engine for neat ethanol would be challenging. Cold starting could be accomplished using reformed ethanol converted into a gas mixture. Another possible drawback of the high heat of evaporation, when using indirect fuel injection, might be formation of fuel films (liquid fuel) in the intake system in rapid load changes. This could be alleviated by using a hybrid system allowing the optimized ethanol engine, when installed into a vehicle, to run more or less on constant load. In general, a hybrid power train would be beneficial for fuel efficiency. Also the option of direct injection of ethanol into the combustion chamber should be evaluated. A mono-molecular fuel like ethanol might make it possible to use a new combustion system like controlled auto ignition or some kind of combined combustion system [Nylund 2004b].

Research in Finland

Finnish activities to study neat (or close to neat) alcohol in spark-ignition engines started at VTT in 1981. Altogether 7 cars and 2 cross-country vehicles were converted to run on E90 or M90 fuel. Two fuel systems were used: a manually operated start-up system with gasoline and an automatic dual-fuel system. However, neither of these systems was fuel flexible, although the dual-fuel system could be operated also on gasoline only. With the dual-fuel system, cold-starting and warming up the engine tool place on gasoline, and at a coolant temperatute of some +70 °C the system automatically switched over to E90 or M90.

After some 50 000 km per vehicle no critical wear was observed, except for valve train systems. The E90 cars were in better condition than the M90 cars. Neat alcohol caused severe corrosion problems in the fuel system components, and driveability especially for the cars with the simple gasoline start-up system was poor [Nylund, eeci].

In 1990's VTT carried out tests on the emission performance of alternative fuels for light-duty vehicles within the IEA Agreement on Alternative Motor Fuels (Annex V) [Nylund 1996]. 14 cars running on different fuels were tested at various temperatures. Four cars were FFV's running on alcohol-gasoline blends, and two of these vehicles were subjected to long-term field testing. The results showed durability problems with materials of the FFV cars when using M85 fuel. Exhaust emissions increased substantially over the field test, but in general the emissions from the FFV's corresponded well to the emissions from gasoline vehicles down to -7 °C.

A recent study within IEA/AMF (Annex XXII) on particulates from alternative fuels at various temperatures gives a comparison of an up-to-date E85 car with other cars. CO and HC emissions were low both with a conventional gasoline vehicle and the FFV vehicle (E85) at +23 °C, but increased more with E85 than with gasoline as temperature decreased (Figures 16-18). The FFV car used heavy enrichment of the fuel mixture at cold-start, and this could be seen as high CO and HC emissions, but low NO_x emission at low temperatures. In general the aldehyde emissions were low, except for relatively high acetaldehyde emissions for the E85 fuelled FFV car. Test temperature had a strong impact on the emissions of individual hydrocarbons, e.g. 1,3-butadiene and BTEX compounds, E85 showing similar emission levels as the conventional gasoline car. The conventional gasoline car, the E85 car and the LPG car showed extremely low particle emissions at +23 °C, but measurable level at -7 °C. The particle emissions of the CNG car were nil independent of test temperature. E85 indicated lower particle number emissions than the conventional gasoline car [Aakko 2003].

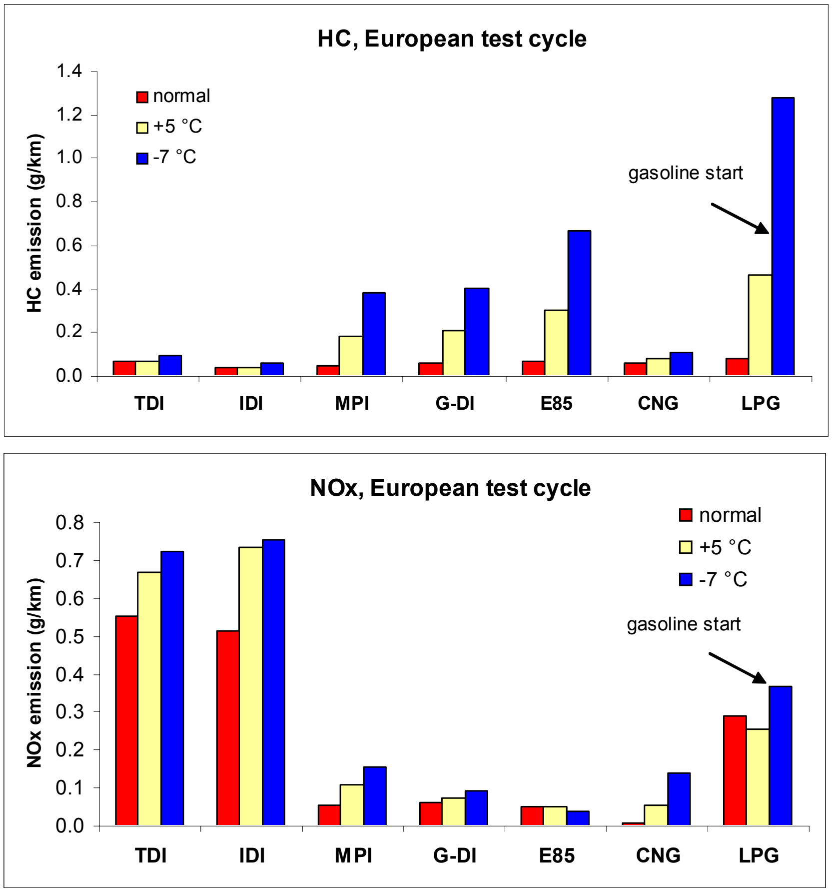


Figure 16. HC and NOx emissions with various cars [Aakko 2003].

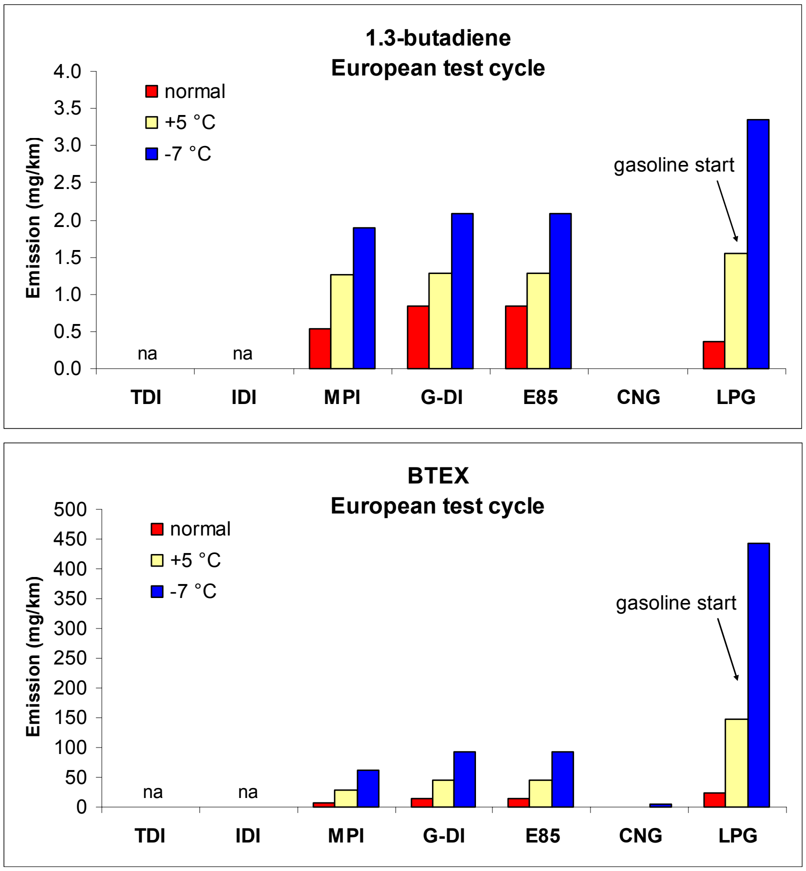


Figure 17. 1,3-butadiene and BTEX compounds with various fuels [Aakko 2003].

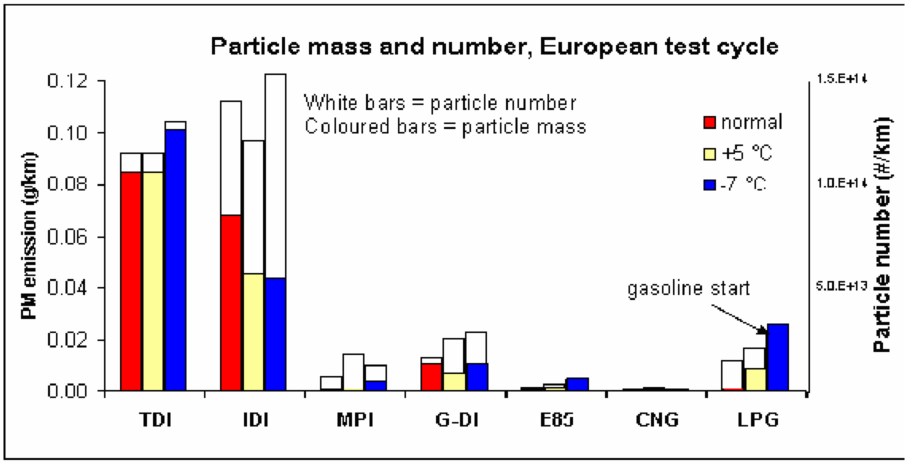


Figure 18. Particle mass and number emissions with various fuels[14] *[Aakko 2003].*

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[14] TDI = turbocharged direct injection diesel, IDI = turbocharged indirect injection diesel, MPI = multipoint injection (conventional gasoline), G-DI = gasoline direct injection, E85 = FFV vehicle (multipoint injection), CNG = dedicated CNG vehicle, LPG = gasoline-LPG bi-fuel vehicle

4.1.6 Compression-ignited engines

4.1.6.1 Neat ethanol

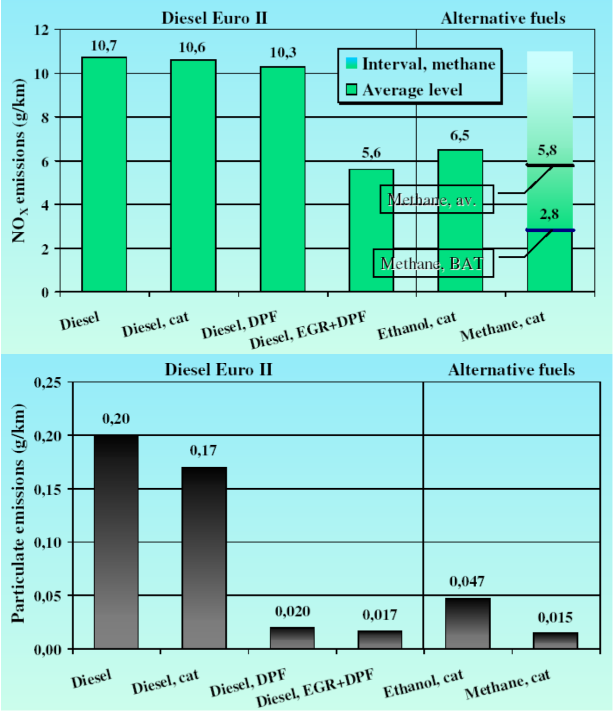

Figure 19. NOx and PM emissions with diesel and ethanol busses [Ahlvik 2001].

One option to use neat ethanol is the spark-ignition FFV-type engine. At the moment most FFVs are not optimized for neat ethanol. Another option would be to use ethanol in compression ignition engines. The properties of ethanol are quite similar to gasoline, whereas diesel fuel is significantly different. If ethanol is going to be used in compression ignition engines, either the engine or the fuel has to be modified, the latter option requiring fuel additives.

Ethanol differs significantly from conventional diesel fuel regarding cetane number, heating value, ignition temperature, vaporization characteristics, and boiling point. Cetane number of neat ethanol is only about 8, whereas today the requirement for diesel in Europe is over 51 [Klass 1998]. Neat ethanol as such will not ignite in conventional diesel engine. Also the lubricity of ethanol is unacceptable for high-pressure injection pumps in diesel engines. The low boiling point of ethanol increases the risk of cavitation, and the high conductivity the risk of corrosion [Peckham 2001, McCormick 2001].

In the past Detroit Diesel manufactured glow-plug equipped heavy-duty engines suitable for methanol or ethanol. However, many problems like engine wear, and glow-plug failures and excessive fuel consumption were encountered. Thus the production of these engines was discontinued.

In Sweden another approach was selected: adding ignition improver and lubricity additive to ethanol making it possible to use the conventional diesel combustion process. In Stockholm and some other Swedish cities city buses manufactured by Scania run on additive treated ethanol. The modifications for ethanol-use include e.g. increased compression ratio, a special fuel injection system and a special catalyst to control aldehyde emissions. The fuel used in ethanol buses in Sweden is called Etamax D. It contains 90% of hydrated ethanol (grade 95%), 7% ignition improver (Beraid 3540), denaturants (2.3% MTBE and 0.5% iso-butanol) and 125 ppm corrosion inhibitor additive [Lif]. Ethanol buses are also running in Mexico, Australia and Denmark.

The emission levels of the Swedish ethanol buses are similar to advanced diesel buses equipped with oxidation catalyst or particle filters, but higher than emission levels of sophisticated CNG buses (higher NO_x). The smoke emission from ethanol buses is almost negligible (likewise buses on gaseous fuels). The first ethanol bus started service in 1985, and in 2000 there were 407 buses running on ethanol in 13 cities in Sweden, 250 busses in Stockholm [Lif]. In 2003 Scania announced that it will discontinue the production of ethanol buses.

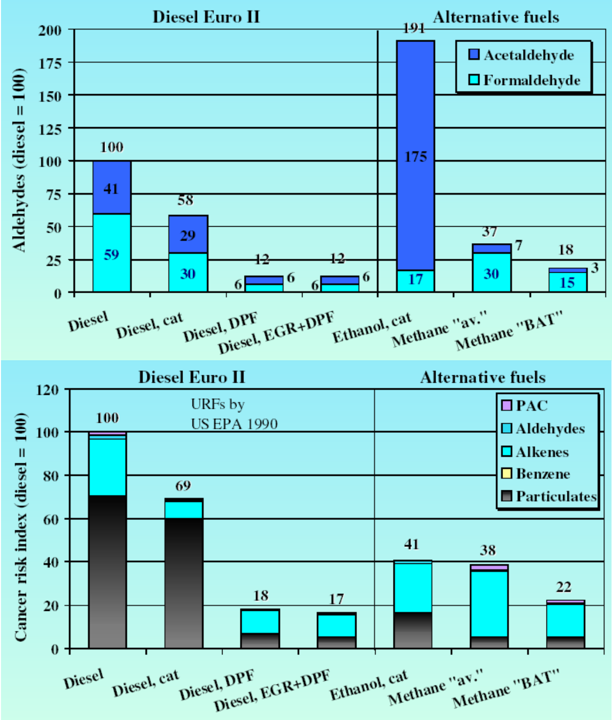

Figure 20. Unregulated emissions with diesel and ethanol busses [Ahlvik 2001].

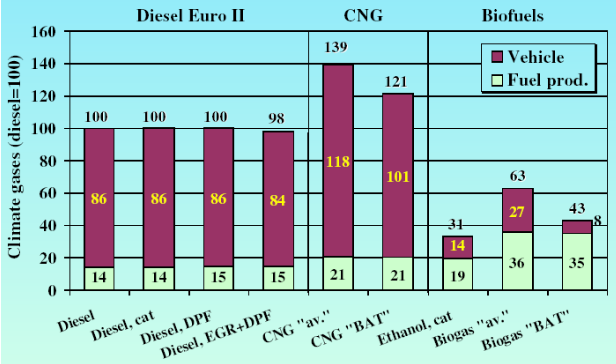

Figure 21. Climate gases with ethanol busses [Alvik 2001].

A comparison of Swedish ethanol buses and diesel buses is given in Figures 19-21. It can be seen that ethanol gives lower NO_X and PM emissions when compared to a Euro II diesel bus, but not if the diesel bus is equipped with EGR and particulate filter (DPF). Acetaldehyde emissions are high for ethanol buses, but the cancer risk index is low (similar EPA factors used as for E85). The major benefit for ethanol, and other biofuels, is the reduction of greenhouse gas emissions [Ahlvik 2001].

Finland

Helsinki University of Technology has conducted studies with alcohol fuels for high-speed Valmet (Sisu Diesel) engines. E.g. the following combustion systems or issues have been studied: injection into the inlet manifold, cetane improver treated fuel, pilot dual-fuel system, cold-start testing, spark- and glow-plug ignition and self-ignition with high compression ratio. Durability problems with fuel system components and spark-plugs were encountered, but such problems can be solved (e.g. engines from Detroit Diesel and Scania). HUT's prototype direct-injection stoichiometric spark-ignition engine equipped with a TWC showed a low NO_x level (~1 g/kWh), comparable with that of stoichiometric gas engines [Nylund eeci].

In mid-1980's VTT converted a Valmet diesel engine to run on alcohol fuel using spark-ignition.The engine was also demonstrated in a Sisu truck. The demonstration showed that it is possible to convert diesel engine for alcohol using rather simple technology (spark-ignition and carburetors). Later on Valmet gas engines were developed based on this experience.

The need for an ignition improver additive significantly increases the cost for running heavy-duty vehicles on ethanol fuels. When developing a new heavy-duty ethanol engine, highest priority should be given to concepts that can do without improver treated fuels. If new ethanol engine would be developed with a diesel-like combustion system, ignition of the fuel has to be secured either by a spark-plug, a glow-plug or by hot re-circulated exhaust gases. Also possibility to use new or combined combustion systems should be evaluated.

In academic research, decomposition of alcohols to hydrogen and carbon monoxide has been has been used to enhance the performance of spark-ignited alcohol engines [Peterson 1994]. One idea could be to produce small amounts of hydrogen on-board a heavy-duty vehicle such as a bus, and use this ethanol derived hydrogen as an ignition enhancer. The desired effect could possibly be achieved by introducing the hydrogen mix into the intake manifold late during the intake stroke. The new heavy-duty should fulfill current and oncoming exhaust regulations, minimum the Euro 4 requirements for the year 2005. Ethanol gives inherently low particulate emissions, but there is probably going to be a need for NO_x control (EGR, lean NO_x or NO_x storage catalyst, perhaps SCR) and control of unburned fuel and aldehydes (oxidation catalyst) [Nylund 2004b].

4.1.6.2 Ethanol-Diesel Blends or E-Diesel

One option to introduce ethanol for diesel engines is to use emulsion type fuels with low concentrations of ethanol. Research and demonstrations on such fuels started a long time ago, work on microemulsion already in the beginning of 80's. Due to technical problems with the first generation of emulsion fuels the interest stalled, until now.

Brazil has used ethanol in gasoline for decades. However, Brazil, and many other countries, consumes more diesel than gasoline. Thus it is understandable that ethanol blended with diesel fuel is an interesting option. When compared to biodiesel, ethanol has the benefit of better market value of side-products [Peckham 2002].

New, improved additives capable to form microemulsions of ethanol and diesel have been developed. The microemulsions are chemically and thermodynamically stable, they are clear and bright blends, unlike the old white "milky" emulsions. Microemulsions are not true solutions, but consist of droplets or micelles at the size of about 1 µm. The fuel properties of ethanol/diesel microemulsions using new additives are better than of conventional emulsions. It has been stated that aromatics in diesel improve the solubility of ethanol [McCormic 2001].

Biodiesel is reported to act as an emulsifier for ethanol. Ethanol/biodiesel might provide a reasonable hybrid mixture as ethanol can reduce NO_x emissions and improve cold flow properties, both of these which are shortcomings of biodiesel. In addition, biodiesel improves e.g. lubricity of ethanol. Both components reduce particulate matter emission [McCormick 2001]. There is also interest for e.g. diesel-ethanol-water blends. However, not much data is available concerning other combinations than diesel-ethanol mixtures.

The main concerns with E-diesel are related to safety issues and the general suitability and performance in diesel engines and vehicles. The properties of ethanol are similar to gasoline. Thus blending ethanol into diesel is somewhat similar as blending gasoline into diesel. The safety risks with E-diesel are even more pronounced in non-road applications (e.g. construction machines and indoor heaters) than in on-road diesel [Peckham 2001].

The general combustion and safety related properties of gasoline, diesel and ethanol are listed in Table 6. The flash point of ethanol is only 13°C. The flash point does not change linearly with the blending ratio of components. Thus even a few percents of ethanol lowers the flash point of diesel close to 13°C. It has been demonstrated that the safety characteristics or risks of diesel fuel containing 10-20% of ethanol are identical to those of neat ethanol. As mentioned before, the denaturant for fuel grade ethanol in U.S. is natural gasoline, and this may also have an adverse impact on the flash point [McCormick 2001].

Storage and handling regulations for fuels are based on the flash point. In Europe diesel fuel is classified as a combustible liquid with a flash point requirement higher than 55 °C. In US the Class II liquid requirement for flash point is higher than 38°C. The flash point of E-diesel is lower than these limits, and thus E-diesel falls into the same class as gasoline. Similar procedures for safety, handling and storage is required for E-diesel as for gasoline (e.g. longer safety distances, special requirements on flame arresters on vents etc.).

With E-diesel, the vapor in the tank is flammable at a wide temperature range (Figure 22). In a gasoline tank the mixture is too rich and in a diesel tank too lean to let the flame to propagate into the tank. Flame-arrester devices have been developed for E-diesel refuelling, but so far the problems have not been completely solved [Peckham 2003, McCormick 2001, Peckham 2001, Weyandt 2002].

A low flash point may create safety risk also within the fuel system of the engine. The flash point issue is gaining even more importance as new fuel injection equipment systems recirculate fuel raising return fuel temperature substantially [Peckham 2002].

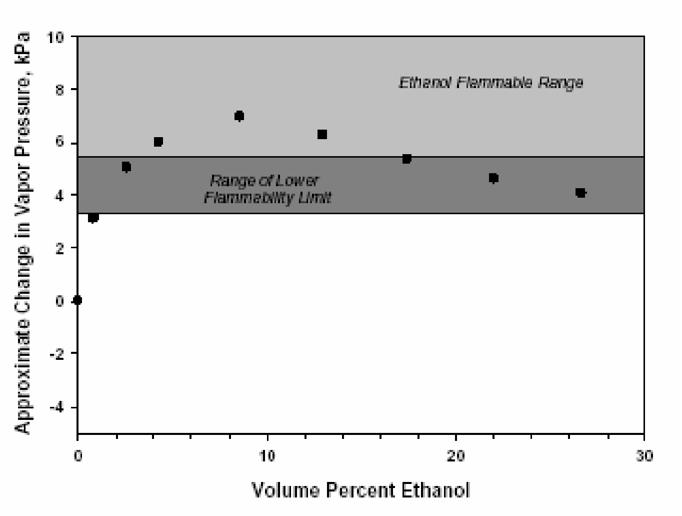

Figure 22. Flammability limits of E-diesel [McCormick 2003].

In addition to the safety concerns there are issues related to the overall suitability of E-diesel for diesel engines, i.e. stability, water tolerance, and other fuel properties including lubricity. The cetane number of ethanol is only 8, whereas the cetane number of diesel fuel in Europe is over 51 and over 40 in US. This means that adding ethanol to diesel will reduce cetane, and therefore cetane improver additives might be needed.

Some studies report that there are problems with elastomers and other materials in the fuel systems when using ethanol blends. E-diesel has also caused vapor-lock problems and power loss. It has been stated that ethanol affects fuel-lubricant interactions resulting in wear in pumps, injectors and cylinder liners. It is well-known that the lubricity of ethanol is poor. The high volatility may lead to cavitation in pumps and injectors, resulting in both component wear and hot restart problems. Bosch has experienced serious problems with injectors and injection pumps during vehicle and engine endurance tests due to low lubricity of E-diesel fuels [Peckham 2001, McCormick 2001]. Reports from emulsifier additive manufacturers claim that emulsifiers increase the lubricity of fuels. One emulsifier manufacturer has reported HFRR less than 300 µm and SLBOCKLE over 5200 g. Proper lubricity performance is a must to get approval from engine/car manufacturers to use E-diesel within normal warranty conditions [McCormic 2001].

The additive of E-diesel should keep the mixture as an emulsion. The presence of water can lead to phase separation, but the manufacturers of emulsifiers claim that water contents up to 3% could be tolerable [Peckham 2001]. In the case of gasohol in US, the water affinity of ethanol has led to blending the ethanol/gasoline mixtures at finished product terminals. Similar procedures would possibly have to be applied for E-diesel. This mean significant investments for blending systems and tanks [McCormick 2001].

Additive manufacturers claim that E-diesels should be stable over a wide range of temperatures down to some -30 °C. In storage tanks the fuel has to be stable over long time periods, a minimum of several months is required. Also the oxidative and biological stability of fuel plus the stability of the additives themselves should be known. However, until now there is not much data on stability issues of E-diesel, and no data on diesel/biodiesel/ethanol blends [McCormick 2001].

Cold flow properties should in principle improve when blending ethanol into diesel. This is also the case proven by laboratory tests, with an exception of cloud point, which increased with addition of ethanol. The cloud point of diesel fuel indicates the temperature at which paraffins start to crystallizate and diesel becomes cloudy. However, this is not the case with E-diesel. It is thought that while cooling E-diesel microemulsion micelles grow to near micron size resulting in a cloudy fuel, which however, flows through fuel filters. Thus cold filter plugging point (CFPP) would be more suitable for E-diesel than cloud point [McCormick 2001].

Due to concerns of safety, liability, and materials and component compatibility it will be difficult to obtain warranties from engine/vehicle manufacturers for E-diesel. In US markets, E-diesel should also pass the *EPA fuel registration requirements,* Tier 1 and Tier 2 emission and health effects testing, a time consuming and expensive process [McCormick 2001]. Small business does not need to fulfill the Tier 1 and 2 testing requirements, so there are small companies registered by US EPA as ethanol-diesel fuel business. These are AAE Technologies with Octel-Starreon (O^2 diesel in North America), Pure Energy in New York, AGP Corn Processing and Corn Plus in USA [Peckham 2001]. Other businesses are also interested in E-diesel. BASF has a concept called Dasol A-8 with 8% ethanol and 2.6% solubilizer, cetane and lubricity additive plus highly reactive polyisobutene for detergency and corrosion inhibition. Dasol was tested in 80 cars in Brazil. Testing was limited to cars with in-line injection pumps [Peckham 2002]. Akzo Nobel produces an additive called Beraid ED [Lif].

The benefits in exhaust emissions claimed for “O^2 diesel” containing 91.5% diesel, 7.5% ethanol and 1% emulsifier are up to 50% reduction in particulate matter and up to 5% reduction in NO_x. Pure Energy’s “E-diesel” containing 15% ethanol and 1-5% cosolvent is claimed to cut 40% of PM and 5% of NO_x, but to increase fuel consumption by 6%. Increased fuel consumption is a direct result of the low heating value of ethanol, 42% lower than that for typical diesel [Peckham 2001]. Generally, the reduction of PM emission with E-diesel is consistent in different studies, with the exception of one study which was carried out using AVL 8-mode duty cycle. Most studies have reported reduced NO_x emissions. Hydrocarbon emissions (presumably mostly ethanol) tend to increase with E-diesel. Also acetaldehyde and acetic acid is expected to be found from exhaust gases with E-diesel. These could be reduced with an oxidation catalyst [McCormick 2001].

Some durability tests from different laboratories on E-diesel have been reported. As an example, the University of Illinois ran 500 hours with a Cummins B5.9 engine. E-diesel resulted in abnormal wear and corrosion on the Bosch fuel pump and the fuel injectors. Material compatibility problems with an electronic sensor on the fuel pump occurred. The pump wear was thought to be due to lower energy content of E-diesel (backlash of the timing device, high fuel rates). No contaminants in the lubricant were seen. The injector nozzle coking was reduced when compared to diesel [McCormick 2001].

A number of field tests with E-diesel are ongoing or completed. A lot of experience has been gained in Brazil, which is one of the countries with a high interest in ethanol/diesel blends. Earlier tests in Brazil showed severe damages in fuel systems with rotary injector pumps. In-line pumps were expected to perform better [Peckham 2002].

One study in U.S. was carried out with three 1999 model-year trucks, two of these running with E-diesel (15% ethanol) and one control vehicle with diesel. After 270 000 miles no fuel related problems were seen. Fuel economy with E-diesel was 11% worse than with diesel. In a field test in Chicago 15 buses running on E-diesel (15% ethanol) and 15 buses on diesel were operated 20 000 miles each. No fuel related problems occurred and no differences in fuel economy were observed [McCormic 2001].

In Sweden fleet tests have been carried out with about 20 heavy-duty diesel vehicles running some 550 000 km in total. [Lif]. In 2003 there were also plans for new tests with Diesohol, an emulsion with 15% ethanol, in a few trucks at the Municipality of Örnsköldsvik [BAFF].

A fleet test in Denmark from 2001-2002 was carried out with two 12 liter Scania trucks running 100 000 km with E-diesel, which contained 10% of ethanol (grade >99.5%), 2% of solubilizer Beraid ED10 and 88% of Danish diesel (ULSD). The following findings were reported: power loss 6-8%, 3-6% increase in fuel consumption, stable fuel (also during winter), normal vehicle performance and less emissions [Lif].

A new E-diesel program started in 2003. This John Deere E-diesel program is carried out with different engine technologies (e.g. three different injection system) covering durability tests, regulated and unregulated emissions (e.g. aldehydes, speciated hydrocarbons PAHs, 1-nitropyrene), emissions at cold temperatures, field tests, material compatibility, flash/flammability and safety tests. The program will provide an extensive analysis of E-diesel performance [Mitchell 2003].

At the end, it has to be noted that E-diesel does not fulfill any current diesel specification[15], and thus it cannot be sold as diesel fuel. However, E-diesel could be

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[15] There are specifications available for emulsified diesel (water-diesel) in France and Italy. E-diesel does not fulfil either these specifications.

used in limited fleets, in demonstration-like use. Even for limited use a specification for E-diesel is needed [McCormick 2001].

4.2 ETBE

Ethers are high-value components for gasoline (Figure 23). Oxygen introduced in the fuel shifts combustion towards lean, and this leads to lower exhaust emissions, especially lower CO emission. Ethers have high-octane numbers, good solubility in gasoline, and compared to alcohols they are less corrosive and their effect of fuel vapor pressure is lesser. Ethers also have a positive effect on mixture formation and startability.

MTBE is has been widely used as oxygenate for gasoline. However, today consumption of MTBE is diminishing due to its solubility in water leading to ground water contaminations in the case of leakages. ETBE is similar to MTBE as regards end-use properties. ETBE is used to some extent e.g. in USA and France. Production in France started in 1993, and has increased up to 0.7% of gasoline consumption in France.

An example of the effect of ETBE on vapor pressure and octane numbers of gasoline is shown in Figures 24-25. Vapor pressure of gasoline is one property influencing emissions. Lowering the vapor pressure decreases the emissions of volatile organic compounds, both pre and after combustion (evaporative and exhaust emissions).

The oxygen content of ETBE is 15.7 wt%, which is lower than the oxygen content of MTBE (18.2 wt%). To obtain 2% oxygen content in gasoline, some 13% ETBE or some 11% MTBE is needed.

High octane numbers of MTBE and ETBE are a benefit as such. In addition, ethers can be used as substitutes for high-octane aromatics, which are an important source of toxic exhaust emissions like carcinogenic polyaromatic hydrocarbons. Ethers reduce harmful constituents of gasoline, e.g. aromatics, olefins and sulfur, simply via the dilution effect.

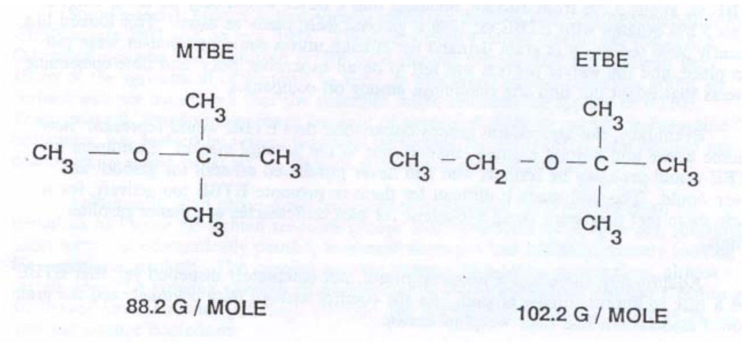

Figure 23. Chemical formula of MTBE and ETBE [Wells 1990].

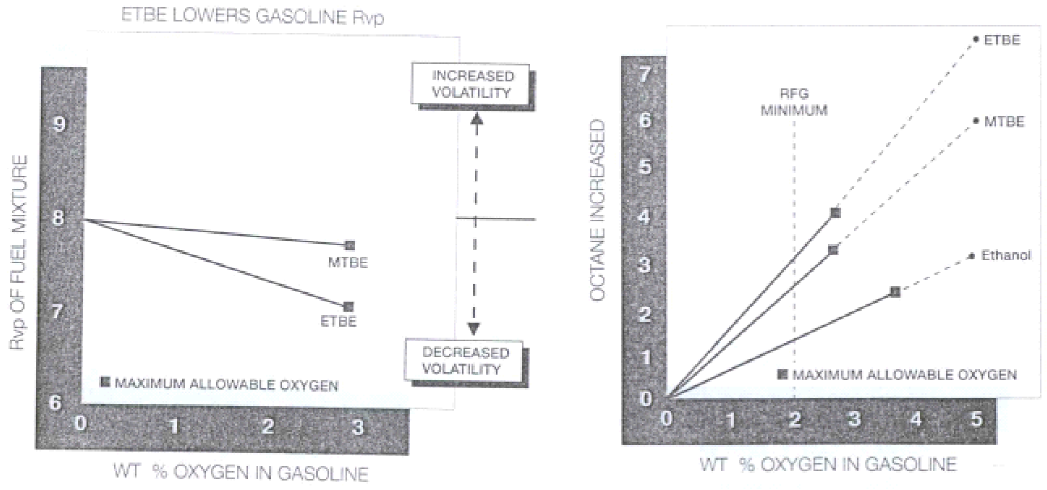

Figure 24. The effect of ETBE on vapor pressure and octane number of gasoline [NN, Fuel reformulation supplement].

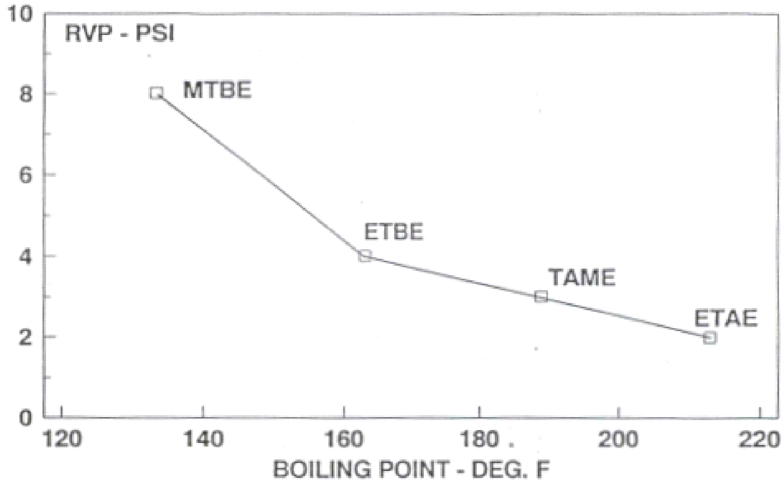

Figure 25. Vapor pressure and boiling point of various ethers [Wells 1990].

<u>Research on ETBE in Finland</u>

Finland has been a forerunner in Europe in research and commercialization of reformulated and oxygenated gasolines. Work on oxygenated gasoline started in 1990 with target to reduce exhaust emissions taking into account the cold climate conditions, e.g. cold-startability. Gasoline/ether and gasoline/ethanol blends with an oxygen content of 0-4% were studied. ETBE showed as good performance as MTBE. Benefits were seen for exhaust emissions, especially for CO emission. The Finnish national oil company Fortum (formerly Neste) launched MTBE containing oxygenated gasoline in 1991, and a tax incentive was granted later on in 1993. The oxygenate in use could well have been ETBE as regards technical performance. However, production costs of ETBE were too high at that time [Nylund, eeci].

As described in previous the Chapter, recent results on gasoline containing ethanol and ETBE (at 2% oxygen level) showed no significant differences in most emission components when compared to reformulated gasoline. As expected, acetaldehyde emission was higher for ETBE and ethanol containing fuels. Particulates and PAH emissions were at the same level, although some indication of lower particulate mutagenicity with ETBE and ethanol blends than with reformulated fuel was seen [Pentikäinen 2003].

4.3 BIODIESEL

4.3.1 Neat vegetable oils

The unesterified vegetable oils are problematic as diesel engine fuels due to high viscosity, high distillation end temperature, deposit formation, engine oil dilution and poor low-temperature operability. Thus the activities for motor fuels have focused on esterified vegetable oils with properties close to ordinary diesel fuel. On the other hand, esterification increases the production costs. Regardless of the technical problems, also the possibilities to use neat vegetable oils have been studied [Nylund eeci].

In Finland, in the early 80's, tests with diesel/vegetable oil mixtures for farm tractors were carried out. As expected, problems with both injector nozzle deposits and engine oil dilution were experienced. Later on a new way of using un-esterified vegetable oil was developed at VTT. Vegetable oil esters are efficient solvents, and thus they can be used as "anti-fouling" additives for neat vegetable oil (a hybrid fuel mix was patented by VTT). A blend containing 75 % diesel, 20 % vegetable oil and 5 % ester was tested in laboratory conditions. This blend, named "Ecodiesel", did not increase injector tip fouling compared to diesel fuel. Afterwards, a 1000 hour durability test was conducted with a Valmet (Sisu Diesel) engine with no special problems. One solution to use un-esterified vegetable oil is the Elsbett-engine, which is specially developed for neat vegetable oils [Nylund eeci].

4.3.2 Vegetable and animal fat based esters

4.3.2.1 Properties

Esters of vegetable oils (VOE) are suitable for diesel vehicles as such, even though some problems, mainly materials related, may occur with older vehicles. Biodiesel mixes easily with diesel fuel at any blend level making it a very flexible fuel component. It has to be noted that the properties of esters depend on the raw materials, e.g. rape seed or used frying oil based esters differ from each other to some extent.

Esters based on animal fats are significantly different than vegetable oil esters, especially as regards natural cold properties, which are poor for animal fat esters. Some selected properties of esters are shown in Table 9.

Cetane numbers of esters are excellent, generally over 50. **Sulfur** content of esters is low, which is a benefit as regards emissions, e.g. the performance of aftertreatment technologies.[16] **Oxygen content** of VOE is about 10%, and no **aromatics** are present. **Lubricity** of VOE is excellent, and VOE can even be used as lubricity additives.

Distillation range of esters is narrow, for methyl ester around 300-340 °C, which may lead to crankcase oil dilution and difficulties in cold-starting. High **viscosity** of esters may affect injection and cold-start.

Natural **cold properties** of vegetable oil esters are not good, and for animal fat esters they are poor. Cold properties can be improved with additives. However, traditional CFPP[17] fuel analysis may give too optimistic view on this improvement when real-word startability is considered [Nylund 2000].

Heat content of esters is lower than for diesel fuel and thus volumetric **fuel consumption** higher. This is to some extent compensated by higher **density** of esters.

Flash point of esters is high, e.g. for RME almost 170 °C. Thus VOEs fall into the same class as diesel as concerns transportation and storage safety regulations. However, if there is any alcohol as impurity the flash point is reduced significantly. About 0.5% methanol in RME decreases flash point below 40 °C, and the fuel cannot be treated anymore in the same way as diesel.

Esters contain triglycerides, glycerol and alcohols as **impurities**. Especially glycerol leads to carbon deposits in engine.

Esters are **polar** compounds, and thus dissolve materials more efficiently than diesel fuel, a phenomenon which may lead to material problems. Sensitive materials are e.g. styrolbutadiene rubber, butadiene, isoprene, silicones, polysulfides and polyurethane. In the beginning of large-scale use of esters there may be cleaning-up effect of distribution and storage systems leading to impurities in the fuel.

Storage stability of esters may also cause problems. Decomposition, oxidation and possibly polymerization may take place, especially in the presence of water. However, biodiesel is said to have better long-term storage properties than the original vegetable oils. On the other hand it has been demonstrated that conventional diesel fuel can be stored for more than 20 years (e.g. Finland has large stockpiles of fuels for crisis situations).

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[16] Diesel Fuel News, November 10 2003: NREL: Yellow-grease biodiesel (from animal fats) can contain 30 ppm sulphur, which is too high for US EPA 2006 mandate for USDL diesel max. 15 ppm.

[17] Cold Filter Plugging Point

Biodiesel is suitable for current diesel engines, nontoxic and biodegradable, and thus an excellent fuel for use in sensitive environments. As a consequence, biodiesel is used e.g. in forest harvesting machinery and machinery used in ski resorts.

Table 9. Biogenic esters for technical purposes.

	Melting range C			
	Oil / Fat	Me. Ester	Et. Ester	Cetane no.
Rapeseed oil	5	0	-2	55
Rapeseed oil	-5	-10	-12	58
Sunflower oil	-18	-12	-14	52
Olive oli	-12	-6	-8	60
Cotton seed oil	0	-5	-8	55
Corn oil	-5	-10	-12	53
Coconut oil	20 - 24	-9	-6	70
Palmkernerl oil	20 - 26	-8	-8	70
Palm oil	30 - 38	14	10	65
Palm stearine	35 - 40	21	18	85
Tallow	35 - 40	16	12	75
Lard	32 - 36	14	10	65

When a fuel is used for transportation, it is crucial to specify the fuel quality requirements. Since 1990's **standards** have been available for RME in several European countries (Austria, Czech, France, Italy, Sweden, and Germany). However, the European standard EN 14214 for FAME for diesel engines was accepted as late as in 2003. In USA, the ASTM D-6751 standard for biodiesel was accepted in 2001 [NBB 2003b].

General information on properties of VOEs can be found from various references, e.g. brochures from UFOP, Statoil, Svenska Ecobränsle, and numerous articles, also from [Ikonen et. al. 2000]. "Handbooks" on biodiesel are available, e.g. Handling and Use Guidelines by [Tyson 2001].

4.3.2.2 Suitability for engines

Biodiesel can be used in most engines manufactured after 1994, although some limitations exist. However, warranty conditions of individual auto manufacturers are not harmonized in any way. At least the VW group (Audi, Seat, Skoda, VW), BMW, MB, PSA (Citroën, Peugeot) and Volvo allow using VOE with some car models within normal warranty conditions [several brochures]. Many manufacturers of engines for non-road applications allow using VOE, e.g. Valmet (Sisu Diesel) engines equipped with in-line injection pumps [Nylund eeci]. In US, 100% biodiesel is accepted by Caterpillar for most of the new engines and by John Deere for some equipment. Other companies (Cummins, DDC, etc.) offer warranties allowing the use of 20 % biodiesel. However, some approvals may be feedstock specific [Tyson 2001].

When using neat VOE as fuel, consumers should be aware of limitations regarding cold weather performance and fuel storage. It might also be necessary to check also seals and gaskets periodically, especially with old engines. The problems associated with storage, fuel system materials and cold weather performance are minimal or avoidable with low-concentration blends, 20% VOE or less.

A recent statement from EMA[18] regarding the use of biodiesel in diesel engines is as follows [EMA Statement]:

- Biodiesel should meet ASTM D6751 or European specification (DIN 51606, EN 14214).
- Up to 5% biodiesel should not cause problems, but blends above 5% should be consulted with the individual engine manufacturers.
- Additives may be needed to improve storage stability and usability in a wide range of temperatures. The seals, hoses, gaskets, and wire coatings should be monitored regularly.
- Biodiesel reduce HC and CO, but increase NO_x emissions when compared to diesel fuel. Therefore, it is not suitable as a means to improve air quality in ozone non-attainment areas.
- Individual engine manufacturers will determine the implications, if any, of the use of biodiesel fuels on their commercial engine warranties.

Also the Statement from FIE[19] in 2000 concluded that injection systems can be designed for neat biodiesel, but in normal equipment blends greater than B5 can cause reduced service life and injection equipment failures [FIE Statement].

4.3.2.3 Emissions

In addition to fuel substitution, today the main motivation to use biodiesel is the possibility to reduce greenhouse gas emissions, and also fuel substitution. However, biodiesel also provides benefits as regards some other emissions associated with health risks from air pollution. Biodiesel contains oxygen, which improves the combustion process. Biodiesel generally reduces CO, HC and PM emissions, and air toxics that are suspected of causing cancer and other health risks. However, biodiesel tends to increase NO_x emissions [US DoE Biofuels].

EPA's Environmental Technology Verification (ETV) Program has verified the following emission implications for using biodiesel: reduction from 0 to 47% for PM and CO, 0-67% for HC, but and increase from 0 to 10% for NO_x. The results are shown in Figures 26-27 [EPA 2002]. The EPA report analyses existing data from relevant studies, and thus represents the current knowledge on general biodiesel perfomance.

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[18] The Engine Manufacturers Association

[19] The fuel injection equipment manufacturers

The EPA report also includes an extensive analysis on the effect of biodiesel properties and feedstock on the exhaust emissions.

The increase in NO_x can hinder the use of high concentrations of RME. Scania announced already in 1997 that the NO_x emission of Scania engines exceeds the limit values with high-concentration RME blends, and also other drawbacks such as material problems arise if RME concentrations higher than 5% are used in their engines. Recently, VW and Audi informed that they may discontinue their approval for 100 % RME in their new Euro 4 emission level cars, since the emissions would not fulfill the limit values. In addition, there are doubts on FAME quality issues arising from the European FAME standard.

EPA report summarizes the effect of biodiesel on the unregulated emissions as follows:

- reduction in formaldehyde, acetaldehyde and acrolein emissions
- reduction in ethylbenzene, xylene and naphthalene
- no significant effect seen for benzene and 1,3-butadiene.

On the other hand, some other studies have reported increases in aldehyde emissions. Significant reductions in overall PAH emissions and mutagenicity of particulate matter with biodiesel have been observed. It was already mentioned that biodiesel reduces PM emissions. It has been observed that particulate matter with biodiesel tends to be “wet”, containing a high share of soluble organic fraction (SOF). However, SOF can be effectively reduced with an oxidation catalyst, and thus the combination of biodiesel and oxidation catalyst offers low particulate emissions [McGill 2003].

One must note that the effect of biodiesel on emission also depends on the quality of the diesel fuel that is used as a basis for comparison. It has been shown e.g. that no significant benefit in particulate phase PAHs is obtained if biodiesel is compared to the Swedish Environment Class 1 diesel fuel [McGill 2003].

There have been many demonstrations on biodiesel over the past decades. One of the latest demonstrations was completed in Montreal, a one-year project with 155 transit buses with B5 and B20 biodiesel blends. This demonstration was interesting due to biodiesel feedstocks: 24% VOE-based, 28% animal fat-based and 48% from used cooking oil. Biodiesel turned out to be a viable fuel option in a region with winter temperatures down to -30°C, and it was a feasible fuel for a transit company of that size [Montreal 2003].

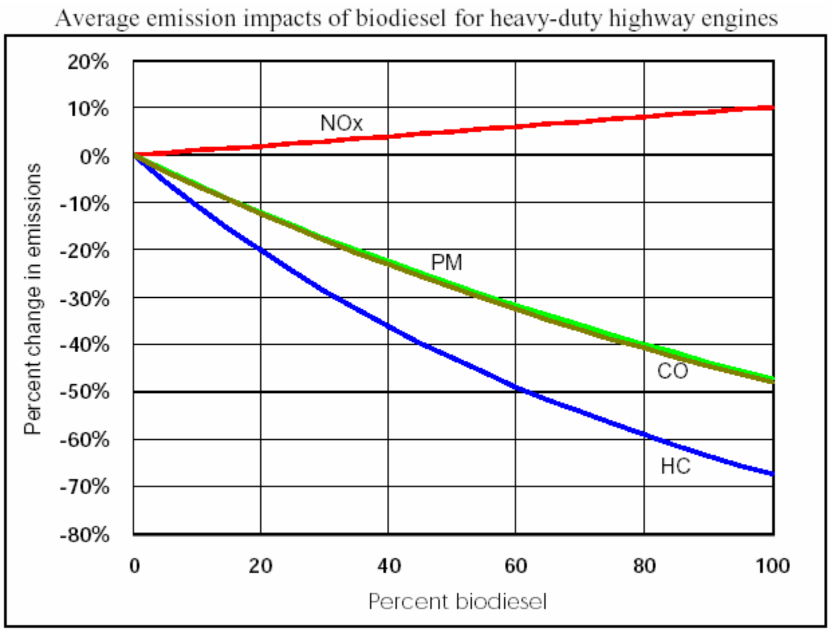


Figure 26. The effect of ester content on regulated emission [EPA 2002].

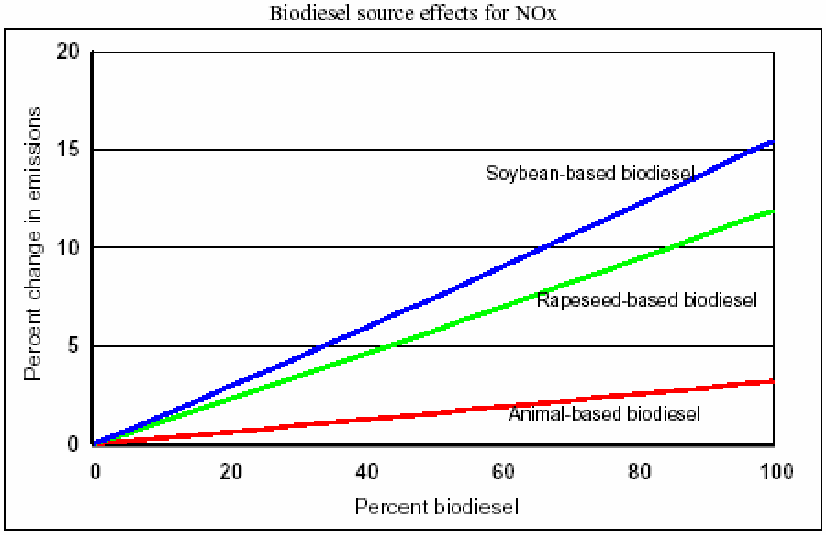


Figure 27. The effect of biodiesel feedstock on NO_x emission [EPA 2002].

Research in Finland

Vegetable oil derived fuels, mainly RME, has been studied in Finland with emphasis on fuel substitution and emission performance. One project targeted to study the suitability of RME for Valmet (Sisu Diesel) engines in off-road applications like farm tractors and combine harvesters started in 1990. Special interest was focused on winter performance and exhaust emissions, and also field tests were included [Nylund eeci]. Some tests were carried out with REE (rapeseed ethyl ester).

As regards regulated emissions, power and fuel consumption, the same kind of results as for other studies were observed for RME. REE performed in the same way as RME. An endurance test showed increased crankcase oil level (dilution effect of RME), but the engine passed the inspections. Combustion characteristics (e.g. combustion flame temperature and rate of heat release) were generally similar between two fuels.

A 2-years field tests involving 6 working machines running on 100% RME was conducted. At first, non-purified RME was used, but this resulted in problems (e.g. filters clogged, injectors coked). With purified RME no problems with overall performance of engines were observed. This emphasizes the importance of fuel cleanliness. In all engines a notable RME dilution of 8... 18 % was found in the crankcase oil, but normal drain intervals could be maintained. The "fried donut" smell was clear, but it did not irritate eyes or breathing. Standard grade RME could be used down to -12 ^{o}C, additive treated winter grade down to -23 ^{o}C. The fuel lines had to be changed to RME compatible material when a combine harvester was stored over winter. Four farm tractor engines were dismantled and inspected: generally, the engines were in good order. As a result, the manufacturer approved the use on 100 % RME within the normal warranty conditions for Valmet (Sisu Diesel) engines.

Some work using RME as a blending component for low-emission diesel has been conducted as a part of diesel fuel development projects. It has been noted that the differences in emissions between RME and a high quality reformulated diesel fuel are not as great as when compared to conventional diesel fuel. However, the emissions and health effects from esters are not yet fully evaluated especially as regards unregulated emissions.

Finland has conducted biodiesel research also within international projects. Within the International Energy Agency Implementing Agreement on “Advanced Motor Fuels” (IEA/AMF) there has been two studies "Characterization of new fuel qualities" [Nylund 2000] and “Emission Performance of Selected Biodiesel Fuels” [Aakko 2000, McGill 2003]. The former study included combustion, emission and cold operability characteristics of a variety of fuels (e.g. RME, TOE and diesel-ethanol). The latter one was a joint project by VTT and Oak Ridge National Laboratory from USA. The work covered nine fuels, e.g. RME, SME and used vegetable oil ester blends. Also in IEA/AMF Annex V and Annex XXII biofuels were included, but with minor role [Nylund 1996, Aakko 2003]. Biofuels were also included in some EU projects, in which VTT participated [Martin 1997].

4.4 GLANCE ON THE OTHER BIOFUEL OPTIONS

4.4.1 Tall oil based fuels

Canada and Finland have shown interest in tall oil based biofuels. As a consequence, both countries have studied tall oil esters (TOE), and Canada also hydrated tall oil. Tall oil esters are in principle similar to vegetable oil esters. However, due to different production process TOE may contain fatty acids, whereas VOE contains glyserides as impurities. TOE contains also sulfur, even up to some 150 ppm, which is a high concentration when current sulfur-limits are considered (e.g. 50 ppm maximum in Europe from 2005).

In Finland tests with TOE has been conducted within national and EU projects [Martin 1997] and also within the IEA/AMF Agreement [Annex X, Nylund 2000]. In the national work several engines from single-cylinder to passenger car and tractor engines have been used. Diesel containing some 30-50% of TOE proved to be the most beneficial as concerns emissions and performance. The NO_x emissions increased some 10-20% with neat TOE, and contrary to RME, also particulate mass emission increased. Injector deposits were smaller with TOE than with diesel fuel. The EU project showed operating problems with diesel containing 20% of TOE, but a significant decrease in particulate matter emission [Martin 1997].

4.4.2 Other biofuels

In principle, many other fuel options than ethanol, biodiesel or ETBE would be available, if biomass could be used as raw material with reasonable costs.

One option would be biogas from the digestion of waste. Biogas means a mixture of methane, CO_2 and water. It can be produced from organic material, e.g. at waste disposal sites, using bacteria in unaerobic environment. After the removal of CO_2 and water the biogas can be used in CNG cars. In Sweden, biogas is used commercially in several locations (e.g. Malmö, Linköping, Stockholm). In some cases, like in Switzerland, biogas is blended into the natural gas pipeline system.

Gasification of biomass, via synthesis gas production, would provide a route to a number of options, e.g. methanol (->MTBE) and diesel-like Fischer-Tropsch fuel.

DME is one of the possible alternatives for diesel engine. The physical properties of DME resemble LPG, with the exeption that the cetane number of DME is high.DME would require a totally new fuel distribution system, and also new engines. Thus DME is an expensive option.

Recently, Daimler Chrysler AG presented a new synthetic fuel made of wood-derived biomass, named "Biotrol". A pilot plant converts the biomass from wood residue into Biotrol fuel, which can be mixed with current fuels. Ongoing research will show if neat Biotrol can be used as a fuel, or whether engine modifications are necessary. The production cost for Biotrol is reported to be 0.7 €/l. Since biofuels are exempted from tax in Germany, Biotrol could be offered at competitively price even today [DaimlerChrysler 2003].

4.5 A SHORT COMPARISON OF THE FUEL OPTIONS

The biofuels that can provide a short-term option as transportation fuels are biodiesel, ethanol and ETBE. Biodiesel is suitable for diesel engines, ethanol and ETBE for gasoline engines. A summary of some properties of these fuels in comparison with gasoline and diesel are shown in Table 10.

Gasoline/ethanol blends with up to some 10% ethanol are suitable for conventional spark-ignition engines without engine modifications. Special cars, so called Fuel Flexible Vehicles (FFV) have been developed to use blends containing up to 85% alcohol (the balance being gasoline). Alcohols as such are not suitable for diesel engines. Two options exist; to modify the engine or to modify the fuel. The latter concept is used in Sweden, where a number of city buses run on additive treated ethanol (ignition improver, lubricity additive). Ethanol blended with diesel fuel has also been studied. In most cases the use of diesel/ethanol blends arise technical problems linked to safety issues and overall suitability on engine.

Methanol is in principle similar to ethanol, and is thus basically suitable for engine applications in the same way as ethanol. Despite of the similarities, there are also differences, e.g. methanol is toxic, corrosive and non-biodegradable. At first, the FFV cars were developed for methanol, later on main attention was switched to ethanol. Alcohols are liquid fuels, this means good energy density, easy re-fuelling and storage. Basically the same kind us distribution system as for conventional liquid fuels can be used. However, corrosion and the affinity of gasoline/alcohol blends to moisture have to be taken into consideration. In addition, both methanol and ethanol burn with invisible flame, which has to be taken into account in the risk assessments.

Alcohols and ethers have high-octane numbers, and can therefore be used as octane boosters in gasoline. Oxygen introduced into the fuel leans off combustion in open-loop systems (lower exhaust emissions). Ethers have many benefits when compared to alcohols: better solubility in gasoline, less corrosive, lesser impact on vapor pressure, positive effect on mixture formation and startability.

Many fossil fuels of today could be biofuels of tomorrow as regards chemical structure. CNG cars can use methane from waste disposal sites as well as fossil methane. Biofuels production via synthesis gas opens up a number of options. Methanol might be produced from biomass in future, and biomethanol could be used as feedstock for MTBE. Also diesel-like Fischer-Tropsch fuels could be biomass-based.

Life cycle analysis is an important factor when evaluating different biofuels/alternative fuel options. CO_2 emissions from transport sector have increased more than CO_2 emissions from other energy sectors between 1990 and 1999. The travelling distances have increased, as well as the number of vehicles. In addition, fuel economy has improved in Europe and Japan, but not in North America. IEA estimates that with current development, the CO_2 emissions from light-duty cars will be 30% above 1990 level in 2010 in the IEA countries [Clean Fuels Report 2002].

For IEA countries the main challenge is to reduce CO_2 emissions from light-duty vehicles. IEA has drafted five supporting strategies. One of them suggests using biofuels, mainly ethanol. Even though many biofuels can substitute fossil fuels, very few of them offer significant benefits in greenhouse emissions. Today's alcohol production from starch containing crops should be replaced by cellulosic feedstocks to gain benefits in greenhouse gas emissions (Figure 28) [Clean Fuels Report 2002].

Table 11 shows an estimate of the land needed to support alcohol production for 10% of gasoline in light-duty vehicles. It seems that in the long-term only ethanol from sugar-rich feedstocks or methanol from cellulosic material could replace 10% of fuel demand. [Clean Fuels Report 2002]

[CONCAWE 2002] published a review on biofuels. A shortened version of conclusions is as follows: *Production of RME and bioethanol gives modest net gains in overall energy balance, even though use of by-products as animal feed or energy source can improve the efficiency. It is not yet clear if practicality and economics will support the use of straw or other biomass, and what real energy and GHG savings can be achieved. The EU target of 5.75% of biofuels by 2010 seems not to be achievable with the EU-15 set-aside land area alone, and no evidence of dramatic yield improvements are on the horizon. Calculations of GHG balance include considerable uncertainties, e.g. the real effect of* N_2O*, and changes in the equilibrium content of carbon when land is put under cultivation. Is it rational to produce biofuels rather than concentrate on bioenergy? Using the high-yield crops for heat and power is more* CO_2*-effective than production of biofuels. The use of land may need a careful optimisation for best use of this limited resource. CONCAWE continues this work, with Eucar and the EU JRC, to analyse various alternative fuels on a well-to-wheels basis.*

The greenhouse gases are only one factor to be taken into account when evaluating biofuels. Feedstock availability, costs and infrastructure are important parameters. In addition, all alternative fuels should be considered in the evaluations, not only traditional biofuels. An extensive Well-to-wheel analysis of energy use and GHGs with various fuel/car options was reported by GM [2002].

GM [2002] concluded that the fuel cell cars on compressed hydrogen from reformed natural gas offer reduced GHG emissions relative to gasoline and diesel. Fischer-Tropsch has higher energy consumption, but GHGs in between of diesel and gasoline. Biofuels offer reduced GHGs, but this depends on N_2O assumptions. Biomass based biofuels (gasification, enzymatic hydrolysis) give lower GHGs than conventional biofuels. Electrolysis-based hydrogen generates high GHG emissions with traditional grid mix, but near-zero level with renewable electricity. North American study was reported separately, but findings were similar for relative rankings.

Table 10. Summary of the selected properties of fuels.

	Gasoline	**Diesel**	**Ethanol**	**ETBE**	**Biodiesel** [a]
Formula	C4-C12	C12-C20	C2H5OH	C6C14O	C19H34O2
Density, kg/m3	750	840	790	745	880
Viscosity at 40°C, cSt	-	~2-4.5	-	-	3.5-5
Distillation range, °C	30-190	170-340	78	73	300-340
C/H/O, wt-%	86/14/0	86/14/0	52/13/35	70/14/16	78/12/10
Octane number, BON [b]	95/98	Na	130	118	na
Cetane number	na	>45	8	Na	>50
Raid vapour pressure, kPa	[c]	-	16/124[d]	10/27[d]	-
Flash point, °C	<0	>56	13	<0	>100
Flammability limits, vol%	1.4-7.6	1-6	4.3-19	?	?
Heat value, MJ/kg	43	43	26	36	36
Flame visibility	Visible	Visible	Not clearly visibly	Visible	Visible

na = not applicable

[a] Biodiesel includes a wide group of different vegetable oil esters, or even fat oil esters. These properties are based on rape seed methyl ester.

[b] RON or MON octane numbers are not relevant for oxygenates. Thus blending octane numbers (BON) are shown here for ethanol and for ETBE.

[c] Raid Vapour Pressure varies in different countries and seasons. Limit for summer gasoline e.g. >70 kPa.

[d] Vapour pressure changes unlinearly when ethanol is added to gasoline, second value is blending vapour pressure (see Chapters 4.1 and 4.2)

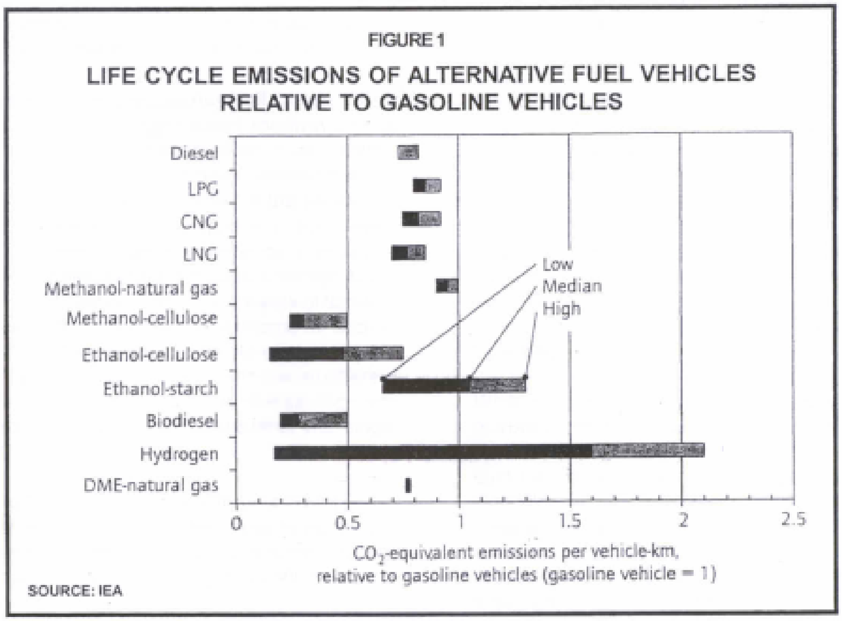
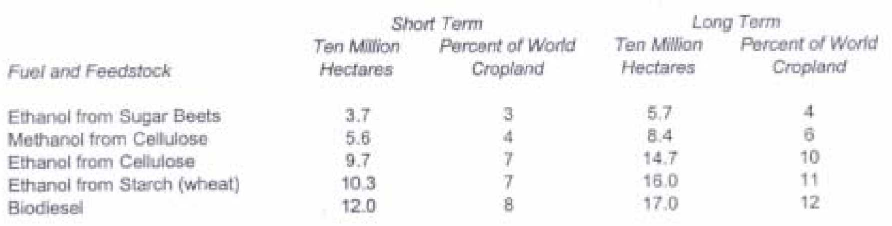


Figure 28. Life cycle emissions of alternative fuel vehicles [Clean Fuels Report 2002].

Table 11. Land needed to replace 10% of gasoline with alcohol [Clean Fuels Report 2002].



	Short Term		Long Term	
Fuel and Feedstock	Ten Million Hectares	Percent of World Cropland	Ten Million Hectares	Percent of World Cropland
Ethanol from Sugar Beets	3.7	3	5.7	4
Methanol from Cellulose	5.6	4	8.4	6
Ethanol from Cellulose	9.7	7	14.7	10
Ethanol from Starch (wheat)	10.3	7	16.0	11
Biodiesel	12.0	8	17.0	12

5 SUMMARY

Finland has proposed a joint project with Japan, USA and Sweden on ethanol as fuel for transportation. This review is targeted to benefit the preparation phase of this possible new project, and can be used as a part of the state-of-the-art review of the possible oncoming project. This review is also targeted to collect information on ethanol for national discussions on liquid biofuels in Finland.

The European Union has given guidelines for transport sector with target values for both biofuels and alternative fuels. So far, heat and power production has been the key priority in Finland in reduction of the greenhouse gas emissions due to the low CO_2 abatement costs when compared to the transportation sector. However, now reactions from Member States are expected also on biofuels for transportation.

The most potential short-term options for liquid biofuels are biodiesel and ethanol. Biodiesel is mainly used as a blending component in diesel, but some engines are approved for operation also on neat biodiesel. Ethanol can be used as a component in gasoline, and is sometimes also added to diesel. At high concentrations ethanol requires special engine technology. The amounts of biofuels and also the range of products could be increased, if synthetic fuels were produced from biomass.

When considering the production potential of liquid biofuels in Finland, it is clear that all possible feedstock options should be taken into account. Agriculture based biofuels from set-aside lands could, with current production technologies, cover less than 2% of the consumption of transportation fuels in Finland. Wood- and waste-based fuels would offer a significant reserve of raw material for liquid biofuels, if cost-effective production processes existed (limitations by competitive use).

Alcohols are liquid fuels, which mean good energy density, easy re-fuelling and storage. Basically the same kind of distribution system as for conventional fuels can be used. However, in the case of gasoline/ethanol blends the distribution system needs special attention to avoid problems caused by water, as blends are very sensitive to moisture.

Fuel properties of ethanol are in many respects similar to gasoline. Thus it can be used in spark-ignition engines as gasoline component, e.g. ethanol up to some 10% can be blended into gasoline and used without modifications in ordinary engines. There is not much experience on the concentrations exceeding 10% with normal cars. The cars running on high-concentration blends (25%) in Brazil are, if not modified, at least recalibrated.

Blending vapor pressures for alcohols are significantly higher than their true vapor pressures. When ethanol is added to gasoline, up to some 5-10% ethanol content vapor pressure increases, but then gradually decreases until at some 30-40% ethanol content vapor pressure is similar as for gasoline, while at higher concentrations vapor pressure is lower than for gasoline. Vapor pressure of ethanol/gasoline blend influences e.g. evaporative emissions.

Biofuels, like ethanol, gain benefit in the carbon dioxide emission (greenhouse gas) when compared to fossil fuels due to CO_2 absorbed by the plants. However, tailpipe CO_2 emissions are roughly equal with gasoline and ethanol. Overall "toxicity" of the emissions of alcohol fuels is generally less than that of reference gasoline despite of the higher acetaldehyde emissions (acetaldehyde less toxic than e.g. 1,3 -butadiene and benzene). Some indications of lower mutagenicity of particulates with ethanol (and ETBE) containing fuels than with gasoline have been observed.

Special cars, Fuel Flexible Vehicles (FFV), have been developed for high concentration alcohol blends (up to 85%, the balance being gasoline). Gasoline improves the cold-startability, which is poor for ethanol due to low vapor pressure and high heat of evaporation. Gasoline also improves safety as flames become visible. The reduction in emissions depends on how well the engine and the emission control system are designed and "tuned" for ethanol. The cars today have been designed to meet stringent emissions regulations, but there still seems to be a potential for emission reductions substituting gasoline for high-concentration ethanol blends.

Also heavy-duty diesel engines can use ethanol with certain limitations. The properties of ethanol are similar to gasoline, thus engine modifications (e.g. glow-plugs or pilot injection) or additives in fuel are needed, if ethanol is to be used in compression ignition engines. E.g. cetane number and lubricity of ethanol are unacceptable for conventional diesel engines. The emissions level of the Swedish ethanol buses are similar to advanced diesel busses equipped with oxidation catalyst or particle filters, but higher than emission levels of advanced CNG buses (higher NO_x). The particle and smoke emissions from ethanol buses are almost negligible. Acetaldehyde emissions are high for ethanol buses, but the cancer risk index low.

One option to use ethanol in diesel engine is a low concentration ethanol/diesel blend (or emulsion). Generally, benefits in PM and NO_x emissions with E-diesel have been observed. The main concerns with this E-diesel are safety issues and the general suitability for diesel engines (low cetane, low lubricity). In addition, e.g. stability, water tolerance, and other fuel properties of E-diesel are problematic. Due these concerns it will be difficult to obtain approvals from engine/vehicle manufacturers for E-diesel (liability for warranty)..

Biodiesel is suitable for current diesel engines, nontoxic and biodegradable, and thus an excellent fuel for use in sensitive environments. As a consequence, biodiesel is used e.g.

in forest harvesting machinery. Many manufacturers, especially for non-road engines, allow the use of biodiesel within normal warranty conditions. Biodiesel provides benefits regarding greenhouse gases and some emissions associated with health risks from air pollution, but on the other hand biodiesel tends to increase NO_x emissions.

Many reviews have been conducted to assess reasonable policies for the introduction of biofuels. Some of them, like the one published by Concawe and focused on Europe, gave a critical view on the appropriateness of the EU targets for biofuels in transportation. Some other studies have given optimistic views. It remains to be seen how the targets can be met, and if met, and at what costs.

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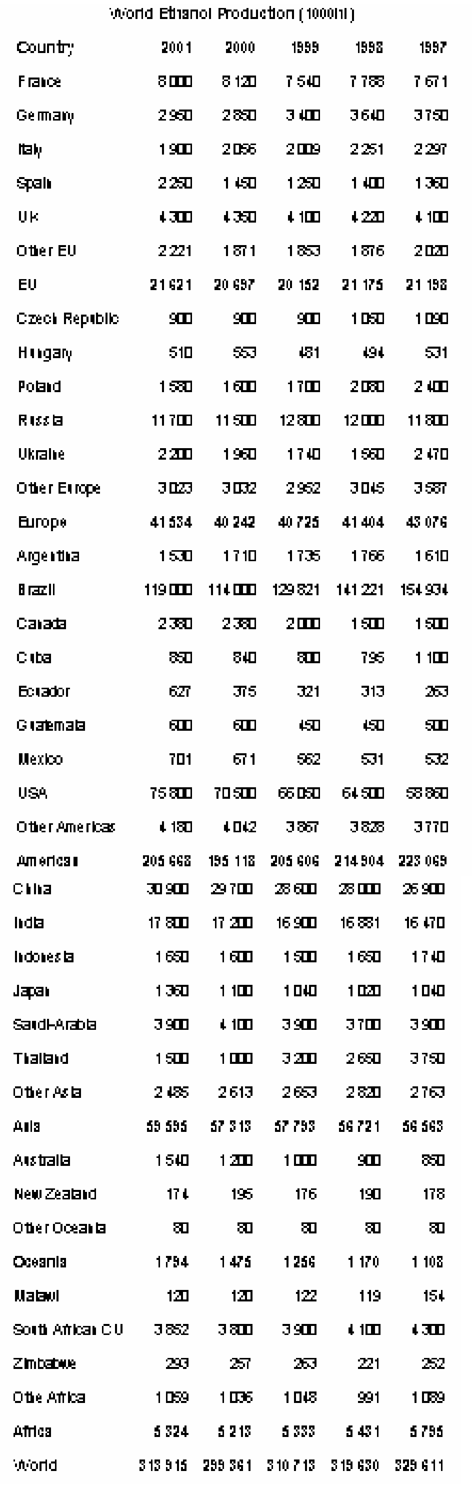

World Ethanol Production (1000hl)

Country	2001	2000	1999	1998	1997
France	8 000	8 120	7 540	7 788	7 671
Germany	2 950	2 850	3 400	3 640	3 750
Italy	1 900	2 056	2 009	2 251	2 297
Spain	2 250	1 450	1 250	1 400	1 360
UK	4 300	4 350	4 100	4 220	4 100
Other EU	2 221	1 871	1 853	1 876	2 020
EU	**21 621**	**20 697**	**20 152**	**21 175**	**21 198**
Czech Republic	900	900	900	1 050	1 090
Hungary	510	553	481	494	531
Poland	1 580	1 600	1 700	2 080	2 400
Russia	11 700	11 500	12 800	12 000	11 800
Ukraine	2 200	1 960	1 740	1 560	2 470
Other Europe	3 023	3 032	2 962	3 045	3 587
Europe	**41 534**	**40 242**	**40 725**	**41 404**	**43 076**
Argentina	1 530	1 710	1 735	1 766	1 610
Brazil	119 000	114 000	129 821	141 221	154 934
Canada	2 380	2 380	2 000	1 500	1 500
Cuba	850	840	800	795	1 100
Ecuador	627	375	321	313	263
Guatemala	600	600	450	450	500
Mexico	701	671	562	531	532
USA	75 800	70 500	66 050	64 500	58 860
Other Americas	4 180	4 042	3 867	3 828	3 770
Americas	**205 668**	**195 118**	**205 606**	**214 904**	**223 069**
China	30 900	29 700	28 600	28 000	26 900
India	17 800	17 200	16 900	16 881	16 470
Indonesia	1 650	1 600	1 500	1 650	1 740
Japan	1 360	1 100	1 040	1 020	1 040
Saudi-Arabia	3 900	4 100	3 900	3 700	3 900
Thailand	1 500	1 000	3 200	2 650	3 750
Other Asia	2 485	2 613	2 653	2 820	2 763
Asia	**59 595**	**57 313**	**57 793**	**56 721**	**56 563**
Australia	1 540	1 200	1 000	900	850
New Zealand	174	195	176	190	178
Other Oceania	80	80	80	80	80
Oceania	**1 794**	**1 475**	**1 256**	**1 170**	**1 108**
Malawi	120	120	122	119	154
South African C U	3 852	3 800	3 900	4 100	4 300
Zimbabwe	293	257	263	221	252
Othe Africa	1 059	1 036	1 048	991	1 089
Africa	**5 324**	**5 213**	**5 333**	**5 431**	**5 795**
World	**313 915**	**299 361**	**310 713**	**319 630**	**329 611**

http://www.distill.com/world_ethanol_production.html