

Delivery of Biofuels – Project Biojakelu Final report

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<p>Summary</p> <p>This report is a summary of the key results of the Tekes-supported consortium project called “Impact of biofuels on the life cycle of fuel station equipment (BIOJAKELU)”. Its aim was to improve the capabilities of the various companies belonging to the value network for fuel service stations in realising the operation based on viable and safe business principles. The emphasis of the report is on safety related issues.</p> <p>The studies of the project involved practical tests on the compatibility between the materials used in the distribution of liquid motor fuels and biofuels and to assess the risks of ignition in the dispensing of biofuels as well as to suggest measures for their minimisation. The results indicate that HVO diesel (like NExBTL) does not require changing current practices; the same applies to petrol containing small amounts of ethanol (up to 10 vol%). On the other hand, safe dispensing of high blend ethanol fuels (HBEF) and RME/FAME biodiesel requires some changes to current practices. The necessary changes are presented in this report.</p> <p>As a general conclusion, it can be stated that the introduction of biofuels is a step in a safer direction in the dispensing of motor fuels. The safety of petrol dispensing is the result of long-term experience. When the changes required by biofuels have been implemented, all preconditions for safe dispensing of biofuels are in place.</p>										
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Foreword

This report is a summary of the key results of the Tekes-supported consortium project called “Impact of biofuels on the life cycle of fuel station equipment (BIOJAKELU)”. Its aim was to improve the capabilities of the various companies belonging to the value network for fuel service stations in realising the operation based on viable and safe business principles. The consortium consisted of energy companies, manufacturers and suppliers of service station equipment as well as companies engaged in the design and building of service stations and dispenser systems. The partner companies were: Neste Oil Oyj, SOK ABC, St1 Oy, NEOT Oy, Autotank Oy, J K Pajarinen & Co, Labkotec Oy, Oy U-Cont Ltd, Wavin-Labko Oy, Asennusliike Lahtinen Oy, Hartela Oy, and Tuotekehitys Oy Tamlink as the administrative coordinator. The consortium bought expert services from VTT with Tekes' assistance in support of the companies own R&D efforts. The project was carried out during the period 1.3.2007–31.8.2008.

The emphasis of the final report is in accordance with the project aims on issues related to the safety when delivering and dispensing liquid biofuels. It starts with an introductory review of liquid biofuels based on literature and then presents the goals of the project and finally the actual results of the study. The compatibility of materials used at dispensing stations and the risk of ignition of biofuels were studied separately. The results were reported in detail and confidentially to the consortium during the project. This public summary report focuses on safety-related issues. Conclusions are drawn and recommendations made for the sector.

The authors express their thanks to the Biojakelu consortium and the members of the project management group – Tuotekehitys Oy Tamlink / Jari Erkkilä, SOK ABC / Tiina Vehmala, ST1 Finland Oy / Mikko Reinekari, Neste Oil Oyj / Martti Mäkelä, NEOT Oy / Elina Leskelä, Heidi Hirvelä, Asennusliike Lahtinen Oy / Eero-Matti Lehtiniemi, Gilbargo-Autotank Oy / Risto Viitanen, Hartela Oy / Aimo Valtonen, J K Pajarinen & Co / Vesa Raja-aho, Labkotec Oy / Jarkko Latonen, Oy U-Cont Ltd / Jarmo Hänninen, Wavin-Labko Oy / Teppo Parviainen – for the support received. Special thanks to Björn Herlin from Räddningsverket concerning the ignition risk surveys on the E85 liquid fuel in Sweden, to Martin Glor of the Swiss Institute for Safety and Security for determining the ignition parameters of ethanol-petrol blends, to Seppo Enbom from VTT for work hygiene studies as well as VTT's Riku Vuorinen, Raija Ilmén, Matti Niinistö and Seija Kivi for assistance in carrying out tests.

Finally, we thank Jorma Tiainen for making the first draft of the English translation of report.

Tampere, 16.2.2009

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1 Liquid biofuels

1.1 Starting point

Reducing the dependence on imported energy and slowing down the greenhouse effect are general EU level objectives. Moreover, the development of the prices of fossil fuels requires searching for alternatives. This means added pressures towards increasing the use of biofuels in both power generation and transportation. The European Commission Green Paper “Towards a European Strategy for the Security of Energy Supply” set the target of increasing the share of alternative transport fuels to 20 % by 2020. Directive 2003/30/EC sets the target to 5.75 % (measured in terms of energy content) by 2010.

In the autumn of 2005 the Finnish Ministry of Trade and Industry appointed a work group to study the possibility of promoting the production and use of biofuels for transport in Finland. The group recommended a gradually increasing obligation to use biofuels as a primary means of promotion. The final version of the obligation incorporated even bigger increments than the work group had recommended. In 2008 the obligation is 2 % (energy equivalent), in 2009 it is 4 % and in 2010 it is a conditional 5.75 %. The obligation is energy company-specific but flexible, so that biofuels or fuel containing biocomponents can be sold at the desired place and time, provided that the annual obligation is met. For example, the sale of pure biodiesel in the metropolitan area during summer may suffice to meet the annual obligation of a company. Obligations may also be traded. A company that exceeds its annual obligation may sell the surplus to another company.

European fuel standards EN 228:2004 and EN 590:2004 allow 5 % ethanol in petrol and 5 % methyl ester of vegetable oil (FAME) in diesel without an indication on the fuel meters. Experience has shown that fuels that adhere to these limits can be dispensed safely by appropriately observing current conventions and regulations. Consequently, the Biojakelu Project focused on fuel blends where the share of bio components exceeds the limits permitted by EN 228:2004 and EN 590:2004.

The EN590 standard is being updated to allow increasing the permissible content of FAME to 7 per cent by volume, and a further increase to 10 % is being planned (source: CEN/TC 19/WG 24 N269, 15.5.2008). It is also highly probable that the permissible ethanol content of petrol will increase to 10 per cent by volume in the next few years.

1.2 Production of biofuels

The current range of biofuels is based mainly on cultivated raw materials such as ethanol from sugar cane, maize or grain and vegetable oils such as the biodiesel derived from rape or palm oil. Ethanol is globally the most commonly used biofuel. The USA and Brazil are clearly the biggest producers. The EU's production of biofuels is only a fraction of the production of these countries (Figure 1). Biodiesel, which here refers to the rape seed methyl ester (RME), is the most common biofuel in Europe. In the USA, soy oil is the most common raw material of biodiesel. The production of soy oil is also increasing rapidly in South America, while Asia is increasing the production of palm oil. Palm oil is already produced in large quantities, so its price is lower compared to other vegetable oils. For this reason palm oil is seen as a potential raw material of biofuels in many countries. Animal fats and fermented vegetable oils are also existing alternatives for the production of biofuels, but at present their share of global production is marginal.

As production grows, it is even more necessary to consider the principles of sustainable production. The global rise in the prices of foodstuffs has also invoked some heavy criticism against the use of edible feedstock as raw materials. Therefore, a considerable increase in the use of non-foodstuff-based biofuels such as woody biomass and biowaste can be expected by 2020.

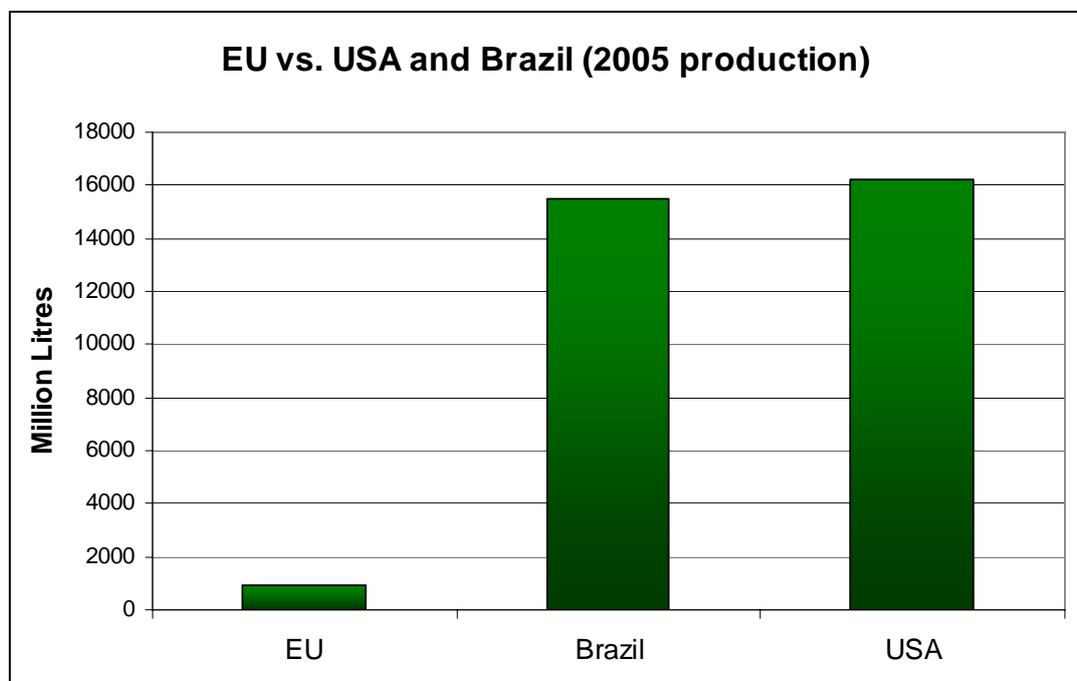


Figure 1. Production of ethanol and biodiesel in the EU, Brazil and the USA. (http://www.ebio.org/downloads/publications/060509_eBIO_WBC_Seville_2006_def.pdf)

1.2.1 Ethanol

Ethanol is produced mainly by fermentation. About 60 % of the ethanol produced in the world is of cultivated sugar-containing plants such as sugar cane and sugar beet – the rest comes mainly from grain. Before fermentation the starch of the grain must be converted to sugar by hydrolysis. In Finland, ethanol is made mainly of barley and to some extent also of potatoes and biowaste. All the ethanol made from barley and potatoes is currently used as raw material for alcoholic beverages and industrial products.

ST1 Biofuels Oy uses an ethanol production process based on fermentation and evaporation that converts biowaste into a 85 % ethanol-water solution in plants typically located close to the place where the waste is produced. The product is converted in a separate dehydration plant into 99.8 % ethanol to be mixed with petrol.

1.2.2 Ethers

Ethers can be produced at oil refineries by making use of the side streams of the refinery. The following ethers are produced for use as liquid fuels: MTBE (methyl-tert-butyl ether), ETBE (ethyl-tert-butyl ether) and TAME (tertiary amyl-methyl ether).

1.2.3 Esters of vegetable oils

Pure vegetable oils are poorly suited for transport fuels. Interesterification, which converts an ester and alcohol into another esters and alcohol (glyserol), makes the vegetable oil more suitable for engines. Products interesterified by methanol are generally called FAME (Fatty Acid Methyl Ester).

In Europe, biodiesel refers to the methyl ester of rape seed oil (RME), where the triglycerides of vegetable oil have been broken down into methyl esters of individual fatty acids. The fatty acid content of different vegetable oils varies considerably, which is why the properties of fuels produced by interesterification also vary. The purity of raw materials is also important. Pretreatment of the raw material commonly includes filtering of solid contaminants, dehydration and removal of possible free fatty acids.

1.2.4 Hydrogenated vegetable oils and BTL

Diesel fuels can also be produced on an industrial scale by hydrogenating vegetable or animal fats. In future biomass gasification combined with the Fischer-Tropsch process will probably become reality (Figure 2). The optimal process size generally grows with the introduction of hydrogenation and later gasification, which also requires bigger investments. The following abbreviations are commonly used for the upgraded products derived from vegetable oils:

- HVO = hydrogenated vegetable oil, e.g. NExBTL
- BTL = Bio-to-Liquids, biomass gasification and liquefaction of gaseous products

A process developed by Neste Oil Corp. converts vegetable oils and animals fats into high quality HVO diesel whose trade name is NExBTL. The first production plant went on stream in Porvoo in the summer of 2007. Production plants using similar technology have also been established, for example, in Brazil.

Fischer-Tropsch liquefaction is a proven technology for deriving liquid fuels from natural gas (GTL, Gas to Liquid). It is currently used, for example, in Malaysia and South Africa. The first commercial BTL plant was built in Freiberg, Germany. However, the application of this familiar technology for biomass has involved many problems (Blades 2005, Shell information www.shell.com, [AMFI Newsletter 3/2006](http://www.amfi.fi) <http://virtual.vtt.fi/virtual/amf/download.html>), so it may take years before BTL can be applied more widely in the production of biofuels.

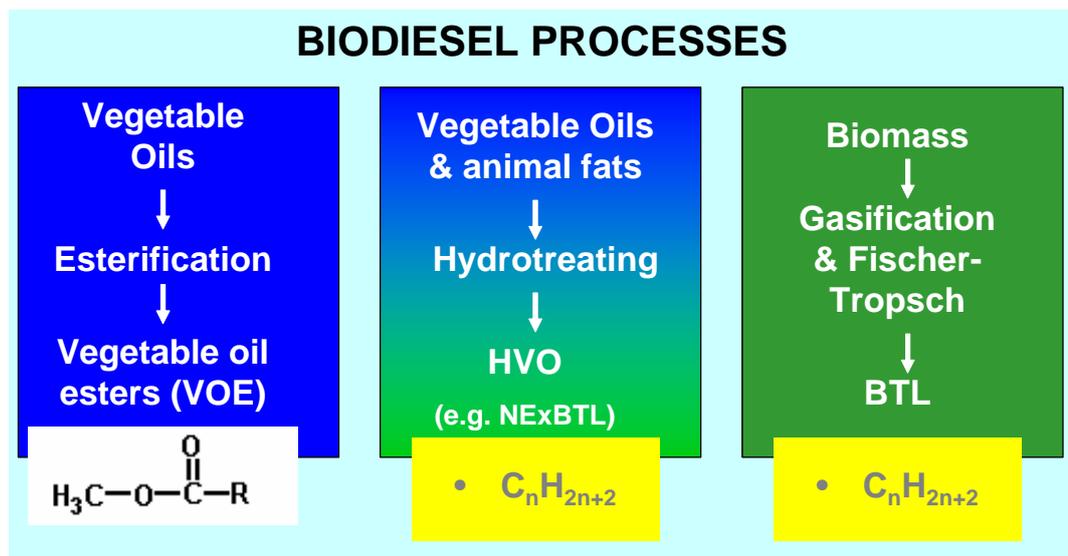


Figure 2. A diagram of different biodiesel processes.

1.3 Properties of biofuels

1.3.1 Ethanol

Standard EN 15376 for ethanol in fuel was enacted by the EU in December 2007 (Table 1). Individual countries that have created their own standards for ethanol mixed with fuel include at least Sweden and Poland. In the USA, standard ASTM D 4806 defines the requirements for anhydrous ethanol that is commonly mixed with petrol at a 10 % ratio.

Table 1. Requirements of European EN 15376 standard for anhydrous ethanol and requirements set by Brazil for ethanol fuels (Nylund et al.)

	Requirements of standard EN 15376:2007	Brazil anhydrous ethanol
Ethanol + higher alcohols	>98.7 w%	> 99.3 vol%
Ethanol		> 99.3 vol%
C3-C5 alcohols	< 2 w%	
Methanol	≤ 1 w%	
Hydrocarbons		max 3.0 vol%
Water	max 0-3 w%	
Density, g/ml		max 0.791
Inorganic chlorine, mg/l	max 20,0	
Copper, mg/kg	max 0.100	max 0.07
Acid content. (acetic acid equiv.)	max 0.007 w%	max 30 mg/l
Appearance	clear	clear, no sediment
Colour		colourless or yellowish
Phosphorous	max 0.50 mg/l	
Insoluble material	max 10 mg/100 ml	
Sulphur	max 10.0 mg/kg	

Ethanol is suited for use in a petrol engine as such. In Brazil it is already widely used. In Europe and USA ethanol is used in petrol at low blends or in the E85 fuel. E85 is 85 % ethanol and 15 % petrol. Petrol is needed to improve cold starting properties, increase the visibility of the flame (for safety) and to denature ethanol. Methanol burns with an invisible flame while the flame of ethanol is barely visible. E85 is used in so-called FFV or Flexible Fuel Vehicles that run not only on petrol or E85 fuel but on any blend of these two fuels. The automation system of the vehicle makes the necessary adjustments so the driver does not need to know which fuel he is using. In Europe the CEN workshop has agreed on a recommendation for the requirements and test methods for E85 fuel (CWA 15293:2005).

Ethanol is a corrosive substance. The most problematic situation arises if water and ethanol are able to separate into different phase. Among alcohols, methanol is more corrosive than ethanol, which requires setting a very low limit for the methanol content of ethanol. A special pHe test reveals even the minutest amounts of acid components in ethanol. A pHe reading of less than 6.5 implies increased risk of fuel pump and nozzle damage, while a reading exceeding 9 may cause problems for plastic parts (Reynolds).

Ethanol contains 35 w% of oxygen, which is reflected in its low calorific value and high fuel consumption measured in litres. The vapour pressure of pure ethanol is clearly lower than that of petrol, but even a small addition of ethanol increases the vapour pressure of petrol. The petrol component of an ethanol containing fuel must therefore be reduced from the normal level to keep the vapour pressure of the end product on an acceptable level. The evaporation point of ethanol is high.

At cold temperatures the preheating of fuel is necessary to improve cold starting and running properties.

Ethanol has a high flash point compared to petrol (Table 2). Flash point means the lowest temperature where fuel vapours are ignited by a burning flame. At temperatures below the flash point evaporation is so slow that a flammable blend is not produced.

A petrol-air blend is flammable when there is roughly 1 to 7 % of petrol in the blend. For instance, in the airspace of tanks petrol content exceeds the higher explosion limit. Low petrol residues in “empty” tanks may form a highly flammable blend with air. The explosion limits of ethanol are wider. On the one hand, at the lower limit more ethanol is needed to form a flammable blend but, on the other hand, ethanol-air blends are combustible up to 19 vol%. The flame speed of ethanol-air blends near the stoichiometric range is also higher than with petrol-air blends. In general the pipes of petrol tanks contain a blend sufficiently rich to prevent the propagation of flame into the tank. Due to the wider explosion limits of ethanol the risk of flame propagation to the tank increases. The formation of a flammable blend in a fuel tank may also be examined in terms of temperatures. Evaporation depends on temperature so a combustible air-fuel blend can only form at a certain temperature range. According to SAE Technical Paper 950401 (www.srv.se, 29.5.2007) the temperature range for petrol is -41 to -10 °C and -33 to +11 °C for E85 fuel. This means that petrol does not form a flammable blend in underground tanks, but E85 fuel does. For this reason, a closer analysis of the ignition risks of ethanol-petrol blends was a central focus of research in the Biojakelu Project.

Table 2. Typical properties of petrol and ethanol.

	Ethanol	Petrol
Density (g/l)	794	about 740
C/H/O, w%	52/13/35	85-88/12-15
Boiling point (o)	78	30-190
Heat of evaporation (MJ/kg)	0.913	0.304
Effective thermal value (MJ/kg)	26.7	about 43
Vapour pressure / 38 °C (kPa)	16.0	45-90
Lower explosion limit (vol%)	3.3	1.3
Higher explosion limit (vol%)	19.0	7.1
Stoichiometric air-fuel blend	9	14.7
Flash point (°C)	13	-43to -9

As a polar compound, alcohol mixes easily with water, which should be taken into consideration in case of fire. Water spray, dry chemicals, CO₂ or alcohol-resistant foam are suitable for extinguishing. With petrols containing over 10 % alcohol, ethanol-related issues must be taken into account in extinguishing. http://hazmat.dot.gov/E-85_042606.pdf

The requirements for materials of E85 tanks, pipes and sensors are higher than those for the materials of corresponding components of conventional petrol tanks.

Literature does not indicate clearly the quantities of ethanol in petrol that affect the durability of materials. Five per cent of ethanol is currently an acceptable content. Material recommendations for the E85 fuel are listed, for example, in the E85 Handbook. <http://www.eere.energy.gov/afdc/pdfs/40243.pdf>. However, the literature survey on the compatibility of materials used at filling stations with different liquid biofuel blends left so many open questions that the Biojaku Project performed extensive test series to gain a better understanding of the issue.

1.3.2 Ethers

Like alcohols, ethers are high-octane oxygen containing components. The advantages of ethers over alcohols include higher calorific value, better tolerance of water, lower corrosive effect and smaller impact on the vapour pressure of petrol. Generally speaking, ethers have the same advantages as alcohols but without their drawbacks.

Among ethers, MTBE (Methyl-tert-butyl ether) has been the most common petrol blending component, while ETBE (Ethyl-tert-butyl ether) and TAME (Tert-amyl-methyl ether) are also quite common. Ethers are polar components but not as polar as alcohols. They blend better with hydrocarbon fuels than alcohols. Ethers contain less oxygen than corresponding alcohols: the oxygen content of most commonly used ethers is 16 to 18 %. When the amount of conventional oxygenates in petrol is limited by oxygen content, bigger quantities of ethers can be blended with alcohols.

1.3.3 Esters of vegetable oils (biodiesels)

The esters of vegetable oils are suitable for diesel fuels with some preconditions and reservations. The purity of esters is very important. Esters may contain triglycerides, glycerol or alcohol and possible trace amounts of metals from the catalyst used in their production. Glyceride causes carbon fouling in engines as do triglycerides. Alcohols lower the flash point and thus constitute a safety risk. Metal residues may have an adverse effect at least on the exhaust gas after-treatment system. Pure esters are polar compounds that dissolve materials differently from conventional diesel fuels.

The storage life of vegetable oil esters is clearly shorter than that of conventional diesel fuels. During storage, esters may polymerise and oxygenate. Water, light and high temperature aggravate these unwanted reactions. The recommended maximum storage time for esters is six months.

Esters have a high flash point, so they fall in the same safety class as conventional diesel fuels. Even a small amount of alcohol as a contaminant lowers the flash point below the permissible limit for diesel fuels.

Table 3 summarises the quality requirements for diesel fuels (EN 590:2004), requirements for vegetable oil esters specified by standard EN14214 and the properties of rape methyl ester (RME) and hydrogenated biofuel (here NExBTL). RME's advantages are that it lubricates, is aromatic free and has a low sulphur content. Its cetane number is on a level with currently used fuels. RME is

biodegradable, which means that possible leaks are not as harmful as with conventional fuels.

Table 3. Requirements for fuels and properties of biodiesels.

	Diesel, summer grade (EN 590:2004)	FAME EN14214:2004	Data on analysis of an RME	HVO (NExBTL)
Ester content, vol%	max 5	min 96.5	>98.7	-
Boiling point, °C	to 360		347	250to 310
Density / 15 °C, kg/l	0.820-0.845	0.860-0.900	0.8835	0.7780
Viscosity @ 40 °C, mm ² /s	2.0-4.5	3.50-5.00	4.5	2.9 to 3.5
Cloud point, °C	Max -5		0	-5 to -30
Pour point °C			-13	
CFPP, °C	Max -15			
Flash point, °C	>55	min. 120	>178	>60
Residue of combustion wt%	<0.30	max. 0,30	<0.1	<0.30
Ash, w%	<0.01	max. 0.02	<0.01	<0.001
Sulphur, mg/kg	<50	max. 10,0	<1	0
Cetane number	>51	min. 51.0	<51	84 to 99
Thermal value, gross, MJ/kg	44		40.54	44
Copper corrosion	class 1	class 1	1	
Water content, mg/kg	max 200	max. 500	250	
Contaminants, mg/kg		max 24	7	
Oxidation resistance, g/m ³	max 25			
Oxidation resistance, 110 °C, h		min. 6	>6.3	
Phosphorous, mg/kg		max. 10.0	0.5	
Acid value, mg KOH/g		max 0,50		
Iodine value		max. 120	<113	
Acid number TAN, mg KOH/g		max. 0.50	0.17	
Free glycerol, wt%		max. 0.02	<0.004	
Glycerol, wt%		max. 0.25	0.18	
Monoglycerides, wt%		max. 0.80	<0.01	
Diglycerides, wt%		max. 0.20	0.16	
Triglycerides, wt%		max. 0.20	0.07	
Methanol, wt%		max. 0.20	<0.01	
Na+K, mg/kg		max. 5.0	<2.6	
Ca+Mg, mg/kg		max. 5.0	<0.5	
Linolenic acid ME		max 12.0	<9.5	
>4 double bonds		max. 1	<1	

1.4 Properties of hydrogenated diesels

The hydrogenated biofuels discussed here refer to NExBTL diesel. It is a blend of normal and isoparaffins whose properties match those of best commercial diesel fuels: GTL (Gas to Liquid) fuel and the Swedish MK1 fuel. NExBTL is a sulphur free and aromatic free product with a very high cetane number (Table 3). Its density is the only property that deviates from the requirements of EN 590 standard. NExBTL can be blended with conventional diesel fuel at any ratio. No changes are needed in dispensing systems or vehicles. Unlike esters of vegetable oils, hydrogenated biodiesels do not contain oxygen. Cloud point may be adjusted in production within the range -5 to -30°C (Rantanen, L. et al.).

1.5 Use of biofuels in engines

1.5.1 Ethanol-petrol blends

High blend ethanol fuels (HBEF), which refer to liquid ethanol-petrol blend fuels with an ethanol content of over 10 but under 90 per cent by volume (such as E85), are not meant for conventional vehicles but are only used in flexible fuel vehicles (FFV) designed with a view to the requirements of E85. Conventional vehicles do not even run properly with high blend ethanol fuels.

Ethanol can be blended with conventional petrol in small quantities without adverse effects on vehicles. The current max. limit in Europe is 5 vol%. The EU Commission has proposed raising the limit to 10 % (E10), to be more specific, the proposal sets the maximum amount of oxygen in petrol at 3.7 %.

The German Mineralölwirtschaftsverband e.v. (MWV) addressed the introduction of E10 petrol on 20.3.2007 by expressing its concern for the increase in corrosion damages to the fuel systems of old vehicles. If the corrosion of aluminium starts, it is almost impossible to stop. Aluminium containing components have until recently been used, for example, in fuel injection systems and couplings of fuel pipes.

1.5.2 Methyl esters of vegetable oils (FAME) in diesel motors

European diesel fuel may contain a maximum of 5 % FAME. It is not required to indicate the content or even the fact that the fuel contains FAME. The fuel must meet the currently valid EN 590 specification, and FAME must also meet the valid EN 14214 specification. In principle the European FAME specification was made with a view to RME use. Correspondingly, in the USA the properties of soy oil esters were used as the starting point.

Engine manufacturers naturally approve the use of fuels containing 5 % FAME in all engines. Higher contents may be allowed for specific models up to 100 %. These models have undergone thorough testing including long service tests. For instance, Sisu Diesel Oy allows the use of 100 % FAME in all of its engines (press release 8.11.2007). Oil change interval and the replacement interval for oil and fuel filters must, however, be halved. Sisu Diesel also recommends installing a separate

prefilter in the fuel line. Deutz gives a corresponding requirement for the oil change interval. In addition, they forbid increasing the fuel feed, and accept 80 % of the maximum load approved for diesel fuel. Rubber hoses and possible fuel pump membranes must be replaced annually. It is also advised to replace the fuel filter after 30 to 50 hours of operation when shifting from conventional to high FAME content fuel. Periods of non-use exceeding four weeks should be avoided. (Source: Deutz at Agritechnica, 7.11.2005)

In general, old engines tolerate FAME better than the latest models. Sticking of the needle of the injection nozzle and loss of power with high blend FAME fuels have occurred in new engines incorporating the common-rail fuel system. The problems are aggravated when an engine is started after a long interval. In general, the fuel injection pressure of diesel engines has increased in recent years. High pressure means small clearances and tolerances, which sets higher demands for the purity/cleansing properties of fuel.

2 Objectives of the Biojakelu Project

The introduction of new technology always involves risks that should be recognised and managed to make the business profitable. Liquid biofuels are no exception to this rule. For instance, when ethanol is mixed with petrol at higher blends it causes a new type of ageing stress on the equipment and materials of the fuel dispensing chain: tanks, suction pipes, hoses, gaskets, oil separators, various meters, etc. Even meters designed for dispensing petrol do not necessarily work properly with liquid biofuels without changes. Petrol-ethanol blends also involve a higher ignition risk than currently used fuels, which also sets requirements for the equipment and the dispensing chain for safe dispensing of liquid fuels. If factors related to the safe dispensing of liquid biofuels are not identified and managed in advance, there is the risk of supplying or acquiring the wrong kind of equipment that need to be replaced prematurely, which causes extra costs and interruptions in fuel dispensing. Thus the central question from the perspective of business operations is:

How to ensure the usability of new investments far into the future?

Another perspective is based on history. Against this perspective, another central question for business operation is:

How to ensure the safe operation and functionality of existing fuel filling stations with biofuels?

These were the two central questions that the Biojakelu Project set out to answer.

The general objective of the Biojakelu Project was to develop the readiness of the various companies belonging to the value network for fuel service stations to implement their dispensing of biofuels on a commercially sustainable and safe basis. This work will continue in the companies even after the termination of the Tekes project. Company-specific development interests depend on the place of the company in the value chain. A central objective of energy companies is to develop solutions for the safe management of the entire process from the terminal to the customer's tank throughout the life cycle of the filling station, and thus ensure that different biocomponents can be used in higher blends concentrations. The objective of the manufacturers and suppliers of fuel filling station equipment and systems is products that enable safe, reliable and effective fuel dispensing with biofuels. From the viewpoint of the maintenance of the equipment and systems, correct recognition of maintenance needs is essential. The objective of companies specialising in the design and building of filling stations and dispenser systems is to find and develop safe, workable and environmentally friendly solutions for biofuel dispensing over the entire life cycle of the station.

3 Compatibility of materials and liquid biofuels

3.1 Basic principles

The compatibility of metals with blends of hydrocarbons is non-problematic except in one respect. If water enters/becomes bound to the blend, it results in electrochemical corrosion of the metal. Ethanol has the ability to bind water, which means that the resulting corrosion of metals must be taken into account. Delphi's press release from February of 2007 put it as follows: "People often say that the biggest problem with high ethanol contents is that it is very corrosive, but this isn't true," said Julie Galante-Fox, a biofuels specialist at Delphi's technical centre in Rochester, N.Y. (USA). "The biggest issue is that ethanol is hygroscopic. It absorbs water easily, which causes the fuel to dissolve corrosive salts from any available source it comes into contact with. It's not the ethanol that is corrosive, it's what it brings with it." (Delphi Corporation, Luxemburg, Press Release: February 15, 2007)

The combined effect of ethanol and water is particularly strong with some metals. In chemical terms, ethanol is an acid. Metals that tend to form easily soluble hydroxides in mild acid solutions are susceptible to the combined effect of ethanol and water.

The durability of plastics and rubbers depends on the amount and length of time the material in question absorbs fuel. This is controlled by the difference of the so-called chemical potential (activity) between the molecules in the solution and those absorbed in the material. It can be expressed by the following equation:

Equation 1. $\mu = \mu_o + RT \ln(a/a_o),$

where μ = chemical potential of the substance

R = general gas constant 8.314 J/mol K

T = temperature in degrees Kelvin 273.15 + °C

a = activity of the substance, which at low concentrations is roughly the same as the concentration of the dissolved substance (mol/dm³) in the solutions.

subscript o refers to normal state, that is 273.15 K, 101.325 kPa, 1 mol/dm³ (or 0 °C, 1 atm, 1 mol/l)

The equation includes a temperature factor, meaning that events accelerate with increasing temperatures. The significance of activity is shown, for instance, by the diagram in Figure 3.

Activity of EtOH, Toluene, and Isooctane as a function of ether in ASTM Fuel C

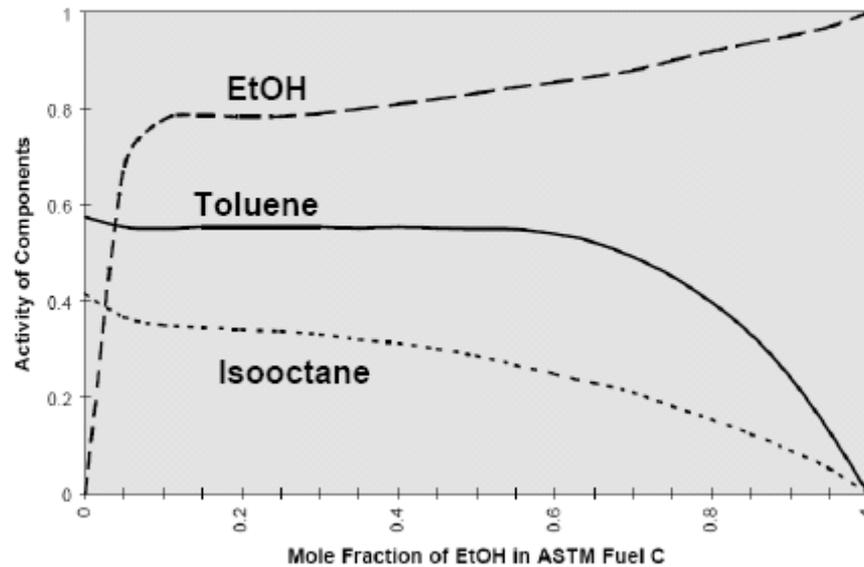


Figure 3. Activity of ethanol, toluene and isooctane in a fuel blend.

Solvent absorbed by plastic/rubber causes various effects such as:

- Chemical reactions with the polymer matrix (dyeing, swelling)
- Extraction of different stabilisers and additives (antioxidants, thermal stabilisers, plasticisers)
- Effects of absorbed solvent on the mechanical properties of the polymer (softening, delamination, becoming brittle)

3.2 Test arrangements

The literature survey at the beginning of the Biojakelu Project on the compatibility of materials used in filling stations with different biofuel blends left many open questions, for which reason the project included extensive tests to gain the necessary understanding. The purpose of the tests was to study the effects of different fuel blends on the materials currently used in the Finnish fuel dispensing chain. The materials were mainly plastics and rubbers. Of metals or metal coated components, zinc-coated parts and aluminium and brass parts were tested. Stainless steel materials were not tested because they are known to withstand all fuels.

Companies participating in the project supplied material samples and preliminary information on whether a certain material came into permanent contact with a liquid fuel or was only exposed to vapours. Fuel may condense intermittently onto surfaces exposed to fuel vapours due to temperature changes. In the tests these materials were tested by pouring just a small amount of fuel into a jar. Thus most of the material was exposed to fuel vapours.

The fuel blends used in the tests, supplied by Neste Oil Corp, were:

- Regular 95 octane petrol (marked BE95),
- Petrol containing 10 vol% ethanol (E10),
- Petrol containing 22 vol% of ethers (MTBE, ETBE; marked BE+EE),
- Fuel containing 85 vol% of ethanol (E85).
- Regular diesel (DIES)
- NExBTL diesel (D100) and
- FAME (RME) ester type biodiesel from rape oil

The compositions of liquid fuels are shown in more detail in Tables 4 and 5.

Table 4. Composition of petrol blends used in the tests of Biojakelu.
(Source: L. Rantanen-Kolehmainen, Neste Oil Oyj)

	Unit	BE95	E10	EtherBE	E85
Density	kg/m ³	750	760	752	787
Aromatics	vol%	34	37	31	5
Alkanes and Cycloalkanes	vol%	45	47	39	7
Olefines	vol%	7	5	6	1
Oxygen content	m%	2,3	3,8	3,9	30
Ethanol	vol%	0	10	0	81
MTBE, TAME ethers	vol%	13	1	23	3
Oxygenates Total	vol%	14	11	24	87

BE95R = Commercial 95 petrol containing ethers as oxygen compounds

E10 = Petrol containing 10 vol% ethanol but no ethers

EtherBE = Ether-petrol blend based on commercial BE95R where the ether content has been increased so that the oxygen content of the blend equals that of E10.

E85 = Fuel with nominal ethanol content of 85 vol%

Table 5 Composition of diesel blends used in the tests of Biojakelu.
(Source: L. Rantanen-Kolehmainen and Martti Mäkelä, Neste Oil Oy)

	Unit	DIR0/-10	NExBTL	FAME(RME)
Densitys	kg/m ³	844	780	883
Aromatics	vol%	20	0	0
Alkanes and Cycloalkanes	vol%	80	100	0
Olefines	vol%	0	0	0
Oxygen content	m%	0	0	11
Oxygenates Total	vol%	0	0	100

DIR 0/-10 = Commercial summer diesel

NExBTL = Hydrogenated vegetable oil diesel, NExBTL

FAME (RME) = rape-methyl-ester biodiesel

Plastic and rubber samples were tested with both 1000 h and 3000 h exposure times. Metal samples were tested with the 3000 h test to reveal possible corrosive effect clearly enough.

Materials supplied for the tests were tested either by submerging them completely in the fuel blend or by pouring only a small amount of fuel in a glass jar, exposing most of the material sample to fuel vapours. After the test period the samples were taken out. Clearly visible changes such as softening and swelling were examined in this connection. After the tests the samples were allowed to dry to standard weight at room temperature and permanent weight changes were determined for the samples weighed before the test.

Pump hoses and underground pipe materials were tested in two ways: by submerging a piece of hose completely in the fuel blend or filling a length of hose sealed at both ends by the liquid fuel.

3.3 Results

3.3.1 General

A general observation based on the results was that a test time of 3000 h for plastic and rubber materials did not yield results different from the test time of 1000 h. Therefore, tests on these materials may in future be conducted with an exposure time of 1000 h. A test time of 3000 h used with metals was sufficient to

reveal some changes. However, the changes were so insignificant that in future a test time of up to 5000 hours is recommended.

The results are presented by material groups below. Test results are also compared with literature survey data. Details on weight changes and visual observations after the tests were reported previously in the confidential research report VTT-R-03571-08.

In the light of the tests, only E85 requires changes in materials. Regular petrol (BE95R), ether containing test petrol (BE+EE) and ethanol containing petrol (E10) had similar effects on materials. All currently used materials can be used with these petrol blends without changes.

NExBTL diesel does not require changes compared with regular diesel. FAME affects elastomers (rubbers) like a plasticiser. This should be taken into account especially in the case of flat gaskets and pump hoses.

3.3.2 Metals

Among metals only electro-galvanised surfaces and unalloyed aluminium had developed incipient pitting in the E85 blend. According to literature, zinc parts are not recommended for use with ethanol, and aluminium should always be given a projective coating. Recommended protective coatings include anodisation (resistant to wear but is electrically insulating) or chemical nickel coating (resistant to wear and is electrically conducting).

Alloyed aluminiums included in the tests performed well. Literature does not give an indication of their usability. The anodisation of aluminium offers an indirect way to examine the compatibility of the material with ethanol containing liquid fuels. The ability of ethanol to absorb water into the blend increases the corrosive properties of the blend. Anodisation is in principle based on the utilisation of the corrosive properties of aluminium. If aluminium can be anodised easily – as pure unalloyed aluminium – it is also highly susceptible to corrosion. High-alloy aluminiums are difficult to anodise, and, accordingly, the resistance of these aluminium grades in the tests corresponds to their anodisation properties.

Brass parts also displayed tarnishing of glossy machined surfaces. This is a normal phenomenon, for example, in urban atmospheres. Brass contains zinc, so it should corrode in ethanol containing liquid fuel blends. According to literature, brass parts may no longer be used with E85 blends. Here the results again contradicted literature data. Brass alloys are used in water pipe fittings, and such brass alloys probably also withstand the effect of ethanol. The zinc content of these brass alloys is clearly under 40 %, and suitable additives have been used to inhibit dezincification.

Other fuels had no effect on the metal samples.

Stainless steel withstands all fuels.

3.3.3 Plastics and elastomers (rubbers)

Hydrocarbons absorbed in plastics caused yellowing. NExBTL diesel was an exception, it did not produce this effect.

Polyolefines (polypropylene and polyethylene) did not dissolve in any liquid fuel blend. Fluoroplastics were also insoluble in any liquid fuel blend.

Filler containing polypropylene lost a bit of its rigidity in other blends except E85. The rigidity loss is caused by the absorption of hydrocarbons between the talcum used as filler and the polypropylene matrix, which in a way lubricate the structure.

Softening due to solvent absorbed through the filler in the material is the more pronounced, the more filler the (plastic) material contains.

PVC is used both for pipes (hard PVC) and cable sheaths (soft PVC). The dissolving of plasticisers from soft PVC cause hardening. The material becomes brittle and cracks and disintegrates over time. During the 3000 h test the material had already become so brittle that the cable sheath cracked when bent. No changes were detected in the hard PVC pipe in the test.

Polyester-type polyurethane (rigid PUR) withstood the 3000 h test well. However, with ethanol blends it lost part of its gloss indicating some reactions.

Chlorinated rubber and nitrile retained their elasticity, as did SBR rubber, although it dissolved and swelled a lot. Conventional vulcanised black rubber used, for instance, in V-belts cannot withstand any liquid fuels.

The durability of rubbers is affected by the type of fillers and the composition of the blend. This was revealed by tests on nitrile rubber samples. Some of the nitrile rubber samples (goose bumps) lost elasticity, some did not. One nitrile rubber swelled at coarse filler particles. This is probably due to the fact that either the blend containing mainly nitrile but also some other material was designated as nitrile rubber, or the roughness of coarse fillers were used. The filler grain size is known to affect elasticity.

Rubbers and plastics are designated according to their main component. Thus the mixing ratios of components, fillers and processing additives may vary greatly between manufacturers. For this reason it is difficult to give an unambiguous recommendation on the durability of a material. It can only be determined by material testing.

3.3.4 Underground fuel pipe systems

Stainless steel pipe samples were not included in the tests because they are known to withstand fuels. There were three pipe materials with polyethylene casing. All three are usable. White corrugated pipe material only yellowed.

No liquid fuel had evaporated from sealed pipe samples through the walls. No changes were observed in them. The zinc-coated plug of the corrugated tube sample had clearly reacted in the E85 blend. This result further confirms the notion that zinc is not suitable for use if the fuel blend contains a lot of alcohol.

It should be noted here that the currently used two-layer pipes are excellent and the older single-layer PE pipes should be replaced with them when changes related to ethanol blends are made at filling stations.

3.3.5 Pump hoses

Current diesel hoses are also well suited for NExBTL liquid fuel. FAME has a softening effect on rubber materials which has to be considered in practice. Only polyester-based polyurethane is suitable for the E85 blend. A hose suited for regular petrol can be used with other liquid fuels (BE95R, E10 and BE+EE) as until now. The test on hoses lasted 3500 h.

3.3.6 Valves, fittings, etc.

Of traditional pipe joints, the glue and flax joint is preferable to mere glue. Glue dissolves, which means that a joint held together by only glue may start to leak over time. Flax retards dissolution and is the better solution.

The 1¼" ball valve was stiff after tests with the E10 ja BE+EE fuel blends. Once the handle could be turned, the stiffness disappeared. It is probably a question of the plastic and steel sticking together which happens when the valve remains for long in the same position. Some NExBTL had seeped between the ball and the gasket. In practice that means that the valve leaks even though it is supposed to be closed.

3.3.7 Tank coatings

Some tested tank coatings (epoxy paints) became clearly duller from contact with the E85 blend. Other liquid fuels did not have a similar effect. During the 3000 h of testing no other changes were observed in the coatings. The dulling is due the slow dissolving of the binder, which in the case of the epoxy paint affects the surface meaning that the protective properties of the coating are not affected. Since it is known that the dullness is the result of less than 2 µm roughness of the surface of the coating, the phenomenon cannot be considered alarming, especially knowing that the recommended tank coating thicknesses are over 200 µm.

3.4 Discussion

Rubbers were the most reactive materials in the tests. Liquid biofuels, with the exception of NExBTL diesel, dissolved rubber materials. In the case of some rubbers this led to their hardening. Despite the dissolving effect, most still retained their elasticity even if they swelled a lot. NExBTL generally only caused swelling and softening in rubbers. Any possible dissolving effect was minor. Regular diesel was no different than NExBTL liquid fuel. FAME had a clear impact on the elasticity of rubbers. It acts like a plasticizer as it is absorbed in elastomers (rubbers). With flat gaskets this may in time cause the gasket to slip out of place. Other effects could not be observed.

Regular BE95R also affected many materials. E10 is not much different from regular 95-octane petrol. According to the results, ether-containing petrol would

appear to be more aggressive toward some rubber materials than other liquid fuel blends. However, there is no big difference compared to regular petrol.

The test fuels contained no water. Water is known to accelerate strongly the corrosion of metals. If entry of water into tanks and fuel lines can be prevented, many problems are avoided. According to literature, E85 may contain a maximum of about 5 wt% of water (about 4.5 vol%). Water causes increased corrosion and blistering of coatings (paints). Blistering of paints can be prevented by selecting paint systems suitable for submersion that also withstand hydrocarbons. These paints are generally two-component epoxy paints.

The inclusion of water changes recommendations as to metals as follows. Carbon steel is corroded by water and must be protected completely, for instance, by coating with an epoxy paint suitable for submersion. The recommendations for aluminium and zinc parts reported earlier do not change. Brass may undergo dezincification with the introduction of water. Thus in fuel lines, it is recommendable to use brass parts in fuel lines that do not suffer from dezincification.

Nylon is the only plastic or rubber material that absorbs water to any appreciable extent. Water strengthens and toughens nylon, and therefore the water absorbed by this material actually improves its properties. Thus, the presence of water cannot be considered to affect adversely nylon materials.

Based on the tests conducted during the project, water separates from the E10 blend together with ethanol into an ethanol-water blend. On the other hand, E85 binds more water to itself, and as the amount of water gets too large, water and ethanol separate into different phases.

According to field data, there have been hardly any problems in relation to condensation water with current petrol grades. Petrols contain ethers which, like ethanol, are polar compounds. Such compounds carry out condensation water at nearly the rate it is created in a tank in a normal situation. Thus, it is likely that condensation water will be no bigger problem with the E10 grade than with the currently used grades of petrol.

Diesel fuel is less capable of binding water than petrol. Pipe samples taken from an old dismantled service station revealed that. The petrol pipes were clean, but the diesel pipe was covered with a thin layer of rust. It appears that condensation water had caused corrosion in the storage tank, and rust had gradually migrated and covered the inner surface of the pipe. The same is likely to hold true also with the NExBTL product.

FAME is a methyl ester of fatty acids. As such, it is prone to biofouling especially if water becomes bound to it. It does not withstand storage as well as other liquid fuels. Due to its composition, it may also form a varnish-type film on some metals. Should it hydrolyze, it produces very weak fatty acids that can react and, thus, corrode metal. On the other hand, the entire product is then also degraded and useless.

3.5 Conclusions and material recommendations

3.5.1 Ethanol-containing fuels

Increasing ethanol content up to 10 vol% requires no changes in materials. Some dispenser equipment manufacturers guarantee resistance of currently used materials up to 15 vol% of ethanol. That was, however, not tested as part of the Biojakelu Project. As ethanol content increases (high blend ethanol fuels, HBEFs), the following restrictions apply.

Metals

The following metals must not come into continuous contact with fuels of high ethanol content.

- galvanised parts
- unanodised, unalloyed aluminium
- brass that has not been inhibited against dezincification

NOTE1! Alloyed/anodised aluminium and brass parts may be used for vapour/filling pipes, but it is better to use more durable materials even for them such as stainless steel (Grade 304).

NOTE2! Anodising (electrolytic oxidation) of aluminium provides a protective surface layer. The anodic oxide film is, however, an insulation meaning that proper earthings must be ensured.

Plastics and rubbers (elastomers)

The following plastics/rubbers must not come into continuous contact with fuels of high ethanol content.

- externally plasticised PVC (electric cabling)
- polyether-based polyurethane
- polyamide (nylon), unless classified for use with fuels
- ordinary black rubber

NOTE! The resistances of the products of different manufacturers vary also in the case of HBEF-resistant plastics and rubbers.

3.5.2 NExBTL diesel

Materials currently used with diesel fuels can also be used with NExBTL.

3.5.3 FAME biodiesel

Actual material changes are not necessary. Yet, in the case of elastomer/rubber parts and, especially, flat gaskets the strong plasticising effect of the substance must be considered. That is likely to require either shorter maintenance intervals compared to systems dispensing diesel, or use of a different material.

With FAME also the following factors are to be taken into account:

- it may form a varnish-type film on some metals (Cu, Fe)
- if it binds water, it could provide favourable conditions for bacterial growth (biofouling).

4 Ignition risks of biofuels

4.1 Basic principles

The ignition of a liquid fuel requires that a relatively large accumulation of energy discharges into an air-fuel blend at a narrow ignition range. Thus, fuel and oxygen (air) in the form of a flammable fuel-air blend and a source of energy that ignites the blend must be present at the same time. That source of ignition may be either heat (fire) or an electrostatic spark where energy discharges as heat. The smallest possible amount of energy that needs to discharge for ignition to happen is the Minimum Ignition Energy (MIE) of the fuel-air blend.

As the content of the flammable substance (liquid fuel) in air become low enough, the energy required to ignite the blend becomes so large that ignition is not possible in practice. This limit is called the lower explosion limit. The upper explosion limit, again, is defined as the limit above which the content of the flammable substance in air is too rich to ignite. The area between these limits is the ignition range which can be defined by flammable substance contents (vol%) of air. Since vapour content over a liquid surface depends on the temperature of the liquid, explosion limits can also be examined in terms of temperatures where the saturated vapour content reaches the lower and upper explosion limit. That gives us the lower and upper ignition temperatures. The flash point may be regarded as the lower explosion limit. Below the lower ignition temperature, the blend is too lean to ignite while above the upper temperature it is too rich to ignite.

Open flames are absolutely forbidden at filling stations, terminals and in their vicinity. That is why the Biojakelu Project focused on the electrostatic spark as the igniting energy source. A spark may result from faulty electrical equipment or the sudden discharge of a local surplus charge (electrostatic discharge). An electric charge is always generated when two different media move in relation to each other. If the generated charge cannot go to earth, it accumulates and the possibility of its uncontrolled discharge exists. A charge accumulates when proper earthings are missing. An unearthed metal object is a highly potential source of an igniting electrostatic spark.

Petrol is a highly flammable liquid of Inflammability Class IIA. Safe dispensing of petrol relies on regulations and recommendations developed on the basis of experience. Ethanol is classified as a more flammable substance than petrol (Class IIB) which requires some changes in the handling and dispensing of the liquid compared to petrol. An ethanol-petrol blend containing a maximum of 90% ethanol falls into inflammability class IIA, but due to the wider ignition range of ethanol over petrol, the conditions under which ethanol-petrol may ignite are wider than with petrol (See Table 2).

The explosion limits of ethers (MTBE, ETBE, TAME) are quite close to those of petrol. Therefore, we may assume that the flammability of ether-petrol (where the

ether components' share of the total liquid volume is significantly smaller than that of petrol) corresponds closely enough to that of "pure" petrol for all practical purposes.

Pure biodiesels or hydrogenated diesels differ hardly at all from regular diesel fuel as to flammability. The flash point of pure diesel is high (>55 °C) which makes its ignition risks small compared to petrol. However, things change if the diesel contains significant amounts of alcohol as a contaminant or intentionally mixed in. Alcohol lowers the flash point sharply making the blend highly flammable under normal conditions. This situation was not studied in the Biojakelu Project.

4.2 Test arrangements

The literature survey at the beginning of the project concerning the ignition risks of liquid biofuels provided some useful data, especially as regards the E85 blend. The data increased further during the project as a broad study on the ignition risks of E85 conducted in Sweden (Persson et al.) was completed and the results became available for this project. Yet, the literature survey left many questions unanswered for which answers were sought through practical tests. The questions we were most keen to get answers for are:

- Which ethanol-petrol blend ratio would require changes to the current practices?
- What are those changes?

The main focus of the tests were the E10 and E85 fuel blends. Literature contained hardly any information on the ignition risks of E10. Information about E85, on the other hand, was too ambiguous which required doing own tests. Regular 95-octane petrol was used as a reference in the tests. Part of the tests were run on a petrol blend containing 22 vol% of ether (BE+EE). Used blends were supplied by Neste Oil Corp. and similar in composition to those of the material tests (Table 4).

The ignition risk tests of the Biojakelu Project targeted two areas: definition of the ignition parameters of liquid fuels conducted at the SWISSI (Swiss Institute for Safety and Security) laboratory in Switzerland and partly at the PTB (Physikalisch-Technische Bundesanstalt) laboratory in Germany, and the liquid fuel charging tests at Autotank's dispenser test bench in Tampere. The vapour pressure, minimum ignition energy and ignition range of tested liquid fuels were measured in order to define ignition parameters.

Fuel charging tests looked into the impact of the various components, filters, suction tubes, hoses and pumping rate on the charging of liquid fuel. The electrical conductivity of fuels was also determined. The charging of liquid fuel was determined by measuring the electric charge that accompanied the fuel as it was discharged from the dispenser into the measuring vessel which was a so-called Faraday cup (that simulates the petrol tank of a passenger car and enables accurate electrostatic charge measurement). Both the person filling the vessel and the vessel were earthed. The liquid fuels for measurements were taken from 50 litre earthed tanks. A series of measurements included about 20 charge

measurements for each liquid fuel. The system was pumped empty of the previous fuel and flushed with the fuel to the measured next before switching blends.

The charge values measured for interpreting the results of charge measurements were converted into the equivalent energy that would have accumulated in a typical passenger car filled with 50 litres in a situation where the earthing of the car was defective. Stored energy was compared to the minimum ignition energy of the fuel to assess any possible ignition risk.

A more detailed report on the test arrangements and results is provided in confidential research reports VTT-R-00799-08 and SWISSI 07.GL.021.307740.

4.3 Results

4.3.1 Ignition parameters

Ignition parameters (flash point, ignition range, MIE) and vapour pressure were determined for the E10 and E85 ethanol-petrol blends and 95-octane petrol (BE95R) to clarify the differences between BE95R and E10. The ignition parameters of the ether-petrol blend were not determined since they were already known to be close to those of petrol. The results as to ignition parameters are presented in Table 6 and those for vapour pressure in Figure 4. The results were complemented with corresponding values for pure ethanol derived from literature (Source: Nabert *et al.*).

Table 6 Key ignition parameters of BE95R, E10, E85 and pure ethanol

	BE95R	E10	E85	Ethanol
Flash point	< -30 °C	< -30 °C	< -30 °C	+12 °C
Lower explosion limit	1.0 vol%	1.3 vol%	3.0 vol%	3.1 vol%
Upper explosion limit	5.8 vol%	6.8 vol%	11.5 vol%	27.7 vol%
Minimum ignition energy [mJ]	0.31 < MIE < 0.38	0.27 < MIE < 0.30	0.30 < MIE < 0.33	

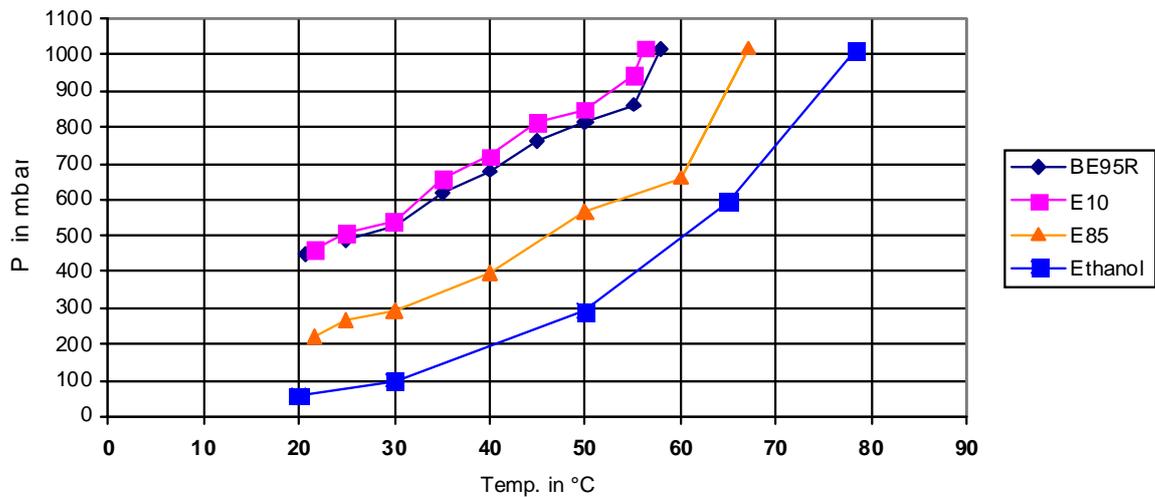


Figure 4 Vapour pressure of BE95R, E10, E85 and ethanol at various temperatures

The results show that the minimum ignition energy of ethanol petrols E10 and E85 is on a level with petrol: all are flammable liquids that are to be handled with care.

The ignition parameters of E10 correspond closely to those of petrol. That means that with E10 no ignitable fuel-air blend forms within the tank under normal conditions since the blend is too rich to ignite. The same applies to ether-petrol.

The ignition range of E85 is wider than with petrol, but not nearly as wide as might appear from just looking at the values of petrol and 100 % ethanol. The vapour pressure of petrol is so much higher than that of ethanol that the bulk of the E85 vapour consists of petrol components. The Swedish test results corroborate this assumption (Persson *et al.*). Thus, petrol – not ethanol – dominates the ignition properties of "fresh" E85 (here "fresh" refers to a liquid fuel blend stored only for a short time in a full tank), and the ignition risks are about the same as with petrol: a flammable liquid fuel-air blend does not form within the E85 tank when a considerable amount of liquid fuel remains there (more than 10-20 %, the amount depends on the blends' vapour pressure and temperature).

The situation regarding the ignition risks of E85 does, however, change essentially if the tank is nearly empty or if it has been warm intermittently (e.g. an aboveground tank in the sun). Then ethanol's share of the E85 vapour increases and the ignition parameters of the blend approach those of ethanol. Tests run with PTB showed that it is possible for an ignitable fuel-air blend to exist within an E85 tank when it is filled to less than 10-20 % of capacity. If the tank fill amount is 1 %, the blend may ignite even at about 20°C (Fig. 5 Brandes *et al.*). The figure also shows that the phenomenon occurs only when the ethanol content of a fuel exceeds about 60 vol%. At lower ethanol contents the ethanol-petrol blends are in practice too rich to ignite.

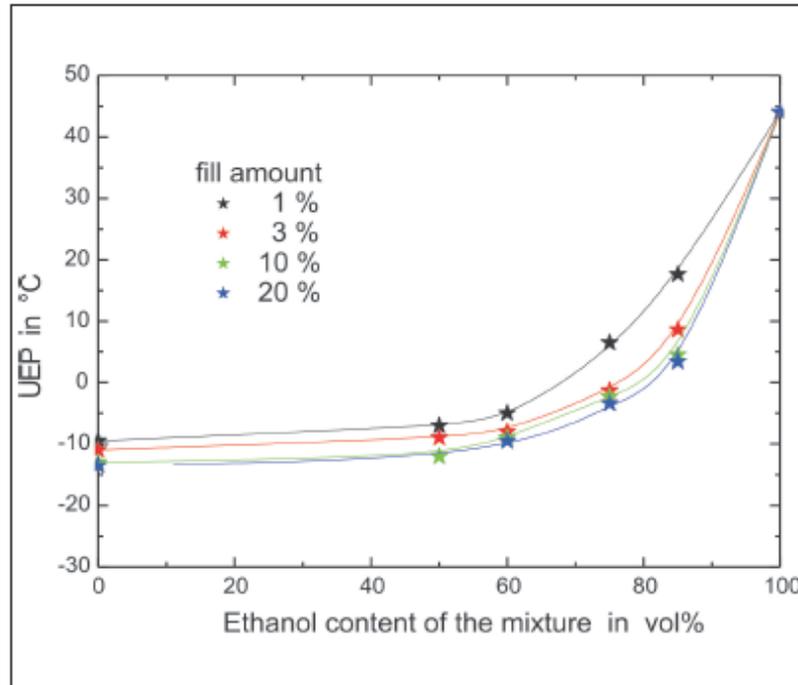


Figure 5 Upper explosion point's dependence on ethanol content of ethanol-petrol blend at different tank fill amounts (Source: Brandes et al.)

4.3.2 Electrical conductivity of liquid fuels

The conductivity of liquid fuels is a major factor in the accumulation of a charge in fuels when system earthings are in good condition. The conductivities of the liquid fuels subjected to measurement of their charge accumulation were determined at 21 °C using the equipment presented in DIN 51412 standard. The results are shown in Figure 6. The conductivity of the ether-petrol used in tests was much the same as that of BE95R. On the other hand, the addition of 10 vol% ethanol increased the electrical conductivity of the liquid fuel blend significantly. In literature, 1000 pS/m conductivity is considered the limit beyond which the risks from electrostatic charging are clearly reduced due to the shorter relaxation time (Smallwood). The conductivity of E10 was already an order of magnitude larger than that limit – not to speak of the high conductivity of E85.

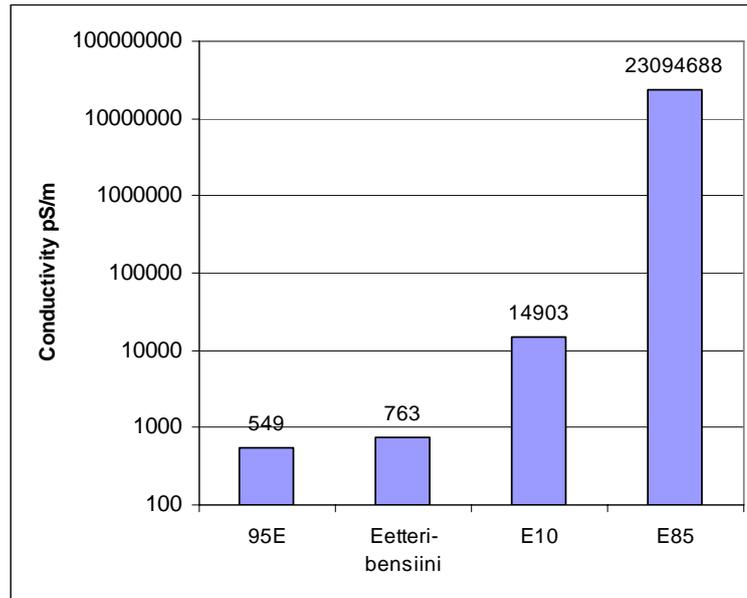


Figure 6 Electrical conductivity of BE95R, ether-petrol, E10 and E85

4.3.3 Accumulation of charge in liquid fuel in fuel dispenser

Fill-up using regular BE95R petrol generated an estimated maximum energy charge of 2.5 mJ in the body of a passenger car which is about 8-fold compared to the 0.3 mJ minimum ignition energy of petrol. The ether-petrol blend became more charged than petrol, the maximum value being about 50-fold to the minimum ignition energy. The results correlate closely with those of a German study (Von Pidoll), where the energy of petrol was 17 mJ in a corresponding situation. Thus, it can be stated that although ether-petrol accumulated a bigger charge than the other tested blends, it did not accumulate an exceptionally strong charge – similar values have been measured from commercial petrols.

During measurement, the charging of the ethanol-petrol blend dropped significantly. With E10 the maximum energy was 0.016 mJ which is far below the minimum ignition energy of the fuel. E85 did not become charged in the used dispenser (i.e. the accumulated charge transferred via the system's earthing route directly to earth and did not migrate with the liquid fuel to the measuring vessel).

Of the various components of the fuel dispenser unit, the entity consisting of the hose and nozzle had a controlling influence on the charging of the liquid fuel flowing into the tank (in the measurements the vessel) excluding the properties of the liquid fuel itself. The hose used in the tests was new. With an old worn hose, of reduced conductivity, the fuel would probably have accumulated a stronger charge. Therefore, attention must be paid to the proper functioning of the nozzle earthing also when dispensing ethanol-petrol. Current earthing instructions, intended for petrol dispensing, can thus also be recommended for the dispensing of E10 and HBEF.

None of the studied liquid fuels accumulated a strong charge in the suction tube. This is probably mainly due to the slow flow rate of liquid fuel at the filling station. In a terminal environment the situation may be different.

4.4 Discussion

There are three areas that require special attention as to ignition risks at a liquid fuel filling station (Fig. 7):

- A) The zone covering the fuel nozzle and the tank's fill spout
- B) Storage tanks
- C) The zone around the storage tank's filler hole and breather pipe.

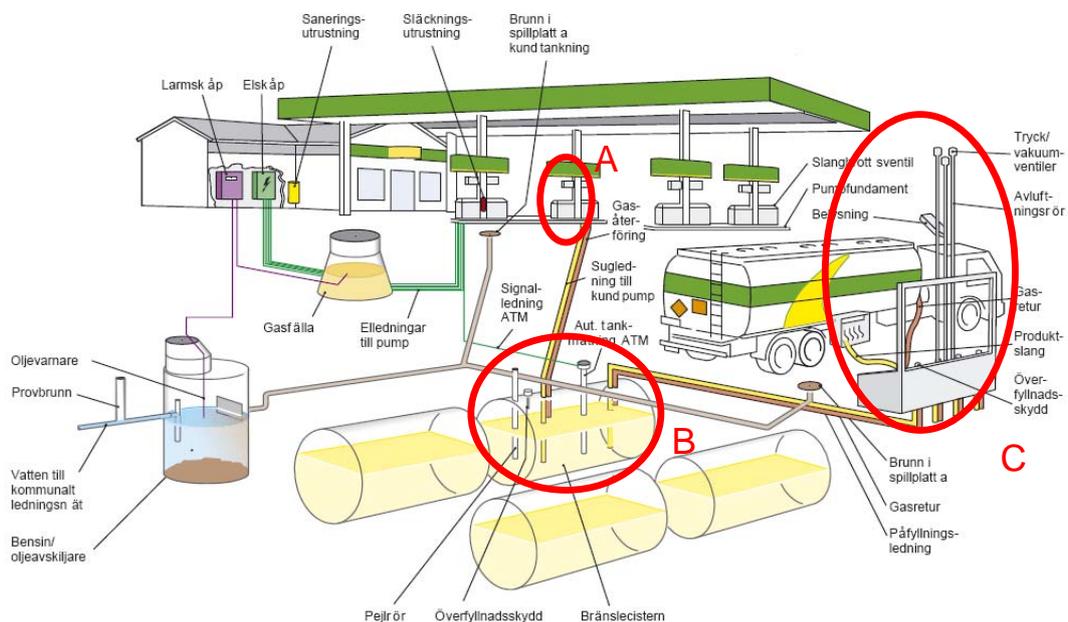


Figure 7 Plan of filling station and areas critical for ignition risks

During normal filling activity the presence of a flammable fuel-air content is probable within the zone formed by the fuel nozzle and the filler hole. In the case of ethanol-petrol blends, the volume of the flammable zone is greater than with regular petrol. However, the volume of the flammable zone can be effectively reduced by introducing Stage II vapour recovery system which is recommended with HBEF dispensers. BE95R and ether-petrol may become dangerously charged but E10 or E85 cannot, as far the system earthings are in proper condition.

Significant ignition risks in relation to liquid fuel storage tanks occur in the dispensing of E85 in situations when the tank is almost empty, i.e. its fill amount is less than 10-20 %. Then a flammable fuel-air blend may be present inside the tank. It requires paying special attention to the elimination of any possible sources of ignition such as:

- elimination of sources of electric sparks by focusing on the control of electrostatic charging and monitoring of the condition of electrical equipment

- prevention of the spread of an external ignition into the tank by a flame arrester element and by locating the tank underground.

Safety can also be improved by keeping the tank always sufficiently full of HBEF. This requires active controlling of the liquid fuel level.

The presence of a flammable concentration in the zone of the storage tank's filler and breather holes is also likely in the normal filling operation of the storage tank. The situation is in many respects like in Zone A of Figure 7.

The results of the charge accumulation tests were interpreted based on the estimated charge accumulated in a normal passenger car in a filling situation. A similar survey may also be conducted on other targets such as metal jerrycans which may accumulate a lot of electrostatic energy unless properly earthed since their capacitance is considerably smaller than a car's. Small capacitance allows high potential and thereby a large accumulation of energy. For instance, the maximum electrostatic energy accumulated in a 20 litre unearthed jerrycan was estimated at 6.5 mJ with BE95R liquid fuel. That is more than the maximum of 2.5 mJ accumulated in the body of a car. With E10 liquid fuel the jerrycan accumulated a maximum of only 0.04 mJ which is still clearly below the minimum ignition energy of the blend. This emphasises the fact that ethanol-petrol is a small step in a safer direction as concerns ignition risks when the dispensing of fuel is in other respects organised responsibly.

4.5 Conclusions

Based on the results of the Biojakelu Project, the introduction of ethanol-petrol is a step in a safer direction compared to the dispensing of regular petrol when fuel is dispensed responsibly in accordance with instructions.

The following safety aspects should nevertheless be considered when dispensing HBEF to ensure that the step improves safety:

- A Stage II vapour recovery system should be incorporated into fuel dispensers. This would allow reducing essentially the volume of the flammable zone around the tank opening. It is recommended that gases are returned to the HBEF tank which increases the petrol vapour content of the tank's airspace. Equipping the fuel dispenser with a flame arrester would for its part improve safety in any possible hazardous situation.
- The presence of a flammable fuel-air content in the HBEF tank must be prevented, or alternately, the ingress of external ignition or spark into the tank by a flame arrester element. The presence of a flammable blend can be prevented by installing the HBEF tank underground in a place of even temperature and by keeping it filled to over 10 % (and by returning the petrol vapours to the HBEF tank). If the presence of a flammable content in the tank cannot be eliminated with certainty, the vent pipe is to be equipped with a proper flame arrester element to minimise ignition risks. Then, it is recommendable to equip also the Stage I vapour recovery pipe with a flame arrester element.

5 Other safety aspects

5.1 Labelling of HBEF grades

High blend ethanol fuels are intended for vehicles whose materials and engine fuel system are designed for HBEF (so-called FFVs). HBEF is not recommended for use in regular vehicles. Thus, HBEF is to be labelled conspicuously (using a different colour) on the bank of pumps and the filling site, and the order of the nozzles is to be standardised.

5.2 Work hygiene

The addition of ethanol to petrol increases slightly the volatility of certain petrol components such as benzene. However, the change is not significant from the viewpoint of work hygiene. Ethanol as such is less harmful to human beings than petrol. Thus, it can be estimated that the exposure of drivers of delivery trucks and service personnel to ethanol-petrol stays clearly below the reference and limit values required by work hygiene. Consequently, the addition of ethanol to petrol does not call for any changes in the methods of preventing exposure to petrol fumes applied today. Appropriate respirators and, where necessary, protective clothing should be available for employees in case something out of the ordinary occurs.

5.3 Overall management

The Biojakelu Project answered the question of what changes are needed in present practices to allow safe dispensing of liquid biofuels. The key changes will be published as annex D of SFS 3352 Standard concerning filling stations for flammable liquids. In order that safe dispensing of liquid biofuels can be realised genuinely and comprehensively, it is necessary to inform all persons who have an impact on the safety and functioning of liquid fuel dispensing of the changes made. They include all members of the business value chain: service station personnel, transportation people, product storage people, authorities and service station installation and maintenance personnel. That requires training and establishment of common rules. The output of the project are hopefully a good opening in that direction.

6 Conclusions

This report is a summary of the key results of the Tekes-supported consortium project called "Biojakelu - Impact of liquid biofuels on the life cycle of fuel station equipment". The focus of the report are the questions concerning the safety issues related to liquid biofuels. The experimental studies of the project focused specifically on the compatibility between the materials used in dispensing liquid biofuels and various liquid biofuels as well as assessment of the ignition risks related to dispensing liquid biofuels and recommending measures to minimise them.

The project gave quite a few direct or indirect answers to the key questions from the viewpoint of the project:

- *How to ensure the usability of new investments far into the future?*
- *How to ensure the safe functioning of currently operating service stations and their compatibility with biofuels?*

Based on the material tests, it can be stated that adding ethanol to petrol up to 10 vol% does not require changes in materials. As the ethanol content increases (high blend ethanol fuels, HBEF), the situation changes. The following materials are not to be placed in continuous contact with liquid fuel of high ethanol content:

- zinc-coated parts
- unanodised, unalloyed aluminium
- brass that has not been inhibited against dezincification
- externally plasticised PVC (electric cabling)
- polyether-based polyurethane
- polyamide (nylon), unless classified for use with fuels
- regular black rubber

The resistances of the products of different manufacturers vary also in the case of HBEF-resistant plastics and rubbers.

As concerns diesel fuels, it may be said that materials currently used for diesel can also be used with NExBTL. FAME biodiesel, on the other hand, has a strong softening effect on elastomers (rubbers) which calls for either a shorter maintenance interval compared to regular diesel dispensing systems or use of a different material. FAME may also form a varnish-type film on some metals (Cu, Fe), and should it bind with water, it can provide favourable conditions for bacterial growth (biofouling).

Ignition risk assessments indicated that introduction of ethanol-petrol is a step in a safer direction compared to dispensing of regular petrol provided that the dispensing of the fuel is realised responsibly and in accordance with instructions. The following safety aspects should nevertheless be considered when dispensing HBEF to ensure that the step improves safety:

- A Stage II vapour recovery system should be incorporated into fuel dispensers
- HBEF dispensers are recommended to be equipped with an appropriate flame arrester element

- The presence of a flammable fuel-air content in the HBEF tank must be prevented by locating the tank underground in even temperature and by keeping it always more than 10 % full
- If a 10 %+ fill amount of the HBEF tank cannot be reliably ensured, the vent pipe of the tank must be equipped with an appropriate flame arrester element.

In final conclusion it can be stated that based on the results of the Biojakelu Project, the introduction of liquid biofuels must be considered on the whole a step in a safer direction compared to the dispensing of petrol. Safe dispensing of petrol is the result of long experience. Biofuels bring some changes to these established practices. As soon as these changes become entrenched, all preconditions for the safe dispensing of liquid biofuels exist.

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