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Biogasoline options for conventional spark-ignition cars

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Title

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Abstract

The purpose of this study is to explore feasible gasoline biocomponents supplementary to ethanol, and to assess their exhaust emissions performance. Although ethanol is the dominant liquid biofuel globally, technical restrictions limit its use in conventional gasoline cars to 10–15 v/v% (bio-energy 7–10%). Since current conventional cars will continue to take the major share of gasoline car fleets for at least the next 10–20 years, it is necessary to establish and assess biocomponent options for them. Today, higher ethanol blending ratios are possible only with the use of flexible fuel vehicle (FFV) technology.

The European Union requires renewable energy to have at least a 10% share of transport energy by 2020, and even higher shares are being attempted regionally. Biocomponents alternative or supplementary to ethanol are therefore desired in the gasoline pool. Interesting gasoline biocomponents are bioethers, biobutanols and biohydrocarbons. Oxygenated and non-oxygenated biocomponents can be combined to increase the bio-share of gasoline.

This study consists of a literature review of the production processes, and an evaluation of the end-use performance of gasoline biocomponents. The results show that there are many options for increasing the bio-energy content of gasoline to 20% or more without increasing the gasoline oxygen content to a higher level than can be tolerated by E10-compatible gasoline cars.

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Executive summary

The purpose of this study is to explore feasible gasoline biocomponents supplementary to ethanol, and to assess their exhaust emissions performance.

Although ethanol is the dominant liquid biofuel globally, technical restrictions limit its use in conventional gasoline cars to 10–15 v/v% (bio-energy 7–10%). However, current conventional cars will continue to take the major share of gasoline car fleets for the next 10–20 years at least, and it is therefore necessary to establish and assess biocomponent options for them. Today, higher ethanol blending ratios are possible only with the use of flexible fuel vehicle (FFV) technology.

The European Union requires renewable energy to have at least a 10% share of transport energy by 2020, and even higher shares are being attempted regionally. Biocomponents alternative or supplementary to ethanol are therefore desired in the gasoline pool. Interesting gasoline biocomponents are bio-ethers, biobutanols and biohydrocarbons. Oxygenated and non-oxygenated biocomponents can be combined to increase the bio-share of gasoline.

This study consists of (a) a literature review of the production processes, and (b) an evaluation of the end-use performance of gasoline biocomponents, based on the literature and experimental work.

PROCESS OPTIONS

The current interest in renewable fuels has led to a substantial investment in the research, development and commercialization of biofuel processes. For biogasoline, efforts have been devoted almost solely to ethanol. However, there are several pathways other than fermentation towards biocomponents for gasoline (Figure 1).

This study focused on the thermochemical routes for the production of gasoline components from biomass. Traditional fermentation routes, as well as etherification, are described briefly as references.

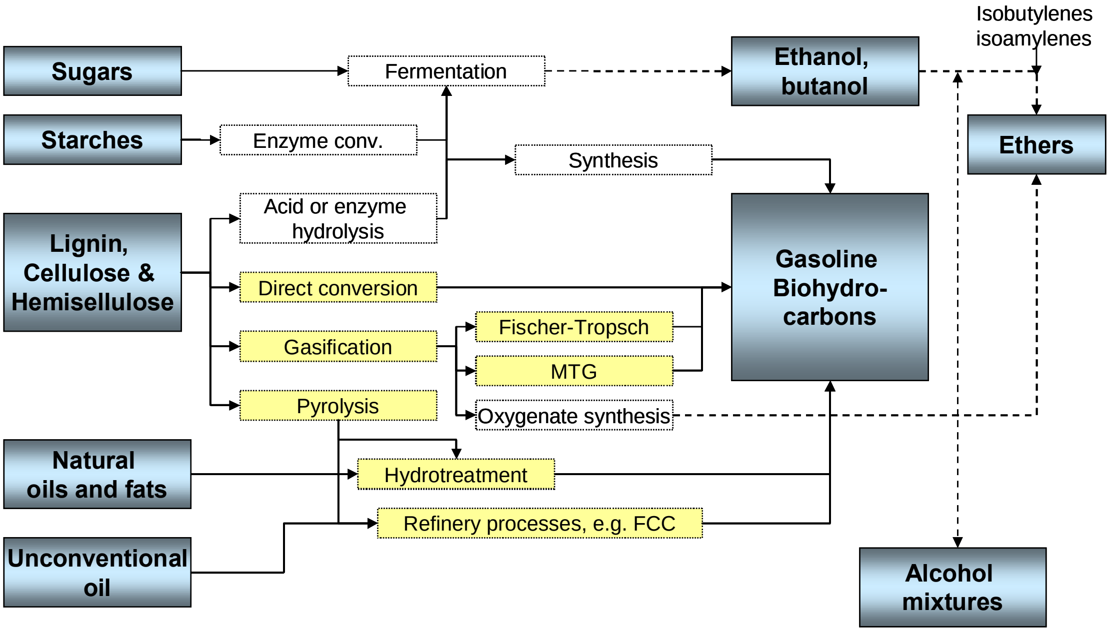

Figure 1. Overview of biogasoline production options (Aakko-Saksa, based on Holmgren et al. 2007, Huber et al. 2006).

Solid, liquid or gaseous hydrocarbon-rich feedstock can be gasified to synthesis gas (CO and H_2), which can be further refined to higher value products. The most prominent thermochemical technologies for gasoline production from fossil feedstocks had already been developed by the 1980s. Biomass-based processes, however, require additional steps such as more thorough gasification gas cleaning.

Thermochemical pathways for producing gasoline from synthesis gas include the methanol-to-gasoline (MTG) and Fischer-Tropsch liquefaction routes. New processes are also under development.

Methanol to gasoline (MTG)

ExxonMobil MTG process – Mobil (currently ExxonMobil Research and Engineering Company) developed their ZSM-5-catalyzed, fixed-bed MTG process in the 1970s. The process included gasification to synthesis gas, the methanol synthesis,

Bio-oxygenates, e.g. ethanol, biobutanol, higher alcohols, bio-ethers.

Biohydrocarbons via gasification/FT or MTG, hydrotreatment (HVO), refinery co-processing, for example.

ExxonMobil MTG: gasification and methanol–DME–gasoline synthesis.

- **Fossil natural gas**-based MTG plant in New Zealand 1986–1996.
- **Fossil coal-based** MTG plants under consideration.

Haldor Topsøe TIGAS: The methanol and DME synthesis are combined.

- **Fossil natural gas**-based demonstration in 1980s.
- **Biomass wood-based** demonstration in Des Plaines, USA.

methanol dehydration to form dimethylether (DME), and further dehydration in the MTG synthesis to form a variety of hydrocarbons. The first industrial-scale natural gas-based MTG plant operated in New Zealand from 1986 to 1996, with production up to approximately 800 000 t/a of gasoline. The conversion of synthesis gas to methanol was approximately 75%, and the methanol to gasoline conversion 100%. Approximately 85–90% of the product hydrocarbons were suitable gasoline components. The MTG process is exothermic, and therefore requires effective heat removal. The catalyst requires frequent regeneration, and is eventually destroyed. An additional distillation step is required to separate methanol from water. However, the process does produce a high yield of sulphur- and nitrogen-free gasoline. The energy efficiency of the process is 50–60% from natural gas and higher if heat is utilized. The fluidized-bed MTG process was demonstrated in Wesseling in 1982–1984.

Several operators have announced their plans to utilize ExxonMobil's MTG technology in fossil coal-to-liquid processes. These include Shanxi Jincheng Anthracite Coal Mining Co. Ltd. (JAM), DKRW Advanced Fuels, and Synthesis Energy Systems.

Haldor Topsøe's MTG process – Haldor Topsøe's integrated gasoline synthesis process (TIGAS) produces gasoline from methanol using ExxonMobil's HZSM-5 catalyst. However, in the TIGAS process, the methanol and DME syntheses are combined in a single synthesis loop. Less steam and a lower pressure are required in the TIGAS process than in the MTG process. A natural gas-based TIGAS process was demonstrated in 1983–1986 in Houston. A biomass-based TIGAS demonstration plant in Des Plaines, USA, start-up in 2012, will convert wood (25 tpd) to gasoline. In future, Topsøe plans to build industrial plants that will use more than 1 000 tpd of wood. The energy efficiency of the wood-based TIGAS process is about 60% and higher if heat is utilized. Topsøe's partners in the project include UPM Kymmene.

Lurgi's MtSynthesis is one option to produce hydrocarbons from methanol, gasoline as a side product.

Fischer-Tropsch process (FT)

One route for converting a variety of feedstocks to liquid fuels is a combination of gasification and Fischer-Tropsch liquefaction. Currently, many companies are utilizing or planning to utilize Fischer-Tropsch technology in diesel production from coal, natural gas or biomass. Only Sasol has an FT-based production line specially designed for gasoline production.

Sasol uses the FT process for gasoline production from coal at the Secunda facility in South Africa (and for diesel and chemicals elsewhere). The current pro-

Gasification and Fischer-Tropsch (FT) liquefaction can be optimized for gasoline, diesel or even methane.

- **Fossil coal-based gasoline** is produced by Sasol in South Africa (up to 875 000 tons/a).
- **Fossil natural gas-based** GTL plants currently produce mainly **diesel**.
- **Biomass-based FT fuels** are not produced commercially.

cess, called the Sasol Advanced Synthol (SAS) process, takes place at high temperature and pressure. The catalyst is iron-based and in fluidized form. The production rate is up to 875 000 t/a (1300–2400 tpd). The product range from the SAS process includes mainly C_1-C_{20} hydrocarbons. In partnership with Qatar Petroleum, Sasol has also built the Oryx GTL plant in Qatar, which produces mainly diesel from natural gas. Highly paraffinic naphtha is produced as a side product and cracked to ethene for the polymer industry.

Virent's "BioForming" process

Virent Energy Systems Inc. has developed a "BioForming" process for producing liquid fuel from various biomass resources. The biomass is first fractionated, and the sugars are processed by an acid hydrolysis or enzymatic technique. The hydrocarbons are either hydrogenated or hydrogenolyzed, and then reformed in an aqueous-phase reforming reactor (APR) to hydrogen, CO_2, alcohols, ketones, aldehydes and alkanes. Organic acids and furans are by-products. The ZSM-5 catalyst can be used to convert suitable oxygenates to gasoline-range hydrocarbons. Kerosene and diesel can also be produced by other refining processes.

Virent Energy Systems Inc. "BioForming" process:
- **Sugars are converted to alkanes**, oxygenates and other compounds.

Virent's BioForming process has the ongoing activities including a new pilot plant and the involvement of a significant industrial partner (i.e. Shell). However, the process includes several catalytic and separation units, indicating high investment costs in the commercialization phase.

Refinery integrated and co-processing

Biofuels can be produced in traditional petroleum refineries. Natural oils and fats can be used as co-feeds in petroleum streams, or in units specifically developed for those feedstocks. FT crude, processed pyrolysis oil and tall oil are also options as feedstocks in refineries. The traceability of the bio-share of products presents challenges in these cases.

Bio-feedstocks can be used in petroleum refineries, e.g. oils, fats, FT crude, processed pyrolysis oil, tall oil, etc.

Products consist of hydrocarbons in the gasoline and diesel distillation ranges, for example.

Several companies currently produce hydrotreated oils and fats commercially to so-called HVO renewable diesel. A gasoline fraction is also formed as a side product. These companies include Neste Oil (NExBTL technology), Petrobras (H-Bio), Galp Energia, UOP/Eni (Ecofining™), Syntroleum (Biofining™), Tyson and ConocoPhillips.

Alcohol processes

Alcohols are produced by the fermentation of sugar- or starch-rich plants. Ligno-cellulosic ethanol production requires additional conversion using enzymatic hydrolysis.

Alcohols can also be produced via thermochemical pathways, e.g. by gasification/alcohol synthesis.

Ethanol is produced commercially by the fermentation of sugar- or starch-rich plants. The conversion of starch crops requires an additional process step involving their hydrolysis into glucose. Ligno-cellulosic ethanol production requires the conversion of biomass cellulose and hemicellulose into fermentable sugars using advanced enzymatic or acid hydrolysis. Alternative routes for converting various biomasses to alcohols include thermochemical processing, for example biomass gasification followed by fermentation.

Biobutanol can be produced from starch and sugar feedstocks or ligno-cellulosic feedstocks using processes resembling those for ethanol. Fossil butanol is produced from propene. The traditional acetone-butanol-ethanol (ABE) fermentation process suffers from low yields of butanol. Currently, most biobutanol production technologies under development are based on fermentation. Piloting or announced production of bio-based butanol are in progress by several companies.

The US company Exelus Inc. has developed catalytic processes for producing higher alcohols from biomass. A mixture of alcohols has a higher octane number, lower blending vapour pressure and higher energy density than does conventional ethanol. The process consists of biomass deconstruction, stabilization, deoxygenation and the separation of water from the product. Exelus has developed a catalyst that is selective for longer carbon chain alcohols.

The Canadian company SyntecBiofuel Inc. has developed a process that converts biomass and municipal solid wastes into ethanol, methanol, n-propanol and n-butanol. The process consists of biomass gasification, syngas cleaning and alcohol synthesis. The mixture of alcohols manufactured by gasification and alcohol synthesis has the trade mark name Ecalene. The product consist of methanol 30%, ethanol 45%, propanol 15%, butanol 7% and hexanol 2%.

Etherification

Fuel ethers are preferred to alcohols as gasoline components. Bio-ETBE, bio-TAEE, bio-MTBE and bio-TAME are produced from bio-ethanol or biomethanol and fossil isobutylenes or isoamylenes.

Fuel ethers are preferred to alcohols as gasoline components. Biomethanol can be converted into methyl-tertiary-butyl-ether (bio-MTBE) and bio-ethanol into ethyl-tertiary-butyl-ether (bio-ETBE) in a catalytic reaction with isobutylene. When biomethanol and ethanol react with isoamylenes, tertiary-amyl-methyl-ether (bio-TAME) and tertiary-amyl-ethyl-ether (bio-TAEE) are produced. Isobutylenes and isoamylenes are currently fossil feedstocks. Production of these ethers is quite simple.

Economics

There is very little publicly available information on the economics of biogasoline processes other than the traditional. The economic evaluations of processes using coal and natural gas are based on low-cost feedstock, and the capacity of the process is usually very high. Biomass is a more expensive feedstock, and plant capacities are small.

END USE OF BIOCOMPONENTS – LITERATURE

Gasoline properties are specified in legislation and standards to ensure the general performance and operability of the fuel in an internal combustion engine, and to take environmental aspects into account. Exhaust emissions from spark-ignition engines can be controlled efficiently using a three-way catalyst (TWC), but only with a stoichiometric air/fuel ratio. Lambda sensors, which monitor this ratio, do not necessarily operate properly with high-oxygen fuels. European legislation therefore imposes a maximum oxygen content in gasoline of 3.7 m/m%. High blending ratios of oxygenates can be used in flexible fuel vehicles (FFV cars), which are equipped with linear-type lambda sensors. Generally, exhaust emissions from cars, and the effect of fuel, are emphasised during cold starts and heavy driving conditions, and at low ambient temperatures. Summary of the end-use aspects of selected gasoline components is shown in Table 1.

Methanol – Up to 3 v/v% methanol is allowed in gasoline in Europe. Methanol is an extremely aggressive alcohol towards materials, and there is a high risk of phase separation, for example. The infrastructure in Europe has not been constructed to tolerate methanol. However, methanol is used as a racing fuel, and in China as a fuel component. Biomethanol can be used in the production of for instance bio-ethers for gasoline (bio-MTBE or bio-TAME).

Ethanol – European legislation allows the blending of 10 v/v% ethanol into gasoline. It increases the volatility of gasoline, which, however, can be adjusted by match-blending. The vapour pressures of ethanol/gasoline blends are at their highest with ethanol contents of 5–10%, and then start to decline. When ethanol is blended into gasoline, volatile organic gas emissions (evaporative and in exhaust gas) increase. Acetaldehyde emissions increase substantially with ethanol, and NO_x emissions may also increase. Ethanol is aggressive towards materials. Ethanol presents a phase-separation risk, and anhydrous ethanol is therefore required for low-level blending. In favour of ethanol are its high octane numbers and reduced particulate matter emissions.

Butanol – European legislation allows a maximum of 15.0 v/v% of butanol isomers to be blended with gasoline. With regard to end-use aspects, butanol offers many benefits compared with ethanol as a gasoline component: higher energy content (lower volumetric fuel consumption), lower vapour pressure (lower evaporative emissions), higher blending ratio, lower water affinity (lower phase-separation risk), less aggressive towards materials and suitable for the current fuel infrastructure. The drawbacks of butanol compared with ethanol concern its lower octane numbers and higher production costs.

The max. oxygen content of gasoline is 3.7 m/m% in Europe. The following **oxygenates** are allowed:

- 3 v/v% methanol
- 10 v/v% ethanol
- 12 v/v% isopropanol
- 15 v/v% tert-butyl alcohol
- 15 v/v% isobutyl alcohol
- 22 v/v% ethers C_5 or C_{5+}
- 15 v/v% other oxygenates.

Biohydrocarbons can be used as gasoline components provided fuel requirements are fulfilled.

Combinations of bio-oxygenates and biohydrocarbons offer pathways towards **high bio-energy fuels compatible with conventional cars**.

Ethers – The conversion of alcohols to ethers produces gasoline components with excellent fuel properties. The octane numbers of ethers are high, and vapour pressures low. Car tests with fuel ethers in gasoline have shown good driveability. Typically, CO and HC emissions are reduced, but NO_x and aldehyde emissions slightly increased, when ethers are used in gasoline. Ethers are compatible with current cars and fuel distribution system. Ethers are not considered to present a risk of phase separation or other water-related problems. Some ethers tend to form peroxides, so stability inhibitor additives are recommended. Ethers have already been used for decades as gasoline components. In Europe, ETBE, MTBE and TAME are used as fuel ethers, whereas MTBE is banned in the USA because leaking storage tanks led to groundwater problems.

E85 – Special flexible fuel vehicles (FFV) can use gasoline containing up to 85% ethanol[1]. Due to the low heating value of E85 fuel, fuel injectors are designed for higher fuel flows than in conventional gasoline cars. Fuel consumption is therefore about 35% higher with E85 fuel than with gasoline. FFV cars must inject excess fuel in cold starts, which leads to increased exhaust emissions until the car has warmed up. E85 fuel generally reduces emissions (CO, HC, NO_x, PM and evaporative) compared with gasoline, but not necessarily at low temperatures. E85 fuel increases acetaldehyde emissions substantially. The most significant barrier to the use of E85 fuel is the need for special FFV cars, infrastructure and safety measures.

Hydrocarbons from biomass – Gasoline-range biohydrocarbons are advantageous because they are fully compatible with conventional gasoline, cars and current infrastruc-

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[1] In the US, so-called P-Series fuel, consisting of butane, pentanes, ethanol and biomass-derived methyltetrahydrofuran (MTHF), is accepted for FFV cars.

ture. However, biohydrocarbons are not consistent with each other. Their properties depend on the production processes and feedstocks used. Product quality ranges from high-aromatic and high-octane qualities to paraffinic low-octane hydrocarbon mixtures. Biogasoline mixtures may contain varying quantities of olefins.

Very limited data are available on the fuel properties or performance of gasoline components obtained by biohydrocarbon processes. No information is available for the new MTG products and other novel processes. Gasoline in South Africa contains components from the gasification/FT process, but it goes through different refinery processes, so different batches are not comparable. Various feedstocks can be used as co-feeds in the refinery. Octane numbers for FCC gasoline are higher when oils and fats are used as feedstocks than when petroleum crude oil is used. When the feedstock is a pyrolysis oil fraction, the gasoline is aromatic. The high olefin or aromatic contents of gasoline components limit their blending ratio in gasoline.

Fuels: Bio-energy share 7–29%, and 78% for the E85 fuel.

Biocomponents: Ethanol, isobutanol, n-butanol, ETBE and renewable hydrocarbon.

Tests

- European driving cycle at -7 °C with three cars: two conventional cars (MPFI, FSI) and an FFV car.
- Regulated and unregulated exhaust emissions. Fuel consumption and CO_2 emissions.

The existing production of hydrotreated renewable diesel (HVO) leads to a gasoline fraction as a side product. This gasoline component is paraffinic, oxygen-, aromatic- and sulphur-free. Exhaust emissions with this component are studied for the first time in this report (experimental part).

HIGH-BIOSHARE GASOLINE – EXPERIMENTAL

Gasoline biocomponents, *isobutanol, n-butanol, renewable hydrocarbon component, ethanol and ETBE,* were studied experimentally. Additionally, a market-grade E85 fuel and a fossil gasoline reference fuel were included in the fuel matrix. The biofuel's bio-energy content was a major parameter in the fuel matrix. The bio-energy share varied from 7–29%, and was 78% for E85 fuel.

- The 7% bio-energy level represented currently used biocomponents, ethanol (10 v/v%) and ETBE (22 v/v%).
- The 14% level represented either butanol or biohydrocarbon alternatives at concentrations of 15–17 v/v%.
- The 21% bio-energy level for conventional cars was achieved by combining non-oxygenated biohydrocarbon with oxygenated biocomponents.

- The 21% bio-energy level for the FFV car was achieved by blending ETBE and/or ethanol with isobutanol or n-butanol (high oxygen content).
- E85 fuel represented the highest bio-energy level, 78%.

The test fuel matrix was divided into two sets: five high-oxygen fuels (6–30 m/m% oxygen) and nine low-oxygen fuels (0–4 m/m% oxygen). Fuels with high oxygen contents are not necessarily compatible with conventional spark-ignition cars. These fuels were therefore tested only with the FFV car. A paraffinic, oxygen-, aromatic- and sulphur-free renewable gasoline component represented liquid biohydrocarbons from different processes. This biogasoline component is a hydrotreated vegetable oil product (HVO) manufactured from vegetable oils and animal fats.

Emissions tests using the European emissions driving cycle were carried out at -7 °C with three cars: multi-point fuel injection car (MPFI), direct-injection car (FSI) and FFV car. The MPFI and FSI cars represent conventional cars, which are not necessarily compatible with high oxygen-containing fuels.

Emissions measurements included both regulated and unregulated exhaust emissions species[2]. Exhaust emissions consist of, for example, carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NO_x), hydrocarbons (HC) and particulate matter emissions (PM). A number of exhaust emissions from mobile sources have also been found to be toxic or to present a risk to human health or the environment, for example 1,3-butadiene, benzene, formaldehyde, acetaldehyde and particulate matter[3]. Polycyclic organic matter, mutagenicity and ozone-forming potential were also studied.

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[2] Different calculation methods for hydrocarbon emissions for E85 fuel are compared in the report.

[3] Results published by Aakko-Saksa, P., Rantanen-Kolehmainen, L., Koponen, P., Engman, A. and Kihlman, J. (2011) Biogasoline options – Possibilities for achieving high bio-share and compatibility with conventional cars. SAE 2011-24-0111. September 2011. (www.sae.org).

Total exhaust risk factors

CO, HC (with and without methane), NO_x, particulate matter, 1,3-butadiene, benzene, formaldehyde and acetaldehyde emissions were included in the calculation of the total risk factors for exhaust emissions[4]. From these, NO_x, particulate matter, 1,3-butadiene and benzene were the most significant contributors. Risk factors for regulated and unregulated emissions were normalized and summarized for each fuel.

In this study, different cars had different responses to fuel changes. However, most biofuels had an exhaust toxicity similar to or lower than that of fossil fuel (Figure 2). This applies to fuels containing ethanol, isobutanol, ETBE and/or renewable hydrocarbon components. The most beneficial emission behaviour was achieved with fuel containing ETBE and the Renewable gasoline at bio-energy content of 21%.

RESULTS – CONVENTIONAL CARS

- o Most biofuels had exhaust toxicity similar to or lower than that of fossil fuel.
- o Indications of increased 1,3-butadiene with butanols.
- o Most beneficial fuel of those studied : ETBE + Renewable gasoline. Bio-energy 21%.
- → **High bio-share, over 20%, is achievable for E10-compatible gasoline cars without increasing oxygen content excessively**.

RESULTS – FFV car

- o Wth E85 fuel exhaust emissions were more noxious than for fossil gasoline, but with E30 fuel similar to gasoline.
- o Most beneficial high-oxygen fuel studied: ethanol + ETBE. Bio-energy 19%.
- → **Low emissions and high bio-energy content are achievable for FFV cars by reducing the ethanol content**.

One of the isobutanol-containing fuels increased the overall exhaust toxicity with the MPFI car, but not with the FSI or FFV cars. n-Butanol-containing fuel indicated an increased overall exhaust toxicity with the FSI and FFV cars. A possible tendency of butanol to form precursors of some harmful exhaust species, such as 1,3-butadiene, warrants further research.

E85 fuel with the FFV car had the highest toxic exhaust emissions risk factor, which was substantially reduced when the ethanol content was reduced from 85 to 30 v/v%. The best emissions behaviour for high-oxygen fuels was achieved with fuel containing 20 v/v% ethanol and 15 v/v% ETBE. In addition, improved engine and emissions control technology is expected to reduce the exhaust toxicity of FFV cars.

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[4] Risk factors for regulated emissions were based on external costs defined in Directive 2009/33/EC and on Finnish national values. Risk factors for the unregulated emissions are based on values defined by OEHHA (2009).

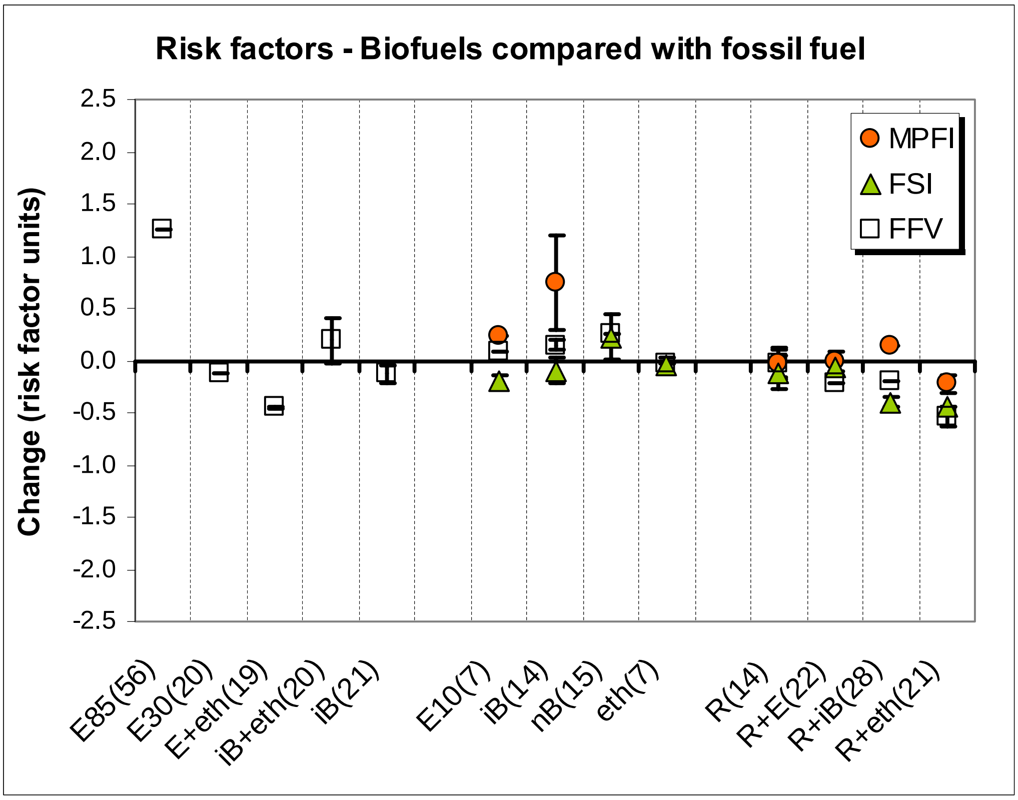

Figure 2. Risk factors for exhaust toxicity calculated from CO, HC (with and without methane), NO_x, particulate matter, 1,3-butadiene, benzene, formaldehyde and acetaldehyde emissions with biofuels compared with fossil gasoline. European test cycle at -7 °C.

Polyaromatic hydrocarbons and the mutagenicity of particles

Little attention has been paid to particulate matter emissions from gasoline cars. Emissions levels have been low for TWC-equipped spark-ignition cars, but this situation is changing with the introduction of direct-injection gasoline technologies. In addition, the ambient temperature has a substantial effect on gasoline car emissions, including particles.

In this study, the direct-injection FSI car was the highest emitter in terms of particle-associated PAH emissions and the mutagenic activity of the particles. With the MPFI car, only minor differences between fuels were observed in the PAH or mutagenicity results.

Hydrocarbon fuels resulted in the highest PAH emissions, while the oxygenated fuels generally reduced PAH emissions. However, with E85 fuel in the FFV car, PAH emissions and the mutagenic activity of particle extracts were elevated.

PAH emissions and **mutagenic activity** (Ames test) of particle extracts:

- The highest emitter was the direct-injection FSI car.
- The oxygenated fuels reduced PAH emissions and the mutagenicity of particles; E85 fuel increased emissions.

Ozone-forming potential

Ethanol used as a low-concentration blend in gasoline had a relatively small impact on the ozone-forming potential of car exhaust gas, whereas a very high ozone forming potential was observed with E85 fuel. Isobutanol and ETBE in fuel slightly increased the ozone-forming potential.

CONCLUSIONS

The purpose of this study was to explore feasible gasoline biocomponents alternative or supplementary to ethanol, and to assess their exhaust emissions performance. When evaluating new fuel components, it is important to ensure that their performance is acceptable throughout the well-to-wheel chain, including production and end-use aspects such as infrastructure, car compatibility, health and environmental effects.

There are limitations in the use of ethanol as a gasoline biocomponent…

Ethanol is the dominant liquid biofuel globally, either as such or as feedstock for ETBE. However, technical restrictions limit the use of ethanol in conventional gasoline cars to 10–15 v/v% (bio-energy 7–10%). Higher ethanol blending ratios are possible with flexible fuel vehicle (FFV) technology.

The biofuel targets for transport energy are challenging. Therefore, biocomponents alternative or supplementary to ethanol are desired for the gasoline pool to *achieve high bio-share fuels compatible with conventional E10-compatible cars*.

There are many biocomponent options…

Ethanol is produced traditionally by fermenting sugars and starches. However, the use of ligno-cellulosic feedstocks requires an advanced enzymatic or acid hydrolysis step. Alcohols could also be produced by gasification followed by fermentation or alcohol synthesis. Biobutanol and higher alcohols can be produced using processes resembling those for ethanol. Alcohols can be converted into ethers, which are preferred to alcohols as gasoline components.

There are pathways for producing gasoline-range hydrocarbons from biomass. Gasoline can be produced via gasification and a "*methanol to gasoline*, *MTG*" liquefaction route, such as Exxon-Mobil's MTG and Haldor Topsøe's TIGAS processes. Gasification and *Fischer-Tropsch liquefaction* are used in diesel production, with a gasoline fraction formed as a side product. Alternatively, the process can be optimized for gasoline production. An example is Sasol's coal-based production line, which is specially designed for gasoline production. Virent Energy Systems Inc. has developed a *"Bio-Forming" process* for producing gasoline from biomass.

Biofuels can be produced in *petroleum refineries*. For example, natural oils and fats, tall oil, FT crude or processed pyrolysis oil could be used as co-feeds in refineries, or in units specifically developed for those feedstocks. Currently oils and fats are hydrotreated commercially by several companies to produce renewable diesel (HVO). As a side product, an renewable gasoline fraction is formed.

End-use aspects must be taken into consideration…

Technical reasons limit blending ratio of ethanol in gasoline. Butanol isomers have many benefits compared with ethanol as a gasoline component. The conversion of bio-alcohols to ethers produces preferred gasoline components with excellent fuel properties. However, the oxygen tolerance of conventional gasoline cars limits the blending ratio for all oxygenates.

Gasoline-range biohydrocarbons are advantageous because they are fully compatible with gasoline, cars and current infrastructure. However, biohydrocarbons are not consistent with each other. Their properties depend on the production processes and feedstocks used.

High bio-energy gasoline options compatible with conventional cars…

Combinations of bio-oxygenates and biohydrocarbons in gasoline were studied experimentally. Biocomponents included *isobutanol, n-butanol, ETBE,* and *a renewable hydrocarbon component* as alternatives or supplementary to ethanol. The results emphasize car emissions at low temperatures (-7 °C).

The results show that there are many options for increasing the bio-energy content of gasoline to 20% or more without increasing the gasoline oxygen content to a higher level than can be tolerated by E10-compatible gasoline cars (Figure 3). This means that various fuels with high bio-energy contents and different chemistries can be used with conventional gasoline-fuelled cars. In most cases, using ethanol, isobutanol, n-butanol, ETBE or blends of these together with renewable hydrocarbon components in gasoline does not significantly or harmfully impact emissions from conventional E10-compatible cars. The preferred combination of a renewable component with oxygenates indicated a reduced exhaust toxicity compared with fossil fuel. A possible tendency of butanol to form precursors of some harmful exhaust species, such as 1,3-butadiene, warrant further studies.

E85 fuel with the FFV car clearly had the most harmful exhaust emissions and the highest ozone-forming potential. These adverse effects can be substantially reduced by using a lower ethanol content, for example 30 v/v%. In this case, the bio-energy content of gasoline could be increased by using biohydrocarbon components. Improved engine and emissions control technology is expected to reduce the exhaust emissions of FFV cars.

The toxicity of gasoline car exhaust particles at low ambient temperatures increases health concerns in general, though this is not primarily a fuel-related problem. In addition, ammonia emissions were high for the cars studied.

Renewable hydrocarbons for gasoline already exist, for example as a side product from renewable HVO diesel production. There are also promising pathways towards gasoline biohydrocarbons from cellulosic feedstocks. These processes and products warrant further studies to evaluate aspects such as economy and well-to-wheel greenhouse gas emissions.

Gasoline biocomponents are summarized in Table 1.

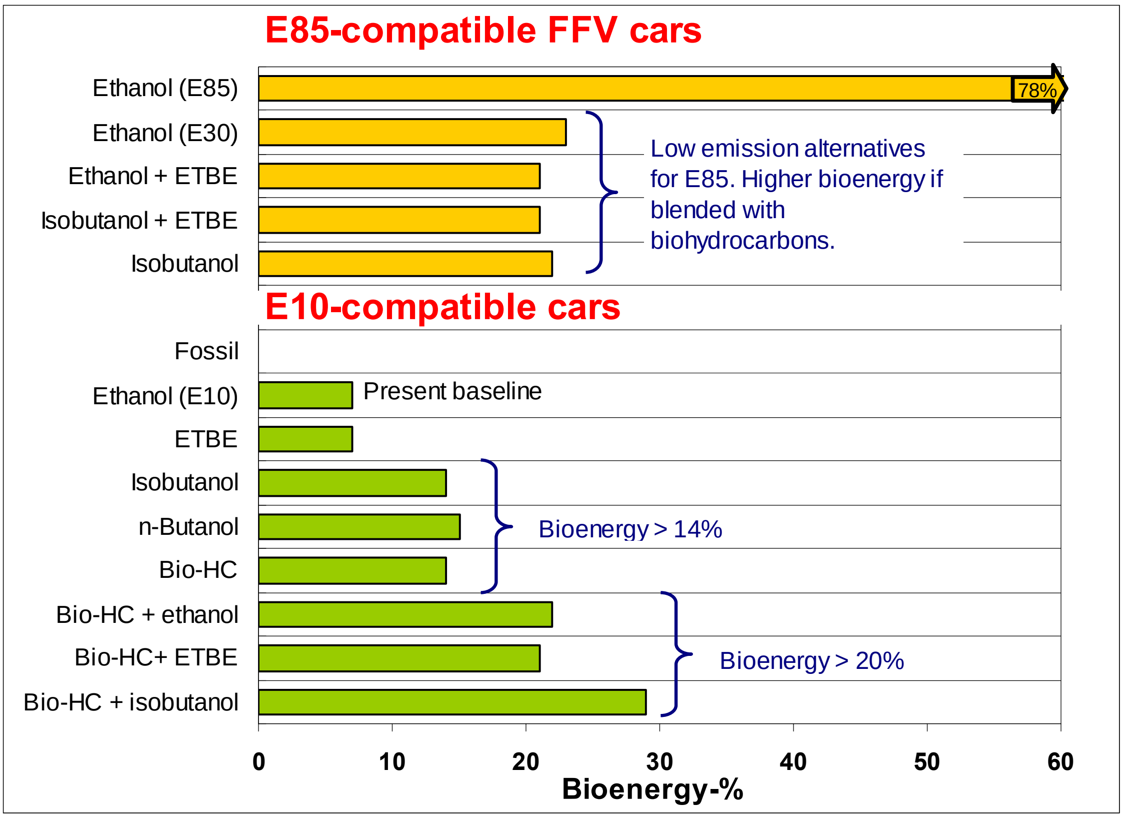

Figure 3. High bio-share fuels for E10-compatible cars are available.

Table 1. Summary of biocomponent options for gasoline.

	Product	End-use "Pros"	End-use "Cons"	Note
Hydrocarbons for gasoline from non-edible feedstocks				
MTG, ExxonMobil: New Zealand / Wesseling – Presently fossil	Alkanes 53/67 wt-% Alkenes 12/6 wt-% Naphthenes 7/7 wt-% Aromatics 28/27 wt-% (Durene: isomerization needed)	+ Compatible hydrocarbons. RON 92.2/96.8 MON 82.6/87.4	No data.	Not commercial currently. Coal-based 0.4–0.8 US$/l [d]. Biomass-based 0.53–0.95 US$/l.
TIGAS	Old demo: C_{5+} 78–80 wt-%, LPG 15–18 wt-%, benzene 0.1 wt-%, some aromatics, naphthenes, olefins[a] Sulphur-free	+ Compatible hydrocarbons. Old demo: (RON+MON)/2=87	No data.	Demo from biomass (wood) in the US.
FT gasoline	Example of 70% Sasol batch: aromatics 32% [a, b]	+ Compatible hydrocarbons. Properties depend on upgrading. Presumably resembles gasoline.	No data.	Commercial from fossil feedstocks. Demos from biomass.
Virent's BTL "BioForming"	Example batch: C_3-C_6 alkanes, some alkenes, aromatics and oxygenates [a]	+ Partially compatible hydrocarbons.	No data.	Under development.
Pyrolysis oil as hydroprocessing feed	Aromatic gasoline [a]	+ Compatible hydrocarbons. Presumably resembles gasoline.	No data.	Under development.
Hydrocarbons for gasoline from edible feedstocks				
HVO gasoline, hydrotreatment of oils and fats	Paraffinic, and oxygen-, aromatic- and sulphur-free renewable gasoline.	+ Compatible hydrocarbons. + Resembles gasoline.	– Low octane numbers.	Commercial (experiments in this report)
Oils and fats as refinery FCC feed	Higher RON than with crude oil feed.	+ Compatible hydrocarbons. Presumably resembles gasoline exhaust.	No data.	
Oxygenated biocomponents for gasoline				
Ethanol up to 10 v/v%	Ethanol	+ High octane numbers. + Reduced PM emissions.	– High volatility. – High evaporative emissions. – High aldehyde emissions. – Limited compatibility. – Phase separation risk. – Aggressive towards materials.	Bio-ethanol commercial from edible feedstocks ~0.6–0.7 US$/lge [d] Bio-ethanol demos from cellulosic feedstocks ~1.1 US$/lge [d]
E85 fuel [c]	Ethanol	+ High octane numbers. + Low CO, HC, NO_x, PM and evaporative emissions at normal temperature.	– Requires special FFV cars and infrastructure. – High acetaldehyde emissions. – High cold-start and cold temperature emissions. – Poor cold startability.	

Butanol up to 15 v/v%	Isobutanol or n-butanol	Compared to E10: + Higher blending ratio. + Lower evaporative emissions. + Higher energy content. + Lower fuel consumption. + Lower phase separation risk.	– Lower octane numbers than for ethanol.	Activities on production from biomass. Higher production costs than for ethanol.
Ethers	ETBE, TAEE, MTBE, TAME	+ Compatible. + High octane numbers. + Low vapour pressure. + Low CO and HC emissions. + No phase separation risk. + High energy content, low fuel consumption. + Good driveability of cars.	– NO_x and aldehyde emissions increase. – Groundwater issues in the case of leakages.	– Commercial from biomass (ETBE).
Methanol	Methanol		– High vapour pressure. – Toxic – Unsuitable for gasoline infrastructure – Extremely aggressive towards materials. – High phase separation risk.	Can be used in ether production.

[a] Volume of aromatics and olefins limited in gasoline. [b] FT crude from SAS: C_1-C_{20}. ~55% olefins, 25% alkanes, 10% oxygenates, 10% aromatics. C_7-C_{11} hydrocarbons into liquid fuels. [c] P-Series fuels for the FFV cars accepted in the USA, but not widely used (butane, pentanes, ethanol, methyltetrahydrofuran). [d] Plant gate prices with certain assumptions. lge = litre gasoline equivalent.

Preface

The European Union requires renewable energy to achieve at least a 10% share of transport energy by 2020, and even higher shares are being attempted regionally. Ethanol is the dominant liquid biofuel globally. However, technical limitations restrict the ethanol content to 10–15% in conventional cars. Higher ethanol blending ratios are possible only by using flexible-fuel vehicle technology (FFV) designed to use any proportion of ethanol and gasoline. Conventional cars, however, will represent the major share of the car fleet for the next 15 to 20 years at least. Alternative fuel options compatible with the existing fleet are therefore needed to increase the bio-share of gasoline above 10% by energy content. This can be achieved by using, for example, combinations of different renewable components and ethanol in gasoline.

In this study, vehicle exhaust emissions and performance were studied for various renewable components in gasoline. Several biogasoline components were included in the fuel matrix: ethanol, ETBE, isobutanol, n-butanol and renewable hydrocarbon gasoline produced from hydrotreated vegetable oils and fats. The bio-energy share in the test fuels varied from 7–29% by energy, and the oxygen content from 0–11%m/m. In addition, fossil gasoline and E85 fuel were used as reference fuels. Experimental work was carried out at -7 °C with three cars: two conventional and one FFV. The measurements included regulated and unregulated exhaust emissions. The results show options for increasing the bio-energy content of gasoline to up to 30% for use with conventional gasoline-fuelled cars.

A literature study on thermo-chemical production processes was carried out in 2009–2011 as part of “Fundamental studies of synthesis gas production based on fluidized-bed gasification of biomass” (UCG-FUNDA) and the TransEco research project “Biogasoline options for conventional cars”. The aim of the study was to gather basic information about the biomass-based production of gasoline and gasoline components, excluding all enzymatic routes. The main focus of the study has been on the process descriptions. A short literature-based economic comparison of the processes has also been included.

This research project, “Biogasoline options for conventional cars”, is a member of the fuel research cluster of the TransEco research programme. Planning and work were carried out by VTT and Neste Oil. The support of the Ministry of Employment and the Economy for this work is acknowledged. The results will also be reported in scientific articles to enable their distribution in international forums. One of the scientific articles is already published[5].

Espoo, December 2011

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[5] Aakko-Saksa, P., Rantanen-Kolehmainen, L., Koponen, P., Engman, A. and Kihlman, J. (2011) Biogasoline options – Possibilities for achieving high bio-share and compatibility with conventional cars. SAE International Journal of Fuels and Lubricants, 4:298-317 (also SAE Technical Paper 2011-24-0111).

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List of abbreviations

AA	Acetaldehyde
Ace	Acenaphthene
Acro	Acrolein
Acy	Acenaphthylene
AFR	Air/fuel ratio
Ald.	Sum of aldehydes
An	Anthracene
Arom.	Aromatic content
APR	Aqueous phase reforming
BaA	Benz[a]anthracene
BaP	Benzo[a]pyrene
BaP	Benzo[a]pyrene equivalent (sum of TEF x mass emissions)
BbF	Benzo[b]fluoranthene
13BD	1,3-Butadiene
BghiP	Benzo[ghi]perylene
BjF	Benzo[j]fluoranthene
BkF	Benzo[k]fluoranthene
Benz., Bz.	Benzene content
BMEP	Brake mean effective pressure
BON	Blending octane number
bpd, bbl/d	Barrels per day
BTEX	Sum of benzene, toluene, ethyl benzene and xylenes
BTG	Biomass to gasoline
BTL	Biomass to liquid
BuA	Butyraldehyde
BzA	Benzaldehyde
CEN	The European Committee for Standardization
CFR	Cooperative Fuel Research(CFR^{TM}) engine
Chr	Chrysene
CrA	Crotonaldehyde

CO	Carbon monoxide
CO_2	Carbon dioxide
CTL	Coal-to-liquid
DBahA	Dibenz[ah]anthracene
DDGS	Dried distiller’s grains with solubles
DI	Direct-injection
DIPE	Diisopropyl ether
DME	Dimethylether
DMBA	7,12-dimethylbenz(a)anthracene
DMSO	Dimethyl sulphoxide
DNPH	Dinitrophenylhydrazine
DOHC	Double overhead camshaft
DVPE	Dry vapour pressure equivalent
E10(7)	Test fuel containing 10% ethanol as 7 E_{eqv}% bio-energy
E30(20)	Test fuel containing 30% ethanol as 20 E_{eqv}% bio-energy
E70, E100	Evaporated (vol-%) at 70 and at 100 °C
E85(56)	Test fuel containing 85% ethanol as 56 E_{eqv}% bio-energy
ECE15	ECE15 portion of the European driving cycle
ECU	Engine control unit
E+eth(19)	Test fuel containing ethanol and ETBE as 19 E_{eqv}% bio-energy
E_{eqv}	Energy equivalent
EGR	Exhaust gas recirculation
ETBE	Ethyl-tertiary-butyl-ether
eth(7)	Test fuel containing ETBE as 7 E_{eqv}% bio-energy
EUDC	Extra-urban driving cycle
F	Fluoranthene
FA	Formaldehyde
FBP	Final Boiling Point
FC	Fuel consumption
FCC	Fluid catalytic cracking
FFV	Flexible-fuel vehicle
FID	Flame ionization detector
FKM	Polymer

Flu	Fluorene
Fossil(0)	Fossil hydrocarbon test fuel, 0 E_{eqv}% bio-energy
FSI	Fuel stratified injection
FT, F-T	Fisher-Tropsch processing technology
FTIR	Fourier transform infrared
FTP	Federal test procedure
GC	Gas chromatography
GTBA	Gasoline-grade tert-butanol
GTL	Gas-to-liquid
H2	Hydrogen
HC	Hydrocarbons
HexA	Hexanal
HPLC	High-performance liquid chromatography
HVO	Hydrotreated vegetable oil, hydroprocessing technology product
hp	Horsepower
HGT	Heavy gasoline treatment
HVP	High vapour pressure
iB(x)	Test fuel containing isobutanol as x E_{eqv}% bio-energy
iB+eth(20)	Test fuel containing isobutanol and ETBE as 20 E_{eqv}% bio-energy
IDI	Indirect-injection
IEA	International Energy Agency
IP	Indeno[1,2,3-cd]pyrene
IR	Infrared
JAM	Shanxi Jincheng Anthracite Coal Mining Co. Ltd.
lge	Litres gasoline equivalent
LHV	Lower heating value, corresponding net calorific value or lower calorific value
M85	Fuel containing 85% methanol
MeCr	Methacrolein
m/m%	Mass per mass percentage
MIR	Maximum incremental reactivity
MON	Motor octane number

MPFI	Multi-port fuel injection
MS	Mass Spectrometry
MTBE	Methyl-tertiary-butyl-ether
MTG	Methanol to gasoline
MTHF	Methyltetrahydrofuran
mTol	m-Tolualdehyde
N	Nitrogen; naphthalene if in PAH context
nB(15)	Test fuel containing n-butanol as 15 E_{eqv}% bio-energy
NEDC	New European driving cycle
NExBTL	Neste Oil's proprietary hydrotreatment process and product using vegetable oil or animal fat as feedstock
NH_3	Ammonia
NMHC	Non-methane hydrocarbons
NMOG	Non-methane organic gases
nm	Nanometre
NO_3	Nitrates
NO_x	Nitrogen oxides (NO and NO_2)
NO_2	Nitrogen dioxide
N_2O	Nitrous oxide
O	Oxygen
OBD	On-board diagnostics
OFP	Ozone-forming potential
P	Pyrene
PAH	Polyaromatic hydrocarbons
PAN	Peroxyacetyl nitrate
Phe	Phenanthrene
PM	Particulate matter
POM	Polycyclic organic matter
PrA	Propionaldehyde
P-Series fuel	Accepted in the USA for FFV cars, consisting of butane, pentanes, ethanol and MTHF
R	Renewable gasoline component, non-oxygenated hydrocarbons
R(14)	Test fuel containing R as 14 E_{eqv}% bio-energy

R+iB(28)	Test fuel containing R and isobutanol as 14 E_{eqv}% bio-energy
R+E(22)	Test fuel containing R and ethanol as 22 E_{eqv}% bio-energy
R+eth(21)	Test fuel containing R and ETBE as 21 E_{eqv}% bio-energy
RHO	Carbonyl compounds
ROH	Alcohols
RON	Research octane number
RPM	Rounds per minute
RVP	Reid vapour pressure
S	Sulphur
SAS	Sasol advanced synthesis
SOF	Soluble organic fraction of particulate matter
SI	Spark ignition
T50	Temperature at which 50 vol-% of fuel is evaporated
TBA	Tert-butanol
TAEE	Tertiary-amyl-ethyl-ether
TAME	Tertiary-amyl-methyl-ether
TEF	Relative toxic equivalency factor for individual PAH compound
TIGAS	Topsøe integrated gasoline synthesis
THC	Total hydrocarbons
tpd	Tonnes per day
TSI	Turbo stratified injection
TWC	Three-way catalyst
URF	Unit risk factor
VA	Valeraldehyde
VOC	Volatile organic compounds
vol-%	Volume percentage
VP	Vapour pressure
v/v%	Volume per volume percentage
wt-%	Weight percentage
ZSM	Zeolite-Socony-Mobil
XTL	GTL, BTL and CTL
ΔrH	Enthalpy, kJ/mol

1. Introduction

There are many options for gasoline biocomponents. Oxygenates, such as alcohols and ethers, have been used as gasoline components for decades. At first, the motivation for using oxygenates was to increase the octane numbers of gasoline; it then shifted to using ethers to reduce exhaust emissions. Now, if produced from biomass, oxygenates could provide a biocomponent contribution to gasoline.

Ethanol is the dominant biocomponent in gasoline. Traditionally, ethanol has been produced from sugar-rich crops, but now processes to utilize lignocellulosic non-edible feedstocks are being developed. Ethanol can be blended up to some 10–15% (bioenergy 7–10%) in gasoline while maintaining compatibility with conventional cars. In the USA, this so-called “blending wall” has already been reached. In Brazil, cars are modified for gasoline containing up to some 25% ethanol. High ethanol blending ratios are possible only with the use of flexible-fuel vehicle technology (FFV). However, conventional cars will represent the major share of the car fleet for the next 15–20 years at least.

Biocomponents other than ethanol could also be blended into gasoline, for example ethers, butanol and biohydrocarbons. Many options are more compatible than ethanol with gasoline cars and current infrastructure. In particular, non-oxygenated hydrocarbons could be options. Synthetic hydrocarbon fuel from coal and natural gas, “FT gasoline”, has been used for a long time in South Africa. Gasoline-range hydrocarbons can also be obtained from biomass using other processes. However, the technical and economic feasibility of production processes vary, and the availability of sustainable feedstocks is another issue. The selection of the optimal feedstock, process and end product is complicated, particularly when regional differences are taken into account.

The European Union requires renewable energy to achieve at least a 10% share of transport energy by 2020, and even higher shares are being attempted regionally. Alternative fuel options that are compatible with the existing car fleet are therefore needed to increase the bio-share of gasoline above 10% by energy content. This study explores possibilities for increasing the bio-share in gasoline by using, for example, combinations of different renewable components and ethanol in gasoline.

Content of this study

In this study, various gasoline components and combinations are studied. Feedstock issues are not considered here. Instead, the focus is on the following tasks:

- Production processes for gasoline biocomponents
- End-use properties of biogasoline options
- Experimental work with the selected biogasoline options.

With regard to production processes, the literature study excludes the production of ethanol because those issues are covered in a number of other studies. The main attention is given here to thermochemical processes. The fuel properties of potential biocomponents for gasoline and their compatibility with the current car fleet and infrastructure are evaluated. Laboratory tests are carried out to study the compatibility of selected fuel candidates for conventional spark-ignition cars. In the experimental part, the performance and exhaust emissions of fuel components are studied with cars over defined test cycles on a chassis dynamometer.

2. Production processes

Ethanol and ETBE are predominantly used in gasoline by EU member states to meet renewable energy targets. In addition, mature production processes exist for bio-origin ethers other than ETBE, i.e. bio-MTBE, bio-TAME and bio-TAEE.

New production processes are under development. Biobutanol is regarded as a promising biocomponent for gasoline. In addition, the production of a number of liquid biohydrocarbon components could be feasible from thermochemical processes, for example:

- ***Gasification combined with Fischer-Tropsch***
- ***Gasification combined with "Methanol-To-Gasoline"***
- ***Hydroprocessing of oils and fats (HVO gasoline)***
- ***Refinery-based processes, e.g. pyrolysis oil as co-feed.***

Biobutanol or gasoline biohydrocarbons are not yet commercially available. HVO gasoline is a side product of existing HVO biodiesel production.

There is very little publicly available information on the economics of biogasoline processes other than the traditional. However, economic evaluations of thermochemical processes for obtaining gasoline biocomponents seem promising.

2.1 General

The current interest in renewable fuels has led to a substantial investment in the research, development and commercialization of biofuel processes. For biogasoline, efforts to date have been devoted almost solely to ethanol. Biohydrocarbons for gasoline are much less studied. In the literature study of production processes, the purpose was to collect publicly available information on the thermochemical production routes for gasoline from biomass. Fermentation routes, as well as etherification, are described briefly as references. An overview of biofuel production options is shown in Figure 2.1.

Thermochemical conversion routes include processes in which solid, liquid or gaseous hydrocarbon-rich feedstock is gasified and catalytically conditioned to synthesis gas, which then can be further refined to higher value products such as gasoline and diesel. Synthesis gas is a mixture of carbon monoxide (CO) and hydrogen (H_2) that can be converted to various fuels and chemicals (Figure 2.2). The most prominent thermochemical technologies for gasoline production depicted in this report had already been developed by the 1980s for the utilization of coal or natural gas supplies. However, biomass-based processes would require additional steps, for example more thorough gasification gas cleaning.

The Fischer-Tropsch (FT) process is a common liquefaction process for synthesis gas. Coal-to-liquids (CTL) and gas-to-liquids (GTL) processes are well-known technologies today, and the development of a gasification/FT process to utilize biomass is in progress. Gasoline production using Fischer-Tropsch technology was covered only briefly in this study, because the principal product of the process is usually diesel.

The emphasis of this work was on thermochemical pathways for producing gasoline from synthesis gas, particularly the methanol-to-gasoline route (MTG). In this respect, ExxonMobil’s MTG process and Haldor Topsøe’s TIGAS process were covered. However, less well known technologies were also reported in as much detail as was possible to obtain from public sources.

Biofuels can also be produced in traditional petroleum refineries. Natural oils and fats can be used as a co-feed in petroleum streams, or as such in units specifically developed for those feedstocks. Cellulosic feedstock could be converted into pyrolysis oil, which could be further processed in petroleum refineries (Holmgren et al. 2007). FT crude is also an option as a feedstock for refineries. These options are only briefly covered in this literature review.

In addition to fermentation, alcohols can be produced with thermochemical processes. Summary of current status of MTG, FT gasoline and thermochemical butanol processes is presented in Table 2.1.

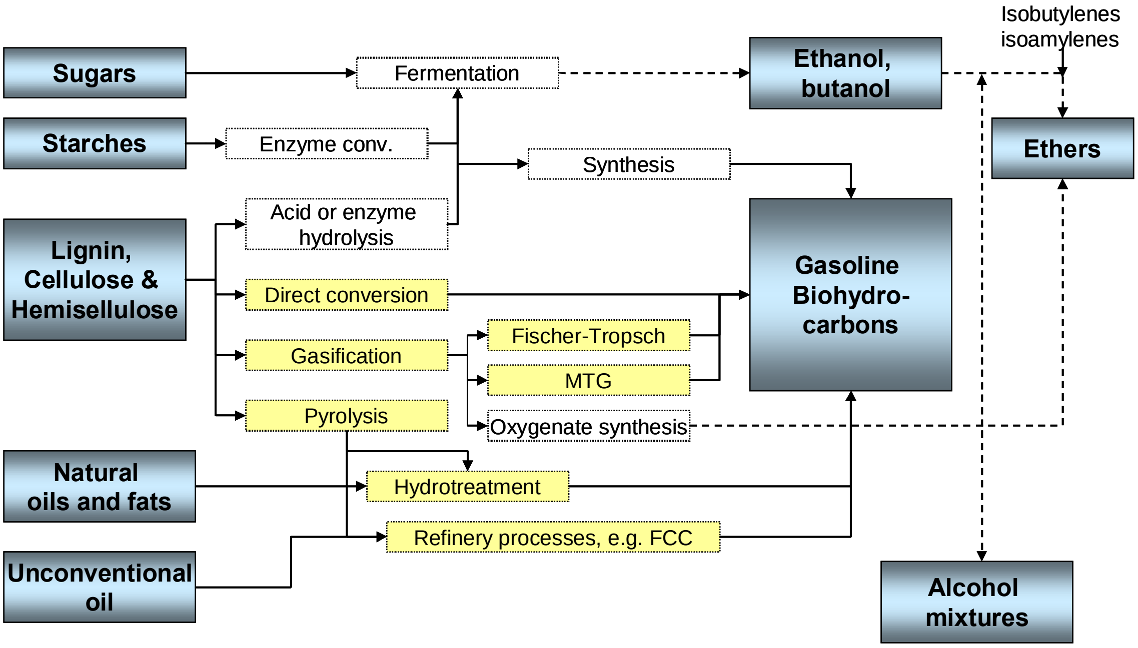


Figure 2.1. Overview of biogasoline production options (Aakko-Saksa based on Holmgren et al. 2007, Huber et al. 2006).

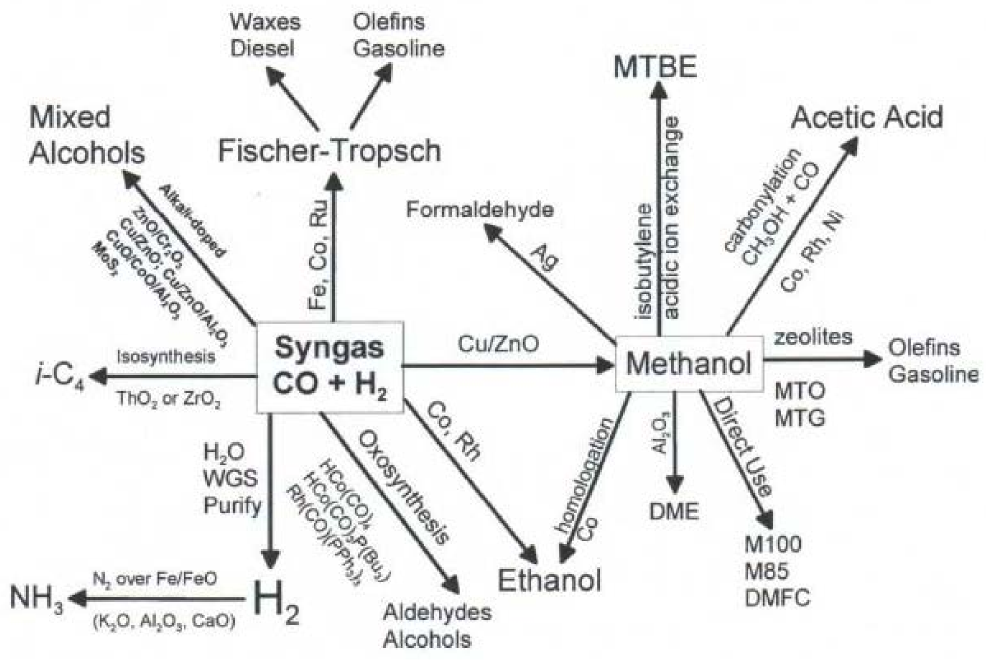
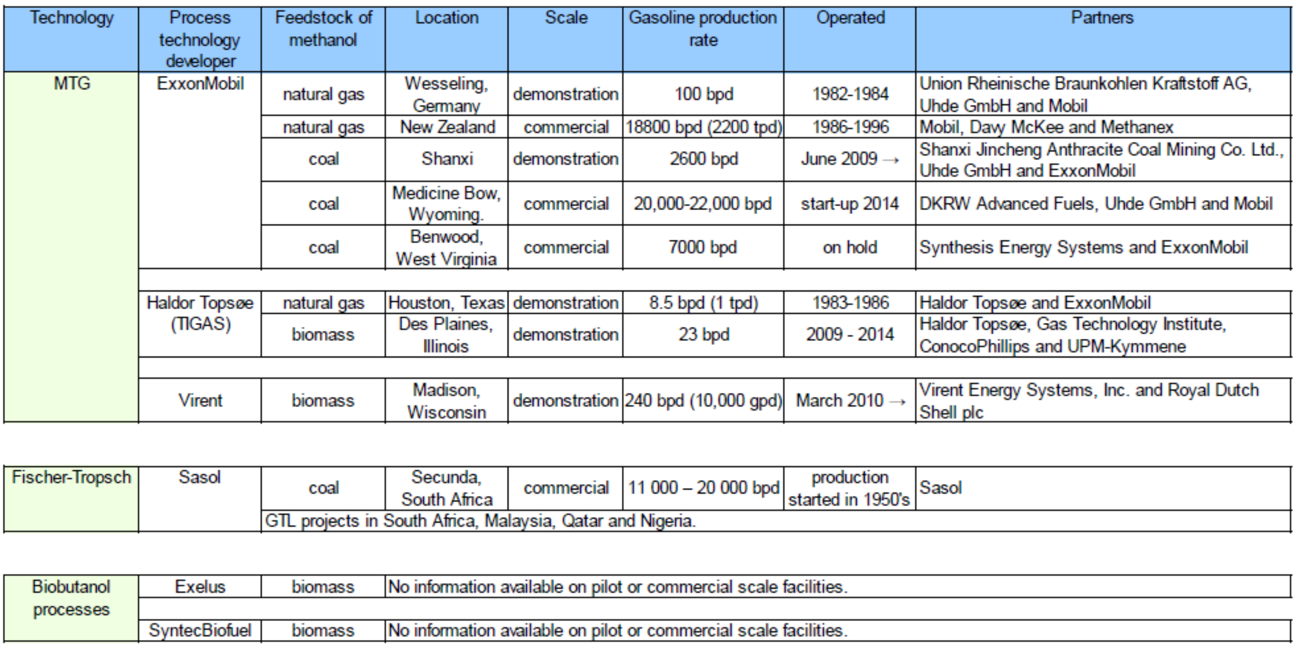


Figure 2.2. Synthesis gas process options (Dayton 2007).

Table 2.1. Summary of current status of MTG, FT gasoline and thermochemical butanol processes.



Technology	Process technology developer	Feedstock of methanol	Location	Scale	Gasoline production rate	Operated	Partners
MTG	ExxonMobil	natural gas	Wesseling, Germany	demonstration	100 bpd	1982-1984	Union Rheinische Braunkohlen Kraftstoff AG, Uhde GmbH and Mobil
		natural gas	New Zealand	commercial	18800 bpd (2200 tpd)	1986-1996	Mobil, Davy McKee and Methanex
		coal	Shanxi	demonstration	2600 bpd	June 2009 →	Shanxi Jincheng Anthracite Coal Mining Co. Ltd., Uhde GmbH and ExxonMobil
		coal	Medicine Bow, Wyoming.	commercial	20,000-22,000 bpd	start-up 2014	DKRW Advanced Fuels, Uhde GmbH and Mobil
		coal	Benwood, West Virginia	commercial	7000 bpd	on hold	Synthesis Energy Systems and ExxonMobil
	Haldor Topsøe (TIGAS)	natural gas	Houston, Texas	demonstration	8.5 bpd (1 tpd)	1983-1986	Haldor Topsøe and ExxonMobil
		biomass	Des Plaines, Illinois	demonstration	23 bpd	2009 - 2014	Haldor Topsøe, Gas Technology Institute, ConocoPhillips and UPM-Kymmene
	Virent	biomass	Madison, Wisconsin	demonstration	240 bpd (10,000 gpd)	March 2010 →	Virent Energy Systems, Inc. and Royal Dutch Shell plc
Fischer-Tropsch	Sasol	coal	Secunda, South Africa	commercial	11 000 – 20 000 bpd	production started in 1950's	Sasol
		GTL projects in South Africa, Malaysia, Qatar and Nigeria.					
Biobutanol processes	Exelus	biomass	No information available on pilot or commercial scale facilities.				
	SyntecBiofuel	biomass	No information available on pilot or commercial scale facilities.				

2.2 Alcohol processes

Methanol production

Biomethanol was once produced by the destructive distillation of wood. Today, methanol is mainly produced from fossil natural gas by gasification to synthesis gas and liquefaction step. However, biomass could be used instead of natural gas as feedstock. Methanol can be further converted into hydrocarbon fuels as presented in Chapter 2.4.

Worldwide methanol production was 45.6 million metric tons in 2010. About 18% of methanol was used as fuel. Methanol was used as MTBE in Europe and Asia, and also as such in China. Not much biomethanol is produced or used as fuel. (Methanol institute 2011). Chemrec AB, BioMCN and Carbon Recycling International have activities on biomethanol.

Ethanol production

Ethanol is produced commercially by the fermentation of sugar-rich feedstocks, such as sugarcane, sugar beet and sweet sorghum, or starch-rich plants such as wheat and corn (Sims et al. 2008, IEA 2011). The conversion of starch crops requires an additional process step over the conversion of sugar crops into ethanol: starch must be hydrolyzed into glucose. The economics of the starch-based process depend on the value of co-products, such as dried distiller's grains with solubles (DDGS) and fructose (IEA 2011).

Ligno-cellulosic ethanol can be produced by the conversion of biomass cellulose and hemicellulose into fermentable sugars by advanced enzymatic hydrolysis or acid hydrolysis. The sugars are further fermented into ethanol. Cellulosic ethanol can perform better than starch-based biofuels in terms of energy balance, GHG emissions and land-use requirements (IEA 2011, Sims et al. 2008).

Alternative routes for converting various biomasses to alcohols include thermochemical processing, for example biomass gasification followed by alcohol synthesis (Anon. 17, Syntec Biofuel). Alcohols can also be produced by gasification followed by fermentation (Datar et al. 2004). The biochemical production of ligno-cellulosic ethanol has been covered in a recent publication by Suokko (2010).

Production of biomethanol by wood distillation is a historical process. Today, biomethanol is produced from glycerol. However, biomethanol could be produced from any biomass that can be converted first into synthesis gas (Methanol Institute 2011).

Butanol by fermentation

The production of butanol from biomass has attracted much less interest than that of ethanol. However, butanol is more suitable than ethanol as a gasoline substitute. Butanol has a higher energy density, it can be distributed with existing fuel pipelines and it can be blended with gasoline up to 40% (Shapovalov and Ashkinazi 2008; Demain 2009; De Guzman 2009). Biobutanol can be produced from starch and sugar feedstocks or from ligno-cellulosic feedstocks using processes resembling those used for ethanol. The so-called acetone-butanol-ethanol (ABE) fermentation process, using bacteria such as *Clostridium acetobutylicum,* can be used for the production of biobutanol from sugar (IEA 2011). However, yields of butanol tend to be low, and butanol is inhibitory towards the bacteria traditionally used (Ramey and Yang 2004).

Currently, most biobutanol production technologies are based on fermentation. For example, Butamax Advanced Biofuels LLC (a joint venture between BP p.l.c. and DuPont) (Anon. 12, Butamax 2010), Swiss Butalco GmbH (Anon. 13, Butalco 2010), American Gevo Inc (Anon. 14, Gevo 2010) and ButylFuel LLC (ButylFuel 2010) have developed their own fermentation-based biobutanol processes. Advanced Biofuels LLC (a joint venture of BP and DuPont) has piloting and optimization phases in progress for bringing bio-based butanol to the market. Results were published first for n-butanol, but isobutanol is mentioned later in this context (Hess 2007, Anon. 12). Potera (2009) announced a process for producing isobutanol from glucose using a genetically altered strain of *E. coli* bacteria. In Russia, a biobutanol factory using woody biomass is expected in 2011 (ETP 2011).

Butanol by catalytic process

Butanol is produced traditionally from petroleum-derived propene using the oxo process. First, propene is hydroformylated with a rhodium-, ruthenium- or cobalt-based catalyst, yielding aldehydes. Hydrogenation of the aldehydes produces n- and isobutanol. The production costs for the oxo process are high compared with those for petroleum-derived gasoline production. The oxo process has therefore not been regarded as a suitable route for biofuel production. The butanol produced by the oxo process is used mainly as a solvent or as a precursor for other chemicals (Shapovalov and Ashkinazi 2008; Burridge 2004).

Fermentation is the primary technology considered for the production of fuel biobutanol. Only a few technologies have been developed for producing biobutanol without fermentation. Typically, butanol is one of the product components in these processes. The US company Exelus Inc. engineers and licenses catalytic processes. Their biomass-to-gasoline (BTG) process produces a mixture of alcohols with a higher octane number ((RON+MON)/2 > 105), lower blending vapour pressure and higher energy density than those of conventional ethanol. The process consists of biomass deconstruction, stabilization and deoxygenation, and the separation of water and the product (Figure 2.3). Biomass deconstruction is achieved without any biological methods in a liquid-phase reactor. The reaction temperature is about 200 ºC. Undegraded lignin is separated from the liquid product. Both stabilization and deoxygenation take place in a fixed-bed reactor. Exelus has developed a novel catalyst for the deoxygenation. The catalyst is highly selective for longer carbon chain alcohols instead of low-value methane and ethane. The process can use any kind of biomass, such as wood, grass and agricultural waste. The process reactants, for example water and hydrogen, can be produced internally (Anon.16 Exelus).

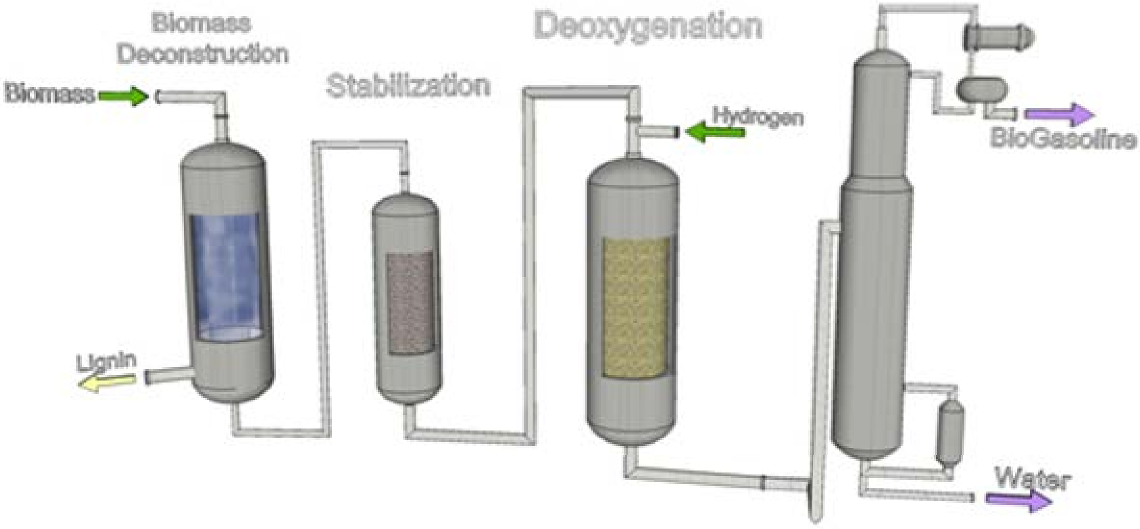


Figure 2.3. Exelus biomass-to-gasoline process. Figure by Exelus (Anon.16).

A Canadian company, SyntecBiofuel Inc., has developed a process that converts biomass and municipal solid wastes into ethanol, methanol, n-propanol and n-butanol (Anon.17 Syntec Biofuel). The process catalysts are also designed by SyntecBiofuel. The process consists of biomass gasification, syngas cleaning, alcohol synthesis in a series of fixed-bed reactors and the separation of alcohols by distillation (Figure 2.4). SyntecBiofuel has one patent (US7384987) (Iordache-Cazana and Smith 2008) and one patent application (Caili 2010) concerning the catalysts for the production of ethanol and other lower oxygenated aliphatic compounds from synthesis gas. The catalyst in the patent application is a combination of molybdenum, cobalt and an alkaline earth metal or alkali promoter. The process conditions for the alcohol synthesis are 240–270 ºC, 69–83 barg (1000–1200 psig) and a H_2/CO molar ratio of 1. In patent US7384987, the catalyst is a combination of an active metal component, a mixed metal component and a promoter. A wide range of metals is listed in the patent as possible catalyst components, for example Pd, Zr, Ce, Li, Mo, K and W. The process conditions are similar to those given in the application, but covering a wider range. The reaction temperature is 200–350 ºC, pressure 34–207 barg (500–3000 psig) and the H_2/CO molar ratio from 1/2 to 4/1.

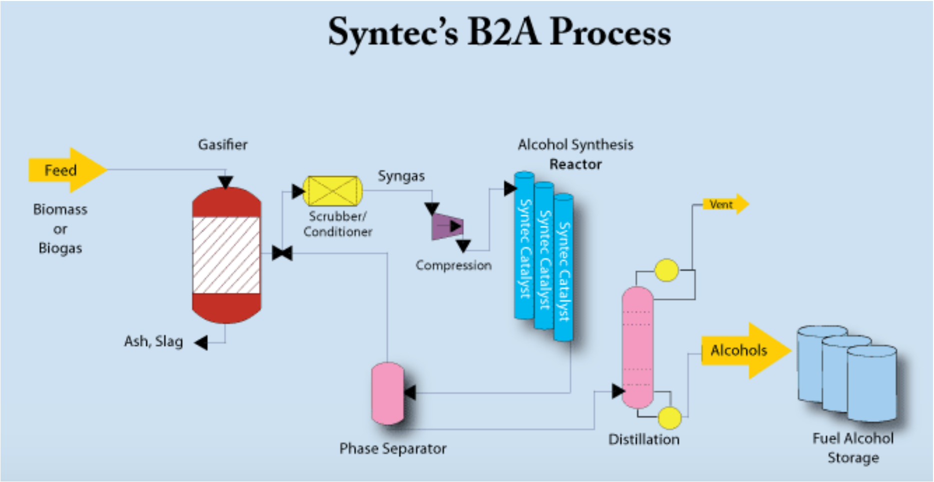


Figure 2.4. Syntec biomass-to-gasoline process. Figure from (Anon.17 Syntec Biofuel).

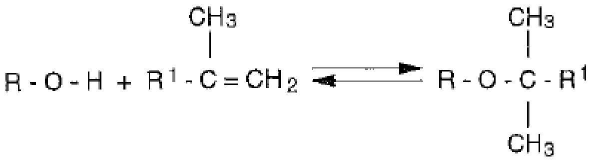
Ecalene

Ecalene is the trade mark name given to a mixture of alcohols that may be used as a fuel or as a fuel additive. The typical composition of Ecalene is methanol 30%, ethanol 45%, propanol 15%, butanol 7% and hexanol 2% (Wikipedia 2011). Ecalene can be manufactured via gasification and alcohol synthesis.

2.3 Etherification

Fuel ethers can be produced from alkenes and alcohols as shown in equation (1) (Kivi et al. 1991). Methanol can be converted into methyl-tertiary-butyl-ether (MTBE) and ethanol into ethyl-tertiary-butyl-ether (ETBE) by catalytic reaction with isobutylene. When methanol and ethanol react with isoamylenes, tertiary-amyl-methyl-ether (TAME) and tertiary-amyl-ethyl-ether (TAEE) are produced (EFOA 2011).

Isobutylenes and isoamylenes are at present fossil feedstocks, for example from oil refineries. Ethanol used in both ETBE and TAEE production is a bio-origin feedstock. Methanol used in MTBE and TAME production is currently fossil feedstock produced mainly from natural gas, but bio-origin methanol could also be used (EFOA 2011).



$$R-O-H + R^1-\overset{\displaystyle CH_3 \atop |}{C}=CH_2 \rightleftharpoons R-O-\underset{\displaystyle | \atop CH_3}{\overset{\displaystyle CH_3 \atop |}{C}}-R^1 \qquad (1)$$

R, R^1 = alkyl groups

The production of MTBE, ETBE, TAEE, and TAME ethers is quite simple. Furthermore, MTBE units can be switched to ETBE production because both have similar synthesis processes. It is also possible to develop facilities that can produce both ETBE and MTBE to meet changing world markets. Almost the same applies to TAEE and TAME. The production of diisopropyl ether (DIPE) is more difficult (Arteconi et al. 2011).

A more detailed description of production processes for MTBE, ETBE, TAME, TAEE, DIPE and some other oxygenates is available from a review published by Arteconi et al. (2011).

2.4 Methanol-to-gasoline (MTG)

Gasoline was first produced from methanol on an industrial scale in the 1980s. Today, interest in this process has revived due to rising crude oil prices. The synthesis gas required for methanol production can be produced from natural gas, coal, biomass or carbon-containing waste. The variety of possible raw materials and the mature technology make the MTG process an interesting option for both biogasoline producers and coal-rich countries, such as China and the USA, seeking to be more self-sufficient in fuel production. Currently, the ExxonMobil Research and Engineering Company (referred to below as ExxonMobil) and Haldor Topsøe have their own MTG processes.

2.4.1 ExxonMobil's MTG process

Mobil (at present ExxonMobil) developed the MTG process and a suitable zeolite catalyst called ZSM-5 (Zeolite Socony Mobil 5) in the 1970s. The catalyst is well suited to gasoline production due to its useful pore size, for the hydrocarbon molecule, and shape selectivity. Typically, gasoline production begins with synthesis gas generation and treatment. The synthesis gas is produced either from natural gas by steam reforming or from solid materials by gasification. If the H_2/CO molar ratio of the product gas is not suitable for methanol synthesis, it is adjusted using the water gas shift reaction.

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \text{ (steam reforming)} \qquad \Delta_r H = +206 \text{ kJ/mol} \tag{2}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \text{ (water gas shift reaction)} \qquad \Delta_r H = +206 \text{ kJ/mol} \tag{3}$$

The next process step is the synthesis of methanol from synthesis gas.

$$2H_2 + CO \leftrightarrow CH_3OH \qquad \Delta_r H = -92 \text{ kJ/mol} \tag{4}$$

Next, the crude methanol is dehydrated to form dimethylether (DME).

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \qquad \Delta_r H = -11.8 \text{ kJ/mol} \tag{5}$$

DME is further dehydrated in the MTG synthesis to form a variety of hydrocarbons. The MTG synthesis is an exothermic reaction.

$$2CH_3OH \rightarrow C_2\text{-}C_5 \text{ alkenes} + H_2O \rightarrow \text{alkanes, cycloalkanes, aromatics} \qquad (6)$$

Naturally, the chemistry of the MTG reaction is complicated, and the equation above is a very simplified version. The individual MTG processes in New Zealand, Germany, China and USA are presented in Chapters 3.1.1–3.1.4 below (Packer 1988; Sørensen 2008).

2.4.1.1 New Zealand MTG plant

The first industrial-scale MTG plant was built in New Zealand in 1986. The owners of the plant were Mobil (25%) and the New Zealand government (75%) (Heinritz-Adrian et al. 2007). The plant was constructed adjacent to the Motunui methanol synthesis plant, owned by Methanex, the world's largest methanol producer. MTG production was active for ten years until 1996 when it became uneconomical to produce gasoline. The plant was sold to Methanex, who converted it to methanol production. The MTG plant was demolished in 2004 (Radtke et al. 2006; Anon. 1 Methanex).

The feed gas for the methanol synthesis was from local natural gas supplies. The methanol synthesis process was designed by Davy McKee (at present Davy Process Technology) and had two production lines. The Motunui plant produced approximately 5200 t/day of crude methanol. The methanol process consisted of desulphurization, saturation, steam reforming, compression of the synthesis gas to 100 bar and methanol synthesis (Figure 2.5). The steam reforming of the natural gas was carried out at a temperature of 800 ºC with a nickel catalyst. The product was synthesis gas, which consists mainly of carbon oxides, hydrogen, methane, nitrogen and steam. The methanol synthesis took place at 50 bar and 270 ºC in the presence of a copper-zinc catalyst (reaction 3). Some additional carbon monoxide was also produced during methanol synthesis by the water gas shift reaction (reaction 2) from carbon dioxide. The once-through conversion from carbon oxides to methanol was about 40%. Methanol and water were separated from the product gas mixture by condensation, and the remaining gas was recycled back to the methanol synthesis. The crude methanol had a water content of approximately 20% (Packer 1988).

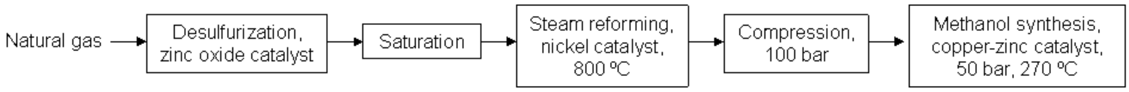


Figure 2.5. Methanol synthesis process (Packer 1988).

The MTG plant consisted of five production lines and had a daily gasoline production of 2200 t. First, the crude methanol was vaporized, then fed to the DME reactor (Figure 2.6). The temperature for the DME synthesis was 300–320 °C, and the catalyst was alumina (Al_2O_3). The product was an equilibrium mixture of DME, water and methanol. The once-through conversion of methanol was approximately 75%.

The next process step was the fixed-bed MTG reactor, which contained Mobil's ZSM-5 catalyst. The temperature of the feed gas was 400–420 °C, and the gas was a mixture of DME synthesis product and recycled gas containing light hydrocarbons, CO_2 and hydrogen. The product mixture from the MTG reactor had a water content of 56 wt-%, and 96 wt-% of the remaining product was hydrocarbons. The MTG conversion was 100%, and 85–90% of the product hydrocarbons were suitable gasoline components. In the next process step, water, recycling gas and hydrocarbons were separated, the hydrocarbons being distilled to separate light ends, light gasoline, heavy gasoline and high vapour pressure (HVP) gasoline (Figure 2.7).

The product composition is presented in more detail in Table 2.2. The average octane numbers of the gasoline were 92.2 (RON) and 82.6 (MON) (Tabak et al. 2008). The heavy gasoline still required additional treatment because it contained 3–6 wt-% durene (1,2,4,5-tetramethylbenzene), which has a high melting point (79 °C) and therefore causes icing in the fuel injection system. Typically, a conventional gasoline contains 0.2–0.3 wt-% durene. In the heavy gasoline treatment (HGT), durene was isomerized to isodurene, which has a lower melting point (-23.7 °C) (Packer 1988).

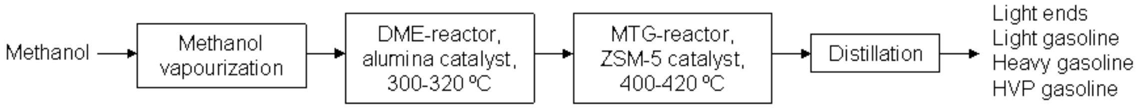


Figure 2.6. MTG synthesis process (Packer 1988).

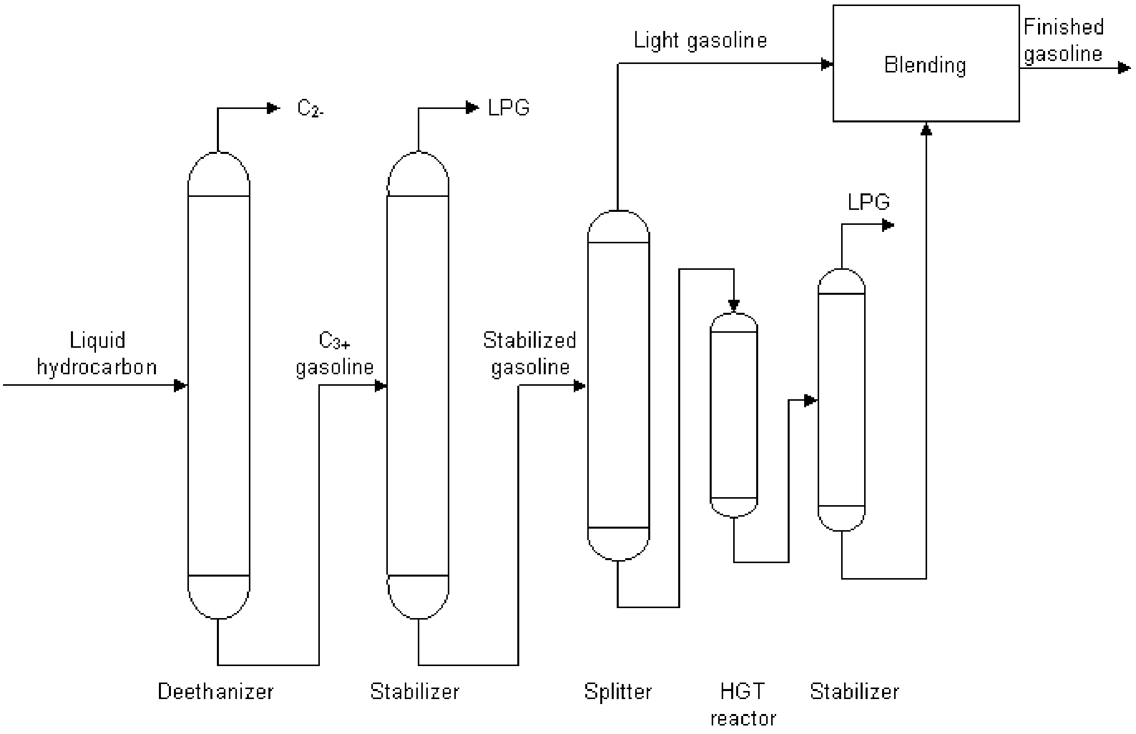


Figure 2.7. MTG product distillation section (Anon.2 Uhde).

Table 2.2. Compositions of hydrocarbon product and gasoline (Packer 1988).

Hydrocarbon product composition	**wt-%**	**Gasoline composition**	**wt-%**
light gas	1.4	highly branched alkanes	53
propane	5.5	highly branched alkenes	12
propene	0.2	naphthenes (cycloalkanes)	7
isobutane	8.6	aromatics	28
n-butane	3.3		
butenes	1.1		
C_{5+} gasoline	79.9		

In addition to the high durene content in the heavy gasoline, the MTG process has some other problems. The process is very exothermic (1740 kJ/kg methanol consumed) and therefore requires effective heat removal. The catalyst also requires regeneration every 3–4 weeks, due to coking, and is eventually destroyed due to dealumination and loss of crystallinity caused by steam. If methanol conversion in the MTG process is not complete, the remaining methanol will dissolve in the water phase of the product mixture. An additional distillation step is therefore required to separate methanol from water. A more technical problem in the process is the band aging occurring in the fixed-bed MTG reactor. This means the reaction takes place only in a narrow band of the catalyst bed. Coke deactivates the front part of the catalyst bed, causing the active zone to move down in the catalyst bed. (Packer 1988).

The advantages of the process are the flexibility of the raw material, sulphur- and nitrogen-free gasoline, an energy efficiency of 50–60% (from natural gas to gasoline), the complete conversion of methanol and a high yield of gasoline (Packer 1988). The energy efficiency is higher if heat is utilized in the integrated process.

2.4.1.2 Wesseling demonstration plant

The Wesseling demonstration plant was built by Mobil, the German engineering company Uhde GmbH and the German oil-refining company Union Rheinische Braunkohlen Kraftstoff AG. The plant's production was 100 bpd, and it operated from 1982–1984. In the Wesseling plant, the MTG-reactor employed a fluidized bed, in contrast to New Zealand, where a fixed-bed reactor was used. A simplified flow diagram of the process is presented in Figure 2.8 (Kam et al. 1981; Lee 1982).

In the fluidized-bed process, both DME synthesis and gasoline synthesis took place in the same reactor. The catalyst was ZSM-5; the particle size was not specified in any of the sources. However, during the cold flow studies before the start-up, a Davison CCZ-11 catalyst with a particle size of approximately 40–80 µm was used. The catalyst was regenerated continuously with air. The catalyst bed had an average temperature of 413 ºC and pressure of 1.72 barg. The hydrocarbon yield was approximately 43.5 wt-% of methanol charge, with the remainder of the product mostly water. The C_{5+} gasoline content of the initial hydrocarbon product was 60 wt-%. After alkylation, the gasoline yield including the alkylate was 88 wt-%. A more detailed product composition is presented in Table 2.3. The octane numbers of the gasoline were 96.8 (RON) and 87.4 (MON). According to the process developers, the fluidized-bed process had several advantages over the fixed-bed process: the gasoline yield was higher; temperature control and heat removal were easier; and the need for recycling was minimal, reducing the operating costs.

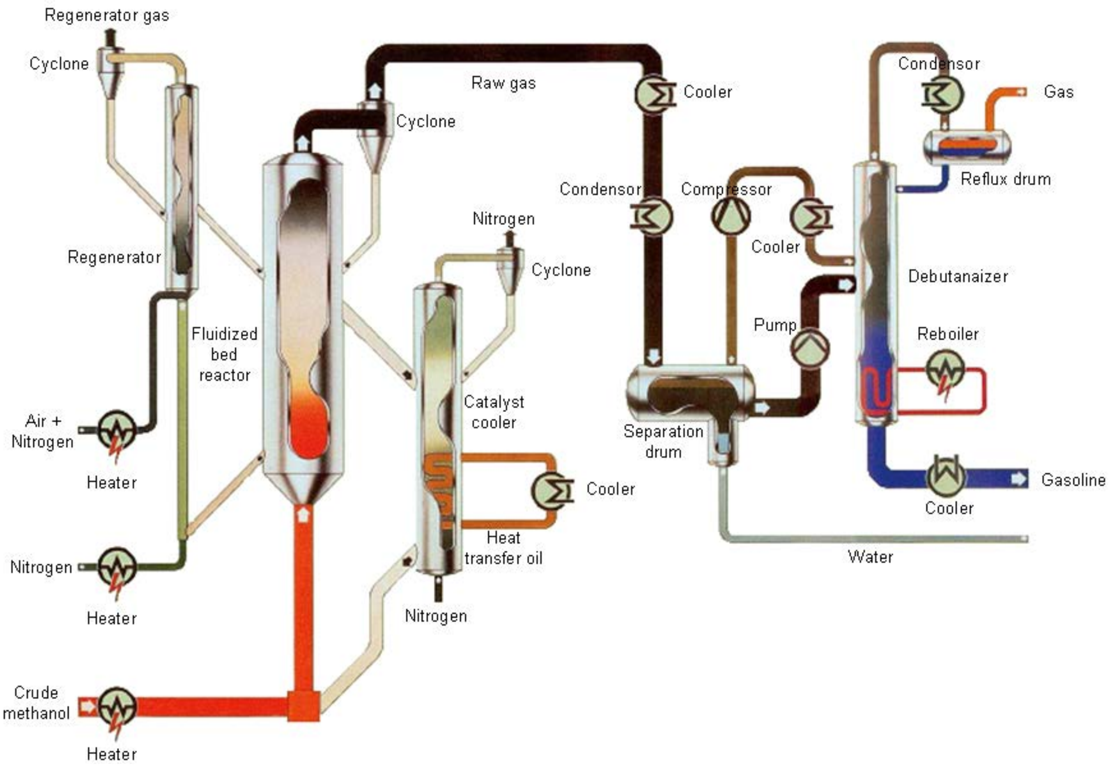


Figure 2.8. Flow diagram of fluidized-bed MTG process. Original picture by [3]. Picture has been modified to include information from (Lee 1982).

Table 2.3. Fluidized-bed MTG hydrocarbon product content, gasoline components and composition (Kam et al. 1981).

Hydrocarbon product	**wt-%**	**Gasoline components**	**wt-%**	**Gasoline composition**	**wt-%**
light gas	5.6	butanes	2	saturates	67
propane	5.9	alkylate	28	olefins	6
propene	5.0	C_{5+} gasoline	70	aromatics	27
isobutane	14.5				
n-butane	1.7				
butenes	7.3				
C_{5+} gasoline	60.0				

2.4.1.3 Shanxi demonstration plant

In 2006, Uhde and Shanxi Jincheng Anthracite Coal Mining Co. Ltd. (JAM) agreed to build a 2600 bpd MTG demonstration plant in Shanxi province, China. The raw material for methanol production is coal, which is abundant in Shanxi province. The process engineering is by Uhde, while the MTG technology is from ExxonMobil. According to ExxonMobil, the process design for the Shanxi plant represents second-generation fixed-bed MTG technology, which reduces capital and utilities costs. The Shanxi plant had a successful start-up in June 2009 (Tabak et al. 2008; Anon.2 Uhde; Hindman 2009).

2.4.1.4 Future investments

DKRW Advanced Fuels and its subsidiary Medicine Bow Fuel & Power LCC are building an MTG plant (20 000–22 000 bpd) in Medicine Bow, Wyoming. DKRW is a US company aiming to develop, own and operate hydrocarbon conversion technologies and facilities. The MTG technology is from ExxonMobil, while the basic process design is from Uhde. The methanol process is designed by Davy Process Technology and Johnson Matthey Catalysts, both part of the Process Technologies Business of Johnson Matthey Plc. The facility will also produce power and Fischer-Tropsch diesel and naphtha (13 000 bpd). The synthesis gas for methanol and Fischer-Tropsch production is produced by the gasification of bituminous coal. Gasoline production is planned to start in 2014 (Tabak et al. 2008; Anon.3 DKRW Advanced Fuels; Anon.4 DKRW Energy LLC).

Synthesis Energy Systems, a US coal gasification company, has bought 15 licences for ExxonMobil's fixed-bed MTG technology (Anon.5 ExxonMobil). They planned to build their first 7000 bpd MTG facility in Benwood, West Virginia. The raw material for the synthesis gas was coal. According to a PR Newswire article from 2008 (Anon.6 Synthesis Energy Systems), Synthesis Energy Systems has ceased development of the Benwood plant due to the global economic situation.

2.4.2 Haldor Topsøe's TIGAS process

Haldor Topsøe's integrated gasoline synthesis process (TIGAS) was also developed when crude oil prices were high in the 1970s and 1980s. Originally, it was designed for remote areas where natural gas would be available at low prices. The low crude oil prices during the 1990s made the TIGAS process uneconomical, and the process was put on the shelf. Interest in the TIGAS process has now revived, and the process will become commercially available once a new demonstration plant has been built and operated successfully (Topp-Jørgensen 1988; Anon.7 Haldor Topsøe).

The TIGAS process, like the ExxonMobil MTG process, produces gasoline from methanol. However, the process chemistry and the process itself are fundamentally different from ExxonMobil's MTG process. The total reaction for the ExxonMobil MTG process from coal-derived gas to gasoline, including reactions (3)-(6) is

$$H_2 + 2CO + H_2O = \text{“}CH_2\text{”} + 3/2H_2O + CO_2 \tag{7}$$

The TIGAS process takes advantage of a much simpler reaction route:

$$3/2H_2 + 3/2CO = \text{“}CH_2\text{”} + 1/2H_2O + 1/2CO_2 \qquad (8)$$

In practice, this means the methanol synthesis and the DME synthesis are combined in a single synthesis loop (Figure 2.9). Because DME production is at its highest in the TIGAS process when the feed gas has a H_2/CO molar ratio of 1 (Figure 2.10), less steam is required for the synthesis gas shift than in the ExxonMobil process, in which the ratio should be around 2. The equilibrium conversion of CO to DME and methanol is also achieved with significantly lower pressure than in the ExxonMobil process (Figure 2.11) (Sørensen 2008; Rostrup-Nielsen et al. 2007).

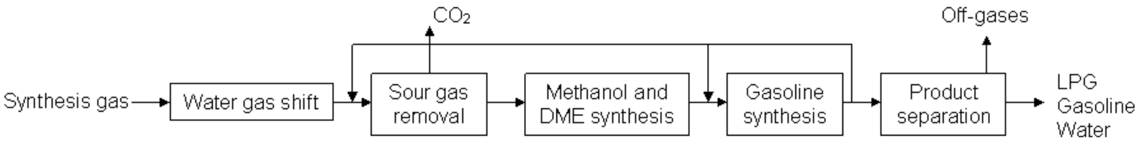


Figure 2.9. TIGAS process. Based on article by Rostrup-Nielsen et al. (2007).

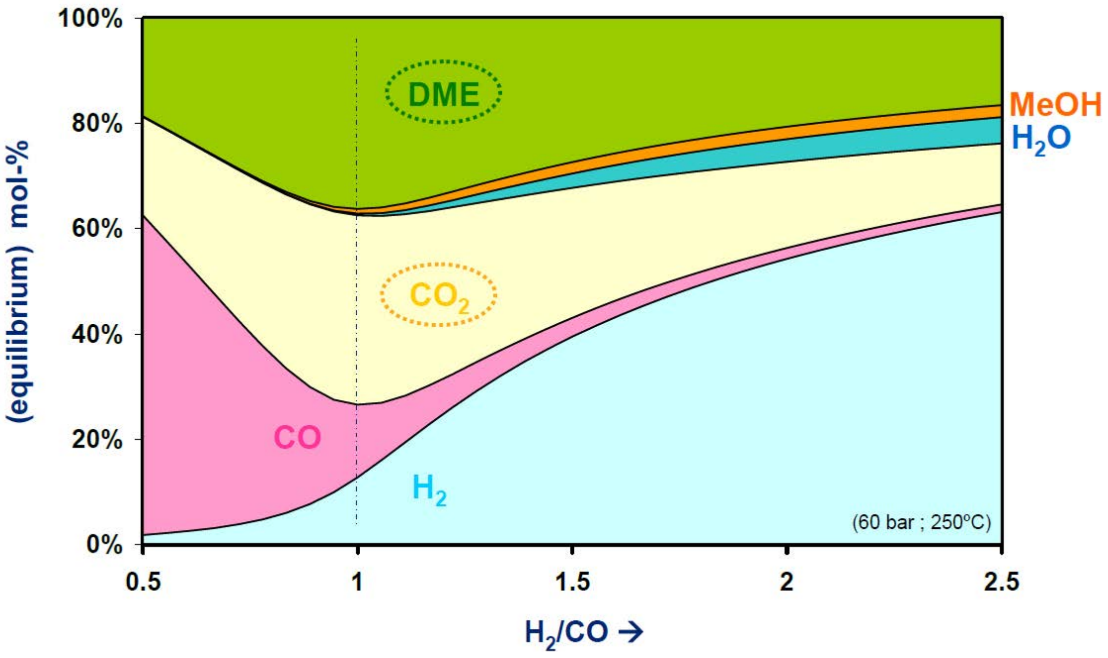


Figure 2.10. Effect of synthesis gas H_2/CO molar ratio on DME production at 60 bar and 250 ºC. Figure from Hansen (2009).

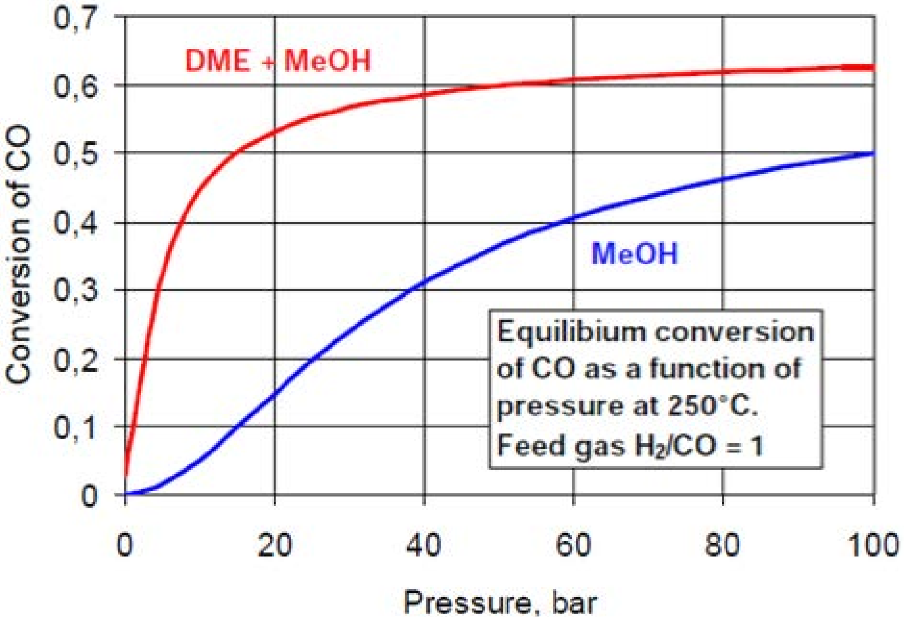


Figure 2.11. Effect of pressure on CO equilibrium conversions. Red: TIGAS process; blue: MTG process with separate methanol synthesis. Figure from Rostrup-Nielsen et al. (2007).

The TIGAS process was demonstrated for the first time in 1983–1986 in Houston, Texas. The feed was natural gas and the production rate 1 tpd. Similarly to the other MTG processes, the catalyst was ExxonMobil's HZSM-5. The gasoline synthesis product consisted of C_{5+} hydrocarbons (78–80 wt-%) and LPG (15–18 wt-%). The benzene content was approximately 0.1 wt-%, and again the product was sulphur-free. The gasoline carbon number distribution is presented in Figure 2.12. The gasoline also contained aromatics, naphthenes and olefins. The octane number was about 87 ((RON+MON)/2) (Topp-Jørgensen 1988; Joensen et al. 2007).

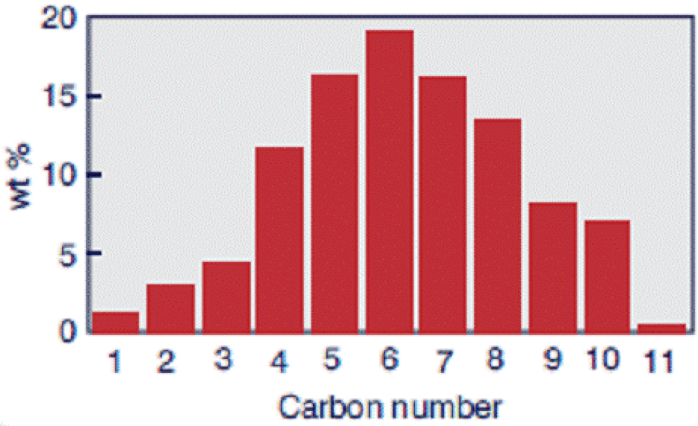


Figure 2.12. Gasoline carbon number distribution in the TIGAS process. Figure from Joensen et al. (2007).

Topsøe will start-up a TIGAS demonstration plant at the Gas Technology Institute in Des Plaines, USA, in 2012. The process will convert wood (25 tpd) to gasoline (approximately 1000 tons/a). In the future, Topsøe plans to build industrial plants that will use more than 1000 tpd wood. The energy efficiency of the wood-based TIGAS process is about 60% (higher if heat is utilized). Topsøe's partners in the project are UPM Kymmene, who will supply the wood, and ConocoPhillips, who test TIGAS gasoline in their existing infrastructure (Anon.7 Haldor Topsøe).

2.4.3 Lurgi's MtSynfuels

The German company Lurgi has developed MtSynfuels process, which can convert methanol into hydrocarbon fuels. Methanol is converted to olefins, which go through olefin oligomerisation. The main products are kerosene/diesel and side products gasoline and LPG (Liebner and Schlichting 2005).

2.5 Fischer-Tropsch process

One route for converting a variety of feedstocks to liquid fuels is a combination of gasification to synthesis gas and the Fischer-Tropsch process for liquefaction. When the feedstock for the Fischer-Tropsch process is natural gas, the product is GTL (gas-to-liquid); when coal, CTL (coal-to-liquid); and when biomass, BTL (biomass-to-liquid). Today, liquefaction of syngas is optimized for diesel fuel production. Some gasoline is also produced.

The Fischer-Tropsch process was developed in the 1920s for the production of synthetic fuel from coal. Today, interest in the technology has been growing for the same reasons as in the case of the MTG process: the Fischer-Tropsch process enables the production of high-quality liquid fuels from synthesis gas. Currently, at least Sasol, Shell, Rentech Inc., UPM Kymmene Oyj and NSE Biofuels Oy (a joint venture of Neste Oil Oyj and Stora Enso Oyj) are utilizing or planning to utilize Fischer-Tropsch technology to produce liquid fuel from coal (CTL), natural gas (GTL) or biomass (BTL)[6] (Anon.10, 18, 19, 20, 21 and Anon.22). However, the main product is commonly diesel; the side products are used for the production of chemicals, for example. Only Sasol has a Fischer-Tropsch-based production line specifically designed for gasoline production.

Sasol is a South African energy and chemical company. In the 1950s, it started developing a Fischer-Tropsch-based process for producing liquid fuel and chemicals from

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[6] Choren Industries GmbH, that was involved in BTL activities, was declared bankrupt in 2011.

coal. Today, this process is used for gasoline production at the Secunda facility in South Africa and in several locations for producing diesel and chemicals. The technology was further developed in the 1980s to increase the production rate from the earlier 2000–6500 bbl/d to 11 000–20 000 bbl/d. The current process is called the Sasol Advanced Synthol (SAS) process. At the Secunda facility, the raw material is coal that is gasified to produce synthesis gas. The gas is fed to an SAS reactor where hydrocarbon production takes place at high temperature and pressure. The catalyst is iron-based and in fluidized form (Gibson 2007; Anon.9 Sasol; Anon.10 Sasol).

The product range for the SAS process is wide, including mainly C_1-C_{20} hydrocarbons. About 55% of the product is olefins, 25% alkanes, 10% oxygenates and 10% aromatics. Ethene, propene, pentene, hexane and octane are separated from the product and either further refined or sold as such. C_7-C_{11} hydrocarbons are used to produce liquid fuel (gasoline at the Secunda facility). Oxygenates from the SAS process are used in alcohol, acid and ketone production (Gibson 2007; Anon.10 Sasol).

In partnership with Qatar Petroleum, Sasol has also built a GTL facility in Qatar. The plant, Oryx GTL, produces mainly diesel from natural gas. Some highly paraffinic naphtha is also produced as a side product. It is cracked to ethene and used in the polymer industry. The Fischer-Tropsch reaction is operated at a lower temperature than in the SAS process, in a slurry phase and with a cobalt catalyst (Anon.11 ORYX GTL).

Fischer-Tropsch crude always needs upgrading into liquid fuels, regardless of the process options. Upgrading can take place not only in refinery units, but also in modular units developed for this purpose. One of these options is Syntroleum’s Bio-Synfining™ process, which can upgrade Fischer-Tropsch wax in addition to oils and fats (Chapter 2.7).

2.6 Virent’s BTL process

Virent’s BTL process is a process to produce liquid fuel directly from sugars. It does not include the gasification step that is an essential part of the gasification/MTG and gasification/FT processes described in previous chapters.

Virent Energy Systems Inc. is a technology and research company based in Wisconsin, USA. They have developed a technology platform called BioForming (Figure 2.13) for liquid fuel production from various biomass resources. The biomass is first fractionated, then the sugars and starches are separated into an aqueous solution. Lignin is usually combusted and used for energy production. The sugars are further processed to C_5-C_6 by an acid hydrolysis or enzymatic technique. Next the hydrocarbons are either hydrogenated to form polyhydric alcohols or hydrogenolyzed to shorter oxygenated hydrocarbons. The required hydrogen can be produced internally. The hydrocarbons are reformed in an aqueous-phase reforming reactor (APR) to H_2, CO_2, alcohols, ketones, aldehydes and alkanes, with organic acids and furans as by-products. The catalyst is, for example, zirconia-supported Pt/Re, the temperature is 450–575 K and pressure 10–90 bar. A ZSM-5 catalyst is used to convert suitable oxygenates to gasoline-range hydrocarbons. Other acid-type catalysts can also be used. The temperature of the condensation step is 648 K. In an experiment with sucrose and xylose, most of the product was alkanes (mainly C_3-C_6) and aromatics. Low levels of alkenes, cyclic alkanes and oxygenates were also produced. Virent have also developed base-catalyzed and dehydration processes to produce hydrocarbons that can be further processed to gasoline-range products (Blommel & Cortright 2008; Anon.8 Virent).

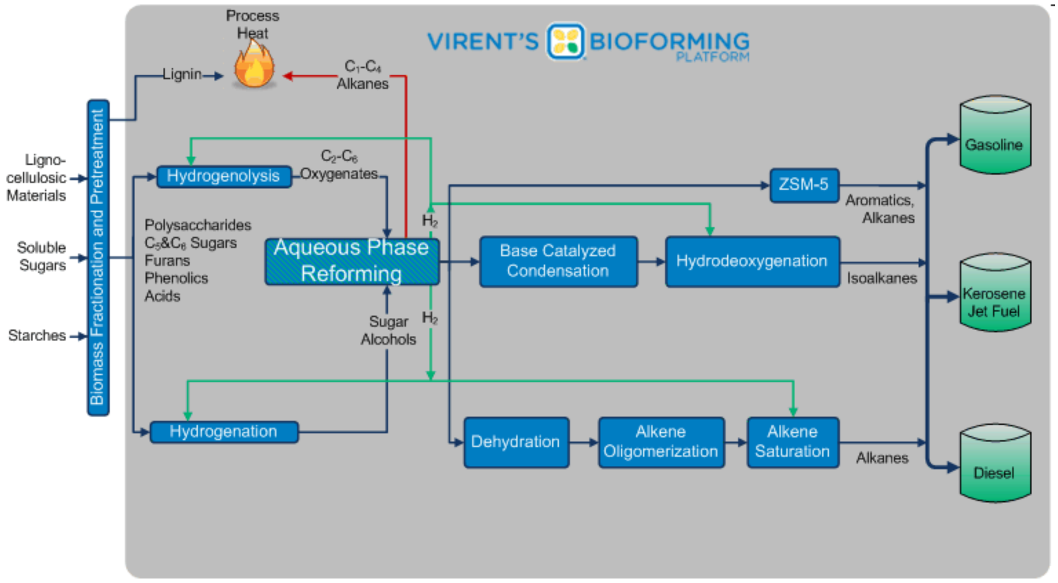

Figure 2.13. Virent's BioForming process. Diagram by Virent (Anon.8).

2.7 Refinery-integrated and co-processing methods

Biofuels can be produced in traditional petroleum refineries. Natural oils and fats can be used as co-feeds in petroleum streams, or as such in units specifically developed for those feedstocks. Cellulosic feedstock could be converted into pyrolysis oil, which could be further processed in petroleum refineries. FT crude is also an option as a feedstock for refineries. Identification and verification of the bio-share in the final products is challenging when bio-origin material is used as a co-feed in petroleum refineries.

2.7.1 Processing of oils and fats

Today, edible oils are mainly used as feedstocks in the processes for converting oils and fats into liquid fuels. Used vegetable oils and animal fats are utilized to some extent. In the future, feedstocks could be algal oil or non-edible oils.

Fluid catalytic cracking (FCC) of vegetable oils and fats has been reported as a promising way to produce biogasoline. In this concept, oils and fats are used as a co-feed into a traditional petroleum refinery's FCC unit. One example of a possible process reported by Holmgren et al. (2007) is shown in Figure 2.14. Oils and fats must be pretreated to remove catalytic poisons such as alkali metals, water and solids. Pretreated feed can be co-processed in the FCC unit to produce gasoline and other high-value products, such as ethene and propene. Gasoline yields from oils and fats are competitive with those from petroleum crude. Less of the heavier, often undesired, products are produced than when the feedstock is petroleum crude (Holmgren et al. 2007).

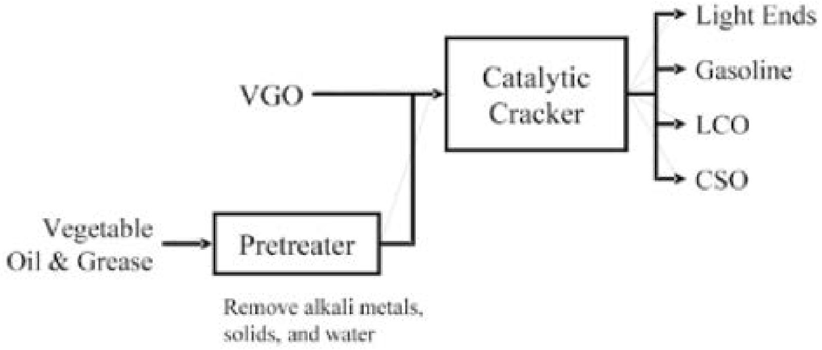

Figure 2.14. Oils and fats as co-feed into petroleum refinery FCC unit.

Hydrotreatment of oils and fats is a feasible option for producing high-quality paraffinic renewable diesel. A gasoline fraction is formed as a side product. Processing can take place in a modular hydrotreatment unit optimized for processing oils and fats, or as co-processing of pretreated oils and fats in the petroleum refinery's existing hydrotreatment unit (Holmgren et al. 2007). At present, few companies produce hydrotreated oils and fats commercially.

Neste Oil in Finland is using its proprietary NExBTL hydrotreatment process, which benefits from the refinery's infrastructure (Rantanen et al. 2005). A NExBTL unit consists of hydrotreatments and the separation of hydrotreated product streams. The main product is NExBTL renewable diesel, but typically some NExBTL renewable gasoline is also formed as a side product. The liquid products are separated into gasoline and diesel fractions by distillation. The production capacity for NExBTL renewable diesel is 340 000 tons/a in Finland, 800 000 tons/a in Singapore and 800 000 tons/a in Rotterdam (Neste 2011).

Dynamic Fuels LLC (a venture of Tyson Foods and Syntroleum) started production of renewable diesel, jet and military fuel using the Syntroleum's Bio-Synfining™ process in 2010. The first facility produces about 220 000 t/a of renewable fuels from animal fats and greases in Geismar, USA. (http://www.dynamicfuelsllc.com/). The Syntroleum's process can also upgrade Fischer-Tropsch wax (Tyson Foods 2007).

Petrobras in Brazil has developed the H-Bio renewable diesel process, which is based on the co-hydrotreatment of vegetable oil and mineral oil. Petrobras originally adopted soybean oil-based H-Bio production in its refineries, but production depends on soy oil prices (Reuters 2008). Galp Energia, Portugal’s largest refinery, and Petrobras plan to build an HVO plant in Portugal using the palm oil produced in Brazil as the feedstock (Petrobras 2010).

ConocoPhillips started co-processing production of renewable diesel from soybean oil in Ireland in 2006. ConocoPhillips is also co-operating with Tyson on using animal fat in HVO production (ConocoPhillips 2007).

UOP/Eni Ecofining™ technology uses catalytic hydroprocessing of vegetable oils to produce hydrotreated biodiesel. The technology is installed at Eni S.p.A.’s facility in Livorno, Italy. Eni is also planning to install other Ecofining units in its refineries in Europe (UOP LLC 2007).

2.7.2 Processing of tall oil

Hydrotreatment technology for converting vegetable oils, animal fats or tall oil into high-cetane diesel fuel was developed in Canada in the early 1990s. The process was licensed from Canmet, Ottawa. A demonstration plant using tall oil fatty acids as the feedstock was started in 1992 by Arbochem Inc. in Canada (Chemical Engineering 1992). Today, this process is known as CanmetENERGY'S SuperCetane Technology (CanmetENERGY 2011).

The Swedish company SunPine is the first company in the world to produce *wood-based* biodiesel from crude tall oil processed from pulp industry by-products. The first tall oil diesel was produced at SunPine’s Piteå plant in 2010. The crude tall oil diesel is upgraded to a high-quality hydrotreated green diesel fuel at a Preem refinery. SunPine’s projected production of is 100 000 m^3/year. According to SunPine, a total of 350 000 m^3 tall oil is available in Scandinavia, but competition for this volume is tough. Preem’s new green diesel will contain up to 20% green components based on the tall oil diesel (Chemrec News 2009).

2.7.3 Processing of pyrolysis oil

The fast pyrolysis of biomass produces bio-oil, which is a challenging product, containing water, acids and other difficult species, resulting in a high oxygen content and high acid numbers. In addition, pyrolysis oil is not soluble in conventional hydrocarbon fuels. Pyrolysis oil cannot be used as such for engines. Pyrolysis oil could be partially upgraded to make it a suitable feed for conventional refineries. Other routes to utilizing pyrolysis oil (direct conversion, gasification/liquefaction, steam reforming) have also been studied (McGill et al. 2008).

Pyrolysis oil can be separated into two fractions: a water-soluble fraction and a heavier pyrolytic lignin fraction. According to Holmgren et al. (2007), pyrolytic lignin is a better feedstock for liquid fuel production than the water-soluble fraction, because of the higher carbon/oxygen ratio. The main product from the hydroprocessing scheme evaluated by Holmgren et al. (2007) is gasoline. In addition, diesel fuel and light hydrocarbons would be produced.

2.8 Economics

There is very little publicly available information on the economics of biogasoline processes other than the traditional. In this report, the objective was to collect the available production costs and to present them in a comparable way.

Some economic evaluations of the coal-based ExxonMobil MTG process in the 1970s and 1980s were summarized in the NREL Technical Report from 2003 (Spath and Dayton 2003). There is also one evaluation of a biomass-based process (Jones 2010). Several studies on the economics of both the coal- and the biomass-based Fischer-Tropsch processes have been carried out recently. However, the main product of these processes is typically diesel. Rostrup-Nielsen et al. (2007) from Haldor Topsøe have published one case study comparing the process economics of TIGAS with cases of combined TIGAS and IGCC. However, this study includes no process data. New processes, such as those of Excelus, SyntecBiofuel and Virent, are still in the development or early demonstration stages, so no economic calculations have been published for these processes. The current interest in coal- and natural gas-based gasoline processes has also led to a number of studies. However, their adaptation to biomass-based cases is difficult. For example, in CTL and GTL processes the raw material is abundantly available at low cost and the capacity is usually very high. Conversely, the biomass-based processes have more expensive feedstock and low capacities, although they are usually subsidized by local governments.

The only publicly available in-depth survey of the economics of a biomass-based MTG process is a recent technical report by NREL (Phillips et al. 2011). The feedstock for the process studied was poplar wood containing 50% moisture (2000 dry tonne/day). The process included feedstock pretreatment, indirect gasification, gas cleanup and conditioning, methanol synthesis and conditioning, ExxonMobil’s MTG synthesis and finally gasoline treatment. Internally produced heat and power were also integrated with the total process. The expected production rate for the plant was about one million barrels/year. Under these conditions, the minimum gasoline plant gate price was calculated to be US$0.52/l and the total project investment US$199.6 million. The challenges in the process were considered to be tar reforming (target 99.9%), methane conversion (target 80%) and the utilization of a fluidized-bed MTG reactor.

The major efforts in the research and development of renewable gasoline are devoted to cellulosic ethanol. The International Energy Agency has estimated the costs of biofuels today and in the future (Figure 2.15). The cost of cellulosic ethanol was estimated to be around US$1.1/l gasoline equivalent (lge) in 2010, and US$0.8/lge by 2050. The figures reflect retail price-equivalents and take into account key steps in biofuel production (IEA 2011). Although cost estimates from different studies are not necessarily comparable, the indication is that the production of biohydrocarbons for gasoline could be competitive with the production of cellulosic ethanol.

The gasoline prices from Jones (2010) and both NREL Technical Reports have been collected in Table 2.4. The original values have first been converted to US$/gallon and then using the CEPCI index to 2007 US$/gallon. In addition, a €/l price was calculated using an exchange rate of €1 = US$1.3705 (European Central Bank, yearly average of 2007). The economics of biogasoline production with refinery integrated processes, and the production of alcohols and ethers, are not covered by this report.

Table 2.4. Production prices for gasoline by the Exxon Mobil MTG process, Brazilian sugarcane ethanol and lignocellulosic ethanol by fermentation.

Feedstock	**Price of product (US$/gallon) original cost year**	**Cost year**	**2007 US$/ gallon**	**2007 US$/litre**	**2007 €/litre**	**Reference**
Coal	0.67–0.87	1977	1.7–2.2	0.45–0.58	0.3–0.4	In Spath and Dayton 2003: [Lee et al. 1980]
	1.25	1979	3.0	0.79	0.6	In Spath and Dayton, 2003: [Wham and Forrester III 1980]
	0.90	1978	2.0	0.53	0.4	In Spath and Dayton 2003: [Edwards et al. 1979]
Biomass	3.1	2008	2.8	0.74	0.6	Jones 2010 (indirect gasification)
	3.9	2008	3.6	0.95	0.7	Jones 2010 (direct gasification)
	1.95	2007	2.0	0.53	0.4	Phillips et al. 2011
Ethanol reference						
Brazilian sugarcane ethanol				US$1.0/lge* (US$0.64/l)		OECD-FAO 2011
Lingocellulosic ethanol by fermentation					€0.2–1.5/lge* p€0.15–1.0l	Suokko 2010
Cellulosic ethanol				US$ 1.1/lge* (US$ 0.72/l)		IEA 2011

* lge = liters of gasoline equivalent

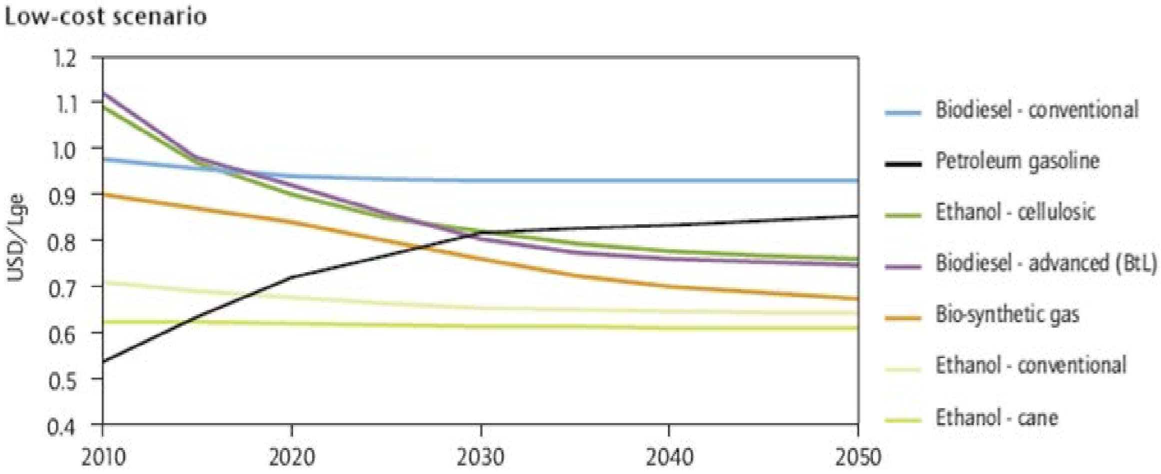

Figure 2.15. Cost estimates for various biofuels compared with gasoline in low-cost scenario (IEA 2011).

3. Biocomponent options

3.1 Vehicle technology

Gasoline cars

Gasoline cars equipped with carburettor engines were available until the late 1980s. Today, spark-ignition engines are port-injection engines, mostly equipped with multi-point fuel injection (MPFI, fuel injected into the intake port). In the 1990s, direct-injection spark-ignition engines with lower fuel consumption appeared on the market. Models using lean combustion with excess air were also introduced in the 1990s, but they have practically disappeared from the market. Spark-ignition engines, whether indirect- or direct-injection, are now based on a stoichiometric air/fuel ratio.

Exhaust emissions from spark-ignition engines using a stoichiometric air/fuel ratio can be efficiently controlled with a three-way catalyst (TWC), in which carbon monoxide and unburnt hydrocarbons are oxidized simultaneously with the reduction of nitrogen oxides. TWCs operate efficiently only in a very narrow lambda window close to the stoichiometric air/fuel ratio. TWCs cannot therefore be used in engines running with a lean mixture, such as diesel engines. The benefit of a lean mixture would be improved fuel consumption, but at the cost of increased NO_x emissions.

Exhaust gas recirculation (EGR) is one of the common technologies for reducing the NO_x emissions of diesel engines, and is also used in spark-ignition engines. NO_x emissions are formed from nitrogen in the air at high temperature. EGR is an internal engine technology, not an exhaust aftertreatment device. With EGR, some of the exhaust gas is returned to the engine cylinders, which lowers the combustion temperature and consequently NO_x emissions. High EGR ratios may increase particle emissions.

Many conventional spark-ignition cars are equipped with a “switching-type” lambda sensor, which operates properly only when lambda is close to 1.0. The lambda sensor monitors the exhaust gas air/fuel ratio as feedback to a closed-loop control system that maintains the stoichiometric air/fuel ratio. This is essential for the proper operation of the TWC. If the fuel oxygen content exceeds a certain limit, a “switching-type” lambda sensor fails to maintain the proper air/fuel ratio. In Europe, the oxygen content of gasoline is limited to 3.7 wt-%, as defined in Directive 2009/28/EC.

FFV cars

Special flexible-fuel vehicles (FFV) are manufactured that use up to 85% ethanol. They are equipped with linear lambda sensors that can adjust the air/fuel ratio to stoichiometric, even if the fuel's oxygen content is high. All materials in FFV cars are compatible with ethanol, which is more aggressive than gasoline towards materials.

Fuel injectors in FFV cars are designed for higher fuel flows than in conventional gasoline cars, due to E85 fuel's low heating value. Feedback control in FFV cars adjusts fuel delivery and ignition timing (EMA Statement 2010). This leads to higher fuel consumption, which can be partly compensated if ethanol's better octane rating is utilized by increasing the compression ratio to achieve better energy efficiency. According to West et al. (2007), fuel consumption is around 33% higher with E85 fuel than with gasoline[7].

FFV cars using E85 fuel must inject excess fuel in cold starts to achieve performance similar to gasoline cars. This leads to increased exhaust emissions until the TWC warms up (Lupescu 2009). Improved engine- and emissions-control technology is expected to reduce the exhaust emissions of FFV cars in cold starts. Catalyzed hydrocarbon traps have been developed to store organic gases in cold starts until they can be removed when the TWC warms up (Lupescu 2009). Intake port heating to reduce non-methane organic gas emissions has been studied (Chiba et al. 2010). Heated fuel injectors have also been studied (Kabasin et al. 2009).

Exhaust emissions with new and old cars

Absolute mass emissions from new cars are smaller than those from old cars. Absolute mass emission differences between different fuels are therefore also generally getting smaller. However, relative differences between fuels may be significant. Furthermore, at cold starts, heavy driving conditions and at low temperatures there may be large differences, absolute and relative, between fuels for all cars.

3.2 Gasoline properties

Engine and aftertreatment technologies impose requirements on fuel quality. Basic fuel analyses were developed to screen the general performance and operability of fuels in internal combustion engines. Fuel properties important in environmental contexts, such

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[7] Editorial: FFV cars typically have large engines, which leads to higher fuel consumption compared with gasoline cars, even in energy equivalent terms.

as compatibility with emissions control devices, were defined subsequently. The functionality and general performance of gasoline can be defined in terms of octane rating, volatility, olefin content and additives, for example. Environmental performance can be defined in terms of aromatics, olefins, benzene content, oxygenates, volatility and sulphur, for example.

Fuel properties are controlled by legislation and by fuel standards. For gasoline, basic fuel properties are defined in Fuel Quality Directive 2009/30/EC in Europe. European standard EN 228 includes a more extensive set of requirements than does the Fuel Quality Directive to ensure the proper functionality of gasoline on the market. Similarly, fuel quality requirements are included in the legislation and standards in various geographical regions or countries. Automobile and engine manufacturers have defined recommendations for fuels in the “World Wide Fuel Charter” (WWFC), in which Category 4 is the most stringent with regard to fuel properties.

Selected requirements for gasoline properties in Europe are shown in Table 3.1.

Table 3.1. Examples of selected gasoline properties and requirements in European Fuel Quality Directive 2009/30/EC and standard EN228:2008. Requirements in the Finnish standard for E10 fuel are also presented.

	Example	**EN 228:2008**	**SFS 5979:en "E10"**	**2009/30/EC "E10"**
Formula	C_4–C_{12}			
Molecular weight, g/mol	~60–150			
Carbon/Hydrogen, % m/m	~86.5/13.5			
Density, kg/m^3	750	720–775	720–775	
Octane number RON/MON	min. 95/85[a]	min. 95.0/85.0	min. 95.0/85.0	min. 95/85[a]
Reid vapour pressure, kPa	45–90[a]	45–60/70[a]	45–60[a]	max.60.0 [a]
Distillation				
Range, °C	30–210			
Final boiling point, °C	<210	max. 210	max. 210	
Evaporated at 70°C, % v/v	20–48	20[a]–48[a]	20–48[a]	
Evaporated at 100°C, % v/v	46–71	46–71	46–71	min. 46.0
Evaporated at 150°C, % v/v	>75	min. 75.0	min. 75.0	min. 75.0
Residue, % v/v	< 2	max. 2	max. 2	-
Olefins, % v/v	<18	max. 18	max. 18	max. 18
Aromatics, % v/v	<35	max. 35	max. 35	max. 35
Benzene, % v/v	<1	max. 1.00	max. 1.00	max. 1.0
Sulphur content, mg/kg	<10	max. 10.0	max. 10.0	max. 10.0
Oxygen content, % m/m	<3.7	max. 2.7	max. 3.7	max. 3.7
Methanol, % v/v	0	max. 3.0	max. 3.0	max. 3.0
Ethanol, % v/v	<10	max. 5.0	max. 10.0	max. 10.0
Isopropyl alcohol % v/v	0	max. 10.0	max. 12.0	max. 12.0
Tert-butyl alcohol, % v/v	0	max. 7.0	max. 15.0	max. 15.0
Isobutyl alcohol, % v/v	0	max. 10.0	max. 15.0	max. 15.0
Ethers, C5+, % v/v	<22	max. 15.0	max. 22.0	max. 22.0
Other oxygenates, % v/v [b]	0	max. 10.0	max. 15.0	max. 15.0
Oxidation stability, minutes	> 360	min. 360	min. 360	
Existent gum (washed), mg/100 ml	<5	max. 5	max. 5	
Copper strip corrosion (3h at 50 °C)	Class 1	Class 1	Class 1	
Lead content, g/l	<0.005	max. 0.005	max. 0.005	max. 0.005
Manganese content, mg/l	<6		max. 6.0	max. 6.0
Energy content (LHV), MJ/kg	~43			
Energy content (HHV), MJ/kg	~45[b]			
Flash point, °C	-40 [b]			
Other properties of gasoline [c]	Viscosity at 15°C: 0.83 mm^2/s; Cetane number: 8-14; Nitrogen ~30 mg/kg; Heat of vaporisation: 275–365 kJ/kg; Autoignition temperature: 300 °C; Flammability limits: 1.4–7.6 vol-%; Vapour density: 2–4; Stoichiometric air to fuel ratio: 14.7.			

[a] Several classes exists. [b] Mono-alcohols and ethers with final boiling point max. 210 °C. [c] Murphy 1998

Sufficient knocking resistance (*octane rating*) is essential for the proper use of fuel in a spark-ignition engine. Increasing the octane rating enables a higher compression ratio, and consequently higher efficiency and higher power output. The ratio of the research octane number (RON) to the motor octane number (MON) varies with the chemical composition of the fuel. The MON is decisive for knocking under high-load conditions, which are particularly critical for the engine. The RON is decisive for high-speed, low-load conditions.

The octane numbers of individual gasoline components are not useful as such, because they do not behave linearly in blends with gasoline (Figure 3.1). *Blending octane numbers* must therefore be defined separately. The response of the components depends on the composition of the base gasoline, and on the blending ratio. In addition, the determination of octane number with a CFR engine is not an exact method. Interlaboratory reproducibility of the results obtained with a CFR engine may be several units. This partly explains the high variability of the octane numbers referred to in the literature.

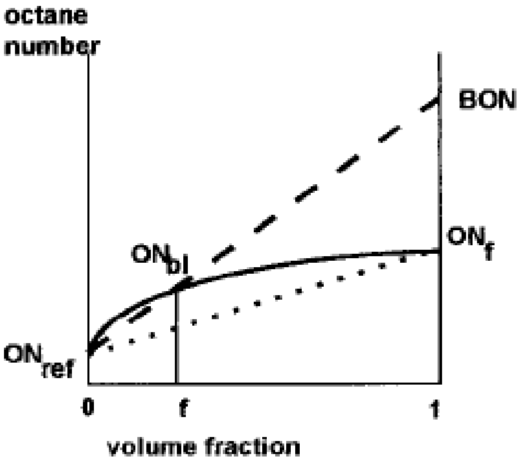

Figure 3.1. ON_{ref} is the octane number of reference gasoline. The solid line illustrates the measured octane numbers of blends with oxygenate. ON_f is the measured octane number of neat oxygenate. The blending octane number (BON) is the calculated blending octane number, which results in the measured ON_{bl} (Golombok 1999).

The *volatility* of gasoline affects evaporative emissions and the driveability of the car. Volatility is specified by the gasoline's *vapour pressure*[8] and *distillation characteristics*. Higher volatility than needed increases evaporative emissions unnecessarily. Appropriate volatility is needed to ensure good cold starting and to avoid driveability problems. However, the extent to which volatility affects the driveability of modern cars is debatable.

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[8] The vapour pressure of gasoline is typically measured at 100 °F (37.8 °C).

The volatility of gasoline is also an issue in the context of safety. The air/vapour mixture in the tank is too rich to ignite in the normal ambient temperature range with gasoline, and too lean with diesel fuel. If the volatility of gasoline is too low, the mixture may become flammable. The volatility of gasoline drops when the ambient temperature falls.

The *olefin content* of gasoline affects engine cleanliness, which is an increasingly important parameter as new sophisticated engines and aftertreatment devices penetrate the market. Olefins in gasoline may also lead to an increase in the concentration of reactive olefins, such as 1,3-butadiene, in the exhaust gases. *Aromatics* affect engine cleanliness, and may include carcinogenic compounds such as benzene. *Additives* may be needed to ensure the gasoline has adequate detergency properties.

3.3 Alcohols as low-level blends

3.3.1 Ethanol and methanol

European legislation allows the blending of 10 v/v% ethanol into gasoline. Ethanol is a problematic gasoline component. It increases the volatility of gasoline, which, however, can be adjusted by match-blending. The vapour pressures of ethanol/gasoline blends are at their highest at ethanol contents of 5–10%, and then start to decline. When ethanol is blended into gasoline, evaporative emissions, and emissions of organic gases such as acetaldehyde, increase. NO_x emissions may also increase to some extent. On the positive side, ethanol tends to reduce particulate matter emissions.

Ethanol is aggressive towards materials. Ethanol presents a phase-separation risk, and anhydrous ethanol is therefore used for low-level blending. With ethanol, the vapour in the air space in the fuel tank is flammable over a wide temperature range. However, the flammability risk of E10 fuel is considered to be close to that of gasoline.

3.3.1.1 Properties

Methanol is one of the economical fuel options considered (Nichols 2003), but it is in many respects very difficult fuel component. However, methanol as such is currently used in China as fuel component, mainly in high-concentration blends (Chapter 3.1.4). Methanol is also used as racing fuel. Methanol was considered as a fuel for fuel-cell cars with an on-board reforming unit, but development stalled. Methanol is used in the production of fuel ethers.

Ethanol is subject to end-use problems, but to a smaller extent than methanol. End-use aspects of ethanol are acceptable with certain conditions. Consequently, ethanol is the dominant biocomponent in the gasoline market.

Selected fuel properties of methanol, ethanol and butanols are shown in Table 3.2.

Table 3.2. Properties of gasoline and some alcohols*.

	Methanol[a]	Ethanol[a]	Iso-Propanol[a]	Sec-Butanol[c]	Tert-Butanol[a]	Iso-Butanol[c]	1-Butanol[c]
Chemical formula	CH_3OH	C_2H_5OH	C_3H_7OH	C_4H_9OH			
Molecular weight, g/mol	32.0	46.1	60.1	74.1			
Oxygen content, % m/m	49.9	34.7	26.6	21.6			
Density 15 °C, kg/l	0.796	0.794	0.789	0.806	0.791	0.802	0.810
Melting point, °C				-115	25.7[c]	-108	-90
Boiling point, °C	65	78	82	100	83	108	117
Octane numbers, neat RON	107[g]-109	108[g]-109					
Blending RON*	127–136	120–135	117[b]	101	104–110[a]	113	94[d], 96
Blending MON*	99–104	100–106	95[b]	91[b] (32[e])	8–-98[a,c]	94	78, 81[d]
Neat vapor pressure at 37.8 °C, kPa	32	16	12		12[i]	3.9 (at 40°C)[k]	2.4 (at 40°C)[k]
Blending vapor pressure, kPa*	214[e]	117[e]	97[e]		62[e]		44[d]
Heating value, MJ/kg	20	27	31		33	33[f]	33[d]
Heat of vaporisation, kJ/kg	1174	838, 839[b]	666[b], 744	562[b]	536[b], 601	579[f], 686	584[h], 592[k], 706
Self-ignition temperature, °C	464	423	399	380[b], 406	478	416, 430	343
Ignition limits, fuel in air, % v/v	7–36	4–19	2–12	1.7–9.8	2.4–8	1.2–10.9	1.4–11.2
Flash point, °C[j]	11	13		31	16	28	34
Stoichiometric air/fuel ratio	6.4	9.0	10.3		11.1	11.2	11.2
Solubility in water, 20 °C, wt-%	fully	fully	fully	37[b]	fully	8.5	7.7

*) Blending properties depend on blending ratio and gasoline composition.

[a] Owen 1995 [b] Prezelj 1987 [c] Cooney 2009 [d] BP 2006 [e] Graboski 2003 [f] Rice 1991 [g] Methanol Institute [h] Zwaja 2010 [i] Unzelman 1991 [j] Material Safety Data Sheets [k] BASF.

The high octane numbers of low-molecular mass alcohols enable them to be used as octane boosters in gasoline. Alcohols tend to increase the research octane number (RON) more than the motor octane number (MON). For example, the blending RON of ethanol is about 120–135, and the blending MON 100–106. The sensitivity (RON-MON) is typically 8–10 units for gasoline. MON is more crucial for the engine than RON, and therefore demands special attention. The high octane numbers of ethanol or methanol enable the thermal efficiency of an engine to be increased, which is utilized in cars equipped with a knocking sensor.

Ethanol forms azeotropes with hydrocarbons of gasoline, which impacts volatility. In particular, the vapour pressure and distillation characteristics of ethanol/gasoline blends are non-linear. Blending *vapour pressures* for alcohols are significantly higher than their true vapour pressures. The vapour pressure of neat ethanol is low at only 16 kPa (Owen and Coley 1995). When ethanol is added to gasoline, the vapour pressure increases with blending ratios of 5–10%, but then gradually declines. With an ethanol content of some 30–40%, the vapour pressure is at the same level as for gasoline without oxygenates (Environment Australia 2002a,b, Furey 1985). The vapour pressures of blends can be adjusted using base fuel with a low vapour pressure.

One notable point regarding the *vapour pressure* of ethanol is its tendency to increase with increasing temperature more quickly than that of gasoline. This phenomenon is illustrated in Figure 3.2 (Tanaka et al. 2006, referred to by Wallace et al. 2009).

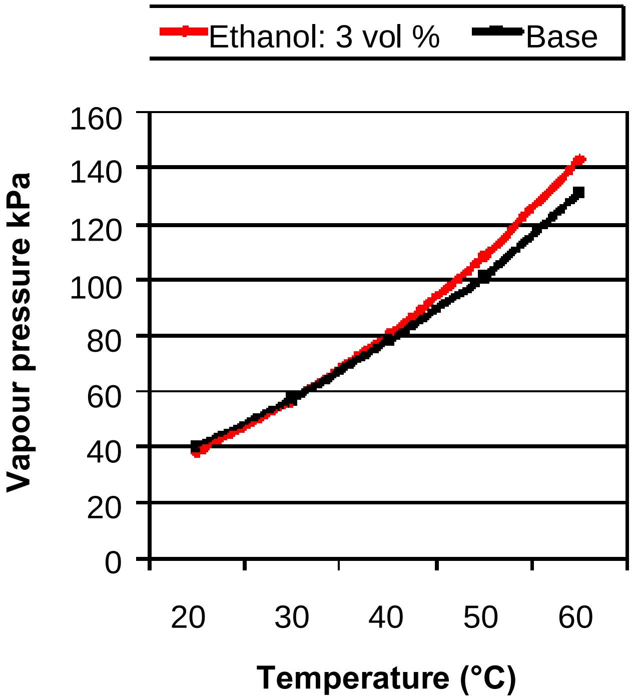

Figure 3.2. Vapour pressure changes for gasoline and a blend containing ethanol 3 vol-% during an evaporation test (Tanaka et al. 2006, referred to by Wallace et al. 2009).

The *distillation* “front-end” increases more than predicted when ethanol is blended with gasoline, due to the azeotropic behaviour of the blend. When ethanol up to 20 v/v% is blended into a hydrocarbon gasoline, the increase in volume evaporated at 70 °C (E70) is as much as 30%. The effect of ethanol on the other parts of distillation curve is smaller (Stradling et al. 2009). The effect of ethanol on distillation is examined in the experimental part of this report (Chapter 4). With the 10% ethanol-containing blend, there is a risk that the E70 limit in standard EN228 might be exceeded, depending on the properties of the gasoline used for blending.

The *heat of vaporization* is higher for ethanol than for gasoline. This leads to problems at start-up and when running a cold engine, due to the cooling effect of the air/fuel mixture. The startability limit of neat methanol is around +5 °C, and of ethanol around +12 °C (Pettersson 1994). This problem can be reduced by using at least 15% gasoline in the fuel. Methanol burns with an invisible flame, which is another reason to add gasoline to methanol (Nichols 2003). The high latent heat of vaporization of ethanol leads to high emissions of organic gases (Chiba et al. 2010), whereas the low combustion temperature of ethanol may lead to a reduction in engine-out NO_x emissions compared with gasoline.

The *energy content* of ethanol is lower than that of gasoline or diesel. The heating value of ethanol is around 27 MJ/kg, in volumetric terms around 21 MJ/l, which is only 65% of the volumetric energy content of gasoline. This leads to a higher volumetric *fuel consumption* with ethanol compared with gasoline. Theoretically, the increase in fuel consumption is about 3.5% with a 10% ethanol blend compared with non-oxygenated gasoline. If the advantage of alcohols' high octane numbers is exploited by increasing the compression ratio of the engine, energy efficiency as kilometres per energy unit of fuel (km/MJ) can be higher for alcohols than for gasoline.

The *density* of ethanol is 0.79 kg/l, which is slightly higher than that of gasoline.

The *oxygen content* of ethanol is 35%. The stoichiometric air/fuel ratio is 9 kg air/kg fuel for ethanol, whereas it is 14.6 kg/kg for gasoline. Modern cars with a closed-loop fuel control system can compensate the leaning effect of fuel, but only to some extent. European Fuel Quality Directive 2009/30/EC, for example, therefore sets a limit of 3.7 wt-% for the oxygen content of gasoline.

Ethanol may reduce the *olefins* and *aromatics* contents of the gasoline pool by a dilution effect, depending on the properties of the base gasoline.

FFV cars were developed for using methanol in the early 1990s. One observation at that time was a need to design a special oil *additive package* to take into account the polar nature of methanol.

The *storage* and *stability* of ethanol blends are special issues due to ethanol's affinity for water and the risk of phase separation. Methanol is an even more difficult alcohol than ethanol in this respect. Ethanol is not only water-soluble, but also hygroscopic. Ethanol transports moisture from the ambient air into the fuel system. The effect of water differs significantly depending on whether the water is dissolved in gasoline or is in a separate phase. A small amount of water in a homogeneous fuel has no adverse effect. If phase separation occurs, the ethanol/water mixture stays as a layer at the bottom of the tank and the octane number of the gasoline layer falls. The engine stalls if it takes in the ethanol/water phase. Furthermore, a mixture of ethanol and water is corrosive.

The risk of phase separation depends on the temperature and the aromatics and ethanol contents of gasoline. The proportion of water that can be absorbed by low-concentration E10 gasoline/ethanol blends varies from around 0.3 to 0.6%, depending on conditions (Owen and Coley 1995, Filho et al. 2008). At low temperatures, the risk of phase separation increases. The higher the ethanol and aromatic contents of gasoline, the higher the proportion of water that can be absorbed by the fuel without phase separation. Phase separation may occur when the critical conditions change. For example, if a tank containing a little ethanol blend is filled with gasoline, the concentration of ethanol in the blend falls. In this situation, the presence of the water originally dissolved in the fuel may be sufficient to precipitate phase separation. The same may happen if the ambient temperature falls. The risk of phase separation is lower if stabilizing agents are used.

To avoid phase separation, anhydrous ethanol is used for low-level ethanol/gasoline blends. The whole chain from supplier to dispenser must be water-free. In practice, anhydrous ethanol is transported by tankers and stored in tanks specially designed for it. Low-level ethanol blends are typically blended at a product terminal or dispenser just before delivery to retail or the end user. Additional cleaning procedures may be needed for ethanol pipelines and tanks, depending on the market area (Owen and Coley 1995).

When non-oxygenated gasoline is used, water accumulates gradually at the bottom of the tank. When alcohol-containing gasoline is used, the alcohol content of the water layer increases and this layer becomes soluble in the gasoline. This dries the tank. Alcohol is sometimes added to fuel for this purpose. However, if there is a lot of water at the bottom of the tank, there is a risk of the alcohol/water layer being drawn into the engine.

Alcohols are aggressive towards *materials*. Methanol is more aggressive than ethanol. However, ethanol is more aggressive towards materials than gasoline. This may lead to early wear or damage to materials and components, swelling of elastomers and corrosion of metals. Materials unsuitable for high-concentration ethanol include natural rubber, polyurethane, cork gasket material, leather, polyvinyl chloride, polyamides, nylon 6/6, plastics, certain thermo- and thermoset plastics, aluminium, zinc, brass, lead and terne (E85 Handbook 2008). The use of these materials with low-level ethanol blends should also be considered. Aluminium in particular should be avoided, because its corrosion product forms a gel. First-generation direct-injection fuel systems with aluminium rails do not tolerate ethanol (ETP 2011). Ethanol may also damage conventional paints, which is a considerable risk during refuelling. Ethanol blends may plug the fuel filter, while ethanol tends to clean impurities from fuel tanks and lines.

In Brazil, there is long experience of blends of around 20% ethanol with gasoline. Examples of modifications to cars relating to this fuel include cylinder walls, cylinder heads, valves, valve seats, pistons, piston rings, intake manifolds, carburettors, electrical systems and nickel plating on steel lines.

Ethanol may dissolve lubricant layers between metal parts, which may increase wear. The conductivity of ethanol may lead to a risk of galvanic corrosion (Walwijk et al. 1996). Consideration must be given to alcohol/gasoline blends in the distribution chain. Materials used in tankers, tanks, lines, seals, hoses and refuelling equipment must be alcohol-resistant. Paasi et al. (2008) reported electrical conductivity and material issues with ethanol/gasoline blends in Finland.

Safety – With ethanol, the vapour in the air space in the fuel tank is flammable over a wide temperature range. With gasoline the mixture is too rich, and with diesel too lean, to be ignitable in the normal ambient temperature range. For neat ethanol, the flammability limits are wide. Vapour barriers or vapour return systems may be needed in the refuelling system to avoid the risk of explosion and poisoning (McCormick 2001). In Finland, Paasi et al. (2008) reported safety factors in the distribution of biofuels. This included an evaluation of the flammability of ethanol/gasoline blends. According to Paasi et al. (2008), the flammability risk with E10 fuel is close to that of gasoline. Safety risks for methanol are higher than those for ethanol. In addition, methanol is toxic, which imposes special requirements on handling (Nichols 2003). On the other hand, denaturants are used in fuel ethanol to make it toxic.

Groundwater issues – If fuel tanks leak, ethanol and gasoline get into the ground. If groundwater is present, ethanol dissolves in it and is biodegraded. One factor that has been studied is the effect of ethanol on the transportation of gasoline in the ground and in groundwater. Deep et al. (2002) reported the effect of ethanol on the rate of benzene biodegradation under non-limiting oxygen and nutrient conditions. The biodegradation of benzene was severely inhibited in the presence of ethanol. Ethanol is degraded preferentially to benzene, which means ethanol has an impact on benzene plume lengths in subsurface environments. Model simulations indicated that benzene plume lengths are likely to increase by 16–34% in the presence of ethanol.

Lahvis (2003) reported the potential effects of low-volume releases of ethanol-blended gasoline in the vadose zone. Model results indicate that the migration of ethanol in the vadose zone is limited to less than 100 cm from the source for releases in sand. In sandy clay, ethanol transport is limited to less than 50 cm. Furthermore, the presence of ethanol in gasoline does not significantly affect benzene transport and mass loading to groundwater. Travel times to groundwater may be more than an order of magnitude greater for ethanol than for benzene, depending on conditions. The model results indicate that the impacts of ethanol and benzene on groundwater from low-volume releases of ethanol-blended gasoline in the vadose zone are not expected to be significant unless the release is near the water table (< 100 cm) or, in the case of benzene, its biodegradation is limited.

3.3.1.2 Ethanol (low-level) – car and engine tests

Few studies on low-concentration ethanol have been published for cars from the 2000s. Studies with cars from the 1990s are still relevant, whereas older studies with carburetted cars do not represent the current car fleet[9].

Some studies, for example Karlsson et al. (2008), reported tests with conventional cars using gasoline containing medium concentrations of ethanol, such as 17% and 43%. However, these are not included in this chapter, which focuses on low-concentration ethanol blends.

Driveability

When ethanol is added to gasoline, it influences the front part of distillation, which may affect hot-weather driveability. Vapour in this part of distillation contains an even higher fraction of ethanol than would be expected based on its share in the gasoline, due to the azeotropic behaviour of the ethanol/gasoline blend. According to Stradling et al. (2009), modern vehicles using multi-point injection technology are less susceptible to hot-weather driveability problems than are older vehicles. The EN228 specification appears adequate for controlling driveability in European vehicles, but further studies are needed should the standard's volatility limits be modified to allow ethanol blends of 10 vol-% and higher (Stradling et al. 2009).

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[9] Background information from selected studies referenced in this Chapter:

Graham et al. (2008): low-concentration gasoline/ethanol blends with three MPFI cars of model years 1998, 2001 and 2003 and one gasoline DI car from 2000. Tests were conducted at +20 and -10 °C. E10 and E20 fuels were tailored to the same vapour pressure as that of the reference gasoline. One of the fuels was splash-blended E10.

Martini (2007) and Concawe (2006): evaporative emissions using various gasoline/ethanol blends with carbon canister-equipped cars. One test fuel set consisted of splash-blended E5 and E10 fuels, the other of blends with adjusted vapour pressures.

Australian study (2008): 21 cars using E5 and E10 splash-blended gasoline/ethanol blends. Seven cars were from the 1990s, seven from around 2003 and seven from 2006 or later.

Durbin et al (2006): the effect of ethanol (0, 5.7 and 10 vol %) and volatility parameters on exhaust emissions. Matrix of 12 fuels was planned to vary ethanol content and mid-range and back-end volatility independently. 12 cars, model years 2002 2003, represented LEV, ULEV and SULEV emissions levels.

Åsman (2006): evaporative emissions within an in-use programme in Sweden.

Egebäck (2005): evaporative emissions of ethanol blended as 5%, 10% and 15% in two vapour pressure gasolines (63 kPa and 70 kPa).

Environment Australia and CRFA (2003): extensive studies on low- and medium-concentration ethanol fuels.

Reviews: One of the reviews carried out within the IEA Advanced Motor Fuels programme was published by Larsen et al. (2009). Karman (2003) reviewed studies published after 1997. Niven (2005) reviewed studies from the 1990s and early 2000s. Summary by AFDC (2009).

Cold-weather driveability is affected by mid-range volatility, defined in Europe by the E100 value. This parameter is linked to exhaust emissions under cold-start conditions. With splash blends of ethanol in gasoline, cold-weather driveability improved somewhat due to the higher volatility of the blends, but the opposite was observed when fuels were tailored at the same volatility levels. Ethanol's high latent heat may affect driveability with a cold engine, and may also have a leaning effect under open-loop engine conditions (Stradling et al. 2009).

Stradling et al. (2009) suggest that current E100 limits in the European EN228 gasoline specification could be modified so that the minimum E100 volatility limits would ideally vary with the ambient temperature and would include an ethanol offset for all volatility classes. The CRC in the USA has developed new fuel parameters (Driveability Indices) that include ethanol offset terms for US vehicles.

Ethanol would prevent icing problems, which are, however, probably relevant only for some old vehicles equipped with carburettors (Owens and Coley 1995).

Evaporative emissions – mechanisms

Evaporative emissions arise from three mechanisms: permeation, leaks (liquid and vapour) and fuel tank venting (canister losses) (Haskew and Liberty 2006). In addition, refuelling produces volatile organic emissions (Larsen et al. 2009). Ethanol may increase the permeation rate through the fuel system. Ethanol is a polar compound and a smaller molecule than typical hydrocarbons, and can pass through the walls of the fuel system (Reynolds 2002). The influence of ethanol on permeation seems to be highest at low ethanol concentrations (Figure 3.3) (Stahl and Stevens 1992).

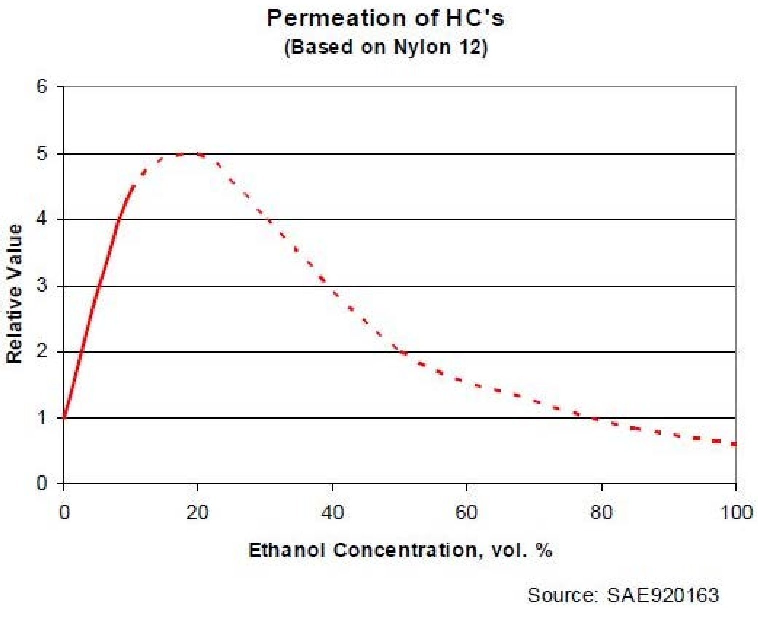

Figure 3.3. The effect of ethanol on permeation (Stahl and Stevens 1992 in Kassel 2006).

An Australian study (2008) observed variations between the results with different cars. This was thought to be due to factors such as the design and volume of the carbon canister and vapour system. Cars with small carbon canisters relative to tank volume struggled with capacity, whereas larger canisters coped better with increased vapour pressure.

Martini (2007) reported that a reduction in canister working capacity due to ethanol may increase evaporative emissions with ethanol. This issue had already been studied in the 1970s and 1980s, with attention given to the higher binding efficiency of ethanol to the activated carbons, and to the tendency of hygroscopic ethanol to carry water into the carbon canister (Croes et al. 1999). According to Martini (2007), heavy hydrocarbons and ethanol are hard to purge from the active carbon in the canister, and trace effects of ethanol may be observed following tests with ethanol-containing fuels. Some carbon types preferentially absorb ethanol, while others do not.

One observation of the Australian study (2008) was that newer vehicles emitted artefacts, remnants of the solvents and adhesives used in the cars. It appeared that these remnants had evaporated completely by the time the car was 8 years old.

Studies showing an increase in evaporative emissions with ethanol

The addition of low-concentration ethanol to gasoline increases the vapour pressure if this is not adjusted. This may lead to rising evaporative emissions. In many areas, legislation allows a higher vapour pressure limit for ethanol-containing gasoline.

AFDC (2009) reports that evaporative emissions increase by 20–80% with splash-blended E10 fuel compared with non-oxygenated gasoline. An Australian study (2008) with 21 cars showed that evaporative emissions, hot-soak and diurnal losses were at least double with splash-blended E5 fuel compared with baseline gasoline. The increase was 50% with splash-blended E10 fuel. Evaporative emissions of benzene, toluene, ethyl benzene and xylenes followed similar patterns in terms of total evaporative hydrocarbon emissions. Alcohol emissions were influenced by the alcohol content of the fuel with some cars, but not with all cars.

Haskew and Liberty (2006) studied the effect of ethanol on permeation with cars from the 2000s, including California “Near Zero” and “Zero Evaporation” evaporation control vehicles. The test fuels covered ethanol contents of 0%, 6%, 10% and 20%. One of the fuels, E6hi, was tailored for higher aromatics content. Haskew and Liberty (2006) concluded that the low-level ethanol blends increased permeation compared with the E0 fuel for all technologies tested. Diurnal permeation rates did not vary significantly between the ethanol blends, and the effect of aromatics was not significant. Despite higher evaporative emissions with ethanol blends, the average specific reactivities of the permeates were lower for the ethanol blends than for E0. The advanced technology systems performed better than the systems of model year 2000–2001 cars. The diurnal permeation rate increased on average from 177 to 484 mg/day for E10 compared with E0 fuel, but only from 36 to 64 mg/day with the “Zero Fuel Evaporative Emissions” system.

Åsman (2006) reported increased evaporative emissions with ethanol in the in-use programme in Sweden. Of 50 tested cars, 20 exceeded the 2 g limit in the EU directive for evaporative emissions, whereas only 2 of 19 cars tested failed in the corresponding programme in Germany. Åsman (2006) concluded that the 5% ethanol content of gasoline in Sweden might be the reason for the high evaporative emissions measured from cars in Sweden. Spark-ignition cars are major sources of vehicle hydrocarbon emissions in Sweden, and evaporative emissions represent some 30% of these emissions.

Egebäck (2005) studied the evaporative emissions with 5%, 10% and 15% of ethanol blended into two baseline gasolines with different vapour pressures (63 kPa and 70 kPa). The level of evaporated hydrocarbons was around 200 ppm with low-vapour pressure gasoline, and 340 ppm with E10 fuel blended in the high-vapour pressure gasoline. Butane used to adjust the vapour pressure of the gasoline was the main component that vaporized during the tests. The evaporation of ethanol followed a trend similar to the evaporation of hydrocarbons.

Environment Australia (2002a) referred to two studies that showed a reduction in diurnal, but an increase in hot-soak, evaporative emissions, leading ultimately to a slight increase in evaporative emissions for gasoline containing 10% ethanol (vapour pressure-adjusted). Higher hot-soak emissions were explained by distillation characteristics.

Studies not showing an increase in evaporative emissions with ethanol

Graham et al. (2008) studied E10 and E20 fuels with MPFI and GDI cars, model years from 1998 to 2003 at +20 °C and -10 °C. Fuels were tailored to the same vapour pressure as gasoline. One splash-blended E10 fuel was also tested. Graham et al. (2008) found no statistically significant differences in diurnal and hot-soak losses between fuels. The ethanol concentration in the evaporative emissions reflected its concentration in the fuel.

Martini (2007) and Concawe (2006) reported that evaporative emissions from cars were dependent on the vapour pressure of the fuel, not on its ethanol content. Ethanol blends with a vapour pressure around 75 kPa had higher evaporative emissions than fuels with a vapour pressure in the range of 60–70 kPa, whether or not they contained ethanol. One observation of this study concerned difficulties in conditioning the carbon canisters of the cars between tests. Martini (2007) observed that evaporative emissions contained relatively high levels of light hydrocarbons (C_4-C_6), low levels of ethanol and significant concentrations of heavier hydrocarbons, such as aromatics. The main sources of the light hydrocarbons are canister bleed emissions and breathing losses, while heavier hydrocarbons may originate through fuel permeation.

Carbon monoxide and hydrocarbons

Larsen et al. (2009) reviewed the literature on exhaust emissions with ethanol blends. They reported that tailpipe CO and HC emissions generally reduced with increasing ethanol content. This was also a conclusion in the reviews by AFDC (2009), Niven (2005) and Karman (2003).

With old cars, enleanment of the air/fuel ratio with ethanol leads to lower CO and HC emissions compared with baseline gasoline. In one study, for example, using E10 fuel resulted in a 25–30% reduction in CO emissions, and a reduction of about 7% in HC emissions compared with baseline gasoline (CRFA 2003).

An Australian study (2008) reported that CO and HC emissions reduced with E5 and E10 fuels compared with baseline gasoline. These emissions trends varied more and absolute differences were smaller for new cars than for older cars.[10] For cars with closed-loop systems and catalysts, benefits in CO and HC emissions with ethanol are gained mainly in cold starts or during heavy acceleration (Graham 2008, Environment Australia 2002a). The exhaust catalyst does not reach the proper operating temperature for some time after a cold start.

Graham et al. (2008) reported that tailored E10 fuel had lower CO emissions than baseline gasoline at normal temperatures and at -10 °C, but that splash-blended E10 resulted in CO emissions 35–50% higher than for tailored E10 fuel at low test temperatures. At normal temperature, there was no statistical difference in NMHC or NMOG emissions between the fuels.

Durbin et al. (2006) studied the effect of ethanol (0 vol-%, 5.7 vol-% and 10 vol-%) and volatility parameters (mid-range and back-end volatility), on exhaust emissions. CO emissions reduced by 6–18% when the ethanol content of the fuel was increased from 0% to 10%, depending on the T50 temperature. NMHC emissions increased with increasing ethanol content if the distillation T90 temperature was high.

1,3-Butadiene, benzene and methane

If ethanol is splash-blended into gasoline, dilution effects may lead to a lower content of aromatics and olefins in gasoline, which may lead in turn to lower benzene and 1,3-butadiene emissions. In many studies, tailpipe benzene and 1,3-butadiene emissions have reduced with increasing ethanol content (Larsen et al. 2009, Graham 2008, Niven 2005 and Karman 2003).

Australia (2008) reported that emissions of benzene, toluene, xylenes, 1,3-butadiene and styrene reduced when E5 and E10 fuels are compared with E0, but not consistently

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[10] Exhaust emission level of new cars is generally lower than that of old cars leading to small differences in emissions between fuels at normal test temperature. In addition, new engine and emission control technologies may affect the fuel responses.

for all cars. This was thought to be due to the performance of the exhaust catalyst in the cold start.

Durbin et al. (2006) studied the effect of ethanol and distillation characteristics on exhaust emissions. The benzene contents of the test fuels were relatively constant. Adding 10% ethanol to gasoline increased emissions of benzene and 1,3-butadiene, but the effect of T50 temperature was greater than that of ethanol.

Methane

Graham et al. (2008) reported that methane emissions reduced as the ethanol content of fuel increased, but not significantly. Larsen et al. (2009) reported that methane emissions increase from 0% to 120% when ethanol is added to gasoline.

Aldehydes

Graham et al. (2008) observed that formaldehyde and acetaldehyde emissions increased as the ethanol content of fuel increased. Differences were not observed between splash-blended and tailored E10 fuel. According to Durbin et al. (2006), adding 10% ethanol to gasoline increased acetaldehyde emissions by 73%. There was an interaction between ethanol content and T50 temperature.

According to Graham et al. (2008), the increase in aldehyde emissions was observed mainly in cold starts and during aggressive driving, and not during stabilized driving.

It is claimed that the risks associated with increased aldehyde emissions from ethanol-blended fuels are negligible, because the absolute emissions are small relative to other hazardous emissions and can be efficiently removed by the catalyst (CRFA). However, acetaldehyde emissions may be significant in cold starts and at low temperatures. This is exaggerated during short journeys.

Ethanol tailpipe emissions

Graham et al. (2008) reported that ethanol emissions with a warmed-up engine were below the detection limit with E10 and E20 fuels. Ethanol emissions are highest in cold starts and at low temperatures. Ethanol seemed to persist in the vehicle system, and a carry-over effect was therefore observed (ethanol was found in the exhaust even with E0 fuel).

Nitrogen oxides

Larsen et al. (2009) reviewed exhaust emissions results with ethanol. In old studies, differences in NO_x emissions with low-level ethanol blends ranged from a 5% reduction to a 5% increase compared with baseline gasoline (CRFA 2003). An Australian study (2008) found no clear trend for NO_x emissions. A study with six cars from the 1990s showed an increase in the NO_x emissions at ethanol concentrations higher than 12 vol-% (Environment Australia 2002). Graham et al. (2008) observed that NO_x emissions increased as the ethanol content increased, mainly during the cold-start part of the test cycle and in aggressive driving conditions. There was no significant difference in NO_x emissions during stabilized driving. The increase in NO_x emissions was substantial for E20 fuel at -20 °C.

An increase in NO_x emissions may indicate a lean mixture outside the limits of the closed-loop control (Environment Australia 2002). Durbin et al. (2006) observed that the effect of the ethanol content on NO_x emissions depended on the distillation characteristics of the fuel. NO_x emissions increased with increasing ethanol content at the low T50 temperature, but not at the high T50 level.

Nitrous oxide

One old study with cars from the 1970s and 1980s showed that there was no significant difference in tailpipe nitrous oxide (N_2O) emissions between gasoline and a 10% ethanol blend with gasoline (Environment Australia 2002). However, Graham et al. (2008) reported that N_2O emissions tend to increase with increasing ethanol content. N_2O emissions are regarded as catalyst-related rather than fuel-related. If ethanol has an effect on N_2O formation, it would mean that ethanol changes the performance of a three-way catalyst.

Particles, PAH and mutagenicity

Particulate matter emissions (PM) are traditionally not regarded as significant emissions from gasoline-fuelled cars equipped with three-way catalysts, because emissions levels tend to be very low. However, there are indications that ethanol reduces PM emissions compared with gasoline. In the study from Australia (2008), lower PM2.5 emissions were reported for E5 and E10 ethanol blends than for gasoline. The PM emissions were 35% lower for E10 fuel than for gasoline with model year 2006 or newer cars.

Pentikäinen et al. (2004) and Aakko et al. (2002) reported an indication of lower particulate PAH emissions and mutagenicity of particulates with ethanol-containing fuel compared with MTBE-containing reformulated gasoline.

Ozone-forming potential

Evaporative, acetaldehyde and NO_x are among the emissions affecting the ozone-forming potential of exhaust gases. AFDC (2009) reported that when tailpipe and evaporative emissions are considered, the ozone-forming potential of exhaust gases is higher for E10 fuel than with gasoline. In contrast, Graham et al. (2008) reported that E10 and E20 fuel blends do not affect the ozone-forming potential for MPFI cars, and ethanol-containing fuels reduced the ozone-forming potential for a GDI car compared with gasoline.

An Australian study (2008) modelled photochemical smog using Sydney as a sample area. In these conditions, an increase in peak ozone concentration was observed in E5/E10 fuel scenarios. A reduction in tailpipe HC and CO did not compensate the increase in volatile organic emissions.

Ethanol summary

Car technology has developed substantially in the past 10–20 years. Many of the studies with low-concentration ethanol blends have been carried out with cars that do not represent today's technology.

In some areas, the volatility of ethanol blends must match gasoline limits. If higher volatility is allowed for ethanol blends, this leads to increased emissions of volatile organic compounds. Even if the vapour pressure is adjusted to a particular level, evaporative emissions may increase due to a higher fuel permeation rate and/or the reduced working capacity of the carbon canister with ethanol-containing fuel.

The major drawback of adding ethanol to gasoline is an increase in emissions of acetaldehyde, which is classified as an "air toxic" substance. A catalyst can efficiently remove aldehyde emissions, but does not always operate properly, for example in cold starts.

Ethanol generally has a positive impact on CO and tailpipe hydrocarbon emissions. However, NO_x emissions tend to increase when ethanol is added to gasoline. The ozone-forming potential tends to increase with ethanol/gasoline blends due to the increased evaporative, acetaldehyde and NO_x emissions.

The ethanol content of fuel does not necessarily influence benzene and 1,3-butadiene emissions, provided the olefin and benzene contents of the fuels are not influenced. Particulate matter emissions are reported to reduce with ethanol. Figure 3.4 and Table 3.3 summarize the emissions studies.

- Evaporative emissions may increase, but this can be avoided by adjusting the vapour pressure and by using advanced vapour canisters in cars.
- NO_x emissions tend to increase.
- Acetaldehyde emissions increase dramatically, formaldehyde only slightly.
- Benzene and 1,3-butadiene emissions may reduce if there is a "dilution effect".
- The ozone-forming potential may increase.
- The effect on emissions is observed mainly in cold starts and during heavy driving conditions.
- Emission trends with fuels vary more, and differences in emissions between fuels are smaller for new cars than for old cars.

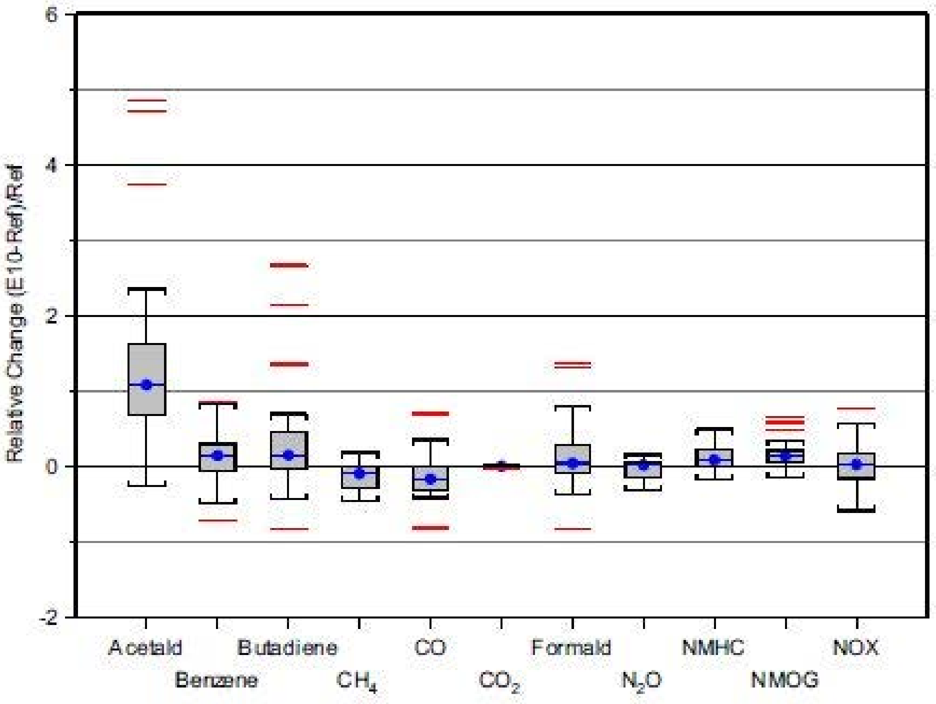


Figure 3.4. The effect of E10 fuel on exhaust emissions (Graham 2008).

Table 3.3. Changes in emissions when E10 fuel is compared with gasoline (negative values = reduction in emissions, positive values = increase in emissions).

	Literature (Change-%)	**Comment**
BENEFITS		
Carbon monoxide (CO)	-32 [a] -25...-30 [b] -16 [c] -95...+27 [d]	Reduction in emissions
Particulate Matter (PM)	-35 [a] -50...-40 [d]	Reduction in emissions
Hydrocarbons (HC)	-12 [a] -7 [b] +9 [c] -70...+20 [d]	Reduction in emissions, but NMHC may increase [c, e]
DRAWBACKS		
Acetaldehyde	+73 [e] +108 [c] ...+3500 [d]	Increase in emissions
NO_x	-5...+5 [b] +1 [a] +3 [c] -60...+30 [d]	Slight increase in emissions
Evaporative emissions	Increase [f]	Increase in emissions
Ozone-forming potential	Increase [c]	Increase in emissions
NOT SIGNIFICANT		
Methane	-9 [c] 0...+120 [d]	No clear effect
Formaldehyde	+5 [c] ...+70 [d]	No clear effect
1,3-Butadiene	-19 [a] +22 [e] +16 [c] -80...-10 [d]	Depends on fuel olefin content
Benzene	-27 [a] +18 [e] +15 [c] -80...-25 [d]	Depends on fuel benzene content
N_2O	+2 [c]	Depends on catalyst

[a] *Environment Australia 2002b* [b] *CRFA 2003* [c] *Graham 2008* [d] *Larsen 2009* [e] *Durbin et al. 2006* [f] *AFDC 2009*

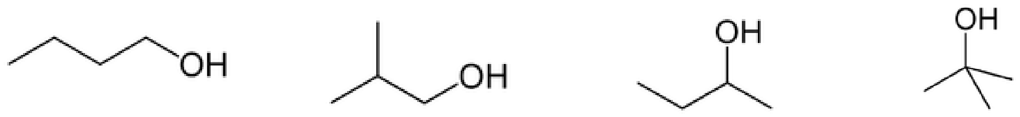
3.3.2 Butanol

European legislation allows a maximum of 15.0 v/v% of butanol isomers to be blended with gasoline. The oxygen limit in Europe would allow some 17 v/v% of butanol blended into gasoline. With regard to end-use aspects, butanol offers many benefits compared with ethanol as a gasoline component: higher energy content (lower fuel consumption), lower vapour pressure (lower evaporative emissions), higher blending ratio, lower water affinity (phase separation), less aggressive towards materials and suitable for current fuel infrastructure without needing high investments. The dilution effect may reduce the contents of olefins and aromatics in the gasoline pool. Adding butanol to gasoline does not require changes in cars or infrastructure. The drawbacks of butanol compared with ethanol concern lower octane numbers and higher production costs.

There are limited studies on exhaust emissions when butanol is used as fuel[11]. Adding 10% n-butanol to gasoline increases the volumetric fuel consumption by 2–3.5%. CO, HC and NO_x emissions do not change significantly; however, contradictory results are also reported. Formaldehyde, acetaldehyde, propene, 1,3-butadiene and acetylene emissions reduced with increasing butanol content, whereas the aromatic emissions reduced in one engine study.

3.3.2.1 Properties

Butanol has four isomers with the same chemical formula, but different structural arrangements: n-butanol, isobutanol, tert-butanol and sec-butanol (Figure 3.5). In the past, “gasoline-grade” tert-butanol (GTBA) was commonly present in gasoline as a co-solvent for methanol and denaturant for ethanol, and via MTBE usage if TBA had been used in MTBE production. TBA solidifies at about 26 °C, and co-solvents are therefore needed to facilitate handling and usage (API 2001). Today, isobutanol and n-butanol (bio-based) are under consideration as blending components with gasoline.



***n*-butanol** ***iso*butanol** ***sec*-butanol** ***tert*-butanol**

Figure 3.5. Isomers of butanol (Wikipedia 2011).

European legislation allows up to 15 v/v% (bio-energy 13%) butanol in gasoline. Isobutanol and tert-butanol are mentioned separately, while other butanol isomers are covered

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[11] Experimental part of this study included fuels containing isobutanol or n-butanol.

in the group of other oxygenates ("other monoalcohols and ethers with a final boiling point no higher than stated in EN 228:2004"). Automobile and engine manufacturers' recommendations for fuels (WWFC 2006) states that *"Higher (C > 2) alcohols are limited to 0.1% maximum by volume."* In the discussion section of WWFC, an explanation is given for limiting alcohols higher than C_2: *"The Charter represents recommendations for a global market, and as such, its specifications will differ in some regards from standards specific for any particular country or location. In this case,* C_3 *and higher alcohols are limited to 0.1% maximum."*

Selected fuel properties of methanol, ethanol and butanols are shown in Table 3.4. Technically, butanol is more suitable than ethanol for use as a gasoline component. Butanol is closer than ethanol to gasoline in terms of heating value, vapour pressure, water tolerance, corrosivity and polarity, for example. More butanol than ethanol can be blended into gasoline within the same oxygen limit. For example, an oxygen content of 3.6 wt-% is equivalent to 10 vol-% of ethanol in gasoline or 16 vol-% of butanol. Adding butanol to gasoline requires no changes to cars or infrastructure.

The octane numbers of butanol isomers are somewhat lower than those of methanol and ethanol. Of the butanol isomers, octane numbers are highest for isobutanol (blending MON 94). For n-butanol, blending MON is as low as 78–81.

Butanol has a lower blending vapour pressure than does ethanol. Essentially, butanol does not significantly increase the vapour pressure of gasoline at any blending ratio (Figure 3.6).

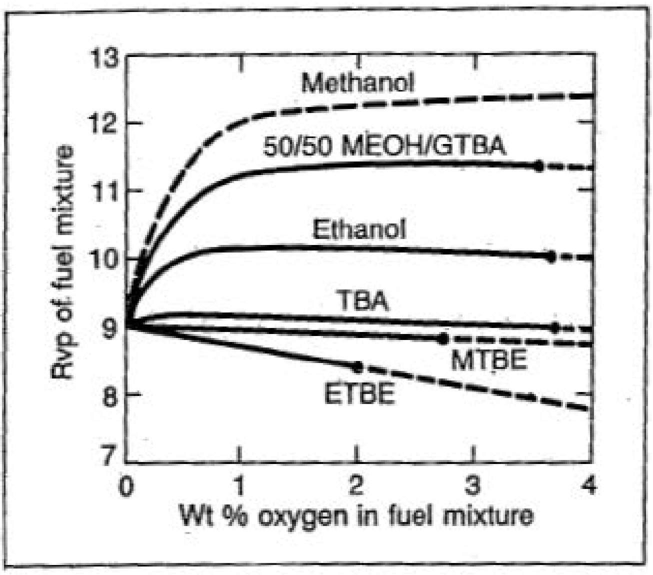

Figure 3.6. Vapour pressures of gasoline/oxygenate mixtures (unit is psi). TBA is abbreviation for tert-butanol (Piel and Thomas1990).

The boiling point of isobutanol is 108 °C, and that of n-butanol 117 °C. These butanol isomers bring higher boiling components into gasoline than does ethanol. Mid-range distillation components increase when butanol is blended with gasoline. The experimental part, Chapter 4, shows that the distillation curves of gasoline/butanol blends may be close to the upper E100 limit (volume evaporated at 100 °C) of European standard EN228.

The *energy content* of butanol is around 33 MJ/kg (27.0 MJ/l), representing some 84% of the volumetric energy content of gasoline. The increase in volumetric fuel consumption with butanol is therefore lower than with ethanol.

The *oxygen content* of butanol is 21.6%. The oxygen content of a fuel determines the stoichiometric air/fuel ratio, which is 11.2 kg air/kg fuel for butanol and 14.6 kg/kg for gasoline. The maximum oxygen content (3.7 wt-%) for gasoline defined in Directive 2009/28/EC is achieved with 16 vol-% isobutanol.

Oxygenates may reduce the content of *olefins and aromatics* of the gasoline pool via the dilution effect, depending on how the refinery blending is optimized.

The *heat of vaporization* of longer chain alcohols, e.g. butanol, is closer to that of gasoline; behaviour at low temperatures is therefore better by default than with ethanol, for example.

The *flame temperatures* of alcohols are generally lower than those of aromatics (Figure 3.7). NO_x emissions can therefore be lower for alcohol fuels than for gasoline. However, if alcohols lead to a rise in combustion temperature due to a leaning effect, NO_x emissions may increase (Piel and Thomas 1990). The flame temperature of butanol is closer to that of gasoline than that of ethanol.

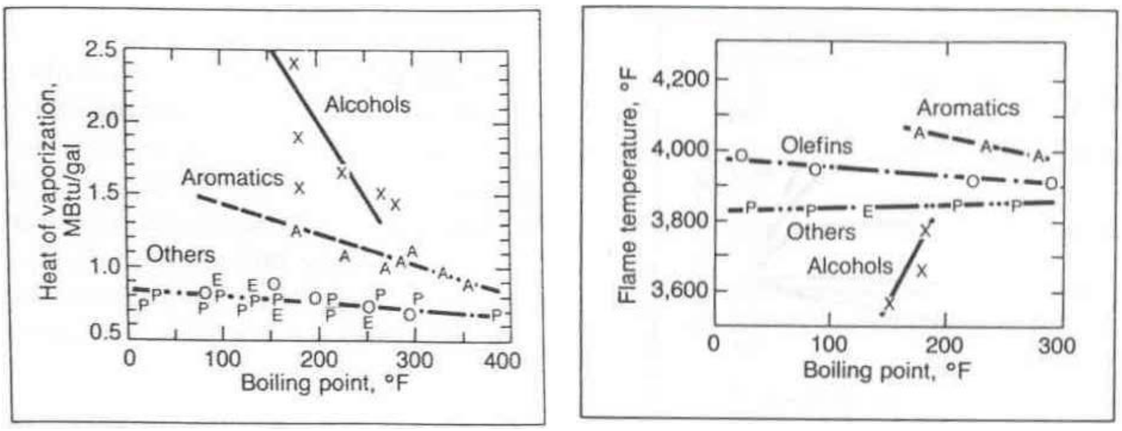

Figure 3.7. Heat of vaporization (left) and theoretical flame temperatures (right) assuming adiabatic and stoichiometric air. O = olefins, P = paraffins, E = ethers (Piel and Thomas 1990).

n-Butanol and isobutanol do not act similarly to ethanol in the presence of *water* (Figure 3.8). When water is added to a 10% n-butanol/gasoline blend, the volume of the water does not increase. Unlike ethanol, the n-butanol remains in the organic phase. However, *tert*-butanol is water-miscible, and *sec*-butanol partially so. The storage and handling of *n*-butanol or isobutanol blended with gasoline do not require expensive investments in the fuel infrastructure (BP 2006).

Butanol has a luminous flame, which is one of the safety factors (McCormick 2001).

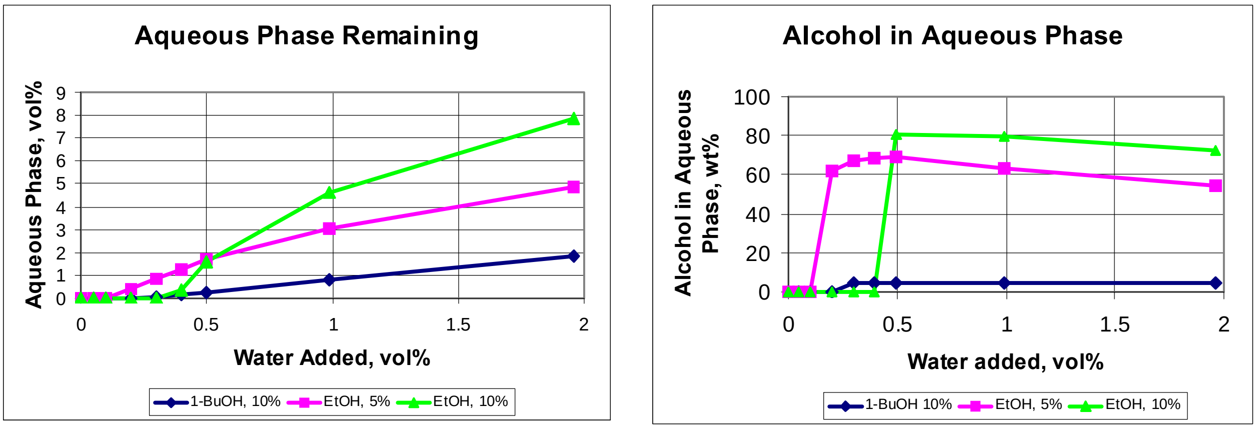

Figure 3.8. Phase separation of ethanol and n-butanol (BP 2006).

Elastomer compatibility for butanol is better than that for ethanol. BP (2006) reported the following results on material tests with n-butanol:

- The increases in weight and volume of viton and nitrile butadiene rubber with butanol are close to those with gasoline.
- No significant changes in the swelling or hardness of elastomers were observed for butanol compared with gasoline.
- Butanol passed 6-week corrosiveness tests with copper, brass, zinc, aluminium, steel and lead. The behaviour of butanol with regard to copper and brass is better than that of ethanol.

Thomas (2009) studied the compatibility of fluoroelastomers with hydrocarbon fuels, ethanol and n-butanol fuels, and their blends. He observed that ethanol blends were the most detrimental to the polymers evaluated.

3.3.2.2 Car and engine tests

General performance

There are a limited number of studies with butanol as a fuel. More studies are conducted with engines than with cars on chassis dynamometers or fleet tests.

An extensive study of cars using *n*-butanol as a gasoline component was published by BP (2006). Activities in this programme included testing of fuel pumps, inlet valve and combustion chamber deposits, exhaust emissions, power and driveability and field trials. However, only parts of the results have been published.

Fuels used in the BP study are shown in Table 3.4. Ethanol and n-butanol were splash-blended into base gasoline. Some properties, such as octane numbers, are therefore different for different fuels.

In tests with Audi A4 Avant 2.0 FSI and BMW CI cars, the effect of n-butanol on power output was lower than that of ethanol. If a car is equipped with a knock sensor, higher octane numbers can be utilized to produce higher power (BP 2006).

In the same study, a significant increase in volumetric fuel consumption was observed for alcohol blends compared with gasoline due to the low energy content of alcohols. The effect was higher for ethanol than for n-butanol. With four cars and fleet vehicles (Figure 3.9), the increase in volumetric fuel consumption varied from 2–3.5% when 10% n-butanol was added to gasoline (BP 2006).

Table 3.4. Properties of fuels used in the study by BP (2006).

	RON* [-] EN 25164	**Density** [kg/m³] EN 12185	**Aromatics** [%(v/v)] EN 14517	**TotalOxygen** [%(m/m)] EN 14517	**FBP** [°C] EN 3405	**Hu** [kJ/kg]
fuel RON 91	91.3	735.6	33.7	0.03	194.3	43423
fuel RON 91 + 5%BuOH	91.4	739.1	32.2	1.22	197.5	42828
fuel RON 91 + 10%BuOH	91.5	742.9	30.9	2.33	192.6	42057
fuel RON 91 + 5%EtOH	92.9	738.0	32.8	1.99	194.4	42477
fuel RON 91 + 5%EtOH + 2.5% BuOH	93.0	739.6	31.8	2.46	194.0	42401
fuel RON91+10%EtOH	95.6	741.0	30.9	3.79	193.9	41640

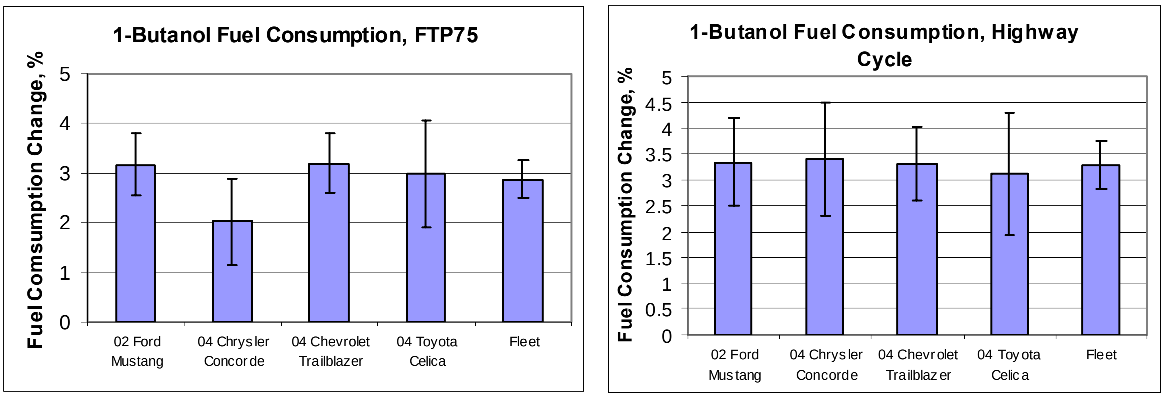

Figure 3.9. The effect on fuel consumption of adding 10% n-butanol to gasoline (BP 2006).

A major part of the studies with butanol has been conducted with engines on engine test benches. Wallner et al. (2009) reported a study using gasoline, 10% ethanol and 10% n-butanol blends in a direct-injection, four-cylinder, spark-ignition engine at engine speeds of 1000–4000 RPM with loads varying from idle to 150 Nm. The brake specific volumetric fuel consumption was lowest with the gasoline baseline fuel, due to its higher energy density compared with alcohol-containing fuels. The 10% n-butanol blend had a lower volumetric fuel consumption compared with the ethanol blend, consistent with differences in energy content. Brake specific volumetric fuel consumption was 3.4% higher for a blend containing 10% n-butanol, and 4.2% higher for E10 fuel compared with gasoline.

Cooney et al. (2009) reported results with n-butanol and isobutanol in a direct-injection gasoline engine. The engine combustion strategy was not changed, and stoichiometric operation was maintained via closed-loop lambda feedback. Brake thermal efficiencies were at the same level for all fuels at low and medium loads, but at high load ethanol and isobutanol benefited from their higher octane numbers compared with gasoline and n-butanol.

Cairns et al. (2009) studied gasoline/ethanol and gasoline/butanol[12] blends, covering a range of oxygen contents and octane numbers, to identify key parameters. A turbocharged multi-cylinder, direct-injection TWC- and EGR-equipped engine was used in this study. Under part-load conditions, 10% ethanol-containing fuel and 16% butanol-containing fuel, with similar oxygen contents, resulted in similar brake specific fuel consumptions.

Black et al. (2010) reported combustion properties and a detailed chemical kinetics model for n-butanol, finding that a higher oxygen concentration leads to faster ignition. Other studies on spray formation, combustion and, for example, laminar combustion

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[12] Cairns et al. (2009) did not specify which isomer of butanol was used.

velocity with n-butanol are reported by Serras-Perreira et al. (2008) and Beeckmann et al. (2009).

Wallner et al. (2009) reported that combustion velocity seemed to be higher for the n-butanol blend than for E10 blend or gasoline in a modern direct-injection four-cylinder spark-ignition engine. In this study, combustion stability did not differ significantly between test fuels, and the brake thermal efficiency was similar between fuels. There were relatively minor differences between the three fuels in their combustion characteristics such as heat release rate, 50% mass fraction burned and coefficient of variation of indicated mean effective pressure at low and medium engine loads. However, at high engine loads, the engine control unit retards the ignition timing substantially when n-butanol blend is used, due to this blend's reduced knock resistance. This was clear when compared with gasoline, and even more pronounced compared with the ethanol blend.

Driveability

Very limited data are available on regulated or unregulated emissions with butanol-containing gasoline. According to Stradling et al. (2009), mid-range distillation is significant for modern vehicles due to interrelated exhaust emissions under cold-start conditions. The experimental part of this study (Chapter 4) shows that the E100 value is high for isobutanol, and close to the upper limit of the EN228 standard for gasoline. E100 is much lower when n-butanol is used in blending than when isobutanol is used. The distillation characteristics of blends depend on the hydrocarbon components used for blending. The heat of evaporation of butanol is close to that of gasoline and substantially lower than that of ethanol, which could positively affect cold-weather driveability.

Exhaust emissions

BP (2006) concluded that HC or NO_x emissions did not change significantly when 10% of n-butanol blend was compared with gasoline in the standard FTP cycle or highway cycle tests with cars. In the highway cycle, a slight reduction in CO emissions was observed (BP 2006).

Wallner et al. (2009) studied gasoline, 10% ethanol and 10% n-butanol blends in a direct-injection, four-cylinder, spark-ignition engine at speeds of 1000–4000 RPM and loads from idle to 150 Nm. No significant differences in CO and HC emissions were observed between the test fuels. The 10% n-butanol blend had the lowest NO_x emissions, and the 10% ethanol blend the highest. The ethanol blend produced the highest peak specific NO_x due to the high octane rating of ethanol and its effective anti-knock characteristics.

Wallner and Frazee (2010) used a direct-injected four-cylinder gasoline engine (GM L850, 2.2 l) with exhaust gas recirculation (EGR) disabled to avoid changes in emissions due to slight changes in the EGR ratio. This study measured both regulated and unregulated emissions. Ethanol, n-butanol and isobutanol were used as blending agents in gasoline. The following results were obtained:

- NO_x emissions reduced with increasing alcohol content.
- Formaldehyde and acetaldehyde emissions increased with the blending ratio of n-butanol and isobutanol.
- A reduction in aromatic hydrocarbon emissions was observed with increased alcohol content.
- Butanol increased emissions of propene, 1,3-butadiene and acetylene (precursors for benzene and particulate matter).

Cooney et al. (2009) reported the results with n-butanol and isobutanol. Ethanol/gasoline and butanol/gasoline blends were tested with blending ratios of up to 85% of the oxygenated fuel. A direct-injection gasoline engine was used in this study. The engine combustion strategy was not changed, and stoichiometric operation was maintained via closed-loop lambda feedback. CO and HC emissions were reduced with ethanol, but remained unchanged with butanol compared with gasoline (Figures 3.10 and 3.11). At low engine loads, there was a slight increase in NO_x emissions with n-butanol. At higher loads, NO_x results scattered more than at lower loads, mainly due to the operation of EGR. The duration of injection is longer for alcohols than for gasoline, under the same load, and these changes affect EGR valve lift. Figure 3.12 shows that NO_x results at high loads are dependent on EGR valve lift.

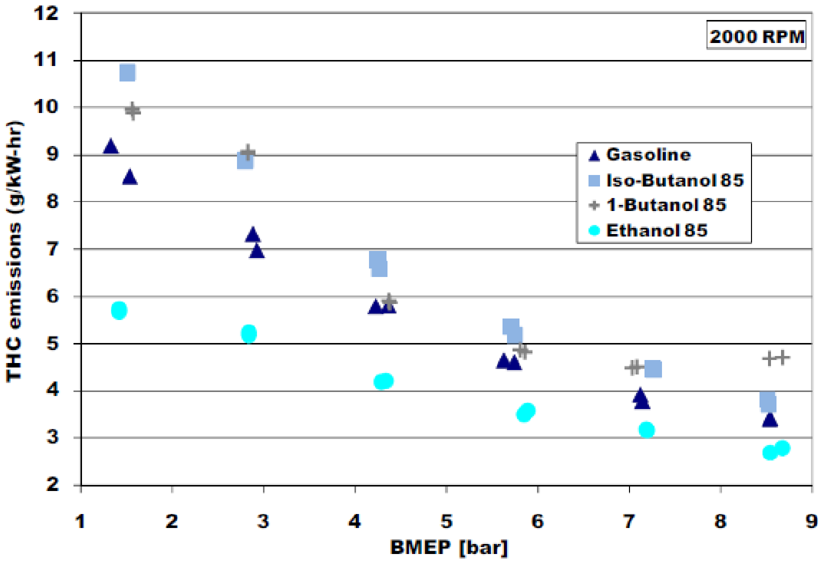

Figure 3.10. THC emissions with gasoline, isobutanol, n-butanol and ethanol blends at a concentration of 85% (Cooney et al. 2009).

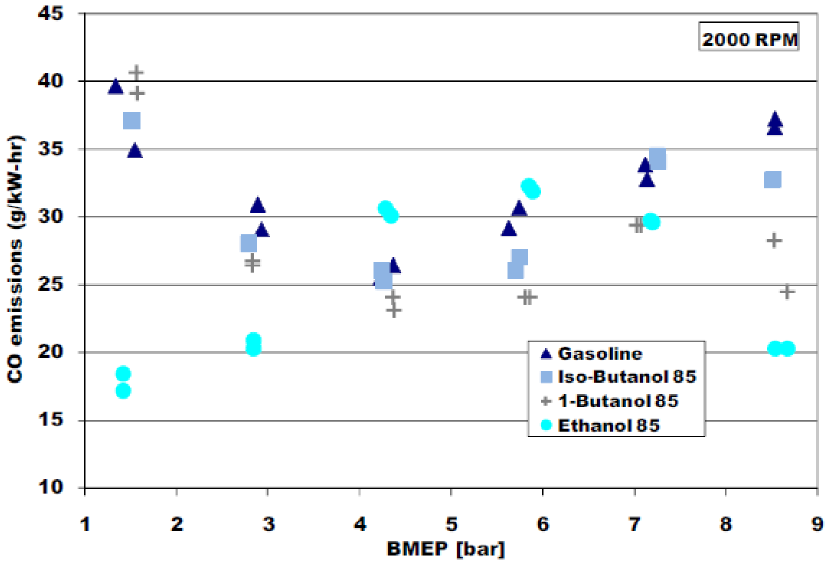

Figure 3.11. CO emissions with gasoline, isobutanol, n-butanol and ethanol blends at a concentration of 85% (Cooney et al. 2009).

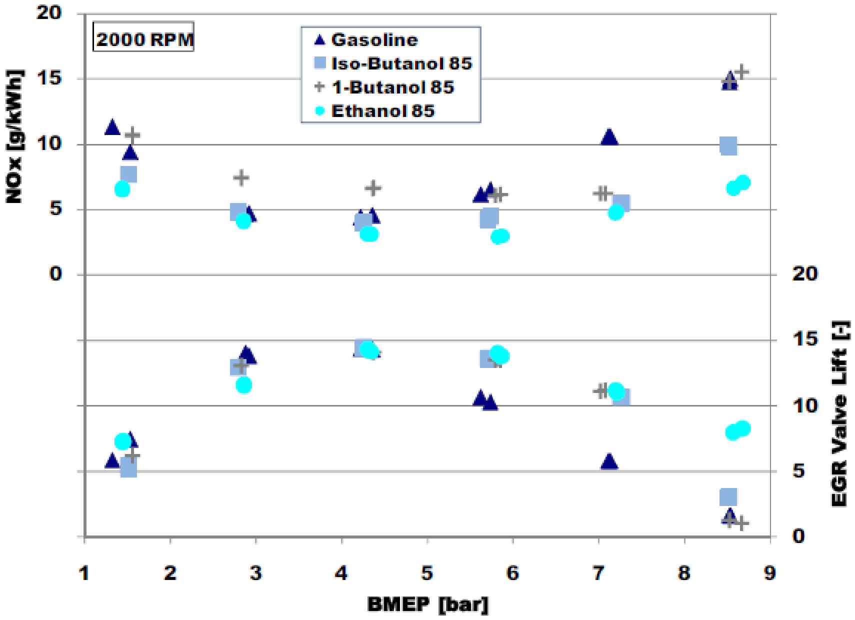

Figure 3.12. NO_x emissions with gasoline, isobutanol, n-butanol and ethanol blends at a concentration of 85% (Cooney et al. 2009).

Yang et al. (2009) studied blends containing 10–35% butanol[13] in gasoline. They observed that engine power was maintained until the butanol content reached 20%, but then dropped. Raw engine HC and CO emissions were reduced, but NO_x emissions increased with increasing butanol content.

Butanol summary

With regard to end-use aspects of isobutanol and n-butanol, these oxygenates offer many *benefits compared with ethanol*:

+ Higher energy content -> lower volumetric fuel consumption
+ Lower vapour pressure -> lower evaporative emissions
+ Higher blending ratio within the same oxygen limit
+ Lower water tolerance -> lower phase-separation risk
+ Less aggressive towards materials
+ Suitable for current fuel infrastructure without needing high investments.

There are also some drawbacks *with butanol compared with ethanol*:

– Lower octane numbers (octane rating of isobutanol is better than for n-butanol)
– Higher production costs.

The few studies on the effect of isobutanol and n-butanol on exhaust emissions have been carried out mainly with engines, not with cars. In a study with cars, CO, HC or NO_x emissions did not change significantly when 10% n-butanol blend was compared with gasoline. Under highway conditions, n-butanol slightly reduced CO emissions (BP 2006).

In studies with direct-injection engines, no significant differences were observed in CO and HC emissions with 10% n-butanol (Wallner et al. 2009) or 85% butanol (Cooney et al. 2009) compared with gasoline. Yang et al. (2009) observed lower HC and CO emissions when butanol was added to gasoline. Cooney et al. (2009) and Yang et al. (2009) observed an increase in NO_x emissions when butanol was added to gasoline. However, Wallner et al. (2009, 2010) reported lower NO_x emissions for n-butanol and isobutanol blends compared with gasoline.

Wallner and Frazee (2010) reported that both formaldehyde and acetaldehyde emissions increased when n-butanol or isobutanol were blended with gasoline. A reduction in aromatic hydrocarbon emissions was observed when isobutanol or n-butanol were added to gasoline, but an increase in emissions of propene, 1,3-butadiene and acetylene.

The effect of butanol on combustion characteristics seems to be relatively small. Cooney et al. (2009) reported that the duration of injection is longer for alcohols than for gasoline under the same load, and that these changes affect EGR valve lift. Ignition

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[13] Yang et al. (2009) did not specify which isomer of butanol was used.

timing was retarded with n-butanol at high engine loads due to the reduced knock resistance. Combustion velocity seems to be higher for the n-butanol blend than for ethanol blend or gasoline (Wallner et al. 2009).

According to Stradling et al. (2009), mid-range distillation is significant for modern vehicles due to interrelated exhaust emissions under cold-start conditions. The experimental part of this study (Chapter 4) shows that the E100 value is high for isobutanol, but much lower when n-butanol is a blending component. The heat of evaporation of butanol is close to that of gasoline, which indicates acceptable cold-weather driveability. However, cold-weather driveability and emissions when using butanol/gasoline blends warrant more attention.

3.4 E85 fuel

Special flexible-fuel vehicles (FFV) can use gasoline containing up to 85% ethanol. Due to the low heating value of E85 fuel, fuel injectors are designed for higher fuel flows than in conventional gasoline cars. Fuel consumption is therefore around 33% higher with E85 fuel than with gasoline. The ignition of ethanol is poor. FFV cars must inject excess fuel in cold starts, which leads to increased exhaust emissions until the car has warmed up. All materials in FFV cars are compatible with ethanol, which is more aggressive towards materials than gasoline. The most significant barrier to E85 fuel usage is the need for special FFV vehicles, infrastructure and safety measures. On the positive side, E85 fuel is not believed to present a risk of water separation.

Fuel evaporative emissions are reported to be lower for E85 fuel than for gasoline, with a potential reduction of some 30% or more. E85 fuel generally reduces CO, HC and NO_x ***emissions compared with gasoline, but not necessarily at low temperatures. Acetaldehyde emissions increase substantially, and formaldehyde emissions to some extent, with E85 fuel. Ethanol emissions tend to increase with E85 fuel, as do methane emissions, whereas 1,3-butadiene and benzene emissions reduce with E85 fuel compared with gasoline. E85 fuel generally produces lower particulate matter and PAH emissions than does gasoline at normal temperatures, but the situation is reversed at low temperatures. The ozone-forming potential of E85 fuel tends to be higher than that of gasoline.***

In the USA, so called P-Series fuel consisting of butane, pentanes, ethanol and the biomass-derived co-solvent methyltetrahydrofuran (MTHF) is allowed for FFV cars.

High-concentration ethanol (up to 85%) can be used in special flexible-fuel vehicles (FFV). E85 fuel is used in Brazil, North America and many European countries, for example. In China, the ministry for standards has approved the nationwide use of methanol as a motor vehicle fuel mixed with gasoline in blends up to M85, containing 85%

methanol and 15% gasoline (Methanol Institute 2011). However, M85 fuel is not discussed in this report.

The properties of neat ethanol are presented in Chapter 3.3. With regard to E85 fuel blends, the most significant remark on fuel properties concerns the low volatility and poor energy content of ethanol. Ignition of ethanol is poor; at least 15 vol-% of gasoline is therefore added to ethanol, and even more to winter-quality. Ethanol is flammable over a wide temperature range, which increases safety risks. The low energy content of ethanol leads to high volumetric fuel consumption.

The CEN workgroup CEN/TC 19/WG 21/TF has developed a proposal for a standard for gasoline containing max. 85% ethanol (E85 fuel): prEN 15293 "Automotive fuels – Ethanol (E85) automotive fuel - Requirements and test methods". The prEN 159293:2009 defines four volatility classes. The ethanol content in Class d (winter grade) is 50–85%, and in Class b (summer grade) 70–85%.

Materials, infrastructure and safety aspects of low-concentration ethanol are described in Chapter 3.3. In many respects, these also apply to E85 fuel. However, E85 fuel is not very sensitive towards water, and hydrous ethanol can therefore be used in the production of E85 fuel. However, in this case ppossible phase separation risk should be considered when refuelling FFV car with low-level ethanol E10. Nevertheless, a number of issues must be taken into account when infrastructure and safety aspects are considered for E85 fuel. Special vehicles, materials, distribution systems and safety measures are needed.

In Finland, Paasi et al. (2008) reported safety factors with regard to biofuels. The report included considerations of materials, electrical conductivity and safety risks. The mixture above the liquid surface in an E85 fuel tank is normally determined by the gasoline fraction. If the tank is less than 10–20% full, or has been warmed, ethanol may determine the flammability of the mixture, which increases safety risks.

Table 3.5. CEN standard proposal for E85 fuel.

	E85 prEN 15293:2009
Octane number (RON)	min. 104.0
Octane number (MON)	min. 88.0
Density at 15 °C, kg/m^3	760.0–800.0
Oxidation stability, minutes	min. 360
Existent gum, mg/100 ml	max. 5
Copper strip corrosion (3h at 50°C)	Class 1
Total acidity (as acetic acid), % m/m	max. 0.005
pHe	6.5–9
Electrical conductivity, µS/cm	max. 2.5
Methanol, % v/v	max. 1.0
Higher alcohols (C3-C5), % v/v	max. 6.0
Ethers (C5 +), % v/v	max. 7.7
Water content, % m/m	max. 0.400
Inorganic chlorides, mg/kg	max. 6.0
Copper, mg/kg	max. 0.10
Phosphorus, mg/l	max. 0.15
Sulphur content, mg/kg	max. 10.0
Sulphate content, mg/kg	max. 4
Appearance	Clear and colourless

Climate related requirements		
	Ethanol and higher alcohols % v/v	Vapor pressure kPa
Class a	[a] -85	35.0–60.0
Class b	70–85	50.0–80.0
Class c	60–85	55.0–80.0
Class d	50–85	min. 60.0

[a] To be decided.

Performance in cars[14]

Research work on E85 fuel is typically conducted by comparing E85 fuel with E5 fuel or with gasoline in the same FFV car. However, FFV cars do not necessarily perform in the same way with low-oxygen fuels as do TWC-equipped conventional gasoline cars, which are optimized for low-oxygen gasoline. Comparisons between the best available FFV technology and the best available gasoline car technology are not common. The development of FFV cars is continuing with, for example, catalyzed hydrocarbon traps, intake port heating and heated fuel injectors.

General performance

Fuel consumption is substantially higher with E85 fuel than with gasoline. The manufacturer's figures for one FFV car are 6.7 l/100 km with gasoline and 8.9 l/100 km with E85 fuel, which equates to 33% higher volumetric fuel consumption with E85 than with gasoline. Ethanol's better octane rating enables a higher compression ratio, which can improve efficiency and fuel consumption to some extent. FFV cars must inject excess fuel in cold starts with E85 fuel to achieve performance similar to that of a gasoline car.

Sensors in an FFV car stabilize slowly after switching between E85 and gasoline fuels, which is a challenging issue for test programmes (Graham et al. 2008). This was also noted in the experimental part of this study.

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[14] Background to articles on the performance of E85 fuel in FFV cars:

Chiba et al. (2010): 4-cylinder 2 l engine using E0 and E85 fuels.

Yanowitz and McCormick (2009): analysis of US EPA certification database and literature. The results from 1979 to 2007 are available in the EPA database. 12 models of 70 FFV models from year 2007. Both E85 and hydrocarbon fuels were used in the tests.

Westerholm et al. (2008), Karlsson et al. (2008): two FFV cars of model year 2005 (Saab and Volvo). Tests at 22 °C and -7 °C, over cold-start NEDC and hot-start Artemis test cycles. Block heaters were not used at cold test temperature.

Graham et al. (2008): One 2004 FFV car and two 2002 Chrysler Caravans (one conventional and one FFV). The FFV cars were tested with E85 fuel and gasoline. Gasoline contained 26 vol-% aromatics and 0.8 vol-% benzene. The article includes a literature review.

West et al. (2007): Saab 9-5 Biopower tests with E85 and gasoline. Measurements included fuel consumption, regulated emissions, individual hydrocarbons and aldehydes.

De Serves (2005): three Ford Focus 1.6 l FFV cars meeting Euro 4 emissions limits. Tests were conducted with E5, E10, E70 and E85 fuels using Artemis and NEDC driving cycles. At -7 °C, E70 fuel was tested both with and without a pre-heater, E85 fuel only with a pre-heater and other fuels without a pre-heater.

Evaporative emissions

Fuel evaporative emissions are lower for E85 fuel than for gasoline (Yanowitz and McCormic 2009). CRFA (2003) reports that the potential reduction of volatile organic compounds with E85 fuel is some 30% or more, thanks to E85 fuel's low vapour pressure. In a study reported by Westerholm et al. (2008), evaporative emissions were also lower with E85 fuel than with E5 fuel in an FFV car.

Haskew and Liberty (2006) studied the effect of ethanol on permeation. The high-level ethanol blend (E85 fuel) tested in the flexible-fuel vehicle system had lower permeation emissions than the non-ethanol (E0) fuel.

Chiba et al. (2010) reported that the evaporative characteristics of E85 fuel lead to the condensation of unburnt alcohol in the combustion chamber. Condensed alcohol is released in cold starts.

Carbon monoxide

Yanowitz and McCormic (2009), Graham et al. (2008) and West et al. (2007) reported lower, or not significantly changed, CO emissions for E85 fuel compared with gasoline. De Serves (2005) observed that CO emissions increased in the cold-start NEDC driving cycle on switching from E5 to E85 fuel. Westerholm et al. (2008) observed that in the hot-start Artemis highway cycle, CO emissions were lower for E85 fuel than for gasoline. At -7 °C, contradictory effects of E85 on CO emission were observed by De Serves (2005) and Westerholm et al. (2008).

Tailpipe hydrocarbons

Graham et al. (2008) and Yanowitz and McCormic (2009) reported a statistically significant reduction in non-methane hydrocarbon emissions (NMHC) for E85 fuel compared with gasoline at normal test temperatures. No consistent differences in HC emissions were observed on switching from E5 to E85 fuel, according to De Serves (2005) and Westerholm et al. (2008).

De Serves (2005) observed that increasing the ethanol content of fuel reduced tailpipe HC emissions in two cars at -7 °C, the opposite being true in one car. Westerholm et al. (2008) observed a strong increase in hydrocarbon emissions for E85 fuel compared with E5 fuel at -7 °C. Aakko and Nylynd (2003) reported that hydrocarbon emissions with E85 fuel were significantly higher than those from a gasoline-fuelled car at -7 °C.

The calculation methodology has a significant impact on the HC emissions results with E85 fuel. This issue is discussed in the experimental part of this report (Chapter 4).

Methane

Higher methane emissions have been observed for E85 fuel than for gasoline (Yanowitz and McCormic 2009). In tests at -7 °C, methane emissions were slightly higher for E85 fuel than for gasoline (Aakko and Nylund 2003).

1,3-Butadiene and benzene

Yanowitz and McCormic (2009) and West et al. (2007) reported that 1,3-butadiene and benzene emissions were lower for E85 fuel than for gasoline. Westerholm et al. (2008) reported that toluene emissions were also lower for E85 fuel. However, differences in emissions were negligible in the hot-start Artemis test cycle. Aakko and Nylund (2003) observed no significant differences in 1,3-butadiene, benzene and toluene emissions between an E85-fuelled FFV car and gasoline cars.

At -7 °C, 1,3-butadiene, benzene and toluene emissions with E85 fuel and gasoline were at the same level (Westerholm et al. 2008). High emissions at low test temperatures may obscure differences between the fuels.

Aldehydes and ethanol

Chiba et al. (2010) measured ethanol, formaldehyde and acetaldehyde emissions during engine cold starts (Figure 3.13 and 3.14). The sum of these constituents represents a major part of non-methane organic gas (NMOG) emissions. The latent heat of vaporization of ethanol is higher than that of gasoline, leading to poor cold-startability and high organic gas emissions. NMOG emissions increased by about 50% in cold starts when E85 fuel was compared with gasoline. Ethanol represented the highest share of NMOG emissions in cold starts.

Yanowitz and McCormic (2009) reported that E85 fuel does not affect NMOG with Tier 2 vehicles.

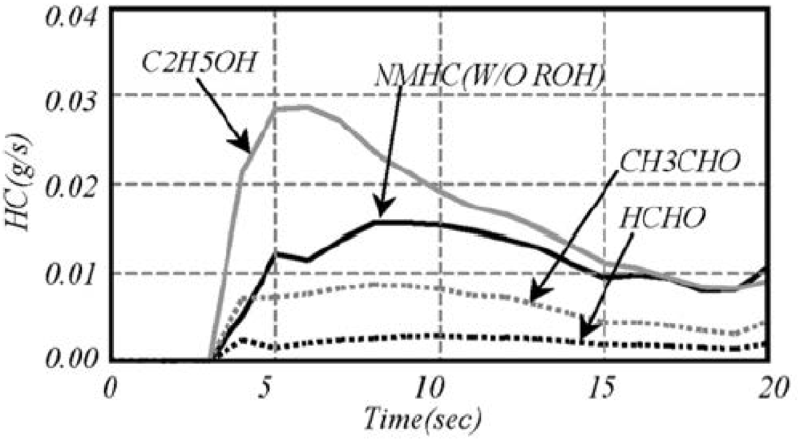


Figure 3.13. Ethanol, formaldehyde, acetaldehyde and total hydrocarbons in cold starts with E85 fuel (Chiba et al. 2010).

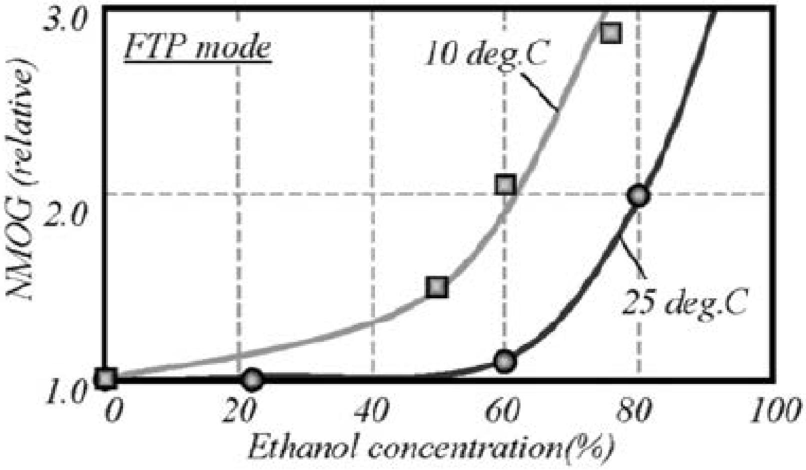


Figure 3.14. The effect of fuel ethanol content on NMOG emissions (Chiba et al. 2010).

Yanowitz and McCormic (2009), Graham (2008) and West et al. (2007) reported that acetaldehyde emissions increased substantially when E85 fuel was compared with gasoline. Yanowitz and McCormic (2009) also observed an increase in formaldehyde emissions. Westerholm et al. (2008) reported that acetaldehyde emissions were 8–15 times higher for an FFV car using E85 than when using E5 fuel. De Serves (2005) also observed a very high increase in acetaldehyde emissions for E85 compared with E5 fuel over the cold-start NEDC cycle.

West et al. (2007) reported that acetaldehyde emissions were lower with E85 fuel than with gasoline in the hot-start US06 test cycle. De Serves (2005) reported that in the hot-start Artemis test cycle, the differences between E85 and E0 fuels were negligible over the test cycle, and aldehyde emissions levels were low in general. In the hot-start Artemis cycle, the catalyst is fully warmed-up and emissions levels are very low.

According to Westerholm et al. (2008), acetaldehyde emissions were more than 100 times higher for E85 than for E5 fuel at a test temperature of -7 °C.

Ethanol emissions are higher for E85 fuel than for gasoline (Yanowitz and McCormic 2009, Westerholm et al. 2008 and West et al. 2007). However, West et al. (2007) observed no differences in ethanol emissions over the hot-start US06 test.

Nitrogen oxides, ammonia

NO_x emissions from FFVs running on E85 fuel are generally lower than or at the same level as those from gasoline-fuelled cars (Yanowitz and McCormic 2009, Graham et al. 2008 and Westerholm et al. 2008). CRFA (2003) estimates that the potential NO_x reduction with E85 fuel is some 20%.

De Serves (2005) observed that NO_x emissions were significantly lower for E85 fuel than for E5 fuel, not only in the first phase of the cold-start NEDC cycle but also in the hot-start Artemis high-way cycle. NO_x consisted almost totally of NO, indicating that NO_2 emissions from these FFV cars were low.

At -7 °C, lower NO_x emissions were observed by Westerholm at al. (2008) for E85 than for E5 fuel with one car, but not with the other car.

Westerholm et al. (2008) observed ammonia formation with one of the FFV cars tested. This occurred over the Artemis hot-start driving cycle and over the NEDC driving cycle at -7 °C.

Particles emissions

An FFV car using E85 fuel generally has a low level of particulate matter emissions. For example, Yanowitz and McCormic (2009) reported lower PM emissions from an FFV car using E85 fuel than from a gasoline-fuelled car. De Serves (2005) also observed one car with lower PM emissions with E85 than with E5 fuel. The emissions levels were very low with other cars. Westerholm et al. (2008) also observed a low level of PM emissions (below 1 mg/km) at normal temperature. Higher PM emissions for E85 fuel than for gasoline were observed at -7 °C, which might be related to cold-start problems with FFV cars using E85 fuel.

Westerholm et al. (2008) and De Serves (2005) measured particle number emissions using the so-called “PMP” protocol, which measures dry particles in exhaust gas. Particle number emissions in the NEDC cycle and Artemis high-way cycle on averaged 10^{11}–10^{12}/km in the study by Westerholm et al. (2008), whereas the level was below 10^{11}/km in the study by De Serves (2005).

Westerholm et al. (2008) reported that particle number emissions were higher for gasoline than for E85 fuel at normal temperature, but that the opposite was true at -7 °C. De Serves (2005) found it difficult to draw conclusions on fuel-related changes in particle number emissions, because cars did not respond consistently to fuel switches.

PAH and nitro-PAH compounds

Westerholm et al. (2008) reported that PAH emissions for E85 fuel were generally at the same level as or lower than for E5 fuel at normal test temperature. At -7 °C, particulate and semivolatile-associated PAH emissions and cancer potency were higher with E85 fuel than with gasoline.

Ozone-forming potential

Yanowitz and McCormick (2009) reviewed studies of the ozone-forming potential of E85 fuel. With Tier 1 vehicles, the ozone reactivity of exhaust gases was lower for E85 fuel than for reformulated gasoline in some studies, although the ozone-forming potential was higher. Cold-start emissions seem to dominate this result. Studies did not consider atmospheric chemistry at individual sites, nor the effect of E85 fuel on NO_x emissions. In the study by Graham et al. (2008), ozone-forming potential seemed to be lower for E85- than for gasoline-fuelled FFV cars.

Jacobson (2007) studied the effect of E85 fuel on cancer and mortality in the USA. He concluded that E85 fuel may increase ozone-related mortality, hospitalization and asthma compared with gasoline. Modelling was based on emissions inventories from 11 studies, each of which included several vehicles. Four studies were from the 1990s, and the others were based on tests with cars up to model year 2007.

Summary for E85 fuel

E85 fuel can be used in special FFV cars. Fuel consumption with E85 fuel is substantially higher, by approximately 33%, than with gasoline. Ethanol's better octane rating enables a higher compression ratio, which can improve efficiency and fuel consumption to some extent.

An E85/FFV car generally produces lower levels of CO and HC emissions than does a gasoline car, but emissions may be higher at low temperatures. NO_x emissions from FFV cars running on E85 fuel are lower than or at the same level as those from gasoline-fuelled cars.

Methane emissions tend to be higher for E85 fuel than for gasoline. 1,3-butadiene and benzene emissions are lower for E85 fuel than for gasoline.

Acetaldehyde and ethanol emissions increase substantially with E85 compared with gasoline, particularly at low temperatures. Formaldehyde emissions increase to some extent with E85 fuel.

An FFV car using E85 fuel generally has particulate matter and PAH emissions levels as low as, or lower than, those of gasoline-fuelled cars. However, at -7 °C, particulate matter, PAH emissions and cancer potency have been higher for E85 fuel than for gasoline.

The ozone-forming potential with E85 fuel has been reported to be higher than that with gasoline, but not consistently.

When the catalyst is fully warmed-up, the differences between fuels reduce. In addition, the engine and emissions control technology of FFV cars is improving; for example, catalyzed hydrocarbon traps, intake port heating and heated fuel injectors have been studied.

The results of Graham (2008) are summarized in Figure 3.15. Other studies are summarized in Table 3.6.

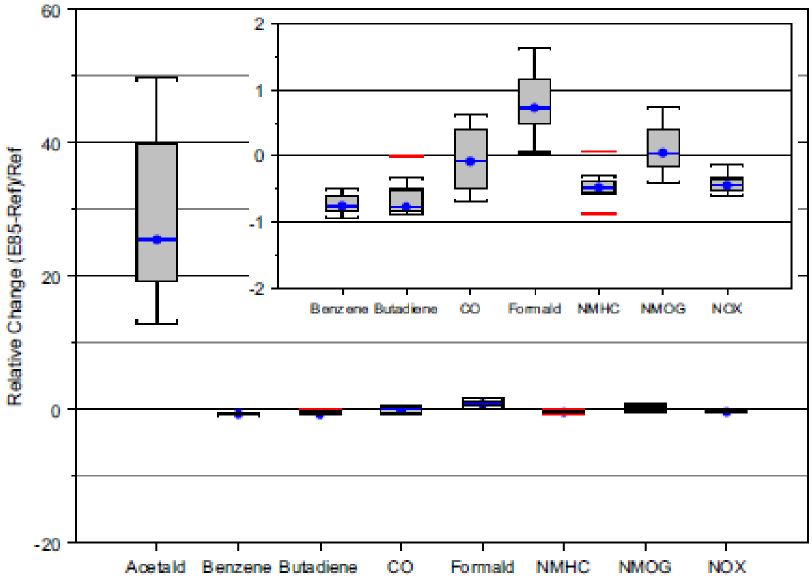


Figure 3.15. E85 fuel compared with reference fuel (Graham et al. 2008).

Table 3.6. Changes in emissions when E85 fuel is compared with gasoline or E5 fuel.

	E85 fuel compared with gasoline or E5 fuel (Change-%)*	Conclusion
BENEFIT IN EMISSIONS		
CO	-38…+320 (8) [a]; -8 (ns) [b]; -20 (ns) [c]	Reduce (increase at cold)
Hydrocarbons	-8 [c]; -48 [b] **	Reduce (increase at cold)
NO_x	-59…+33 (8) [a]; -45 [b]; -18 [c]	Reduce
Ethene	-17 (1) [a]	Reduce
1,3-Butadiene	-17…0 (2) [a]; -77 [b]; -62 [c]	Reduce
Benzene	-85…-62 (3) [a]; -76 [b]; -70 [c]	Reduce
Particulate matter, PAH	+31 (1) [a]; -34 (ns) [c]; (ns) [d]	Reduce or not changed at normal temperature (increase at cold)
DRAWBACK IN EMISSIONS		
Acetaldehyde	+1250…+4340 (6) [a]; +2540 [b]; +1786 [c]; +1304…1614% at -7°C [e]	Huge Increase
Formaldehyde	+7…+240 (5) [a]; +73 [b]; +63 and +54, [c]	Increase
Organic gases (mainly aldehydes)	0…+63 [a];, +5 (ns) [b];, +12; +28[c]	
Methane	+43…+340 (3) [a]; +92 [c]	Increase
PAH emissions and cancer potency	Huge increase at low temperature [d]	Huge increase at low temperature

*) Number of studies reviewed in parentheses. ns = not significant **) NMHC
[a] Jacobson 2007 [b] Graham 2008 [c] Yanowitz and McCormic (2009) [d] Westerholm et al. (2008) [e] Karlsson 2008

3.5 Ethers

3.5.1 General

The conversion of alcohols to ethers, ethanol into ETBE or TAEE and methanol into MTBE or TAME produces gasoline components with excellent fuel properties. Diisopropyl ether (DIPE) is a further option under consideration as a gasoline component. In Europe, Directive 2009/30/EC allows a maximum of 22.0 v/v% of ethers containing five or more carbon atoms in gasoline. Automobile and engine manufacturers' recommendations for fuels, "World Wide Fuel Charter", states that "*Where oxygenates are used, ethers are preferred*" (WWFC 2006).

In the past, MTBE has been widely used as an oxygenate in reformulated gasoline. Oxygenates were initially introduced into gasoline to compensate octanes lost due to the phasing out of lead to enable the use of three-way-catalysts. Oxygenates were subsequently added to the gasoline pool to reduce exhaust emissions. A minimum oxygen limit for gasoline was consequently introduced in the USA and Europe, which led to the widespread use of MTBE in gasoline (Arteconi et al. 2011). In the USA, ethanol has gradually replaced MTBE.

Global fuel ether demand in 2009 was 16.5 million tonnes. Of this, 78% was MTBE, 14% ETBE and the remainder TAME and TAEE. Europe accounted for 26% of ether consumption, and Asia-Pacific 25%. Substantial quantities of fuel ethers are also used in Latin America and the Middle East (EFOA 2011).

In Europe, MTBE and ETBE are the dominant fuel ethers. TAME and the ethanol-based ether TAEE are also used to some extent (Figure 3.16). In Europe, the demand for fuel ethers was about 6 million tonnes in 2009, of which ETBE consumption was around 2.5 million tonnes (~1.6 Mtoe). The total consumption of ethanol, as such and as ETBE, was 2.34 Mtoe in Europe in 2009. A substantial proportion of the ethanol is used as ETBE in Europe, but markets for neat ethanol are increasing (EFOA 2011, Biofuels Barometer 2010).

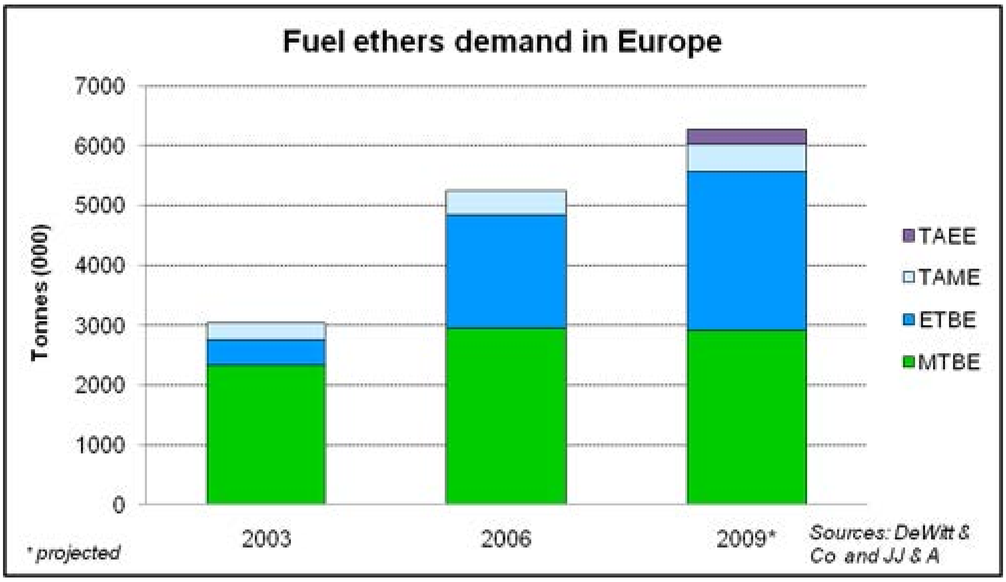


Figure 3.16. Fuel ethers demand in Europe (EFOA 2011).

3.5.2 Fuel properties

The molecular structures of MTBE, ETBE, TAME and TAEE are shown in Table 3.7. Selected properties of ethers are shown in Table 3.8.

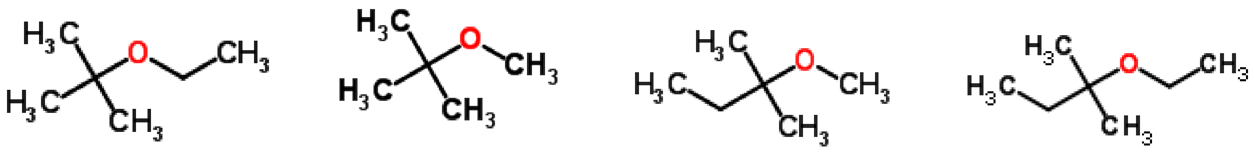
The octane numbers of ethers are high, and they have therefore been used as octane boosters in gasoline (Figure 3.17). The vapour pressures of ethers are low (Figure 3.6). Ethers do not exhibit azeotropic behaviour with gasoline, so blending is therefore predictable with regard to volatility properties. This is a substantial benefit for ethers compared with methanol or ethanol (Wallace 2009). Ethers affect mid-range distillation by increasing the volume distilled at 100 °C (E100), which is observed for ETBE in the experimental part of this study (Chapter 4). The heat of vaporization of ethers is at the same level as for gasoline.

According to Wallace (2009), the addition of ETBE in the mid-range distillation could improve vehicle warm up during cold engine operation with no drawbacks in hot-driveability performance.

Ethers do not contain olefins and aromatics. Splash-blending may therefore reduce the content of these species in the gasoline pool via the dilution effect. Some ethers tend to form peroxides, so the use of stability inhibitor additives is recommended.

The water-solubility of ethers is low, so ethers do not present a risk of phase separation or other water-related problems. However, the water-solubility of ethers is slighlty higher than that of hydrocarbon fuels. In the USA, leaking storage tanks and spills caused groundwater pollution, which led to MTBE bans and the gradual replacement of MTBE by ethanol (EIA 2006).

Table 3.7. Molecular structures of MTBE, ETBE, TAME and TAEE (EFOA 2011).



MTBE *Methyl-tertiary-butyl-ether* *ETBE* *Ethyl-tertiary-butyl-ether* *TAME* *Tertiary-amyl-methyl-ether* *TAEE* *Tertiary-amyl-ethyl-ether*

Table 3.8. Fuel properties of selected ethers and gasoline.

	MTBE[a]	ETBE[a]	TAME[a]	TAEE[f]	DIPE[d]
Chemical formula	C5H12O	C6H14O	C6H14O	C7H16O	C6H14O
Mol. weight, g/mol	88.2	102.2	102.2	116.2	102.2
Carbon/Hydrogen/Oxygen, % m/m	68.1/13.7/18.2	70.5/13.8/15.7	70.7/13.8/15.7	72.4/13.8/13.8	70.5/13.8/15.7
Density 15 °C, kg/l	0.74	0.74	0.77	0.766	0.73
Boiling point, °C	55	73	86	101	68[d,i]
Octane numbers					
Blending RON*	115–123	110–119	111–116	105, 112[k]	105
Blending MON*	98–105	95–104	98–103	95, 98[k]	98[h]
Vapour pressure at 37.8 °C, kPa	55[h]	28 [h,j]	17[h]	7	35
Lower heating value, MJ/kg	35.1	36.5	36.5	-	37.0
Heat of vaporisation, kJ/kg	337[b], 356[e], 462	314, 344[e]	326[b], 354[e]	-	340
Auto-ignition temperature, °C	435[a,g], 460[b]	304[g]	460[g]	-	443[g]
Flammability limits, fuel in air, % v/v	1.6–8.4	1.0–6.8[g]	1.0–7.1	-	1.4–7.9
Stoichiometric air/fuel ratio	11.7	12.2	12.1	12.5	12.1
Solubility					
Fuel in water, 20 °C, % v/v	4.8g, 5.7[k]	1.2g, 2c, 2.2[k]	1.15g, 1.4[k]	0.5[k]	1.1[g]
Water in fuel, 20 °C, % v/v	1.5[g]	0.5[g]	0.6[g]	-	0.6[g]
Odour detection in water, µg/l	15[k]	49[k]	194[k]	-	-
Taste detection in water, µg/l	40[k]	47[k]	128[k]	-	-
Odour treshold, ppb	-	13	-	-	-

*) Depends on blending ratio and gasoline composition.

[a] Owen 1995 [b] Prezelj 1987 [c] Piel 1990 [d] Piel 1992 [e] Nylund 1992 [f] Kivi 1991 [g] API 2001 [h] Nutek 1994 [i] Unzelman 1991 [j] EFOA 2006 [k] EFOA 2011

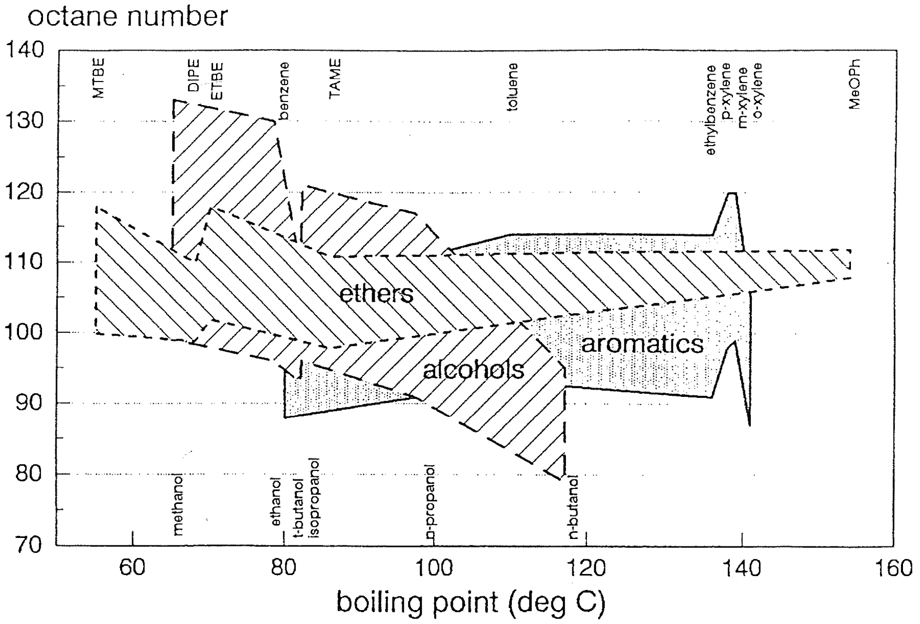


Figure 3.17. Octane numbers as a function of boiling point for oxygenates and aromatics (Oil Gas 1991).

Ethers are compatible with the current car and fuel distribution chain. Normal pipelines and procedures can be used for handling fuel ethers. Furthermore, ethers have already been used for decades as a gasoline component.

The compatibility of fuels with elastomers can be evaluated by volume swell in long-term immersion tests. Engine manufacturers have different criteria for different materials, but swells less than 20% are generally acceptable (Wallace et al. 2009).

Wallace et al. (2009) reviewed the compatibility of ETBE with materials. One study referred to was conducted by ARCO Chemical Company in 1990 with 13% MTBE, 13% ETBE and neat ETBE fuels. ETBE resulted in less swell than premium gasoline for all elastomers studied except for Viton A, which only experienced a small increase. Swelling was slightly higher with 13% MTBE than with 13% ETBE.

Wallace et al. (2009) refer to data on DuPont's website, which includes elastomer compatibility results for MTBE, TAME, ethanol and ETBE (Figure 3.18). In general, ETBE exhibited the lowest seal swell. Higher swelling was observed for ethanol and MTBE.

According to Wallace et al. (2009), swelling was not observed with ethers in a study with elastomers by Japan Auto and Oil Industries.

Permeation is a function of the ability of a fuel to swell elastomers. The other aspect of permeation is as a route to induce evaporative emissions. Ethers that did not exhibit a swelling ability greater than that of gasoline are not expected to increase fuel permeation emissions.

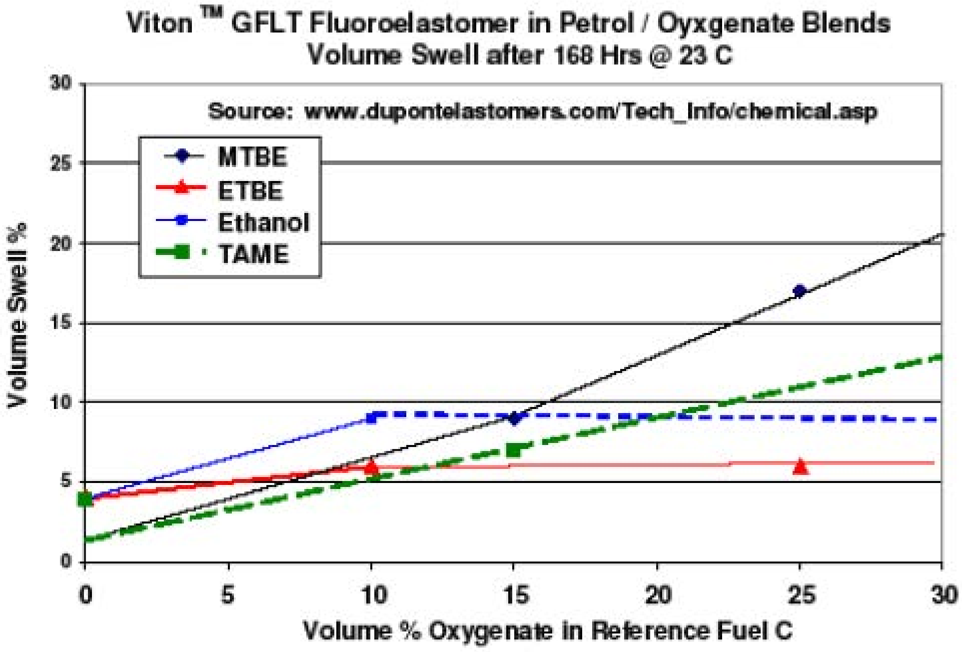


Figure 3.18. Volume swell of Viton GFLT Fluoroelastomer (data from DuPont referred to by Wallace et al. 2009).

3.5.3 Car tests

Wallace et al. (2009) reviewed driveability and emissions tests with ETBE. One driveability study with ETBE- and ethanol-containing fuels with 2–4.3 wt-% oxygen contents was conducted in the early 1990s by Neste Oil. All fuels had good starting properties. The cold-weather driveability performance of a multi-point injection car (model year 1993) was excellent with all fuels tested. In hot-weather driveability tests, drawbacks generally increased with increasing test temperature. However, the differences between fuels were negligible.

Wallace et al. (2009) references a study published by H. Tanaka et al. in 2006. Evaporative emissions tests were conducted with fuels containing 3 or 10 vol-% ethanol or 8 vol-% ETBE. Neither ethanol nor ETBE increased refuelling loss emissions when the vapour pressures of the fuels were tailored to the same level. Running loss emissions with ethanol tend to increase more than with gasoline, despite the vapour pressures of the fuels being similar. The vapour pressure of ethanol increases with increasing temperature more rapidly than that of gasoline or ETBE. Another study published by Tanaka et al. in 2007 was referred to by Wallace et al. (2009). This study with 3% ethanol or 8% ETBE blends showed increased diurnal breathing losses with ethanol, but not with ETBE. It was concluded that this was due to differences in the permeation abilities of the fuels.

Arteconi et al. (2011) conducted a literature review on oxygenates, including MTBE, ETBE, TAME, TAEE and DIPE. With regard to exhaust emissions, a number of studies referred to were from the 2000s: 11 studies on MTBE, two on ETBE, two on TAEE and one on DIPE. All studies that referred to TAME emissions were from the 1990s.

The general trend was that all fuel ethers reviewed by Arteconi et al. (2001) reduced harmful emissions. Emissions reductions depend on the oxygenate type, blending ratio, operating conditions, engine characteristics and many other parameters. Specific observations from this review include:

- CO and HC emissions reduced with fuel ethers. With MTBE, the highest CO reduction was with a 10% blend at low loads
- NO_x emissions slightly increased with MTBE and ETBE, while DIPE reduced them
- Formaldehyde emissions increased with MTBE
- Regulated and unregulated emissions with TAME resemble those for MTBE. However, formaldehyde emissions are higher for TAME than for MTBE
- TAEE increased fuel consumption.

Overall, the effect of fuel ethers on exhaust emissions in new studies seems to follow general trends observed in the 1990s. The older studies are summarized in Figure 3.19.

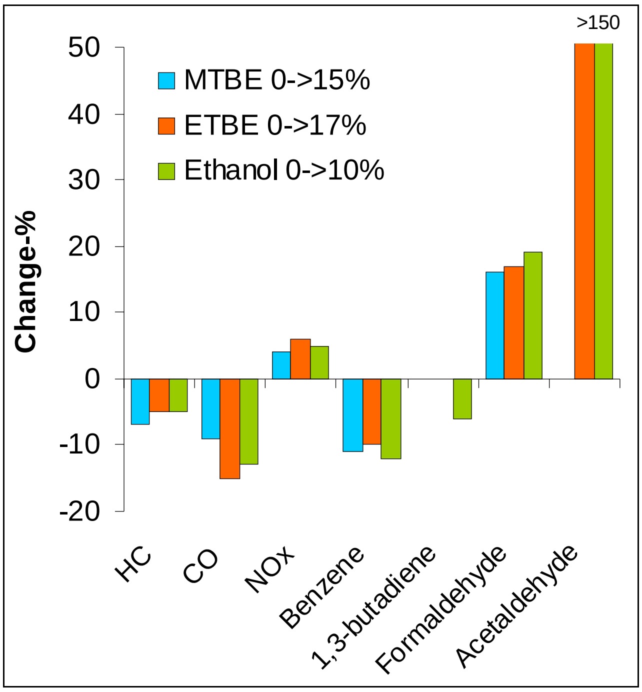


Figure 3.19. The effect of MTBE, ETBE and ethanol on exhaust emissions. Change-% represents the difference in emissions when oxygen-containing fuel is compared with non-oxygenated fuel (Figure by Aakko 2000, data from US Auto/Oil studies from 90's).

3.5.4 Summary

As gasoline components, ethers are preferred over alcohols (EFOA 2006). This is also the conclusion in the World Wide Fuel Charter, which includes the views of engine and automobile manufacturers on fuel qualities (WWFC 2006).

The main benefits of ethers are:

- High octane numbers help refineries achieve required octane levels.
- No azeotrope with gasoline, giving predictable volatility blending properties.
- General reduction of VOC, CO, HC and toxic emissions compared with non-oxygenated gasoline.
- Not aggressive towards normal materials.
- Low solubility with water, so no phase-separation risk.
- Compatible with current cars and infrastructure.

The drawbacks of ethers are higher NO_x and aldehyde emissions compared with non-oxygenated gasoline.

3.6 Biohydrocarbons

Gasoline-range biohydrocarbons are advantageous because they are fully compatible with conventional gasoline, cars and current infrastructure. Biohydrocarbons are not, however, consistent with each other. Properties depend on the production processes and feedstocks used. Product quality ranges from high-aromatic and high-octane qualities to paraffinic low-octane hydrocarbon mixtures. Biogasoline mixtures may contain different amounts of olefins as well as oxygenates. Very limited data are available on the fuel properties or performance of gasoline components obtained from the biohydrocarbon processes under development.

Fossil gasoline is produced by Sasol in South-Africa using the gasification/FT process. The product undergoes different refinery processes, and batches are therefore not comparable. One batch of gasoline containing an FT component exhibited lower HC and CO emissions, but higher NO_x ***emissions, than for regular gasoline with cars. PAH emissions were highest for the FT-containing fuels, although PM mass emissions were among the lowest.***

Various feedstocks, such as vegetable oils, animal fats, hydrated wood-based tall oil, pyrolysis oil fraction or FT crude, can be used as integrated or co-processing feedstocks in the refinery. The existing production of hydrotreated HVO renewable diesel leads to a gasoline fraction as a side product. This gasoline component is paraffinic, oxygen-, aromatic- and sulphur-free. The exhaust emissions with this compo-

nent are studied in the experimental part of this report. If oils and fats are used as feed for the FCC unit, the octane number of the gasoline stream is expected to be higher than when using petroleum crude oil. When the pyrolysis oil fraction is a feedstock, the gasoline is aromatic. High olefin or aromatic contents limit the blending ratio with other gasoline components.

Gasoline-range biohydrocarbons are advantageous because they are fully compatible with conventional gasoline, cars and current infrastructure. Biohydrocarbon products are not, however, consistent with each other, but depend on the production technology and feedstock used. Product quality ranges from high-aromatic and high-octane qualities to paraffinic low-octane hydrocarbon mixtures. Biogasoline mixtures may contain different amounts of olefins as well as oxygenates.

The routes for producing biohydrocarbons for gasoline, explained in Chapter 2, are:

- ExxonMobil MTG process
- Haldor Topsøe’s TIGAS process
- Lurgi’s MtSynfuels process
- Virent’s BTL process
- Fischer-Tropsch process
- Refinery integrated or co-processing.

Very limited data are available on the fuel properties or performance of gasoline obtained from the various biohydrocarbon processes.

The ExxonMobil MTG process has been in operation in New Zealand and Wesseling. The hydrocarbon composition and octane numbers of products from these two MTG plants are shown in Table 3.9. Properties of gasoline (side product) from Lurgi’s MtSynfuels process are also shown in Table 3.9.

Table 3.9. Hydrocarbon composition and octane numbers of ExxonMobil MTG products and Lurgi's MtSynfuels gasoline (Packer 1988, Kam et al. 1981, Liebner and Schlichting 2005).

	New Zealand	**Wesseling**	**Lurgi's MtSynfuels**
Alkanes, wt-%	53	67 (incl. naphthenes)	
Alkenes, wt-%	12	6	6
Naphthenes, wt-%	7		
Aromatics, wt-%	28	27	11
RON	92.2	96.8	92
MON	82.6	87.4	80
Note	3–6 wt-% durene, melting point 79 ºC. Isomerized to isodurene (melting point -23.7 ºC) during treatment.		

Virent's BTL "BioForming" process produce different types of hydrocarbons and oxygenates, depending on the process selected. Depending on the technology selected, the BioForming process can generate hydrocarbons for gasoline, jet fuel or diesel fuel, for example (Huber et al. 2006). In one example batch, the main product contained C_3-C_6 alkanes and aromatics (Figure 3.20). Low levels of alkenes and oxygenates were also produced (Blommel 2008). In this batch, the major part of the hydrocarbons was light (C_3-C_6). In the gasoline pool, the use of the lightest hydrocarbons is limited. High-octane branched alkanes are generally more favourable gasoline components than are low-octane straight-chain alkanes. Aromatics have generally good octane numbers, but the aromatic content is limited for environmental and other reasons. For example, in Europe a maximum of 35 vol-% of aromatics is allowed in gasoline according to Fuel Quality Directive 2009/30/EC.

There are no published data on practical products from Virent's process.

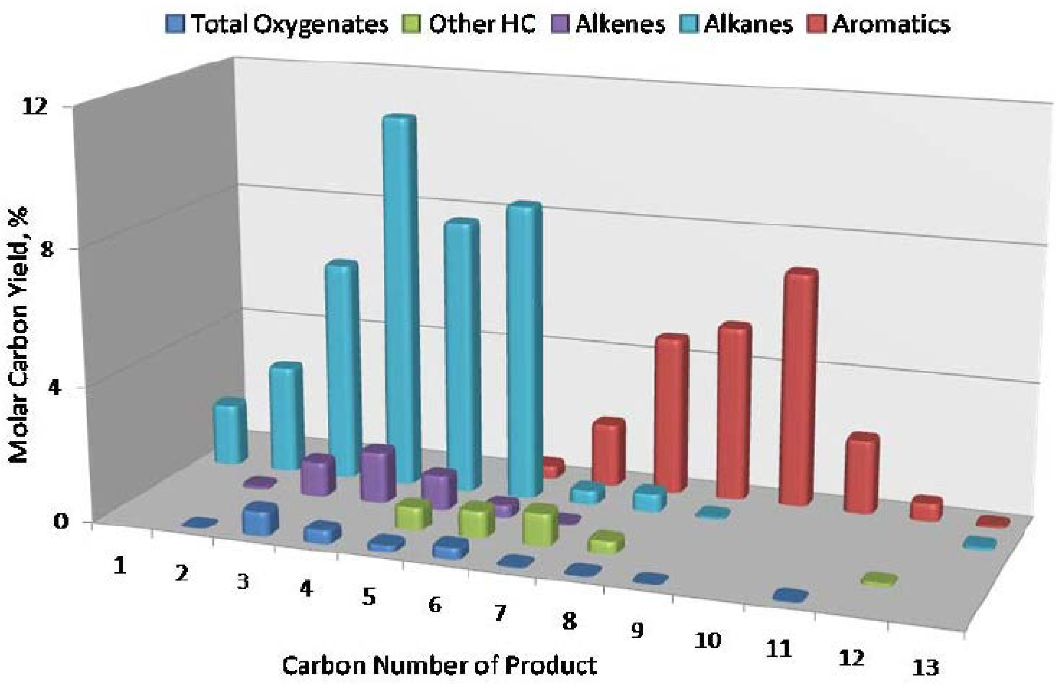
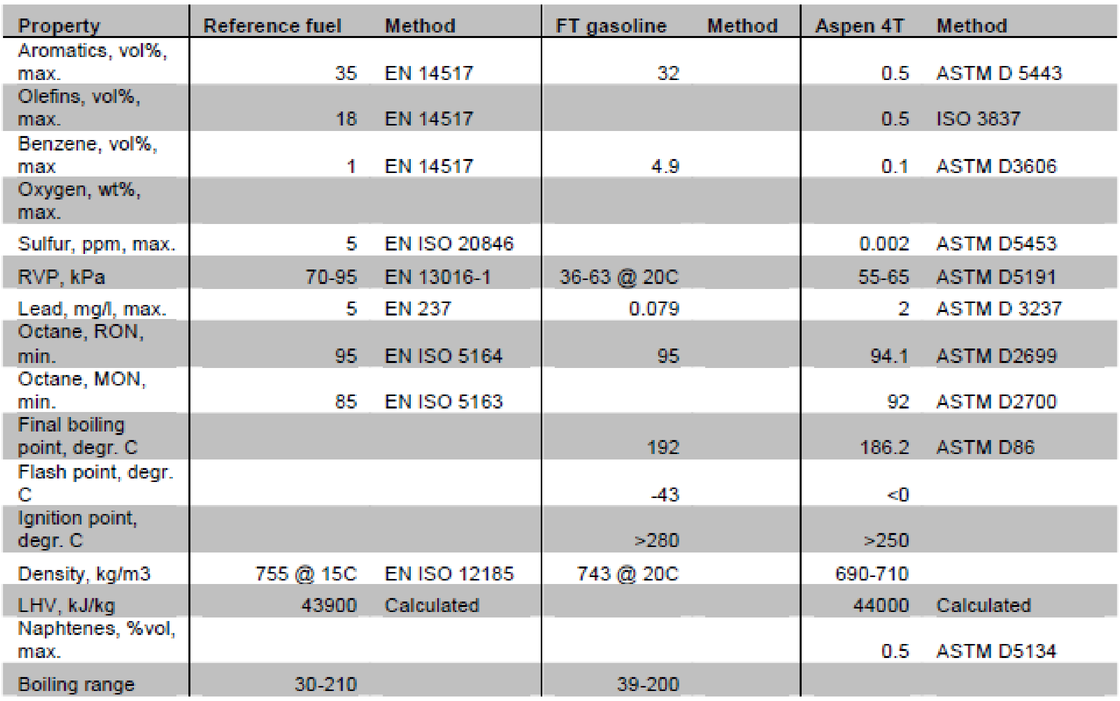


Figure 3.20. An example of the conversion of sucrose and xylose into gasoline-range hydrocarbons using aqueous-phase catalytic conversion and acid condensation (Blommel 2008).

The Fischer-Tropsch processes are currently optimised to produce mainly diesel fuel, although gasoline is formed to some extent. Only Sasol in South Africa has a high-temperature Fischer-Tropsch based production line specially designed for gasoline production. The FT product is treated (for example, by alkylation, hydrotreatment and isomerization) before the blending of the gasoline. Olefins originating from the FT process are treated using the conversion of olefins to distillate (COD) process. Final products containing synthetic fuels must meet requirements for regular gasoline and diesel fuel. Final gasoline consists of alkanes, alkenes and aromatics, and even ethanol and MTBE are used in this gasoline (Larsen et al. 2007).

Larsen et al. (2007) studied Danish gasoline, alkylate and fuel containing 70% FT gasoline. The fuel properties of FT gasoline used in the study are shown in Table 3.10. The aromatic content of this gasoline was 32%. Emissions tests were carried out with a VW Golf 1.6 FSI of model year 2003. HC and CO emissions for FT-containing gasoline were lower than for regular gasoline, but NO_x emissions were somewhat higher. PAH compounds associated with particles were highest with FT-containing fuels, although PM mass emissions were among the lowest. The authors point out that the FT gasoline tested here does not necessarily represent typical FT gasoline. The FT product can undergo different treatment processes that affect fuel chemistry and properties.

Table 3.10. Properties of fuels used in a study by Larsen et al. (2007).



Property	Reference fuel	Method	FT gasoline	Method	Aspen 4T	Method
Aromatics, vol%, max.	35	EN 14517	32		0.5	ASTM D 5443
Olefins, vol%, max.	18	EN 14517			0.5	ISO 3837
Benzene, vol%, max	1	EN 14517	4.9		0.1	ASTM D3606
Oxygen, wt%, max.						
Sulfur, ppm, max.	5	EN ISO 20846			0.002	ASTM D5453
RVP, kPa	70-95	EN 13016-1	36-63 @ 20C		55-65	ASTM D5191
Lead, mg/l, max.	5	EN 237	0.079		2	ASTM D 3237
Octane, RON, min.	95	EN ISO 5164	95		94.1	ASTM D2699
Octane, MON, min.	85	EN ISO 5163			92	ASTM D2700
Final boiling point, degr. C			192		186.2	ASTM D86
Flash point, degr. C			-43		<0	
Ignition point, degr. C			>280		>250	
Density, kg/m3	755 @ 15C	EN ISO 12185	743 @ 20C		690-710	
LHV, kJ/kg	43900	Calculated			44000	Calculated
Naphtenes, %vol, max.					0.5	ASTM D5134
Boiling range	30-210		39-200			

Oils and fats could be used as co-feeds in the FCC units of traditional petroleum refineries. According to Holmgren et al. (2007), the research octane number of the gasoline fraction from an FCC unit is higher with oils and fats as feedstocks than with petroleum crude oil as the feedstock (Holmgren et al. 2007). However, FCC gasoline is used as a normal blending component, and the properties of the final products therefore depend on refinery blending schemes. In principle, the same applies to pyrolysis oil used as a feedstock for a hydroprocessing unit to produce aromatic blending stock (Holmgren et al. 2007). The blending of highly aromatic components in gasoline is limited.

The experimental part of this study used gasoline containing biohydrocarbons from the NExBTL hydrotreatment unit for oils and fats. Neste Oil's NExBTL technology is optimized for the production of renewable diesel fuel, but some gasoline fraction is formed as a side product. According to the manufacturer, this product is a paraffinic, oxygen-, aromatic- and sulphur-free gasoline fraction. The properties of, and results with, this renewable gasoline component are shown in the experimental section (Chapter 4).

3.7 P-Series fuels

In the USA, so-called P-Series fuel can be used as fuel for FFV cars. P-Series fuels are blends of butanes, pentanes, ethanol and the biomass-derived co-solvent methyltetrahydrofuran (MTHF). P-Series fuels are clear, colourless, liquid blends, with a (RON+MON)/2 octane number of 89–93, formulated for use in flexible-fuel vehicles (FFVs). P-Series fuel can be used alone or freely mixed with gasoline in any proportion in an FFV fuel tank. FFV cars are specially designed for E85 fuel (ADFC 2009).

P-Series fuels are Pure Energy Corporation's blends that have been tested for vehicle tailpipe and evaporative emissions. Emissions of criteria pollutants with P-Series fuels were among the lowest of all test fuels, and compared favourably with emissions with E85 fuel. The life cycle greenhouse gas emissions of the P-Series fuels were 45–50% less than those of reformulated gasoline (US DoE Federal Register 10 CFR Part 490).

Currently, P-Series fuels are not being produced in large quantities and are not widely used (ADFC 2009).

3.8 Summary of the end-used aspects from literature

Summary of the end-use aspects discussed in this review (Chapter 3) is shown in Table 3.11.

Table 3.11. Summary of the end use aspects of gasoline components (literature).

ETHANOL (up to 10 v/v%) + High octane numbers + Reduced PM emissions – Increases evaporative emissions – Increases acetaldehyde emissions – Phase-separation risk – Aggressive towards materials	**BUTANOL (up to 15 v/v%) compared with ethanol** + Higher blending ratio (bio-share) + Higher energy content, lower fuel consumption + Lower evaporative emissions + Lower phase-separation risk + Better compatibility with cars and infrastructure – Lower octane numbers – Higher production costs
METHANOL (up to 3 v/v%) Substantial drawbacks, e.g. – Extremely aggressive towards materials – High phase-separation risk – Unsuitable for gasoline infrastructure – Extremely high vapour pressure – Toxic (Methanol can be used in the production of ethers.)	**ETHERS (ETBE, TAEE, MTBE, TAME)** + High octane numbers + Low vapour pressures + Good driveability of cars + Low CO and HC emissions + Compatible with present cars and infrastructure + No phase-separation risk + Used for decades in gasoline – NO_x and aldehyde emissions increase – ETBE may form peroxides – Groundwater risk from leakage
Special FFV cars: E85 fuel[15] + Low CO, HC, NO_x, PM and evaporative emissions at normal temperature – High acetaldehyde emissions, high emissions at low temperature, high fuel consumption, poor cold startability, requires special FFV cars and infrastructure	
All oxygenates: Fuel consumption increases compared with gasoline.	
Biohydrocarbons: Product properties depend on feedstock and process, e.g. o high vs. low aromatic o high vs. low olefinic o high vs. low octane	

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[15] P-Series fuel containing methyltetrahydrofuran for FFV cars is allowed in the US.

4. High bio-share gasoline for conventional cars – experimental

4.1 Introduction

The purpose of the experimental part of this study was to explore feasible gasoline biocomponents, such as bio-ethers, biobutanols and biohydrocarbon components, as alternatives to ethanol, and to assess their exhaust emissions performance.

Ethanol is the dominant liquid biofuel globally. However, technical restrictions limit the use of ethanol in conventional gasoline cars to 10–15 v/v% (approx. 7–10% as an energy equivalent percentage). Generally, fuels with a high oxygen content are not necessarily compatible with conventional spark-ignition cars. Present conventional cars will, however, continue to take the major share of gasoline car fleets for the next 10–20 years at least, and it is therefore necessary to establish and assess alternative biocomponent options for them. Today, higher ethanol blending ratios are possible only by using flexible-fuel vehicle (FFV) technology designed to use any proportion of ethanol and gasoline in the blend.

The European Union requires renewable energy to achieve at least a 10% share of transport energy by 2020, and even higher shares are being attempted regionally. *Ethanol* is readily available, and is used as a biocomponent and as a feedstock in the production of *ethyl-tert-butyl-ether (ETBE)*. Interesting alternative gasoline biocomponents are *bio-ethers*, *biobutanols* and *biohydrocarbons*, which can be combined with ethanol and ether components to increase the share of bio-energy and to improve the quality of gasoline. Biobutanols and biohydrocarbon components are competitive with ethanol, for reasons such as their higher heating value compared with that of ethanol.

The properties and composition of car exhaust gas depend on the engine technology, emissions control devices, engine operating conditions and fuel composition. Exhaust emissions consist of carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NO_x), hydrocarbons (HC) and particulate matter (PM), for example. CO, NO_x and HC emissions from gasoline cars are typically limited by legislation. In some regions, other emissions are also limited, for example NMHC and formaldehyde in the USA, and particulate matter emissions (PM) in Europe. Generally, emissions limited by legislation are called regulated emissions.

Tightening emissions legislation has resulted in a dramatic drop in the regulated emissions from vehicles (Table 4.1). However, the field of exhaust emissions is very complicated. A reduction in one emissions component may lead to an increase in another. Furthermore, atmospheric reactions of exhaust species may lead to unexpected health and environmental effects. A number of exhaust emissions from mobile sources that have been found to be toxic or to present a risk to human health or environment are not regulated by legislation. These are called "unregulated emissions". Typically, the main attention is given to 1,3-butadiene, benzene, formaldehyde, acetaldehyde and polycyclic organic matter, which are defined by the US EPA as "Air toxics" (Chapter 4.2.5).

Particles from gasoline cars have not been studied widely. The main attention is given to diesel particles, which are classified by the US EPA as "likely to be carcinogenic to humans by inhalation" and to have a potential for "a nonthreshold mutagenic effect" (US EPA 2002). However, particle emissions from diesel cars are diminishing with tightening regulations and with the introduction of aftertreatment devices such as diesel particle traps. On the other hand, particle emissions from gasoline cars are increasing with the introduction of direct-injection engines.

Some studies have indicated the significance of particles from gasoline cars, particularly when the ambient temperature changes. Furthermore, a secondary organic aerosol may be formed from aromatic precursors such as toluene (US EPA 2007). The small particle size and the chemical composition of the soluble organic fraction in the particulate matter are generally considered to cause adverse health effects. Particles may adsorb various compounds that may be toxic, mutagenic and carcinogenic (for example PAHs, nitro-PAHs and oxy-PAHs).

When evaluating new fuel components, it is important to ensure that their performance is acceptable throughout the end-use chain, from compatibility with infrastructure and cars to the health and environmental effects of exhaust gases.

Table 4.1. European emissions legislation for light-duty vehicles (www.dieselnet.com).

	Date [a]	CO	NMHC	HC	HC+NO_x	NO_x	PM
Euro 1	1992	2.72	-	-	0.97	-	-
Euro 2	1996	2.2	-	-	0.5	-	-
Euro 3	2000	2.3	-	0.20	-	0.15	-
Euro 4	2005	1.0	-	0.10	-	0.08	-
Euro 5	2009	1.0	0.068	0.10	-	0.06	0.005[b]
Euro 6	2014	1.0	0.068	0.10	-	0.06	0.005[b]
-7 °C [c]	2002	15		1.8			

[a] Dates refer to new type-approvals. The EC Directives also specify a later date for the first registration of previously type-approved models.

[b] Applicable only to direct-injection engines. The limit is 0.0045 g/km using the PMP measurement procedure.

[c] Directive 2001/100/EC, Urban part of test cycle.

4.2 Test set-up

Car exhaust emissions for gasoline biocomponents (isobutanol, n-butanol, renewable hydrocarbon component, ethanol and ETBE) were studied. Additionally, market-grade E85 fuel and a fossil gasoline reference fuel were included in the fuel matrix. The test fuel matrix was divided into two sets: a) five high-oxygen fuels containing 6–30 m/m% oxygen, and b) nine low-oxygen fuels containing 0–4 m/m% oxygen.

The biofuel bio-energy content was a major parameter in the fuel matrix. Fossil energy was substituted with 7–56 E_{eqv}% (7–78% bio-energy). The 7 E_{eqv}% bio-energy level represented currently used biocomponents (ethanol 10 v/v%, ETBE 22 v/v%), whereas the 14 Eeqv% level represented either butanol or biohydrocarbon alternatives (15–17 v/v%). The bio-energy level of 21 E_{eqv}% represented combinations of biocomponents. Market E85 fuel represented the highest bio-energy substitution value, 56 E_{eqv}% (78% bio-energy). When fuels were blended, their properties other than bio-energy content were kept as constant as possible.

Emissions tests using the European emissions driving cycle were carried out at -7 °C with three cars: multi-point fuel-injection car (MPFI), direct-injection car (FSI) and FFV car. Fuels with a high oxygen content are not necessarily compatible with conventional cars, so these fuels were tested only with the FFV car.

Emissions measurements included both regulated and unregulated exhaust emissions species. A special issue concerning the total hydrocarbon measurement for E85 fuel is discussed, and different calculation methods are compared. Total risk factors are calculated and analyzed for exhaust toxicity based on regulated and unregulated

emissions[16]. The role of the polyaromatic hydrocarbons is discussed, whereas the mutagenicity of particulate extracts and ozone-forming potential are not taken into account.

4.2.1 Fuels

The fuel matrix included 13 biofuels and two fossil fuels. The test fuels represented different bio-energy contents, oxygen contents and fuel chemistries (Table 4.2). The fuels, except E85 market fuel and one fossil fuel, were match-blended using fossil gasoline refinery components and gasoline biocomponents. Fuels were blended and analyzed by Neste Oil. VTT purchased Fossil-b fuel from Haltermann (RF-02-03), isobutanol from Merck (MERC1.00985.6025) and n-butanol from Prolabon (PROL20810.323).

The biocomponents used in fuel blending were ethanol, isobutanol, n-butanol, ETBE and a biohydrocarbon component. In this study a paraffinic, oxygen-, aromatic- and sulphur-free Neste Oil Renewable gasoline component was chosen to represent liquid biohydrocarbons from different processes. This biogasoline component is a hydrotreated vegetable oil product (HVO) manufactured from vegetable oils and animal fats using Neste Oil's NExBTL hydroprocessing technology. The main product of the NExBTL technology is renewable diesel, but renewable gasoline is typically formed as a side product.

The test fuel matrix was divided into two sets: high-oxygen containing fuels (oxygen content 6–30 m/m%) and low-oxygen containing fuels (oxygen content 0–4 m/m%). Fuels with a high oxygen content are not necessarily compatible with conventional spark-ignition cars, so five high-oxygen containing fuels were tested only with the FFV car. The low-oxygen fuel matrix contained nine fuels and was tested using both conventional cars and the FFV car. Oxygen-free fossil hydrocarbon gasoline was used as a reference fuel in both sub-matrices.

The biofuel's bio-energy content was a major parameter in the fuel matrix. Bioenergy as an energy equivalent percentage (E_{eqv}%)[17] was calculated using the lower heating values (LHV in MJ/l), given in the European Renewable Energy Directive 2009/28/EC, for both biocomponent and fossil gasoline, and the analyzed biocomponent concentrations for each fuel blend. Fossil energy was substituted with 7–56 E_{eqv}% (7–78% bio-energy). Essentially, three bio-energy substitution levels, 7, 14 and 21 E_{eqv}%, were used. The 7 E_{eqv}% bio-energy level represented currently used biocomponents,

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[16] Published by Aakko-Saksa, P., Rantanen-Kolehmainen, L., Koponen, P., Engman, A. and Kihlman, J. (2011) Biogasoline options – Possibilities for achieving high bio-share and compatibility with conventional cars. SAE 2011-24-0111. September 2011. (www.sae.org).

[17] E_{eqv}% = Bio-energy of blend (MJ/l)/Energy content of gasoline (MJ/l)
Bio-energy % = Bio-energy of blend (MJ/l)/Energy of blend (MJ/l)

ethanol (10 v/v%) and ETBE (22 v/v%), whereas the 14 E_{eqv}% level represented either butanol or biohydrocarbon alternatives in concentrations of 15–17 v/v%. The highest bio-energy level, 21 E_{eqv}%, was designed to represent both oxygenated and non-oxygenated biocomponent alternatives. The 21 E_{eqv}% bio-energy level was achieved either by adding 15 v/v% non-oxygenated bio-hydrocarbon (14 E_{eqv}%) to oxygenated component or simply by increasing the fuel's oxygenate content. Market E85 fuel represented the highest bio-energy substitution value, 56 E_{eqv}%.

Fuels were labelled using biocomponent abbreviations and the corresponding bio-energy content of the blend. For example, E+eth(19) fuel is an ethanol (E) and ETBE (eth) blend with a bio-energy content of 19 E_{eqv}%. The abbreviations iB, nB and R were used for isobutanol, n-butanol and renewable gasoline component, respectively. The generally recognized labelling E10, E30 and E85 was used for ethanol-containing fuels representing approximately 10, 30 and 85 v/v% ethanol.

The bio-energy contents, proportions of biocomponents and oxygen contents of the test fuels are shown in Table 4.2. Figure 4.1 shows the bio-energy and oxygen contents of the test fuels.

Table 4.2. Test fuels.

	Bio-energy		**Volume** [b]	**Oxygen**	**LHV**
	%	**E_{eqv}%**	**v/v%**	**m/m%**	**MJ/kg**
High oxygen content					
E85(56)	78	56	85	29.8	28.9
E30(20)	23	20	31	11.3	38.2
E+eth(19)	21	19	39	10.3	38.4
iB+eth(20)	21	20	36	7.3	40.1
iB(21)	22	21	25	5.8	40.9
Low oxygen content					
Fossil(0)	0	0	0	0.1	43.6
Fossil-b	0	0	0	0.0	42.9
E10(7)	7	7	10	3.7	41.4
iB(14)	14	14	16	3.8	41.6
nB(15)	15	15	17	4.0	41.5
eth(7)	7	7	21	3.5	41.5
R(14)	14	14	15	0.0	43.4
R+E(22)	22	22	26	4.0	41.4
R+eth(21)	21	21	35	3.4	41.6
R+iB(28)	29	28	32	3.8	41.5

[a] E = ethanol, eth = ETBE, iB = isobutanol, nB = n-butanol, R = renewable component. Number in parentheses indicates fuel bio-energy content as Eeqv%.

[b] Volume of ethanol, isobutanol, n-butanol, ETBE and renewable component.

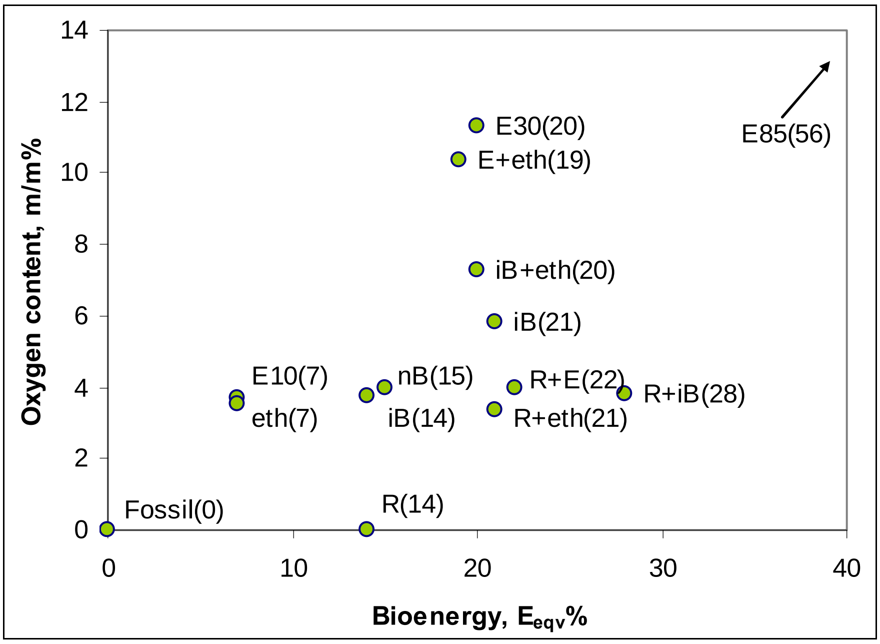


Figure 4.1. Bio-energy and oxygen contents of test fuels.

Selected fuel properties are shown in Table 4.3. When fuels were blended, their aromatic contents, densities, sulphur contents and vapour pressures were kept as constant as possible. The aromatic content of the high-oxygen content fuels was 16–21 v/v%, whereas that of the low-oxygen content fuels was 27–35 v/v%. The benzene content was below 0.5 m/m% in all fuels. The densities of all blended fuels were 740–756 kg/m^3. The sulphur contents of all fuels were below 10 mg/km. The vapour pressures were 69±2 kPa, except for market E85 fuel (34 kPa) and Fossil-b fuel (59 kPa).

Research octane numbers (RON) were within the measuring range of the ASTM D2699 method for the low-oxygen containing fuels, whereas the RON value of the high-oxygen containing fuels must be considered only indicative. RON values were 101–106 for E85(56), E30(20), E+eth(19), iB+eth(20), eth(7) and Fossil-b fuels, but slightly lower, 94–97, for iB(21), E10(7), iB(14), nB(15), R+E(22), R+iB(28), R+eth(21) and Fossil(0). The lowest RON value, 92, was measured for R(14) fuel. Motor octane numbers (MON) in both fuel sets were 86–92 and within the ASTM D2700 method measuring range.

Distillation curves for the test fuels are presented in Figure 4.2. Ethanol (boiling point 78 °C) and isobutanol (boiling point 108 °C), as well as other oxygenates, clearly affect the distillation curves. Fuels containing a biohydrocarbon component are heavier than Fossil(0) gasoline at the front and mid part of distillation. With R(14) fuel, 42.4 v/v% is evaporated at 100 °C (E100), which is outside the limit required in Fuel Quality Directive 2009/30/EC (E100 at least 46.0 v/v%).

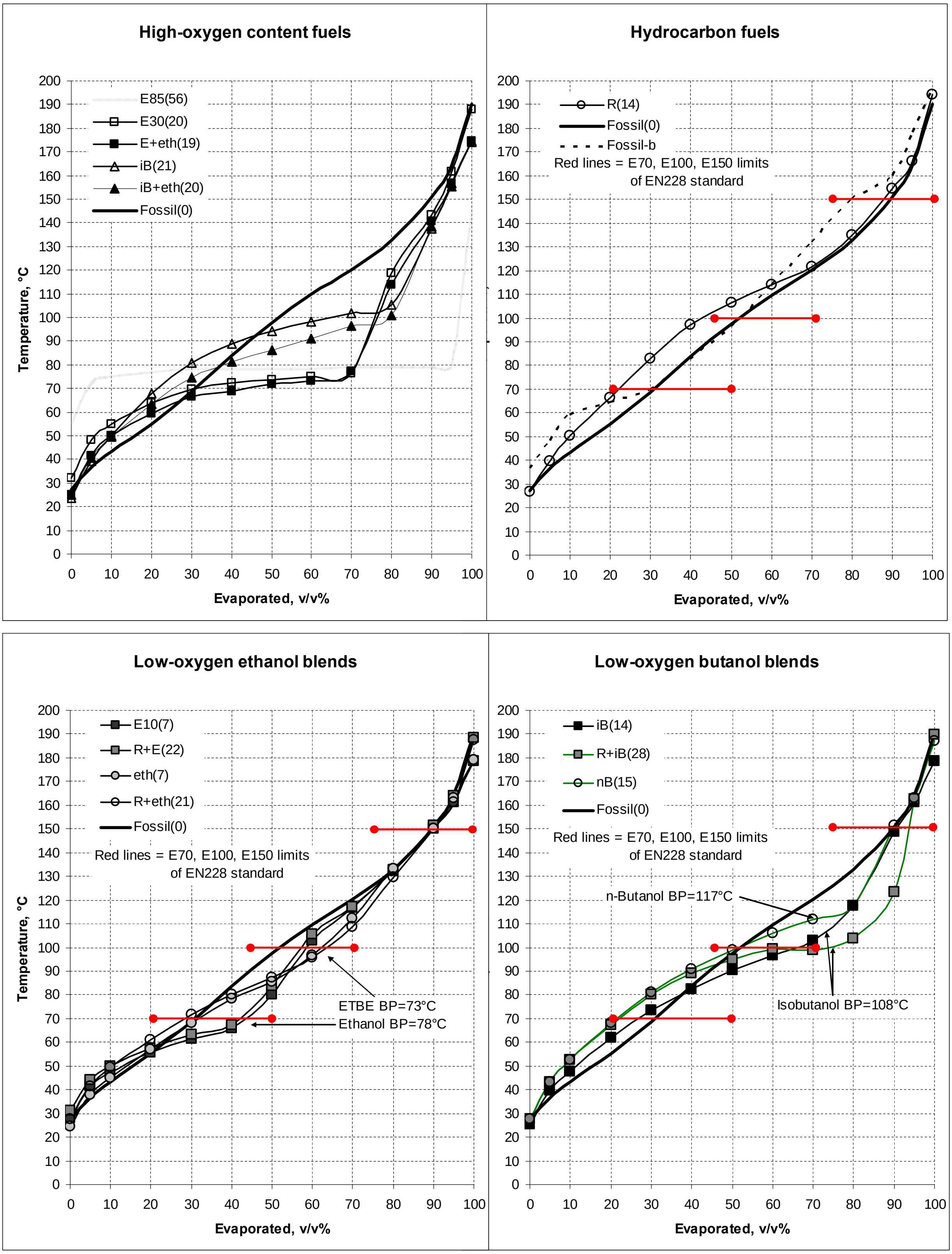
Table 4.3. Selected fuel properties [a, b].

	Density kg/m^3	**Oxygen** m/m%	**DVPE** [b] kPa	**Arom.** [c] v/v%	**Benz.** [d] v/v%	**RON** [e]	**MON** [f]
High oxygen content							
E85(56)	788	29.8	34	5	0.1	~104*	~88*
E30(20)	754	11.3	68	20	0.3	103	90
E+eth(19)	753	10.3	70	21	0.2	106	92
iB+eth(20)	750	7.3	71	16	0.1	101	89
iB(21)	748	5.8	70	18	0.3	97	87
Low oxygen content							
Fossil(0)	736	0.1	67	33	0.5	95	86
Fossil-b	751	0	59	29	0.2	101	89
E10(7)	754	3.7	69	27	0.2	97	86
iB(14)	756	3.8	69	29	0.5	97	86
nB(15)	759	4.0	69	29	0.5	95	86
eth(7)	756	3.5	70	35	0.5	101	89
R(14)	740	0.0	67	35	0.3	92	86
R+E(22)	749	4.0	69	33	0.4	95	86
R+eth(21)	745	3.4	69	32	0.4	97	88
R+iB(28)	752	3.8	69	31	0.3	94	86

[a] E = ethanol, eth = ETBE, iB = isobutanol, nB = n-butanol, R = renewable component. Number in parentheses indicates fuel bio-energy content as E_{eqv}%.

[b] DVPE = dry vapour pressure equivalent [c] Arom. = aromatic content [d] Benz. = benzene content [e] RON = research octane number [f] MON = motor octane number.

* E85(56) was commercial-grade fuel and its octane numbers were not measured. Typically E85 fuel fulfils Swedish standard SS 155480, with a RON around 104 and a MON around 88.



High-oxygen content fuels

Hydrocarbon fuels

Low-oxygen ethanol blends

Low-oxygen butanol blends

Figure 4.2. Distillation curves for the test fuels.

4.2.2 Cars

4.2.2.1 Technical description

Experimental work was carried out with three cars: a multi-point fuel injection car (MPFI), a direct-injection car (FSI) and an FFV car. The MPFI and FSI cars represent conventional cars, which are not necessarily compatible with fuels with a high oxygen content. An FFV tolerates high-oxygen containing gasoline, for example up to 85% ethanol. The MPFI and FSI cars used in this study represented the Euro 5 emissions level, whereas the FFV car represented the Euro 4 emissions level. The characteristics of the cars are shown in Table 4.4.

The MPFI car is equipped with a DOHC, 16-valve engine including variable valve timing (Dual VVT-i) and variable lifting of inlet valves (Valvematic). These features enable the timing of the inlet and exhaust valves to be adjusted, and the efficient adjustment of the air flow into the engine. This enhances the engine´s combustion efficiency and helps improve the fuel consumption (manufacturer’s information).

The FSI car is equipped with a low-displacement engine that combines petrol direct injection with turbocharging. This enhances the engine's combustion efficiency, giving a power output much higher than that of conventional, naturally aspirated engines (manufacturer’s information).

The FFV car used in this study has a turbocharged engine with rated power of 112 kW (150 hp) with gasoline, but 132 kW (180 hp) with E85 fuel. The performance of the FFV car is optimized for fuel containing 85% ethanol. The engine control unit (ECU) detects the fuel’s ethanol content, and increases the maximum turbocharger boost pressure and, consequently, the mass air flow and ultimate power (West et al. 2007). The ECU dithers the air/fuel ratio somewhat depending on the oxygen content of the exhaust gases.

Table 4.4. Characteristics of cars.

Abbreviation	**MPFI**	**FSI**	**FFV**
Model year	2010	2010	2006
Displacement, litres	1.6	1.4	2.0
Engine	4 cyl., 16-v DOHC, Valvematic	4 cyl.	4 cyl. turbocharged
Fuel system	Multi-point fuel injection	Gasoline direct injection	Multi-point fuel injection
Power, kW/min^{-1}	97/6400	90/5000	132/5500
Torque, Nm/min^{-1}	160/4400	200/1500–4000	280/1800
Odometer, km	5 300	21 400	62 000
Fuel consumption, l/100 km [a]	6.6	6.2	9.2
CO_2 emissions, g/km [a]	153	144	230 [b]
Emissions level	EU5	EU5	EU4

[a] Technical data sheet for car [b] Calculated

4.2.2.2 Preconditioning of FFV and OBD results

The FFV car model used in this project requires special adaptation to fuel[18]. Instructions from the manufacturer included driving in on-road conditions before preconditioning on the chassis dynamometer. The adaptation of the car to new fuel was monitored with the following parameters: charge air pressure, ignition timing, injection time and long- and short-term adjustment for fuel adaptation. Measurements were conducted after changing fuel and preconditioning at three constant loads (idle, 10 kW and 30 kW) using an Autocom OBD tester. In addition, data were recorded continuously during selected test runs using an ELM OBD diagnostic card.

With the FFV car, charge air pressure was relatively constant for all fuels measured (Table 4.5). The ignition timing was at the same level at idle and at 10 kW load. At the highest load (30 kW), the most significant difference was observed for E30(20) and Fossil-b fuels (late timing), and R(14) and Fossil(0) fuels (early timing). The respective parameters were not measured for E85(56) fuel.

Adjustment parameters for fuel adaptation behaved exceptionally in the case of the ETBE-containing fuel eth(7), with the adjustment changing significantly at the end of the second European test cycle (test id 10153EB). This test was rejected from the final results. For the other fuels, adjustments did not change over the replicate measurements.

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[18] Later FFV models may be equipped with a so-called flow-by sensor, which enables adaptation to fuel without special preconditioning.

Table 4.5. Parameters recorded for each fuel with the FFV car. With eth(7), fuel adaptation values changed significantly at the end of the second test, which was rejected.

	Charge air pressure			Fuel adaptation						Injection time			Ignition timing		
				Fine			Coarse			ms	ms	ms	°	°	°
	Idle	10 kW	30 kW	Idle	10 kW	30 kW	Idle	10 kW	30 kW	Idle	10 kW	30 kW	Idle	10 kW	30 kW
E+eth(19), beginning	37.0			-1.0			-1.6						8.0		
E+eth(19)	37.1	64.6	115.6	-0.7	3.2	2.0	-1.9	-1.9	-1.9	3.0	5.8	10.5	8.0	34.6	23.0
iB+eth(20)	42.3	66.1	115.9	0.7	2.2	-0.5	0	0	0	3.4	5.6	10.2	8.0	35.5	20.2
E30(20)	39.0	62.5	114.1	-0.4	-3.1	2.0	-2.5	-2.5	-2.5	3.0	5.5	10.4	8.0	35.6	24.4
E10(7)	39.0	65.2	115.9	-0.8	0.1	-0.6	-1.2	0.1	0.1	2.9	5.2	9.5	8.0	35.7	21.0
eth(7)	39.5	64.3	114.7	1.2	-2.7	6.9	-17.3	-15.8	-15.8	2.7	4.9	9.0	8.0	35.7	21.5
R(14)	36.8	63.7	117.8	-0.6	0.6	-0.3	-3.8	-3.8	-3.8	2.5	5.1	9.4	8.0	36.2	14.7
R+E(22)	36.8	65.2	116.5	4.7	-0.2	1.1	0.2	0.2	0.2	2.7	5.5	10.0	8.0	36.0	19.3
R+eth(21)	36.8	64.0	115.0	1.9	1.3	3.2	-0.4	-0.4	-0.4	2.6	5.1	9.6	8.0	36.3	21.3
R+iB(28)	38.6	65.2	116.2	-0.8	-2.1	1.5	-1.3	-1.3	-1.3	3.0	5.2	9.8	8.0	35.6	18.5
Fossil(0)	36.5	65.5	117.8	2.3	1.3	0.4	-1.8	-1.4	-1.4	2.6	5.2	9.5	8.0	36.0	15.8
Fossil(0b)	39.0	64.3	114.7	2.4	-4.7	-12.0	-2.5	-2.5	-2.5	2.7	5.0	9.3	8.0	35.3	24.3

4.2.2.3 Stability of cars

The measurement campaign lasted for two months. The stability of the cars was screened by measuring Fossil-b fuel at the beginning and at the end of the test campaign. The stability of the cars was relatively good, although CO and HC emissions from the FSI car increased to some extent over the measurement campaign (Figure 4.3).

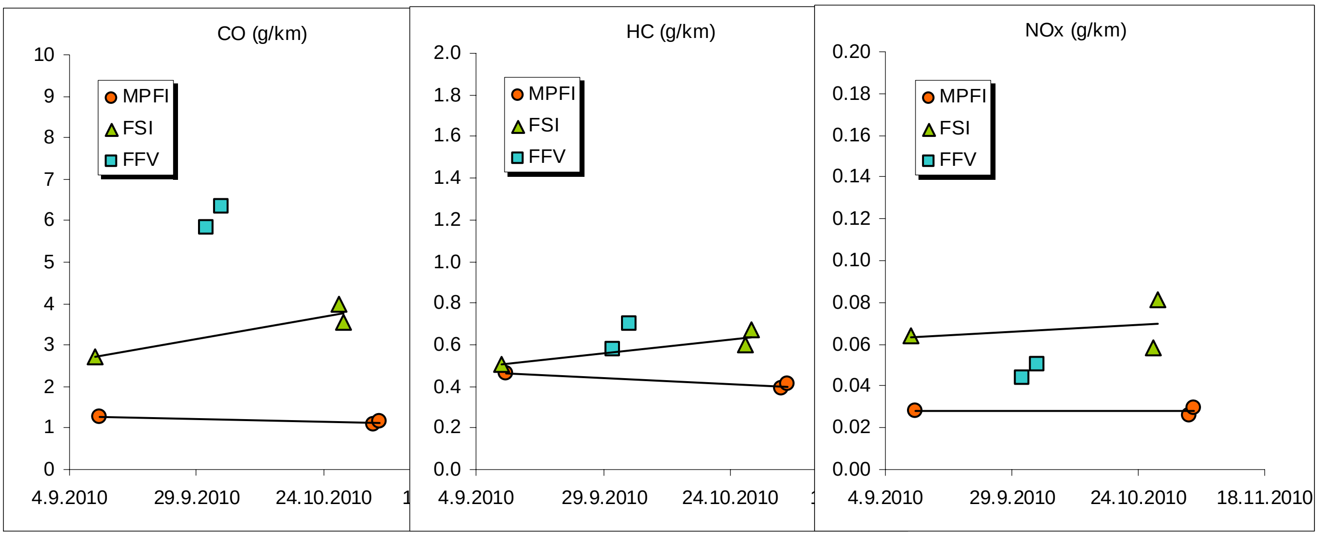

Figure 4.3. Stability of cars over the measurement campaign. Fossil-b fuel was measured at the beginning and at the end of the testing period.

4.2.3 Test Matrix

The tests were carried out at -7 °C with fifteen fuels and three cars. In general, three replicate tests were carried out for each fuel/car combination; in a few cases there were only two replicates. Fuels containing more than 4.0 m/m% oxygen were tested only with the FFV car. Two fuels, eth(7) and nB(15), were excluded from the test matrix for the MPFI car.

The measurements covered the regulated emissions CO, HC, NO_x, and a number of unregulated emissions, for example particulate matter, CO_2, NO, NO_2, NH_3, individual hydrocarbons and aldehydes. In addition, particulate matter was analyzed for PAH compounds and mutagenic activity using the Ames test. In this case, the number of replicate tests is limited. In total, the measurement matrix included the following regulated and unregulated emissions:

- Total hydrocarbons (HC), carbon monoxide (CO), oxides of nitrogen (NO_x), and particle mass emissions (PM)
- Carbon dioxide (CO_2) and fuel consumption
- Aldehydes, including formaldehyde and acetaldehyde
- Individual C_1-C_8 hydrocarbons, including 1,3-butadiene and benzene
- FTIR analysis, including alcohols and ethers
- Polyaromatic hydrocarbons from extract of particulate matter (PAH)
- Ames test from extract of particulate matter.

The numbers of regulated measurements for different fuels and cars are shown in Table 4.6. In addition, preliminary tests and tests of the stability of the cars were conducted. A few measurements were rejected due to failures with the car or the measurement protocol. Several measurements of speciated hydrocarbons were lost when a computer hard disk failed.

Table 4.6. Test matrix for regulated emissions.

	FFV	MPFI	FSI
E85(56)	2		
E30(20)	2		
E+eth(19)	2		
iB+eth(20)	2		
iB(21)	2		
E10(7)	3	3	3
eth(7)	2		2
iB(14)	3	4	3
nB(15)	2		2
R(14)	3	3	3
R+iB(28)	3	3	3
R+E(22)	3	3	3
R+eth(21)	3	3	3
Fossil(0b)	2	3	3
Fossil(0)	2	2	2

4.2.4 Measurement methods

4.2.4.1 Regulated gaseous emissions and CO_2

Tests were carried out in the engine and vehicle emissions test laboratory at VTT. Cars were tested on a chassis dynamometer in a climatic test cell at -7 °C test temperature (Figure 4.4). All equipment used for the measurement of the regulated gaseous emissions (exhaust dilution and collection, concentration analysis, etc.) conforms to the specifications of Directive 70/220/EEC and its amendments (European test). In addition, several parameters were recorded at one-second intervals, for example speed, carbon monoxide (CO), total hydrocarbons (HC) and nitrogen oxides (NO_x). The dynamometer and the basic equipment used for recording the test parameters are described in Table 4.7.

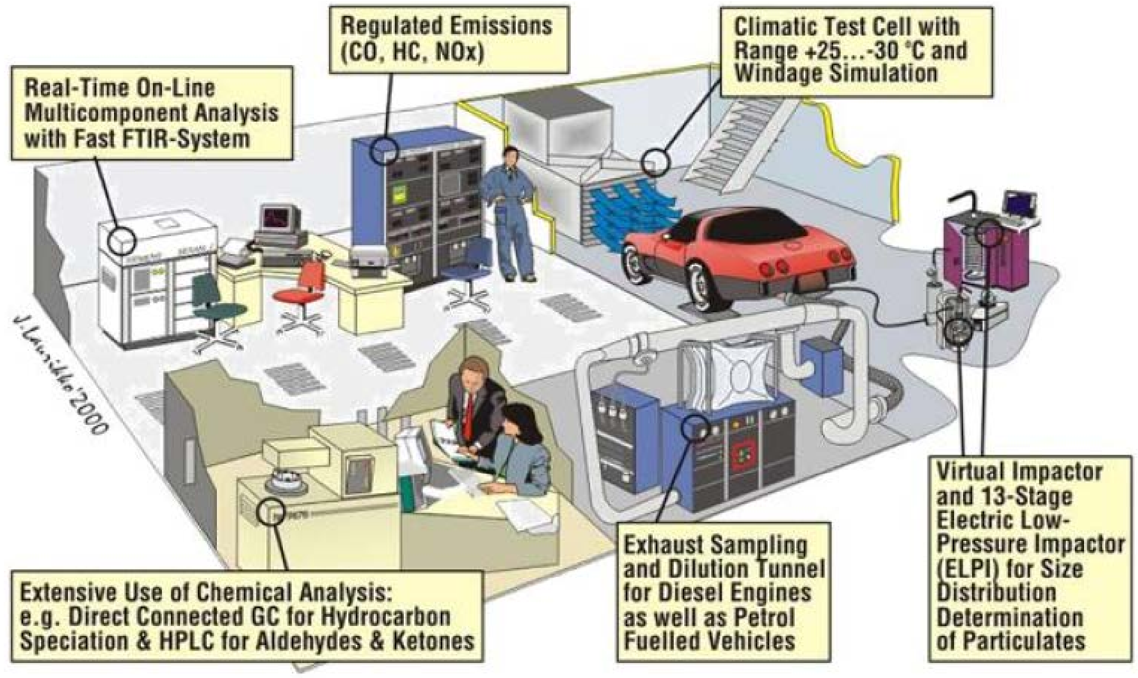

Figure 4.4. Schematic layout of VTT's facility for measuring car exhaust emissions.

Table 4.7. Basic instrumentation for the measurement of regulated emissions.

Equipment	**Manufacturer/type**	**Remarks**
Chassis dynamometer	Froude Consine 1.0 m	DC, 100 kW
Constant volume sampler	AVL CVS i60 LD	Venturi-type
CO, HC, NO_x, CO_2	Pierburg AMA 2000	Regulated gaseous emissions, triple bench

The standardized tests were run in accordance with the European exhaust emissions measurement procedure and driving cycle (Figure 4.5). The European emissions test driving cycle, which totals 11.0 km, was divided into three test phases to study emissions behaviour in cold starts and with warmed-up engines. The first and second test phases each consisted of 2.026 km driving, and the third test phase, the extra-urban driving cycle (EUDC), was 6.955 km.

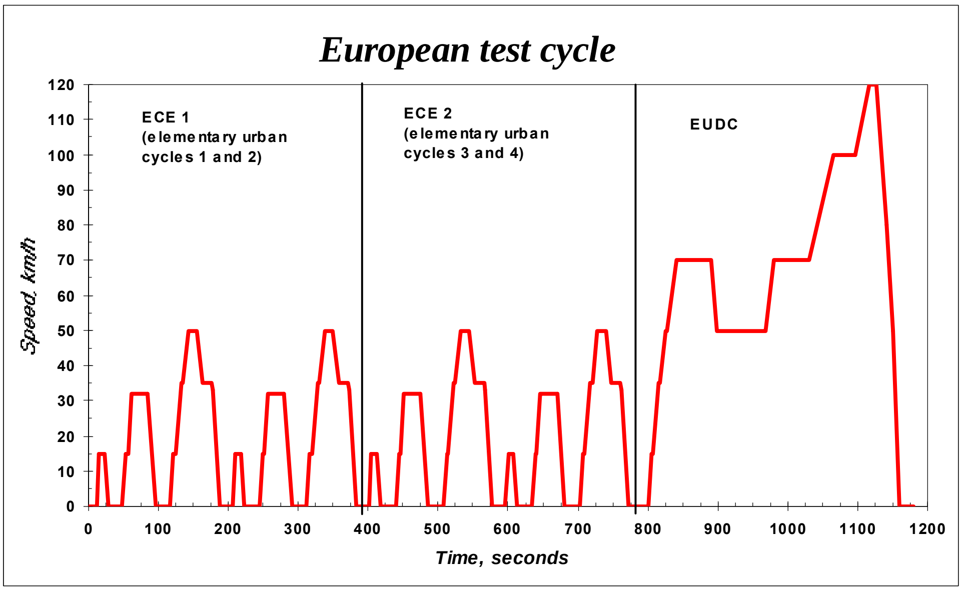

Figure 4.5. European driving cycle in emissions tests.

In these measurements at -7 °C the standard deviations of replicate tests were as follows:

- CO max. ±15%
- HC max. ±10%
- NO_x max. ±15% with the MPFI and FSI cars; max. ±20% with the FFV car
- PM max. ±15% with the FSI car; max. ±20% with the FFV car and ±45% for the MPFI car.

At normal temperature, the standard deviations of the overmentioned regulated gaseous emissions are typically around ±5%. PM emissions are not usually measured with gasoline-fuelled cars.

The standard deviations of the CO_2 emissions and fuel consumption measurements were low (well below ±1%).

Calculation methods

Regulations for exhaust emissions measurements have been developed for the type-approval tests of cars using fuels with defined fuel properties. In this research project, fuel properties varied widely from those defined in the emissions test regulations. Some fuel properties affect the calculation procedure for exhaust emissions. In these measurements, the true oxygen contents and densities of fuels were used in the calculation of the results.

HC emissions from the FFV car

A special issue concerns the total hydrocarbon emissions measured with a flame ionization detector (FID). In addition to hydrocarbons, all carbon-containing compounds, as well as oxygenates, give a response with an FID. This matter is discussed by Sandström-Dahl et al. (2010). In the USA, the FTP emissions measurement procedure takes into account the response of oxygenates with an FID by subtracting methane and ethanol emissions multiplied by their respective response factors from hydrocarbon emissions measured with an FID. In this way, so-called non-methane hydrocarbon emissions (NMHC) are obtained (Equation 9). In the USA, non-methane organic gases (NMOG) are calculated by taking oxygenates into account separately (Equation 10).

In the European emissions regulations, the FID response of oxygenates is not taken into account. However, a higher exhaust gas density is used for the calculation of HC emissions with E85 fuel. In the European emissions test procedure for gasoline cars, a density of 0.619 g/dm^3 based on the formula $C_1H_{1.85}$ is used in the calculation of HC emissions. European Regulation No 692/2008 requires a density of 0.932 g/dm^3 ($C_1H_{2.74}O_{0.385}$) to be used for the calculation of HC emissions from E85 fuel. In the USA, in both cases the HC density used for calculations is 0.619 g/dm^3 at 273 K (0.5768 g/dm^3, 16.33 g/ft^3 at 293 K).

$$NMHC = HC_{FID} - 1.04*CH_4 - 0.66*ROH \qquad (9)$$

$$NMOG = \Sigma NMHC + \Sigma ROH + \Sigma RHO \qquad (10)$$

The effects of different calculation methods on the results are given here for the FFV car using E85 fuel (Table 4.8). Hydrocarbon emissions achieved using the European calculation method for E85 fuel are at the same level as the US NMOG emissions. The NMHC result is naturally low, because methane and alcohol emissions are not included and the higher density of ethanol is not taken into account. In this project, the fuel matrix contained a wide set of fuels with different exhaust HC densities. HC results for all fuels were therefore calculated using the European procedure using a density of 0.619 g/dm^3. The calculation method chosen gives lower HC emissions for E85 fuel than does the EC regulation 692/2008 method.

Table 4.8. HC emissions from FFV car using E85 fuel with different calculation methods.

	HC emissions (g/km)
European [a], density 0.619 g/dm^3	2.4
European [b], density 0.932 g/dm^3	3.6
NMHC (US)	0.6
NMOG (US)	3.4

[a] Directive 70/220/EEC and its amendments before 2008
[b] EC Regulation No 692/2008

4.2.4.2 Aldehydes, individual hydrocarbons and FTIR analysis

Aldehydes were collected from the CVS diluted exhaust gas using dinitrophenylhydrazine (DNPH) cartridges. The DNPH derivatives were extracted with an acetonitrile/water mixture. Eleven aldehydes were analyzed using HPLC technology (HP 1050 UV detector, Nova-Pak C18 column). Attention was given mainly to formaldehyde and acetaldehyde. Other aldehydes analyzed were acrolein, propionaldehyde, crotonaldehyde, methacrolein, butyraldehyde, benzaldehyde, valeraldehyde, m-tolualdehyde and hexanal. The detection limit for aldehydes corresponds to approximately 0.01 mg/km. The maximum standard deviations of replicate tests in this study were around ±15% for formaldehyde and acetaldehyde with the MPFI and FSI cars, but as high as ±25% for the FFV car.

The diluted exhaust gas for individual hydrocarbon analysis was collected from the same Tedlar bags as were used for measuring the regulated emissions. The diluted exhaust gas was drawn from the bags and fed to the gas chromatograph. The hydrocarbons (C_1-C_8) from diluted exhaust gas were speciated using an HP 5890 Series II gas chromatograph (AL2O3, KCl/PLOT column). Hydrocarbons were identified by retention times, and analyzed quantitatively using an external standard method. The hydrocarbons analyzed were methane, ethane, ethene, propane, propene, acetylene, isobutene, 1,3-butadiene, benzene, toluene, ethyl benzene and m-, p- and o-xylenes. The detection limit is 0.02 mol-ppm, which corresponds to approximately 0.1 mg/km for methane, 0.5 mg/km for 1,3-butadiene and 0.7 mg/km for benzene. The maximum standard deviations of replicate tests in this study were around ±15–20% for 1,3-butadiene emissions and ±10% for benzene emissions.

A number of compounds were measured on-line using Fourier transformation infrared (FTIR) equipment (Gasmet Cr-2000). Ahonen (2006) has reported the performance of the Gasmet FTIR equipment with exhaust gases from vehicles. More than 10 exhaust components from the raw exhaust gas were measured at two-second intervals. However, the concentrations of many compounds are low with gasoline-fuelled cars. Detection limits based on manufacturers' reference spectra are summarized in Table 4.9. These detection limits were converted to corresponding mass-based emissions representing the duration of the European test cycle. In Table 4.10, the detection limits are compared with the maximum emissions results measured in this project.

Alcohols results measured with FTIR were used in the calculation of the NMHC and NMOG emissions.

Table 4.9. Detection limits determined from manufacturer's reference spectra at one-second intervals as concentrations and calculated mass emissions over the European test cycle. Maximum emissions observed in this project are also presented.

	Detection limit		**Max. emissions, this project (mg/km)**
	Concentration at 1-second intervals (ppm)	**European test (mg/km)**	
Carbon monoxide (CO)	7	8	8000
Nitric oxide (NO)	13	15	120
Nitrogen dioxide (NO_2)	2/10	4	7
Nitrous oxide (N_2O)	4	4	18
Ammonia	2	1	42
Methane	2	1	165
Ethanol	4	7	2900
Isobutanol	3	9	80
n-Butanol	4	12	80
ETBE	2	8	63
Formaldehyde	5	6	6
Acetaldehyde	5	9	91

The results obtained by FTIR were compared with those from the traditional measurement methods (Figure 4.6). For the CO emissions, the correlation between FTIR and the traditional method is relatively good. General trends for the other exhaust species monitored by FTIR and by traditional methods are in quite good agreement where differences in emissions are high, whereas FTIR does not seem to be applicable for monitoring small changes in emissions.

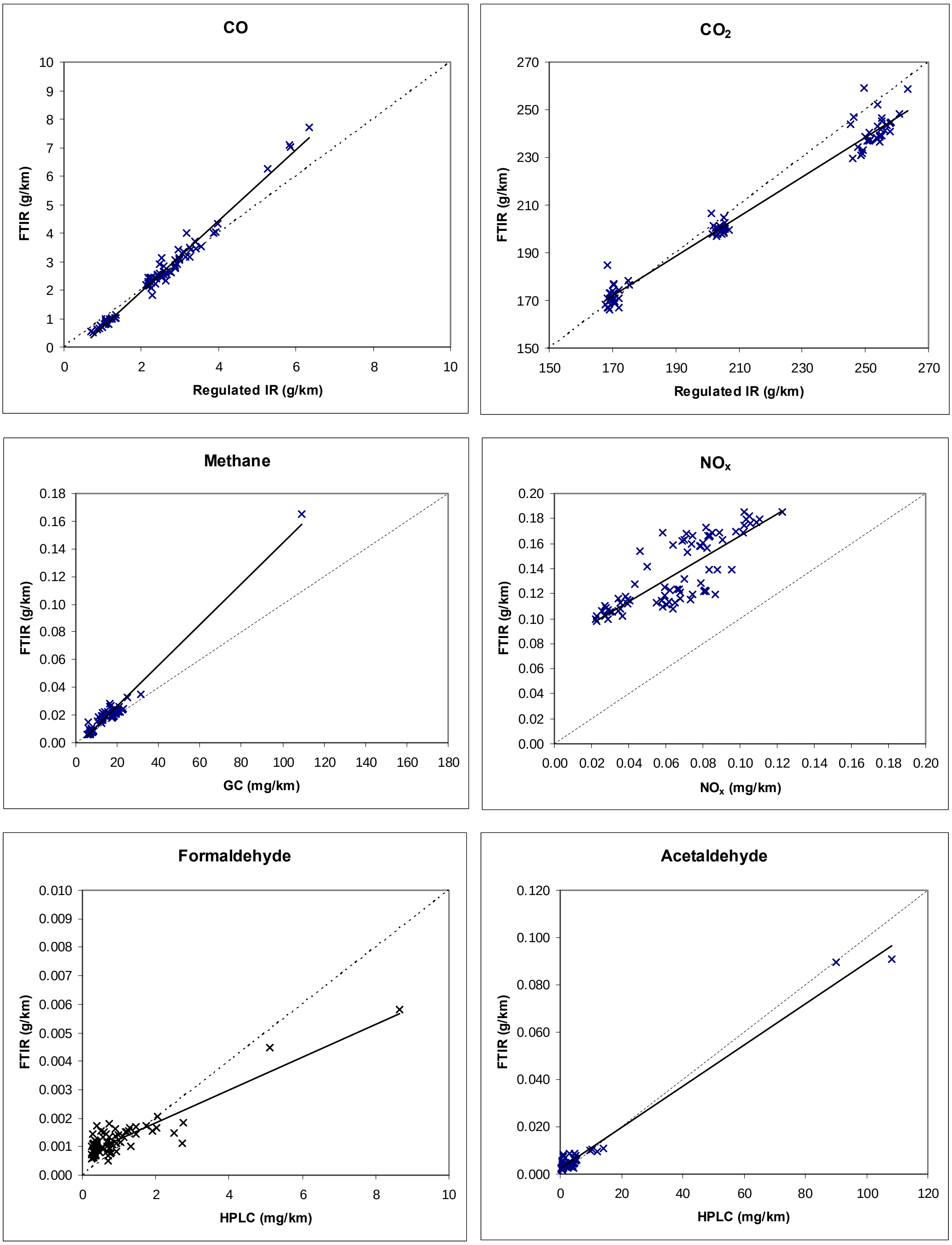

Figure 4.6. Correlation between the results obtained with FTIR and with traditional measurement methods.

4.2.4.3 Particulate matter sampling

Special analyses, particularly Ames mutagenicity assays conducted at several concentration levels in triplicate, require a substantial particulate mass. A high-capacity sampling system for particles was therefore used in these measurements (Figure 4.7).

The high-capacity sampling system was originally developed at VTT in the 1990s for measurements of gasoline cars (Kokko et al. 2000). There are now two high-capacity sampling systems available at VTT. In this project, particulates were collected using a high-capacity collection system, which includes a dilution tunnel (Ø 265 mm), a sample probe (Ø 80 mm), two filter holders in parallel (Ø 142 mm), a blower (Siemens ELMO-G, 2BH1 810-1HC36, 11 kW), a flow meter (Bronkhorst F-106C1-HD-V-12) and a controller (Stafsjö MV-E-80-P-TY-AC100-PN10).

The high-capacity sampling system can control sample flows up to 2000 l/min. In these measurements, a flow of 700–850 l/min was used to obtain appropriate particle masses. Two ∅ 142 mm filters were used in parallel to reduce face velocity and pressure drop on the filters. The filter type used was Fluoropore 3.0 µm FSLW, which is a hydrophobic membrane filter with a pore size of 3.0 µm, an air flow rate of 20 l/min/cm^2, an operating temperature of 130 °C and a porosity of 85%.

A Sartorius SE2-F microbalance was used to weigh the filters. The filters and samples were wrapped in aluminium foil to protect them from light, to avoid changes that could affect the mutagenicity results from the samples. Samples were placed in a freezer before being subjected to Soxhlet extraction for PAH analyses and the Ames tests.

The parameters of the collection system with different cars are summarized in Table 4.10. The velocity of the sonde must be equal to or higher than the velocity of the tunnel in order to obtain a representative sample. In addition, the face velocity on the filter should be 35–100 cm/s (ISO 16180). The high-capacity sampling system was set up to satisfy both requirements.

Table 4.10. Parameters of high-capacity collection system for particulate matter.

	Tunnel			**High-capacity collection system**[a]				
	Flow Nm^3/min	**Diameter mm**	**Velocity m/s**	**Sonde, id mm**	**Flow l/min**	**Velocity m/s**	**No. of filters 142 mm** [b]	**Face velocity cm/s**
MPFI	5.6	265	1.7	80	850	2.8	2	59
FSI	5.6	265	1.7	80	700	2.3	2	49
FFV	7.4	265	2.2	80	850	2.8	2	59

[a] High-capacity particulate sampler specially developed for low-emitting cars.

[b] Particulate filters: 142 mm Fluoropore FSLW 3.0

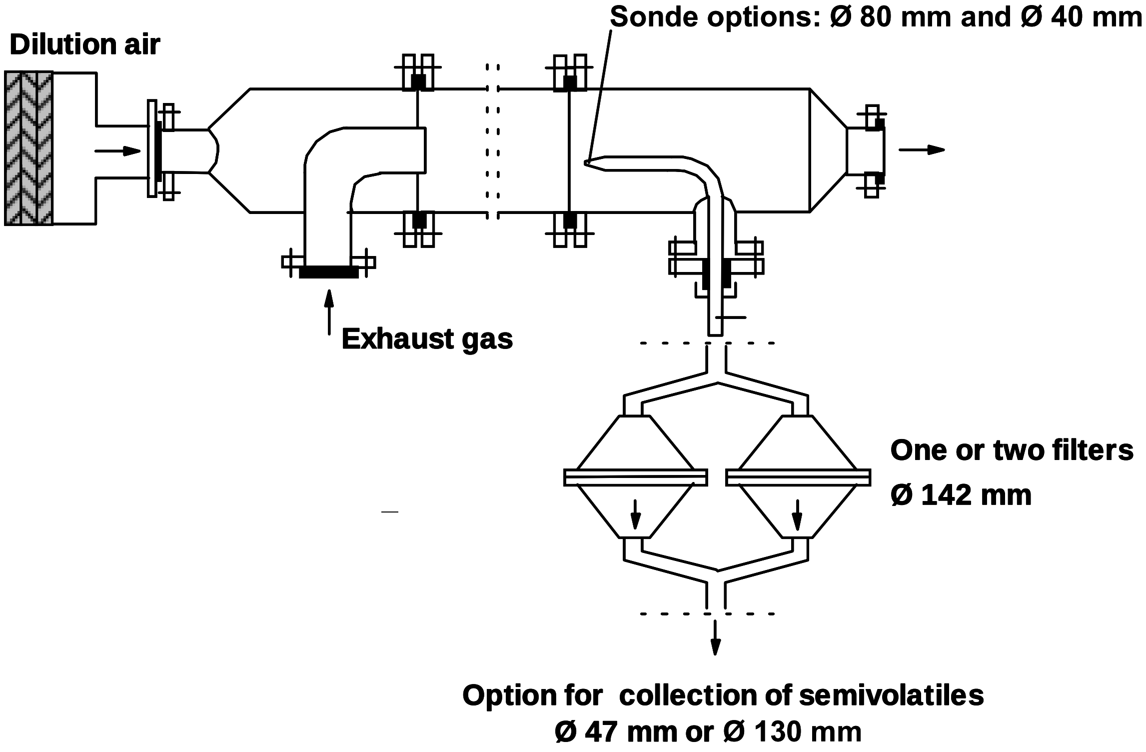

Figure 4.7. Schematic configuration of high-capacity sampling system at VTT.

4.2.4.4 SOF, Soxhlet extraction

Soxhlet extraction is required for the particle filter samples before PAH analysis and the Ames test. Several filters were combined for each extraction batch. An equivalent number of filters was used for the blank control sample.

The solvent used in the Soxhlet extraction of particle filters was dichloromethane. To avoid any unwanted changes in the samples, they were protected from light during and after the Soxhlet treatment. Solvent extraction (6 hours) was used to clean the Soxhlet apparatus. An internal standard was added before extraction, and samples were Soxhlet-extracted for 16 hours. After extraction, the volume was reduced by evaporating the solvent, and the concentrates were divided for the PAH analyses and Ames tests. For the Ames test, the dichloromethane solvent was replaced by dimethyl sulphoxide (DMSO), which is better tolerated by the test organisms used in the Ames assay.

Filters were dried in decanters and weighed. The soluble organic fraction (SOF) was determined by weighing the filters before and after Soxhlet extraction with dichloromethane. The standard deviation of the SOF results depends on the mass of particulate matter on the filters, and on the filter material. For Fluoropore membrane filters, standard deviation of the SOF is typically high.

4.2.4.5 Polyaromatic hydrocarbons and priority PAHs

Analysis method

A set of polyaromatic hydrocarbons (PAHs) was analyzed from the soluble organic fraction (SOF sample) obtained by the Soxhlet extraction of particle samples using dichloromethane. PAH analyses were performed using GC/SIM-MS following purification of the extract by liquid chromatography. EPA 610 PAH mixture from Supelco and PAH-MIX 63 from Ehrensdorf were used to check the calibration standard. The calibration standard was made from pure solid substances of each PAH compound determined. Detection limits were 0.1 µg component/sample, which represents approximately 0.04 µg/km for the MPFI car and 0.08 µg/km for the FSI and FFV cars in this study. The PAH analyses were carried out at Nablabs laboratories.

A total of 30 individual PAH compounds was analyzed (Table 4.11). From these, the sums of 7 and 14 Priority PAHs were calculated.

Table 4.11. The PAH compounds analyzed.

naphthalene
2-methylnaphthalene
1- methylnaphthalene
1,1-biphenyl
acenaphthylene
acenaphthene
dibenzofuran
fluorene
dibenzothiophene
phenanthrene
2-methylanthracene
anthracene
1-methylanthracene
2-phenylnaphthalene
fluoranthene
pyrene
benzo[a]fluorene
benzo[b]fluorene
benz[a]anthracene
chrysene
benzo[b]fluoranthene
benzo[k]fluoranthene
benzo[j]fluoranthene
7,12-dimethylbenz[a]anthracene
benzo[e]pyrene
benzo[a]pyrene
perylene
indeno[1,2,3-cd]pyrene
dibenzo[a,h]anthracene
benzo[g,h,i]perylene
coronene

Priority PAHs

Polycyclic organic matter, POM, defined by the US EPA as “Priority Air Toxic”, consists of hundreds of different compounds, for example pure hydrocarbons (PAH) and hydrocarbons containing heteroatoms (N, S, O). In practice, it is not possible to analyze all compounds found in POM. The US EPA has therefore defined groups of priority PAHs. The sums of priority PAHs are considered to represent individual PAHs better than using B(a)P alone. Hover, even these sums do not take into account for instance substituted PAHs. The US EPA (1998) defined 16 PAHs for inclusion in this group representing POM compounds. Many of these PAHs are classified as carcinogenic (group 1), probably carcinogenic (group 2A) or possibly carcinogenic (group 2B) according to the IARC classification (IARC 2008, 2011). The US EPA has also defined a shorter list of priority PAHs. In a list of mobile-source air toxics defined by the US EPA (2007), 7 PAHs are used to represent POM compounds (Table 4.12).

European directive 2004/107/EC of 15 December 2004, relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air, states that (art. 4-8): "To assess the contribution of benzo(a)pyrene to ambient air, each Member State shall monitor other relevant polycyclic aromatic hydrocarbons at a limited number of measurement sites. These compounds shall include at least: *benzo(a)anthracene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene, and dibenz(a,h)anthracene*." These PAHs are classified in groups 2A and 2B by IARC.

In addition to the US EPA's definitions, there are several other lists of "Priority PAHs" to describe the cancer-related risks of substances. In an earlier Finnish study on gasoline particle emissions (Kokko et al. 2000), a sum of 14 PAHs was presented. This sum of 14 PAH compounds was based on the US EPA priority list of 16 PAHs, from which naphthalene, acenaphthene and acenaphthylene were excluded because these low-molecular weight PAHs significantly decrease the repeatability of the results. On the other hand, benzo[e]pyrene is included in the 14 PAHs despite not being included in the US EPA priority list. This compound is listed by NIOSH and VDI 3872, for example. In later national studies, for example Rantanen et al. (2005) and Murtonen et al. (2010), a sum of 7 PAH compounds is presented in accordance with the US EPA (2007) definition.

Table 4.12 summarizes the US EPA's lists for 16 and 7 priority PAHs, together with the list in European directive 2004/107/EC for 7 PAHs. The US EPA includes chrysene and 7,12-dimethylbenz[a]anthracene in the list of 7 PAHs, whereas the European directive includes benzo[j]fluoranthene.

Table 4.12. **a)** 16 PAHs[19] defined by the US EPA 1998, **b)** 14 PAHs reported in the Finnish gasoline PM study by Kokko et al. (2000). **c)** 7 PAHs defined by the US EPA 2007 and **d)** 7 PAHs defined in European Directive 2004/107/EC. IARC (2011) classification of PAHs in Class 1 or 2 are shown in boldface[20].

	N	Ace	Acy	Flu	Phe	An	F	P	BaA	DM-BA	Chr	BbF	BjF	BkF	BaP	BeP	IP	DBahA	BghiP
IARC	2B	3		3	3	3	3	3	2B*		2B*	2B	2B	2B	1*	3	2B	2A	3
Ring**	2/2	3/2	3/2	3/2	3/3	3/3	4/3	4/4	4/4	4/4	4/4	5/4	5/4	5/4	5/5	5/5	6/5	5/5	6/5
a (16)	x	x	x	x	x	x	x	x	X		X	X		X	X		X	X	x
b (14)				x	x	x	x	x	X		X	X		X	X	x	X	X	x
c (US 7)									X	X	X	X		X	X		X		
d (EU7)									X			X	X	X	X		X	X	

*) IARC classification has changed in 2010 or later. **) No. of rings/aromatic rings

Standard deviation of PAH results

The masses of particulate matter from the FSI car were sufficient for the replicate PAH analyses and Ames tests. With the FFV car, replicate PAH analyses and Ames tests were conducted with one fuel. The sum of 7 PAHs from the replicate tests is shown in Figure 4.8 as µg/mg particles. The standard deviations of replicate measurements are shown as percentages.

The standard deviations of the PAH results were below 6%, except in one case (13%). Repeatability was excellent, taking into consideration that the samples originated from different exhaust emissions test runs and from different Soxhlet extractions. This means the standard deviation includes uncertainties originating from the car, driving cycle, particle collection, extraction method and PAH analysis.

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[19] N = Naphthalene, Ace = Acenaphthene, Acy = Acenaphthylene, Flu = Fluorene, Phe = Phenanthrene, An = Anthracene, F = Fluoranthene, P = Pyrene, BaA = Benz[a]anthracene, DMBA = 7,12-dimethylbenz(a)anthracene, Chr = Chrysene, BbF = Benzo[b]fluoranthene, BkF = Benzo[k]fluoranthene, BjF = Benzo[j]fluoranthene, BaP = Benzo[a]pyrene, IP = Indeno[1,2,3-cd]pyrene, DBahA = Dibenz[ah]anthracene, BghiP = Benzo[ghi]perylene.

[20] Group 1: carcinogenic; Group 2A: probably carcinogenic; Group 2B: possibly carcinogenic; Group 3: not classifiable with regard to carcinogenicity; Group 4: probably non-carcinogenic.

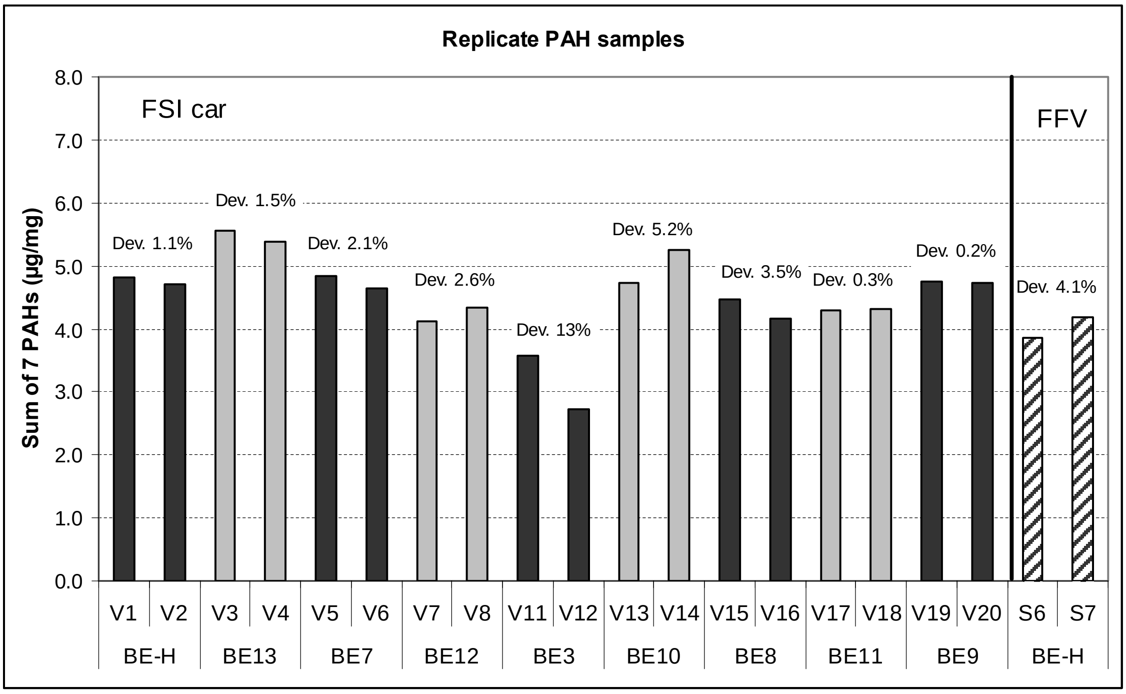

Figure 4.8. PAH results from the replicate European test runs with different car and fuel combinations. Standard deviations are shown as percentages.

4.2.4.6 Ames test

Introduction

The Ames test was originally developed for screening individual, pure chemicals for mutagenicity, and potential carcinogenicity in mammals (Ames et al. 1973a; Ames et al. 1973b; Ames et al. 1975). The short-term in vitro assay is capable of detecting compounds causing either base-pair substitution or frameshift mutations in DNA. The tester strains, specially tailored Salmonella mutants, have been made sensitive to chemical attacks, for example by increasing the permeability of the cell wall to large molecules such as PAHs. To enable indirect mutagens, which are mutagenic in mammals only after metabolic activation, also to be detected, a metabolic activation system has been incorporated in the test procedure. The enzyme system used is isolated from rat livers after a specific induction treatment, and is a simplified simulation of mammalian metabolism.

DNA has essentially a universally uniform structure, so mutations caused in a prokaryotic organism may be equally possible in any other organism. Although chemical carcinogenesis in mammals is known to be a complex multistep process, a mutation in DNA is one of the initial steps of key importance. In the early 1970s, the correlation between carcinogenicity and mutagenicity detected by the Ames assay was estimated to be nearly 90% (McCann et al. 1975; McCann et al. 1976; Rinkus and Legator 1979 and 1981; Ames and McCann 1981). However, more recent validation studies suggest the correlation rate is most probably much lower. Of 301 chemicals demonstrated to be carcinogenic in mice and rats, only 56% exhibited mutagenicity in the Ames reversion assay (ETAD 1998). Nevertheless, the Ames test provides one of the most widely used short-term mutagenicity assays, and is widely applied as a preliminary screening tool for chemicals with potential genotoxic activity. A positive result from the Ames test provides an indication of genotoxic potential that must always be confirmed by some other method capable of predicting more accurately the risk of carcinogenicity in mammals.

In addition to its use with single chemicals, the Ames test has been used for a long time to assess the mutagenicity of a wide variety of complex samples. A number of studies have been published on the assessment of the mutagenicity of diesel exhausts, process emissions, tobacco smoke and air pollution in urban environments, in general. Certain limitations of the test method must be taken into account in these kinds of applications. The sensitivity of the test organisms means they are simultaneously sensitive to any kind of chemical attack. Toxic components may interfere with the target organisms via a number of mechanisms. They may inhibit some vital metabolic reactions of the tester strain, interfere with transport processes in the cell by disturbing the function of the proton motive force or electron transport system, or cause fatal shock reactions. Toxicity may be due to a single toxic component or the cumulative effect of several components. If the mixture contains any component acutely toxic to the test organism, the mutagenicity of the sample may be masked. The test results are therefore only reliable within a non-toxic concentration range. To avoid interference from toxic components, it may be necessary to fractionate the original complex sample into chemical subfractions. Another potential source of error in the assessment of complex samples may be attributable to the metabolic activation system applied. It consists of a range of enzymes responsible not only for metabolic activation but also for a range of deactivation reactions in mammals. Full control of these enzymatic reactions is not possible under the test conditions.

Test method

In this study, the samples were wrapped in aluminium foil and kept in a freezer before the Soxhlet extraction of particle samples with dichloromethane. The extraction took place in the dark, and during all handling phases the filters and samples were protected from light to avoid changes that could affect the mutagenicity results for the samples. Because dichloromethane is toxic to the Ames tester strains, the solvent was replaced by dimethyl sulphoxide (DMSO).

The mutagenicity of the extracted particle samples was assessed by the Ames test using histidine auxotrophic *Salmonella typhimurium* tester strains originating from B.N.

Ames, University of Berkeley, California, USA. The method applied (VTT-4352-91) is based on the original reference method by Maron et al. (1983) and the recommendations of the OECD (1997).

While in the preliminary assays the samples were tested both for direct (without metabolic activation) and indirect (with metabolic activation) mutagenicity, in the final assessment only the indirect mutagenicity of the samples was tested. The tester strain TA98 used in the assessment is sensitive to frameshift-type mutagens. Polycyclic aromatic hydrocarbons (PAH) show indirect mutagenicity, i.e. only after metabolic activation (+S9 mix), whereas nitro-PAHs are direct-acting mutagens. The contribution of nitro-PAH-type compounds to mutagenicity can be studied using tester strains TA98 and the nitroreductase-deficient TA98NR in parallel. Provided the sample exhibits direct mutagenicity in TA98 but not in TA98NR, the presence of nitro-PAHs is likely.

Selection of tester strain

In the preliminary tests, the mutagenic properties of particles from cars were characterized in general, the best applicable tester strains were selected and suitable dose levels of particles were defined. In the preliminary tests the samples were assessed using TA98 with (+S9 mix) and without metabolic activation (-S9 mix), and nitro-PAH-deficient strain TA98NR (-S9 mix). The samples from the FSI car exhibited a substantially higher mutagenicity against TA98 after metabolic activation (+S9 mix) than without it. No indication of the presence of nitro-PAH-type mutagenicity could be demonstrated. Consequently, the samples were assessed only for indirect mutagenicity using strain TA98 with metabolic activation (+S9).

The results obtained at different dose levels are shown in Figure 4.9. The regression line was linear over a range of 0.1–0.8 mg particles/plate. With the FSI and FFV cars, counts per plate already exceeded 1000 with particle masses of 0.4–0.6 mg/plate.

For actual samples, tester strain TA98 was used at five dose levels corresponding to particle masses of 0.1–0.8 mg/plate. For metabolic activation, an S9 homogenate prepared from rat livers induced with phenobarbital and β-naphthoflavone was used. The volume of liver homogenate was 20 μl/plate. The tests were carried out only once using mainly three replicate plates for each dose level. The positive control for indirect mutagenicity was 2-aminoanthracene (0.5 μg/plate). DMSO (100 μl/plate) was used as the solvent control.

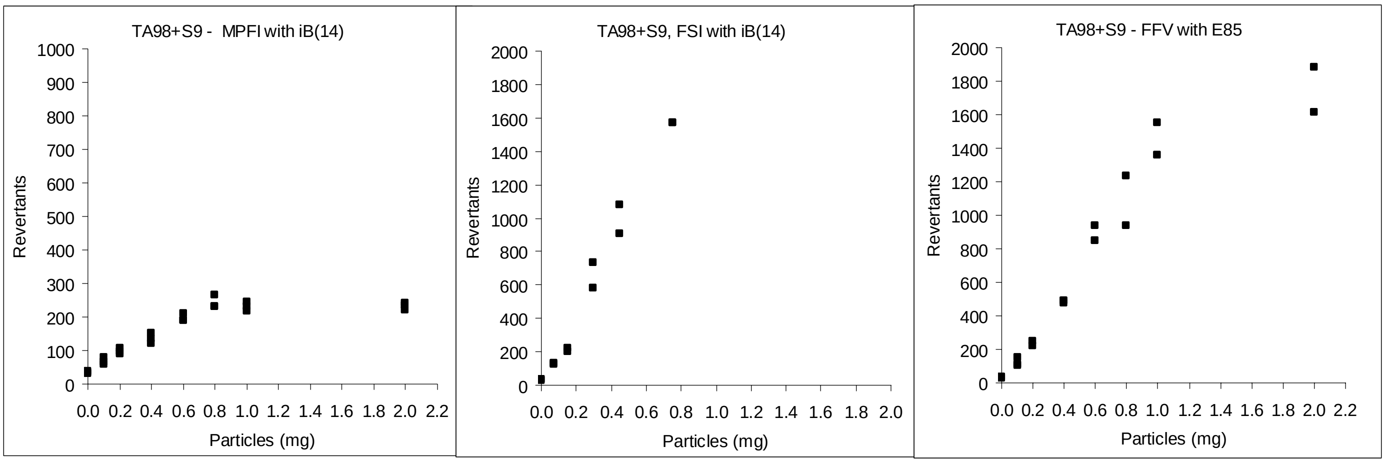

Figure 4.9. Number of revertants per plate with tester strain TA98+S9 in the preliminary tests.

Interpretation of the Ames results

The mutagenic dose response of each sample was calculated by linear regression analysis. The slope (b) within the linear part of the regression line (y = bx + a) describes the magnitude of mutagenic activity, and is expressed as revertants/mg of sample. For a sample to be classified mutagenic it must cause a dose-related, more than two-fold, increase in the number of revertants compared with the solvent control. For comparison, the results were calculated separately as the number of revertants per plate at a dose level of 0.1 mg particle mass (B).

Results were presented as krev/mg of particulate matter and as krev/km.

Repeatability of the Ames test results

Replicate samples from the FSI car were tested for mutagenicity. The FSI car emitted enough particulate mass for the Ames test in each individual European emissions test. In addition, two samples with the FFV car using one fuel were tested for mutagenicity. The Ames results (B) from the FSI and FFV cars' replicate test runs are shown in Figure 4.10 as revertants per mg particles. The standard deviations of replicate measurements are shown as percentages.

The standard deviation of the Ames results from replicate European emissions test runs was below 25% with Ames-B calculation method. The standard deviations of Ames results using the regression analysis calculation method were significantly worse (the standard deviation up to 51%). The replicate samples originated from different emissions test runs, and from different Soxhlet extractions.

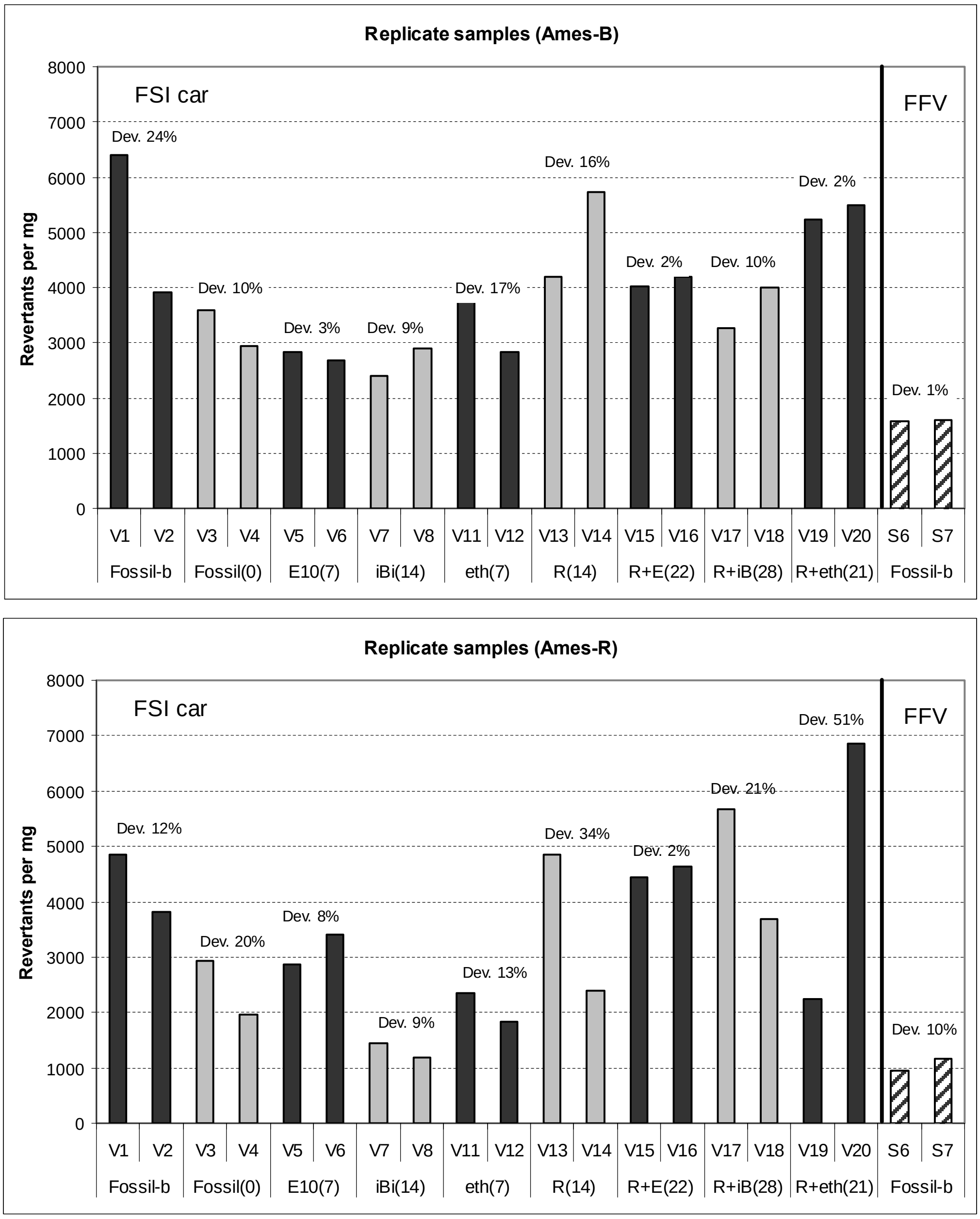

Figure 4.10. Ames results from replicate European test runs with different car/fuel combinations. Results with two calculation methods are shown (Ames-B and Ames-R). Standard deviations are shown as percentages.

4.2.5 Calculation of risk factors

4.2.5.1 Regulated risk factors

Risk factors for exhaust toxicity were calculated separately for regulated and unregulated emissions.

Energy imposes indirect, external costs on society related to impacts in areas such as climate change, the environment, health and accidents. The monetary values of these impacts have been evaluated to determine the lifetime costs of, for example, exhaust emissions from transport vehicles. Directive 2009/33/EC defines these external costs as follows:

CO_2	€30–40/tonne
NMHC (without methane)	€1000/tonne
NO_x	€4400/tonne
PM	€87 000/tonne.

In Finland, Tiehallinto (2001) published external costs for CO and HC emissions in addition to those for NO_x, $PM_{2.5}$ and CO_2 emissions. National values in Finland for CO and HC emissions were defined as follows:

CO	€29/tonne
HC (with methane)	€62/tonne.

Risk factors for regulated emissions were calculated using Equation (11), which includes external costs for CO, HC (including methane), NMHC (without methane), NO_x and PM emissions.

$$\text{“Regulated risk factor”} = \Sigma(F_X * E_X) \tag{11}$$

F = External costs of emissions, €/tonne
E = Emissions in exhaust gas, tonne/km
x = CO, HC, NMHC, NO_x, PM

4.2.5.2 Unregulated risk factors (“priority air toxics”)

There are several lists of “priority air toxics” that define the most harmful compounds that should be taken into account for mobile exhaust gases. These lists have been defined from various starting points, and there are therefore also some differences in the outcomes.

The US EPA's Mobile Source Air Toxic (MSAT[21]) list from 2001 included 21 compounds, among them acetaldehyde, acrolein, benzene, 1,3-butadiene, dioxin/furans, diesel exhaust, ethylbenzene, formaldehyde, n-hexane, metals (6 species), MTBE, naphthalene, styrene, toluene and xylene. In the 2007 rule[22], the US EPA discusses *eight key MSATs* and *gasoline particulate matter*[23]. This MSAT list includes:

- benzene
- 1,3-butadiene
- formaldehyde
- acetaldehyde
- acrolein
- polycyclic organic matter (POM)
- naphthalene
- diesel exhaust
- gasoline PM.

The Health Effects Institute, HEI (2007), reviewed these key MSAT compounds defined by the US EPA. The focus was on the MSATs, for which mobile sources are a significant source and for which effects may be observable at concentrations approaching those found in ambient air. The key questions in the review were: **a)** To what extent are mobile sources a significant source of exposure to this MSAT? Does this MSAT affect human health at environmental concentrations? **b)** Does this MSAT affect human health?

The panel concluded that the contribution of *mobile sources is greatest for 1,3-butadiene, followed by benzene, formaldehyde, acetaldehyde and acrolein*. The evaluation of mobile-source contributions to POM or naphthalene is difficult. The main findings of the HEI (2007) review are as follows:

Acetaldehyde – a) Mobile sources are a significant, but not principal, source. Acetaldehyde is present in some foods, for example. The use of ethanol as fuel may increase acetaldehyde emissions. b) Acetaldehyde is chemically reactive. It causes irritation to the eyes, skin and respiratory tract and induces cellular inflammation. Acetaldehyde is a carcinogen in rodents, but the data on its carcinogenicity in humans are inadequate.

Acrolein – a) Environmental data for acrolein are limited. In addition to its direct sources, acrolein is formed from 1,3-butadiene in the air. The major indoor source is

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[21] US EPA (2001), 40 CFR Parts 80 and 86, Control of Emissions of Hazardous Air Pollutants From Mobile Sources. Final Rule. 29 March 2001.

[22] US EPA (2007), 40 CFR Parts 59, 80, 85, and 86, Control of Hazardous Air Pollutants From Mobile Sources. Final Rule. 26 February 2007.

[23] Particulate matter emission from gasoline-fuelled cars.

tobacco smoke. Environmental concentrations have been close to those causing irritation. b) Acrolein is highly irritant to the respiratory tract. Chronic inhalation results in inflammation. Evidence of carcinogenicity has not been firm.

Benzene – a) Mobile sources are an important source of benzene. b) Benzene increases the risks of acute myeloid leukaemia. Benzene seems to affect haematologic indices at exposure concentrations lower than those reported previously.

1,3-Butadiene – a) Mobile sources are the most important contributors in ambient air in most locales. The lifetime of 1,3-butadiene is short, but its high reactivity results in other MSATs, such as formaldehyde, acetaldehyde and acrolein. Indoor concentrations may be higher than outdoor concentrations due to tobacco smoke, for example. In community studies, there is no direct evidence of health effects from exposure at ambient concentrations. b) 1,3-Butadiene may cause lymphohaematopoietic cancers in high-exposure occupational settings.

Formaldehyde – a) Indoor sources are most important for formaldehyde. Mobile sources are the principal sources of ambient concentrations, but summer photochemical activity contributes more than do direct vehicle emissions. In Brazil, ambient formaldehyde concentrations have increased fourfold as the use of natural gas vehicles has expanded. b) Formaldehyde is an irritant to the eyes, skin and respiratory tract in humans. It has been classified as a human carcinogen. Indoor exposure seems to increase asthma in children. There is no evidence regarding the health effects of outdoor exposures.

Naphthalene – a) Naphthalene is the most abundant PAH in ambient air. Mobile sources are an important, but not principal, source. Tobacco and moth-repellents are indoor sources. There are no studies that assess the health effects at ambient concentrations. b) There is evidence in rodents that exposure to naphthalene leads to inflammation of the nasal tract and tumors of the nasal epithelium, for example. However, there are no data on carcinogenicity in humans. Case reports suggest that exposure may cause effects in blood cells, such as haemolysis and haemolytic anaemia.

POM – a) Polycyclic organic matter includes a mixture of compounds, for example PAHs. POMs are found in the exhaust gas phase, particle phase or both. Mobile sources may be significant contributors to ambient concentrations of POM in urban settings. Cigarette-smoking, food-derived sources, etc., may lead to exposure. Diesel vehicles emit more PAHs than do gasoline-fuelled vehicles[24]. Cold starts account for up to 50% of their PAH emissions from vehicles. Community studies have a limited ability to address the effects of POM alone. b) A few PAH components in POM are potent animal carcinogens. Some of these, for example benzo[a]pyrene, are classified as human carcinogens. Many adverse health effects are reported in highly polluted industrial sites, but the links to POM are not firm. Priority PAHs are discussed in Chapter 4.2.4.

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[24] This study at hand shows that PAH emissions from the gasoline-fuelled cars may be high at -7°C.

One indirect adverse effect of acetaldehyde is reported by Environment Australia (2002): “acetaldehyde reacts with NO_x in the atmospheric photochemical system, and produces peroxyacetyl nitrate (PAN), which is a phytotoxicant and mutagen”.

Calculation of unregulated risk factors

Risk factors for calculating the cancer potency of exhaust gas, as defined by OEHHA (2009), US EPA IRIS (2010) and The Nordic Ecolablelling (2008), are shown in Table 4.13. OEHHA (2009) defines cancer unit risks and potency factors for 107 carcinogenic substances or groups of substances. The US EPA IRIS (Integrated Risk Information System) is a human health-assessment programme that evaluates quantitative and qualitative risk information for effects that may result from exposure to environmental contaminants. The Nordic Swan labelling criteria for biofuels define substances, which are measured in accordance with a particular protocol, and calculate the cancer potency of exhaust gas using risk factors (Nordic Ecolabelling 2008).

The most significant differences in the risk factors defined by different organizations concern ethene and propene emissions, which are included in Nordic Ecolabelling but not in the other definitions. Törnqvist et al. (1994) reported that ethene is metabolized in animals and in humans to a probable human carcinogen, ethylene oxide. Similarly, propene is metabolized to propylene dioxide.

Table 4.13. Substances and risk factors for calculating the cancer potency of exhaust gas according to OEHHA (2009), US EPA IRIS (2010) and Nordic Ecolabelling (2008).

Substance	Unit Risk Factor (µg/m^3)$^{-1}$			Normalized[25]
	Nordic Ecolabelling	OEHHA 2009	US EPA IRIS 2010	
Particulate matter[26]	7 x 10^{-5}	30 x 10^{-5}	insuff. data	177
Benzene	0.8 x 10^{-5}	2.9 x 10^{-5}	(0.22-0.78) x 10^{-5}	17
Formaldehyde	10 x 10^{-5}	0.6 x 10^{-5}	1.3 x 10^{-5}	4
Acetaldehyde	0.2 x 10^{-5}	0.27 x 10^{-5}	0.22 x 10^{-5}	2
Ethene	5 x 10^{-5}			17
Propene	1 x 10^{-5}			3
1,3-Butadiene	30 x 10^{-5}	17 x 10^{-5}	3 x 10^{-5}	100
PAH (including benzo(a)pyrene)	2800 x 10^{-5}			9333

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[25] In the normalization, 1,3-Butadiene = 100, and OEHHA 2009 factors are used for substances other than ethene, propene and PAH.

[26] OEHHA defines “Particulate Matter from Diesel-Fueled Engines”.

Risk factors for unregulated emissions were calculated using Equation (12). Unit risk factors defined by OEHHA (2009) were used in the calculation: 1,3-butadiene 17 x 10^{-5}, benzene 2.9 x 10^{-5}, formaldehyde 0.6 x 10^{-5} and acetaldehyde 0.27 x 10^{-5}. Particulate matter emissions were excluded, because they were already taken into account in Equation (11).

$$\text{“Unregulated risk factor ”} = \Sigma(\text{URF} * c)_x \qquad (12)$$

URF = Unit risk factor (OEHHA 2009), $(\mu g/m^3)^{-1}$
c = Concentration in exhaust gas, $\mu g/m^3$
x = Formaldehyde, acetaldehyde, benzene and 1,3-butadiene

4.2.5.3 Total risk factor

The total risk factors for exhaust toxicity were calculated as the sum of the normalized risk factors of the regulated and unregulated emissions. In the normalization procedure, the risk factor for Fossil(0) fuel was set to 1. This compensates for the different scales of risk factors for regulated and unregulated emissions, as well as for cars' different emissions levels.

4.2.5.4 Risk factors for PAHs and ozone-forming potential

A Working Group of the European Commission prepared a position paper to review knowledge of PAHs in ambient air (EU 2001). As part of the study, toxic equivalency factors (TEFs) relative to benzo(a)pyrene were reviewed. The review results with regard to 14 selected PAHs are summarized in Table 4.11. In addition, supplementary TEFs are shown for fluorene (Flu) and 7,12-dimethylbenz(a)anthracene (DMBA) (Collins et al. 1998).

Table 4.14. Toxic equivalency factors (TEFs) relative to benzo(a)pyrene and selected values used in this study.

	Flu	Phe	An	F	P	BaA	Chr	BbF	BkF	BjF	DMBA	BeP	BaP	IP	DBahA	BghiP
EU (2001)		0.0005–0.01	0–0.01	0–0.06	0–0.081	0.005–0.145	0.001–0.89	0.06–0.14	0.03–0.1	0.045–0.061		0–0.004	1	0–0.232	0.69–5	0.01–0.03
Selected	0.001[a]	0.01	0.01	0.06	0.081	0.145	0.89	0.14	0.1	0.061	(10[a])	0.004	1	0.232	5	0.03

[a] Collins et al. 1998

A total cancer potency for PAHs was evaluated by calculating the BaP equivalent using Equation (13).

$$BaP_{eq} = \sum \left(TEF_x * PAH_x \right) \quad (13)$$

BaP_{eq} = Benzo(a)pyrene equivalent (µg/km)
TEF_x = Relative toxic equivalency factor for individual PAH compounds in Table 4.14
PAH_x = Mass emissions (µg/km) of PAH compounds in Table 4.14

The unregulated risk factor was calculated by using a unit risk factor of 2800 x 10^{-5} for BaP_{eq} in addition to the unregulated risk factor defined in the previous chapter.

For comparison, the risk factor was calculated using the Nordic Ecolabelling methodology taking into account particulate matter, benzene, formaldehyde, acetaldehyde, ethene, propene, 1,3-butadiene and PAH emissions.

Ozone-forming potential

Mobile sources emit volatile organic compounds (VOC) that contribute to the formation of ground-level ozone together with nitrogen oxides in the presence of heat and sunlight.

Ozone causes adverse health effects, for example irritation of the respiratory system, coughing, throat irritation and reduction of lung function. Ozone may aggravate asthma. Potential interactions between ozone and particulate matter emissions have been suggested. There is also evidence of the effect of ozone on, for example, cardiovascular-related morbidity (US EPA 2007). Ozone contributes to damage to plants and ecosystems. Ozone may cause visible injury to leaves and impair photosynthesis. The adverse effects of ozone on forest and other natural vegetation may lead to species shifts and loss from the affected ecosystems, resulting in the loss or reduction of related goods and services (US EPA 2007).

Individual VOC species contribute very differently to ozone and the formation of oxidants. Carter and Atkinson (1987) developed a maximum incremental reactivity (MIR) scale to assess the ozone-forming potential (OFP) of any emitted molecule (Equation 14).

$$\text{OFP} = \Sigma \text{ (MIR x mass emissions)} \quad (14)$$

In this study, OFP was calculated by using the MIR values for selected individual hydrocarbons and oxygen-containing compounds as shown in Table 4.15 (Carter 2010).

Table 4.15. Maximum incremental reactivity (MIR) values of selected compounds (Carter 2010).

	MIR **g ozone/g VOC**
carbon monoxide	0.056
methane	0.0144
ethane	0.28
ethene	9.00
propane	0.49
propene	11.66
acetylene	0.95
isobutene	6.29
1,3-butadiene	12.61
benzene	0.72
toluene	4.00
ethyl benzene	3.04
m-xylene	9.75
p-xylene	5.84
o-xylene	7.64

	MIR **g ozone/g VOC**
ethanol	1.53
isobutanol	2.51
n-butanol	2.88
ETBE	2.01
formaldehyde	9.46
acetaldehyde	6.54
acrolein	7.45
propionaldehyde	7.08
crotonaldehyde	9.39
methacrolein	6.01
butyraldehyde	5.97
benzaldehyde	-0.67
valeraldehyde	5.08
m-tolualdehyde	-0.59
hexanal	4.35

4.3 Car exhaust emissions

Regulated exhaust emissions from all cars tested were generally high over the European test cycle at -7 °C compared with emissions at normal temperature. Cold starts at low test temperatures led to high emissions at the start of the test until the engine and three-way catalyst have warmed up to the normal operating temperature. Exhaust emissions and fuel consumption are reduced with a warmed-up engine (EUDC test phase). However, formaldehyde emissions were relatively high even with a warmed-up engine, which indicates that the catalyst did not remove formaldehyde as efficiently as it removed the other exhaust species.

Regulated emissions were generally lowest for the MPFI car compared with the FSI and FFV cars. In addition, the spread of the results for different fuels was quite narrow for the MPFI car. This indicates the three-way catalyst's short start-up and warm-up periods and the MPFI car's good engine control system.

4.3.1.1 Cold-start cycle at -7 °C

Numerical results are presented in Appendices 1–4. The error bars in the Figures describe the standard deviations of the measurements unless otherwise noted.

Regulated exhaust emissions from all cars tested were generally high over the European test cycle at -7 °C compared with emissions limits at normal temperature (Table 4.15, Figures 4.11 and 4.12). Cold starts at low test temperatures led to high emissions at the start of the test before the engine and three-way catalyst had warmed up to the normal operating temperature.

The CO and HC limits at -7 °C are defined over the ECE15 portion of the European test cycle. The CO end HC emissions over the ECE15 part were within the CO and HC limits at -7 °C for the MPFI, FSI and FFV cars, with the exception of the FFV car using E85(56) and Fossil-b fuels (Figure 4.11, right).

CO emissions from the MPFI car were lower than those from the FSI and FFV cars. In fact, CO emissions from the MPFI car at -7 °C were in many cases lower than the Euro 5 limit at normal temperature. CO emissions from the FFV and FSI cars at -7 °C were more than twice as high as the limit for normal temperature. HC emissions from the FSI car were higher than those from the FFV and MPFI cars. HC emissions from all cars tested were substantially higher than the Euro 5 limit at normal temperature.

NO_x emissions varied between cars and fuels. The MPFI car had very low (lower than the Euro 5 limit at normal temperature) NO_x emissions even at -7 °C. FSI and FFV cars had substantially higher NO_x emissions than did the MPFI car, and were on average well above the Euro 5 limit.

PM results depended on the car. PM emissions from the MPFI and FFV cars were relatively low, in most cases below the 5 mg/km Euro 5 limit for PM emissions at normal test temperature. The FSI car was the highest PM emitter. The PM emissions of the FSI car were 10–20 mg/km.

Overall, regulated emissions were generally lowest for the MPFI car compared with the FSI and FFV cars. Furthermore, the spread of the results for different fuels was quite narrow for the MPFI car. This indicates short start-up and warm-up periods for the three-way catalyst and the MPFI car’s good engine control system.

Table 4.16. Average emissions over the European test cycle (ECE15+EUDC) at -7 °C [a].

	CO g/km	HC g/km	NO_x g/km	PM mg/km	CO_2 g/km	FC l/100 km
MPFI, E10, -7 °C	1.0	0.4	0.03	4	203	8.9
FSI, E10, -7 °C	3.1	0.5	0.07	13	170	7.7
FFV, E10, -7 °C	2.3	0.3	0.10	3	255	11.3
FFV, E85, -7 °C	5.5	2.4	0.05	7	247	15.8
EU5 limit, normal temp.	1.0	0.1 (NMHC 0.068)	0.06	5		

[a] EU5 limits at -7 °C: CO max. 15 g/km and HC max. 1.8 g/km apply to ECE15 portion of the European test cycle.

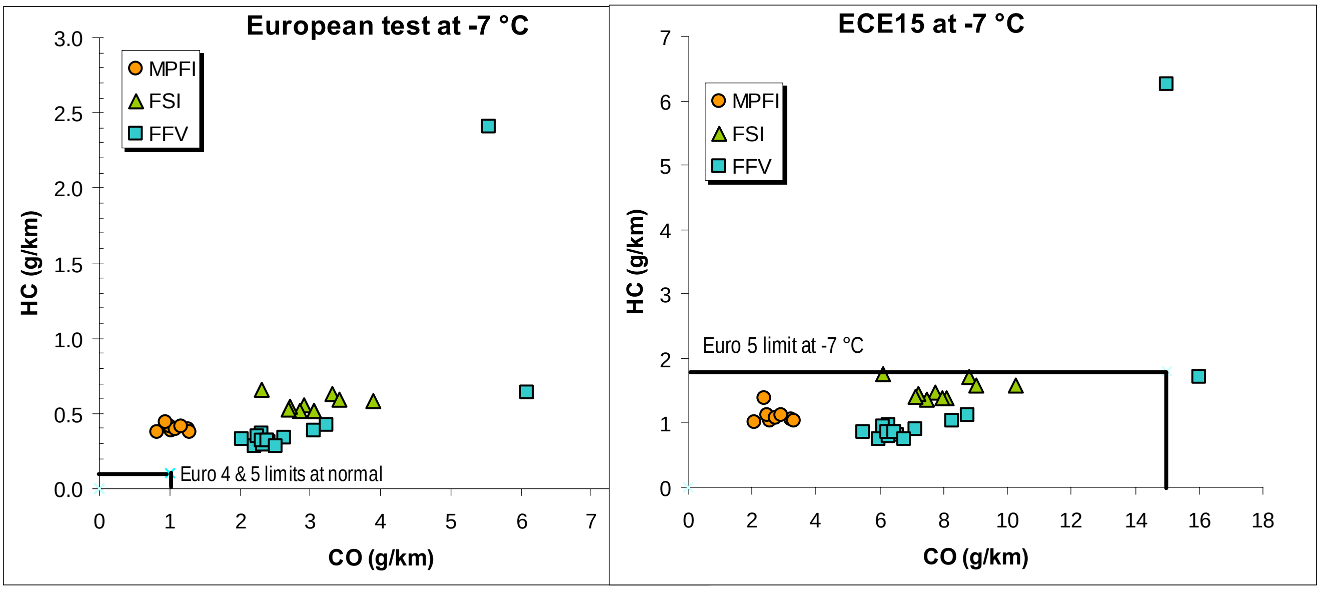

Figure 4.11. CO and HC emissions at -7 °C over the European test cycle (left) and over the ECE15 portion (right) of the European test cycle.

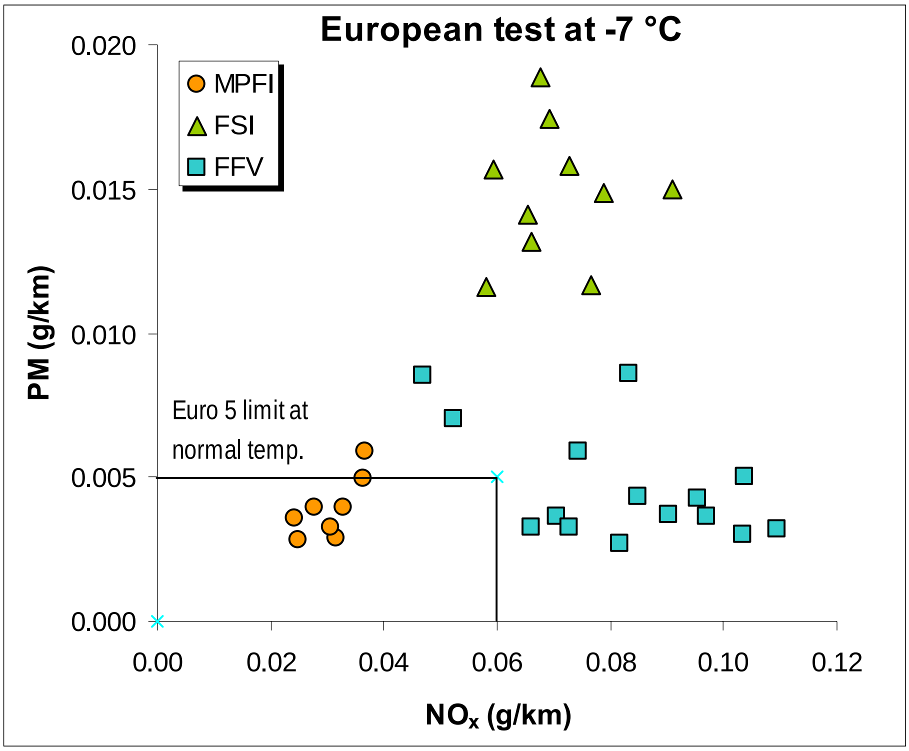

Figure 4.12. NO_x and PM emissions over the European test cycle at -7 °C.

4.3.1.2 Warmed-up cars

The European emissions test driving cycle was divided into three phases to study the behaviour of cold-start and warmed-up engines. In the EUDC part of the test, the engine and catalyst are more or less warmed up, and exhaust emissions are very low.

Figure 4.13 shows that CO, HC, NO_x, acetaldehyde, methane, 1,3-butadiene and benzene emissions in the EUDC test phase are only a fraction of emissions over the European driving cycle including cold-start. CO, HC, acetaldehyde, 1,3-butadiene and benzene emissions in the EUDC part of the test were some 10% of those over the European driving cycle. NO_x emissions were 18% of the respective total result.

CO_2 emissions and fuel consumption are also substantially lower when engine was warm than when engine was cold.

Formaldehyde emissions are relatively high in the EUDC phase of the test cycle at some 45–80% of those over the European driving cycle.

In Appendix 1, the results over the EUDC test phase are shown in parallel with the results over the test cycle to illustrate that emissions diminish once the catalyst has warmed up. Overall, the results of this study emphasize car emissions in cold starts at -7 °C.

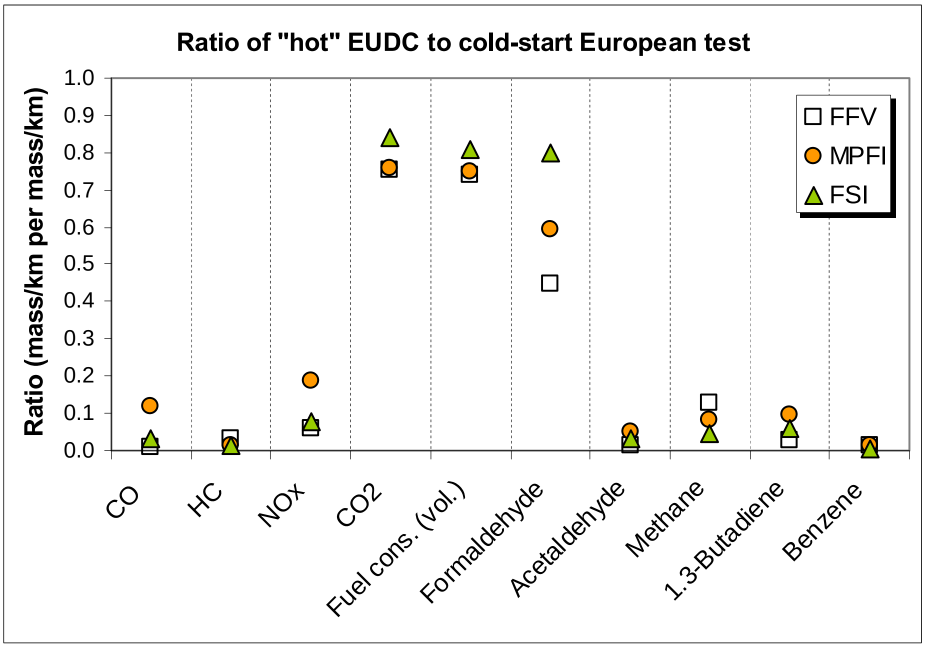

Figure 4.13. Ratio of emissions from the “hot” EUDC phase to the cold-start European test cycle at -7 °C.

4.4 Exhaust emissions and fuel consumption

Volumetric fuel consumption over the European test was significantly higher at -7 °C than at normal temperature, with increases of around 33% for the MPFI car, 21% for the FSI car and 18% for the FFV car. The lower test temperature was also observed to increase CO_2 emissions.

Differences in emissions between biofuels and fossil fuel were not consistent across the cars tested. The FSI car responded more clearly to fuel changes than the MPFI and FFV cars. With the FSI and MPFI cars, CO emissions were lower with biofuels than with fossil fuel, but the NO_x emissions were generally higher. For the FFV car, E85 fuel resulted in high CO and HC emissions, but low NO_x emissions. The NO_x emissions from the FFV car were generally lower for high-oxygen than for low-oxygen fuels. The FSI car was the highest PM emitter. For the FSI car, oxygenates seemed to reduce PM emissions. With the FFV car, PM emissions with E85 fuel were unexpectedly high.

Acetaldehyde emissions were at their highest with ethanol- and/or ETBE-containing fuels. The highest acetaldehyde emissions were observed for E85 fuel. Acrolein emissions were elevated with E85 fuel and butanol-containing fuels. Formaldehyde, butyraldehyde, propionaldehyde and methacrolein emissions were generated by butanol-containing fuels. Alcohol in fuel leads to tailpipe emissions of alcohol, which was seen for instance as high ethanol emissions with E85 fuel.

1,3-butadiene emissions for biofuels were lower than or at the same level as for the fossil fuel, but with some exceptions. Higher 1,3-butadiene emissions were observed for butanol-containing fuels in some cases. The combination of the renewable gasoline component with oxygenates had some beneficial effects on the 1,3-butadiene emissions. The FSI car had the highest benzene emissions. With FFV cars, E85 fuel resulted in the highest benzene emissions regardless of the fuel's low benzene content. Methane emissions were high with E85 fuel, but emissions fell with E30 fuel for the FFV car.

Catalyst-related ammonia emissions were substantial for the three cars tested.

High emissions of heavy PAHs and strong mutagenicity associated with gasoline car particles were observed, particularly for the FSI car. The hydrocarbon fuels and E85 fuel resulted in the most harmful particles in this respect.

4.4.1 Fuel consumption and CO_2

Fuel consumption over the European test was significantly higher at -7 °C than the nominal values announced by the manufacturer for the test at normal temperature, with increases of 33% for the MPFI car, 21% for the FSI car and 18% for the FFV car (Table 4.17). This reflects the substantial impact of the ambient temperature on fuel consumption.

The impact of the lower test temperature was also observed as CO_2 emissions increases of 32% for the MPFI car, 17% for the FSI car and 16% for the FFV car.

Table 4.17. Nominal and measured CO_2 emissions and volumetric fuel consumption.

	MPFI	**FSI**	**FFV**
Nominal CO_2, g/km**	153	144	217*
CO_2, -7 °C, Fossil(0) fuel	203	169	251
Difference- %	*32%*	*17%*	*16%*
Nominal fuel consumption, l/100 km**	6.6	6.2	9.2
Fuel consumption, -7 °C, Fossil(0)	8.8	7.5	10.9
Fuel consumption, -7 °C E10 fuel	8.9	7.7	11.3
Difference-% (-7 °C vs. nominal with Fossil(0))	*33%*	*21%*	*18%*
Difference-% (E10 fuel vs. Fossil(0))	*1.1%*	*2.7%*	*3.7%*

*) For the FFV car, nominal CO_2 emissions are calculated from the nominal fuel consumption.
**) Announced by the manufacturer.

Figure 4.14 shows changes in measured mass-based fuel consumption with biofuels compared with the Fossil(0) fuel, and respective changes in theoretical fuel consumption[27]. Generally, the fuel consumption results followed the theoretical trends with two exceptions: nB(15) and eth(7) with the FFV car resulted in higher fuel consumption than expected, which indicates changes in engine adjustments. This was probably not a fuel-related phenomenon.

Fuel consumption with the oxygen-containing fuels was worse than with the hydrocarbon fuels, as expected. For E10 fuel the volumetric fuel consumption increased by 1.1–3.7% compared with Fossil(0) fuel at -7 °C, depending on the car tested. The theoretical increase in volumetric fuel consumption is 3.4% when 10 v/v% ethanol is added to gasoline.

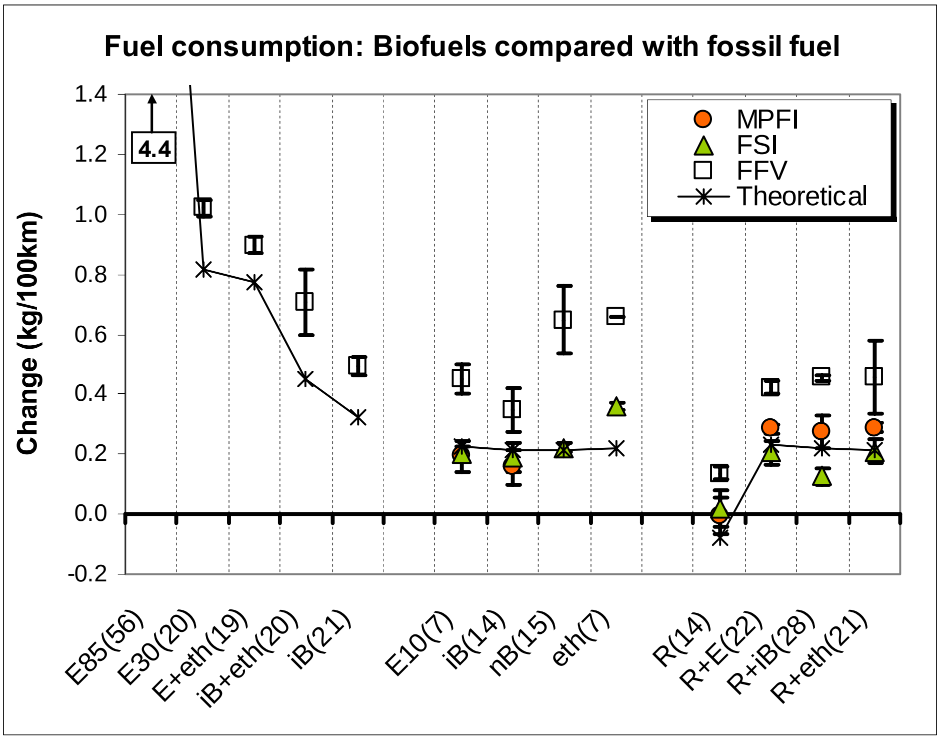

Figure 4.14. Differences in mass-based fuel consumption in absolute terms (change kg/100 km) between biofuels and non-oxygenated fossil fuel. European test cycle at -7 °C.

Tailpipe CO_2 emissions depend on the carbon/hydrogen ratio of the fuel and engine efficiency. The carbon/hydrogen ratios of pure ethanol, butanols and ETBE are lower than that of fossil fuel. This may lead to a reduction in tailpipe CO_2 emissions if oxy-

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[27] The theoretical fuel consumption with each fuel was calculated using the approximate energy consumption of the car (MJ/km) and the energy content of the fuel (MJ/kg). The specific energy consumption of each car was assumed to be constant independently of the fuel. The theoretical carbon dioxide output was calculated, based on the theoretical fuel consumption, and compared with the sum of the measured carbon dioxide and carbon monoxide outputs. In the combustion process, carbon in the fuel is also converted into hydrocarbons and other carbon-containing compounds, but these were not taken into account.

genates are splash-blended into gasoline. However, in this work fuels were match-blended. The carbon/hydrogen ratio depends on both the hydrocarbon and the oxygenate portions of blends. Overall, differences in tailpipe CO_2 emissions between fuels are an extremely small factor in the evaluation of well-to-wheel life cycle CO_2 emissions. Tailpipe CO_2 emissions are therefore not discussed here in detail. However, an overview of absolute emissions levels is shown in Figure 4.15.

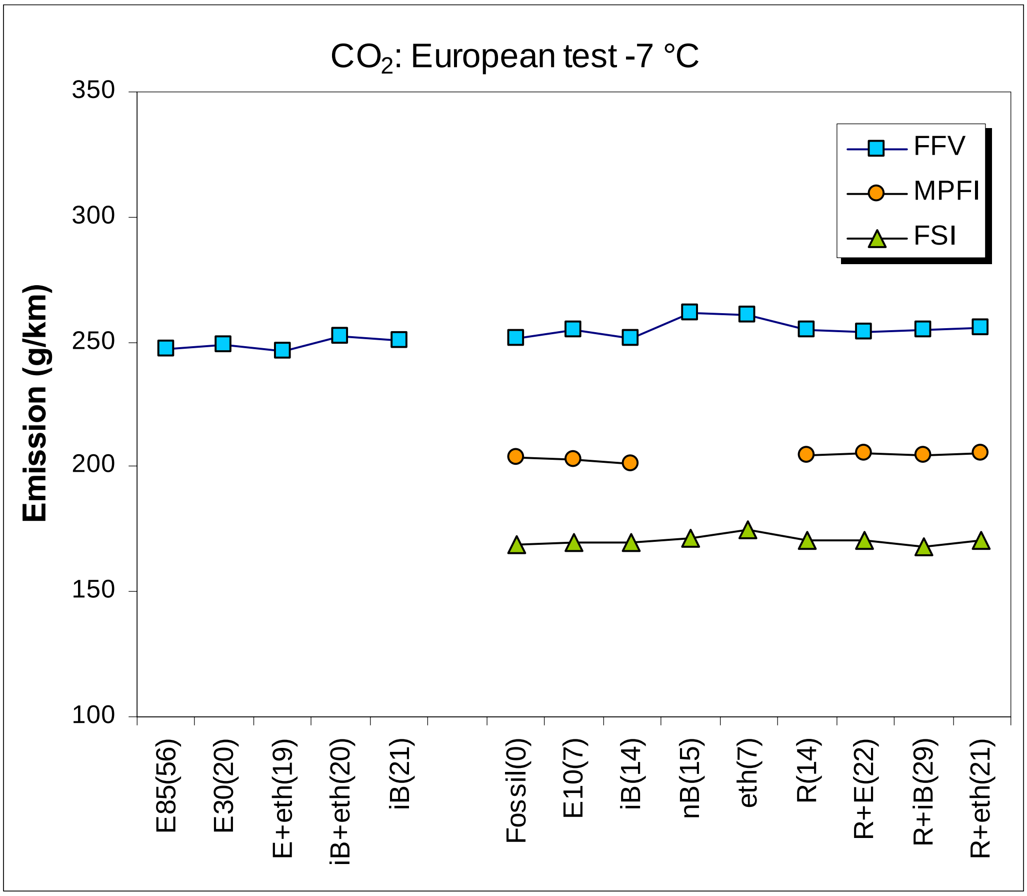

Figure 4.15. CO_2 emissions over the European test cycle at -7 °C.

4.4.2 Regulated gaseous emissions (CO, HC, NO_x and PM)

Emissions changes when biofuels are compared with Fossil(0) fuel for each car are shown in absolute terms in the figures of this chapter. Relative changes are shown numerically in Appendix 1.

Biofuels with high oxygen content

For the FFV car, E85(56) fuel resulted in high CO and HC emissions, but low NO_x emissions. Ethanol’s evaporation characteristics and low combustion temperature may lead to high CO and HC emissions, but low NO_x emissions in cold starts (Chiba et al. 2010). However, adjustments to the FFV car may also enhance this trend.

CO emissions for E30(20), E+eth(19) and eth(7) fuels were higher than those for fuels containing, for example, isobutanol. The NO_x emissions from the FFV car were generally lower for the high-oxygen containing fuels than for the low-oxygen containing fuels. PM emissions with E85(56) and iB+eth(20) fuels were unexpectedly high.

Hydrocarbon emissions with high-oxygen containing fuels are not entirely comparable with those of hydrocarbon fuels. Carbon-containing oxygenates in the exhaust gas have a response in an FID detector, as described in Chapter 4.2. A notable part of the measured HC emissions for ethanol-containing fuels is therefore actually attributable to ethanol and carbonyl emissions.

Biofuels with low oxygen content

Cars representing different engine technologies responded differently to fuel changes. Consequently, differences between biofuels and Fossil(0) fuel were not consistent across the cars tested. Some fuels showed a benefit with one car, but not necessarily with another. The FSI car responded clearly to fuel changes with regard to emissions, whereas the changes for the MPFI and FFV cars were not as clear or systematic.

With the FSI and MPFI cars, CO emissions were lower with biofuels than with Fossil(0) fuel. For the FFV car, changes in CO emissions were small. With the FSI car, HC emissions were lower with biofuels than with fossil fuel, with the exceptions of n-butanol-containing fuel and R(14) fuel. For the MPFI and FFV cars, HC emissions with biofuels were slightly higher than or at the same level as with fossil fuel.

With the MPFI and FSI cars, NO_x emissions were higher for biofuels than for Fossil(0) fuel, with the exception of R+eth(21) fuel. The opposite was observed with the FFV car, for which NO_x emissions were lower with the biofuels than with the Fossil(0) fuel.

The FSI car was the highest PM emitter, with a substantial level of 10–20 mg/km, whereas PM emissions from the MPFI and FFV cars were generally below 5 mg/km over the European test cycle at -7 °C. For the FSI car, oxygenates seemed to reduce PM emissions with the exception of eth(7) fuel.

Remarks

For the FFV car, two fuels behaved differently from the other fuels. E85(56) and Fossil-b fuels resulted in high CO and HC emissions, but low NO_x emissions. The FFV car is equipped with a knocking sensor. However, this does not explain the differences, because the octane number of Fossil-b fuel was at the same level as those of, for example, E30, iB+eth(20) and eth(7) fuels. For E85 fuel, the evaporation characteristics and low combustion temperature of ethanol explain the high emissions of CO and HC, as well as the low emissions of NO_x in cold starts (Chiba et al. 2010). It is more difficult to explain the similar trends with the Fossil-b fuel. One possibility is that car adjustments changed for the Fossil-b fuel. However, monitoring parameters did not reveal this. It is noted that distillation characteristics of these fuels were rather special.

Emissions are generally low in the "hot" EUDC part of European test cycle. However, some emissions for E85 fuel with the FFV car were still high during the EUDC cycle (Appendix 1).

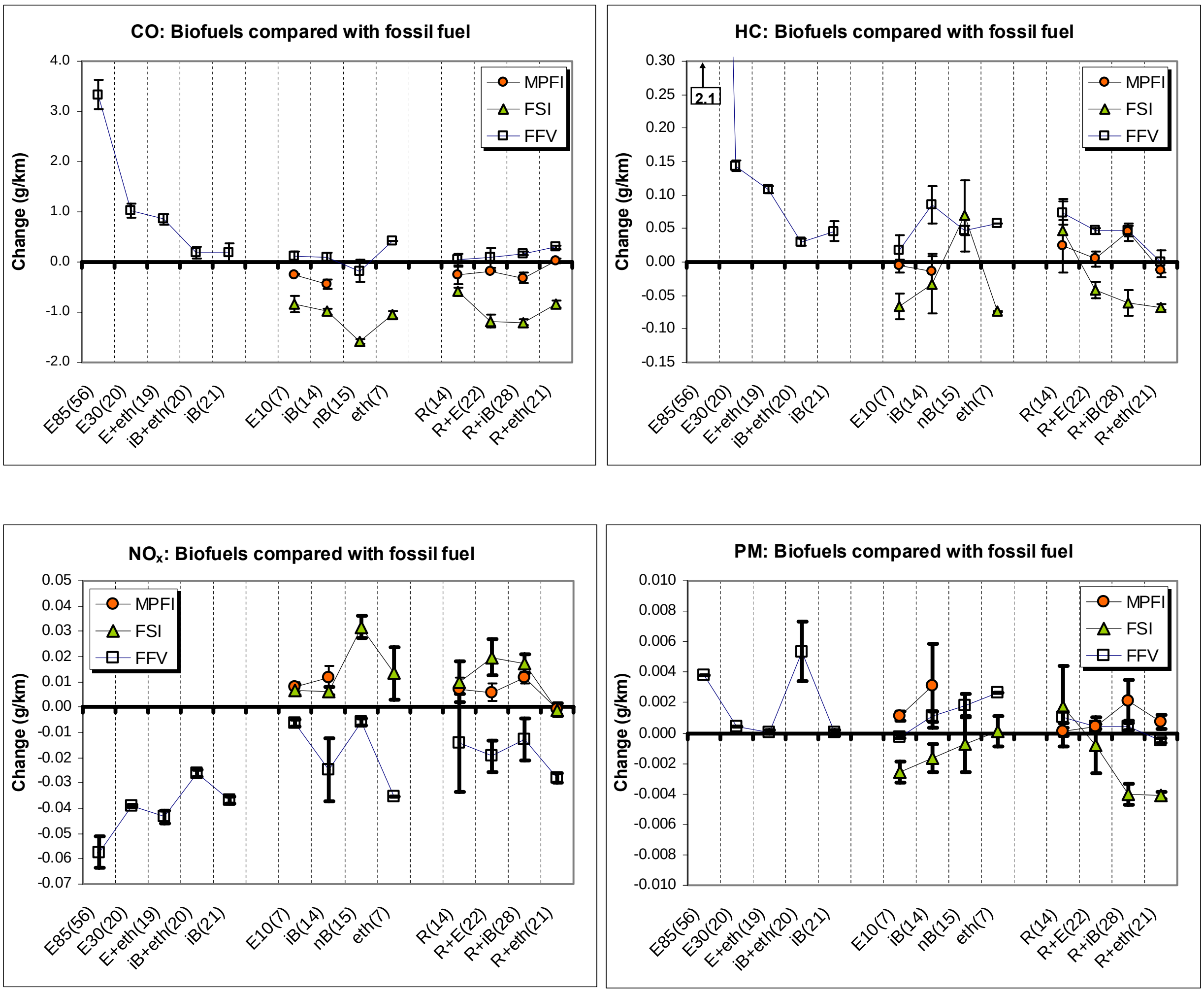

Figure 4.16. Differences in absolute terms (change g/km) between biofuels and non-oxygenated fossil fuel. NO_x and particulate matter emissions over the European test cycle at -7 °C. The PM emissions level for the FSI car was high, whereas the emissions levels for the MPFI and FFV cars were low (close to the detection limit).

4.4.3 Alcohol and ETBE emissions

Absolute differences in alcohol emissions between biofuels and Fossil(0) fuel are shown in Figure 4.17. Ethanol and isobutanol mass emissions with each fuel are shown in Figure 4.18. Numerical results are shown in Appendix 2.

Alcohol in fuel leads to tailpipe emissions of alcohol. Substantial concentrations of ethanol, isobutanol and n-butanol were observed in the exhaust gases, particularly for fuels with high concentrations of respective alcohols. Figure 4.19 shows that the cars responded logically to the fuel's alcohol content.

Ethanol emissions with E85(56) fuel were very high at around 2.5 g/km. Ethanol emissions were only 0.07–0.09 g/km with E30(20) and E+eth(19) fuels. This is only around 4% of the emissions with E85(56) fuel, despite the ethanol contents of these fuels being relatively high. Ethanol emissions were around 0.01–0.02 g/km with fuels containing low concentrations of ethanol and/or ETBE.

Isobutanol-containing and E85(56) fuels generated isobutanol emissions of around 0.03–0.06 g/km. n-Butanol-containing fuel generated n-butanol emissions of around 0.04 g/km.

It is noticeable that E85(56) fuel also generated alcohols other than ethanol, and even ETBE, in the tailpipe exhaust gases. E85(56) fuel generated ETBE emissions of around 0.06 g/km, whereas ETBE-containing fuels only 0.01–0.02 g/km.

A dramatic drop in alcohol and ether emissions was observed when the fuel was switched from E85(56) to E30(20) or lower ethanol concentration fuel.

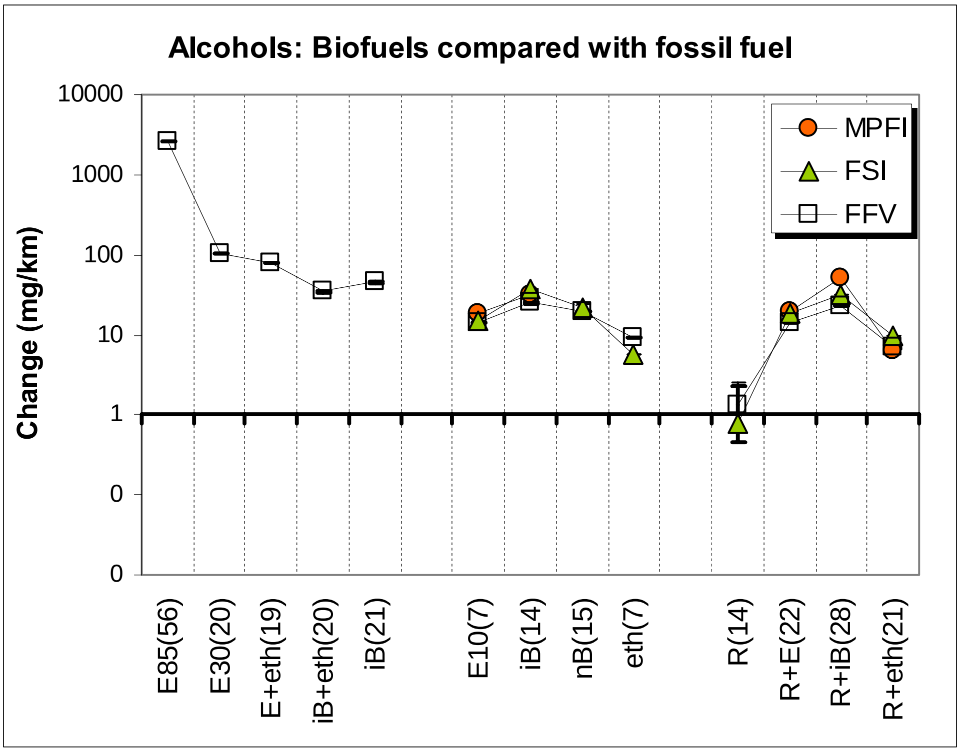

Figure 4.17. Sum of ethanol, isobutanol and n-butanol emissions: changes in absolute terms compared with Fossil(0) fuel. European test cycle at -7 °C. Note: logarithmic scale for y-axis.

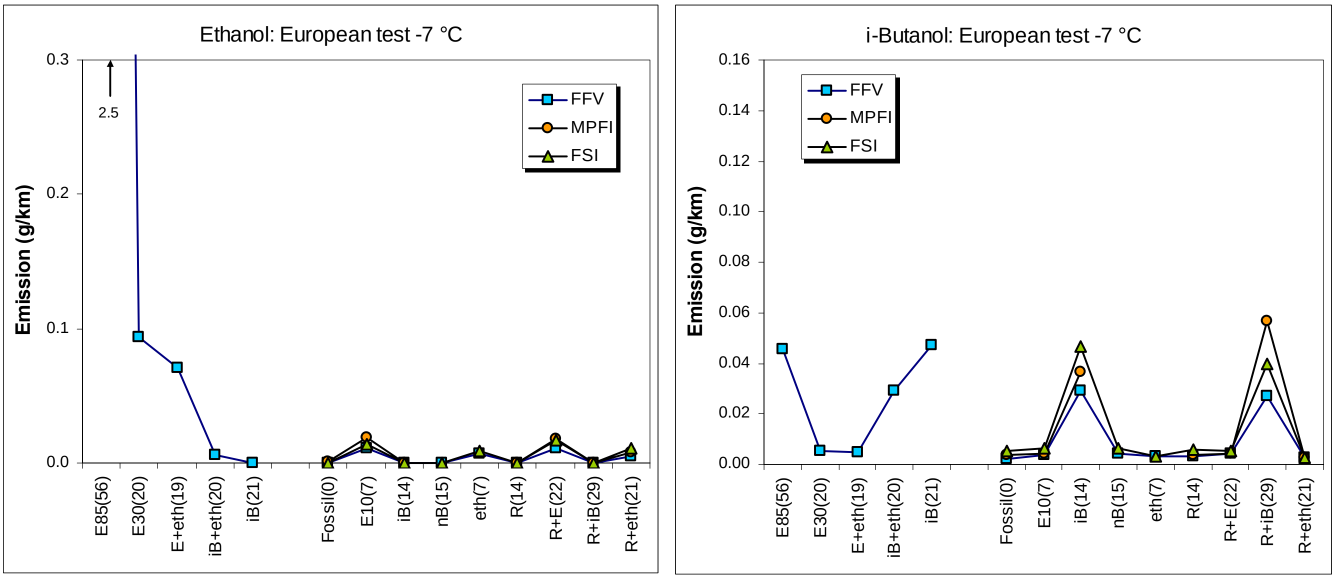

Figure 4.18. Ethanol and isobutanol mass emissions, European test at -7 °C.

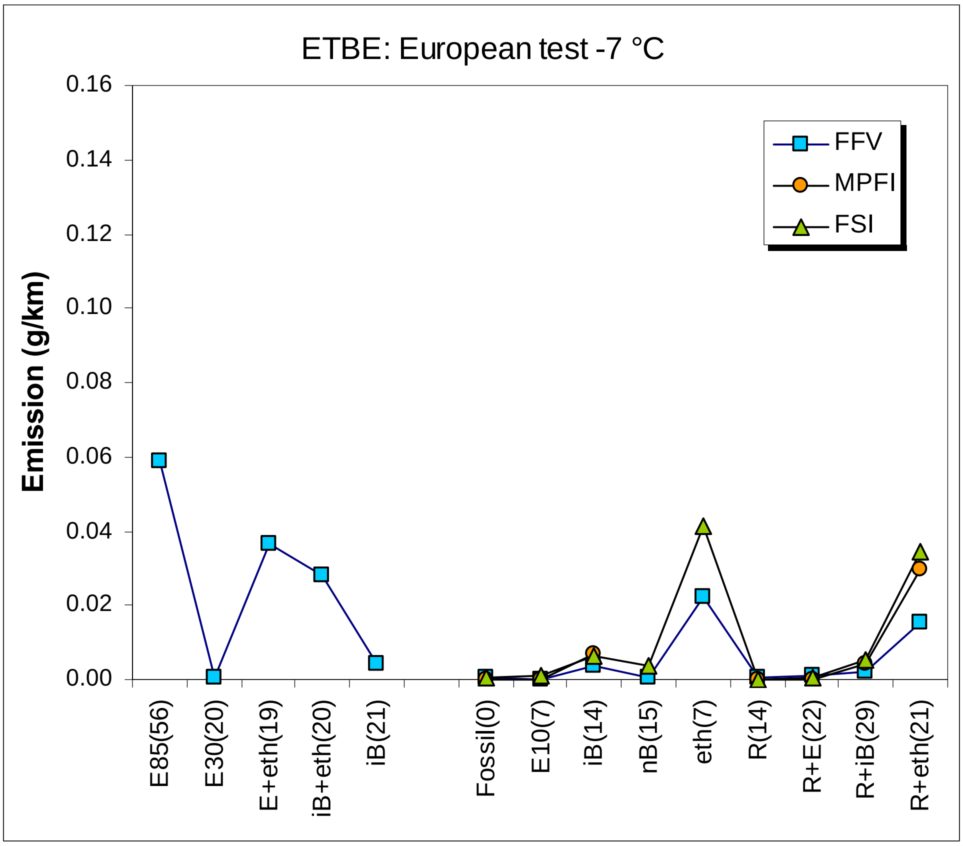

Figure 4.19. ETBE mass emissions, European test at -7 °C.

4.4.4 Aldehyde emissions

The maximum emissions of individual aldehydes measured with the tested cars are presented in Figure 4.20. The aldehydes present significantly in the exhaust gases were formaldehyde, acetaldehyde, acrolein, propionaldehyde, methacrolein, butyraldehyde and benzaldehyde. Formaldehyde and acetaldehyde are also evaluated using risk factor calculations in Chapter 4.6. Numerical results are shown in Appendix 2.

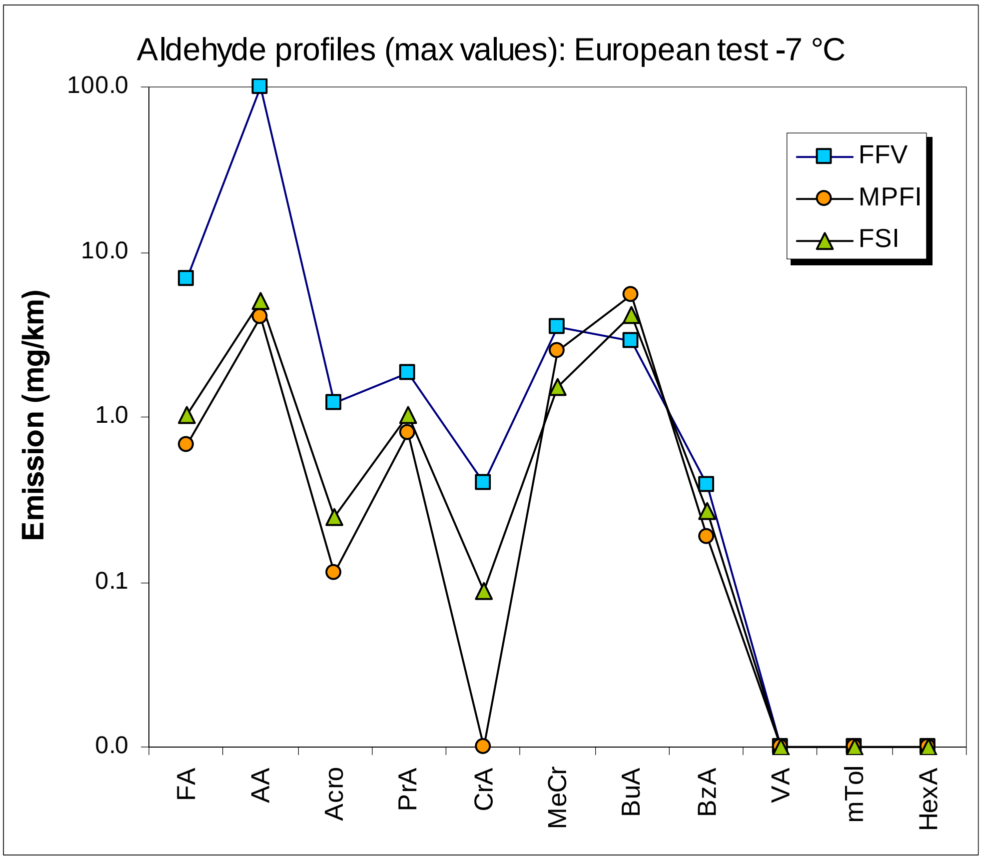

Figure 4.20. Aldehyde profiles of cars (maximum aldehyde emissions) [28], European test at -7 °C. Note: logarithmic y-scale.

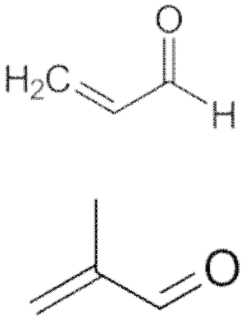

Figure 4.21. Acrolein and methacrolein (Wikipedia).

Formaldehyde and acetaldehyde emissions were higher for oxygen-containing fuels than for Fossil(0) fuel, as expected (Figure 4.22). The highest emissions were observed for E85(56) fuel, with acetaldehyde emissions as high as 98 mg/km and formaldehyde emissions 7 mg/km. With low-oxygen containing fuels, formaldehyde emissions were below 2 mg/km and acetaldehyde emissions below 4 mg/km. The level of formaldehyde emissions was higher for the butanol-containing fuels than for fuels containing ethanol or ETBE. Acetaldehyde emissions were at their highest with ethanol- and/or ETBE-containing fuels. In addition, n-butanol fuel generated acetaldyde in the exhaust.

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[28] FA = Formaldehyde, AA = Acetaldehyde, Acro = Acrolein, PrA = Propionaldehyde, CrA = Crotonaldehyde, MeCr = Methacrolein, BuA = Butyraldehyde, BzA = Benzaldehyde, VA = Valeraldehyde, mTol = m-Tolualdehyde, HexA = Hexanal

In contrast with other emissions, formaldehyde emissions stayed at a relatively high level even with a warmed-up engine in the EUDC part. For example, acetaldehyde emissions dropped to below 0.3 mg/km with a warmed-up engine. This may indicate the inability of the catalyst to oxidize formaldehyde efficiently.

For the nine other aldehydes analyzed, E85(56) fuel resulted in higher *acrolein* emissions than did the other fuels. In addition, acrolein emissions were slightly elevated with butanol-containing fuels. Molecular structures of acrolein and methacrolein are shown in Figure 4.21.

Butyraldehyde, propionaldehyde and methacrolein emissions were generated by butanol-containing fuels. With the FSI and FFV cars, *butyraldehyde* emissions were higher for n-butanol-containing fuel (3–5 mg/km) than for isobutanol-containing fuels (0.5–1 mg/km). Butyraldehyde emissions were higher with the MPFI car than with other cars when using isobutanol-containing fuels (5–6 mg/km), but n-butanol was not tested with the MPFI car. In the “hot” EUDC part, butyraldehyde emissions were around zero with all fuels. Propionaldehyde and methacroleine emissions were generated with isobutanol-containing fuels, but not much with n-butanol-containing fuel.

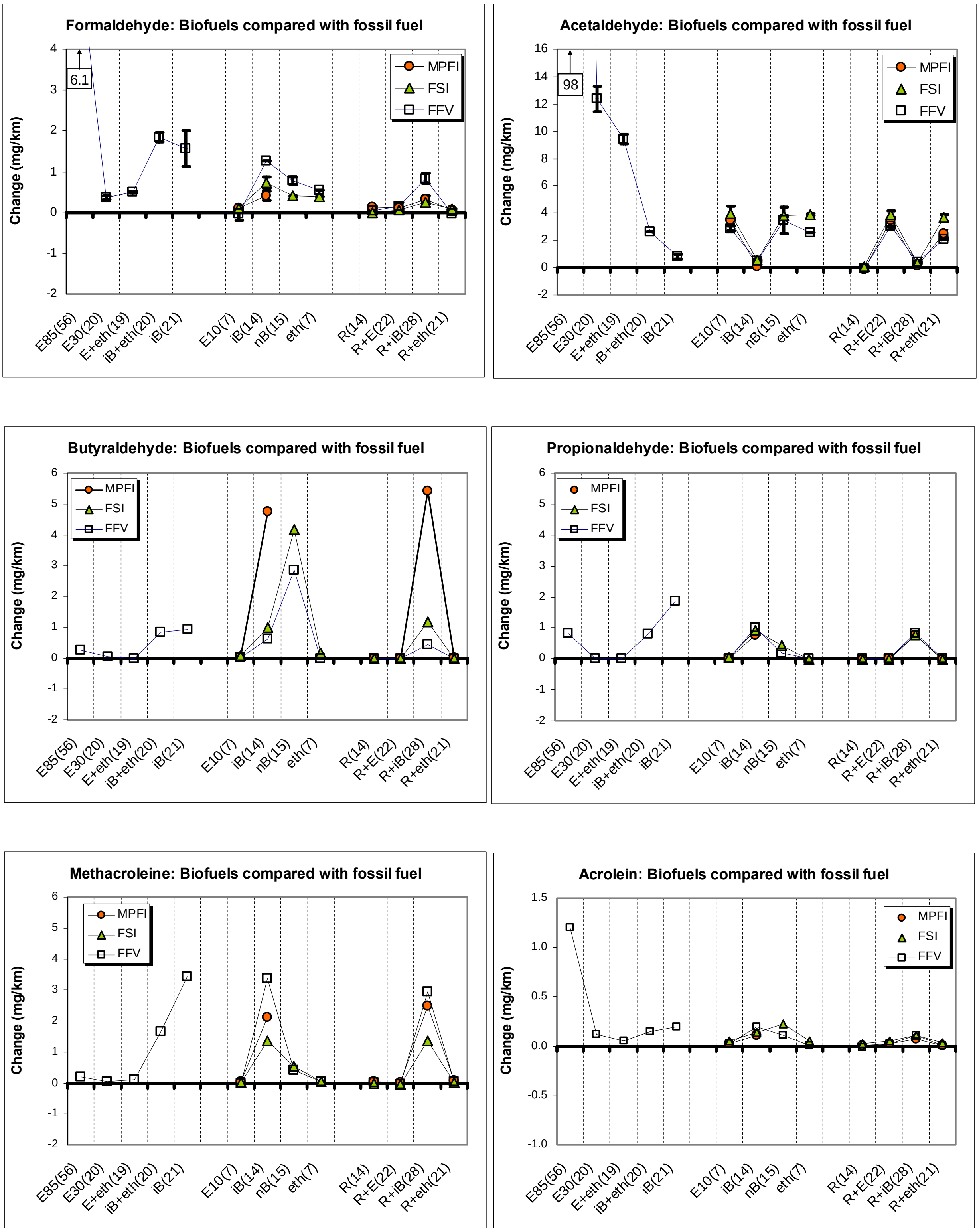

Figure 4.22. Difference in absolute terms (change mg/km) between biofuels and non-oxygenated fossil fuel. Formaldehyde and acetaldehyde emissions over the European test cycle at -7 °C.

4.4.5 C_1-C_8 hydrocarbon emissions

The hydrocarbon profiles of the tested cars, in terms of maximum emissions observed, are presented in Figure 4.23. The highest C_1-C_8 hydrocarbon emissions were observed for methane, ethane, acetylene, toluene and xylenes. 1,3-butadiene and benzene are also evaluated using risk factor calculations in Chapter 4.6. Numerical results are shown in Appendix 2.

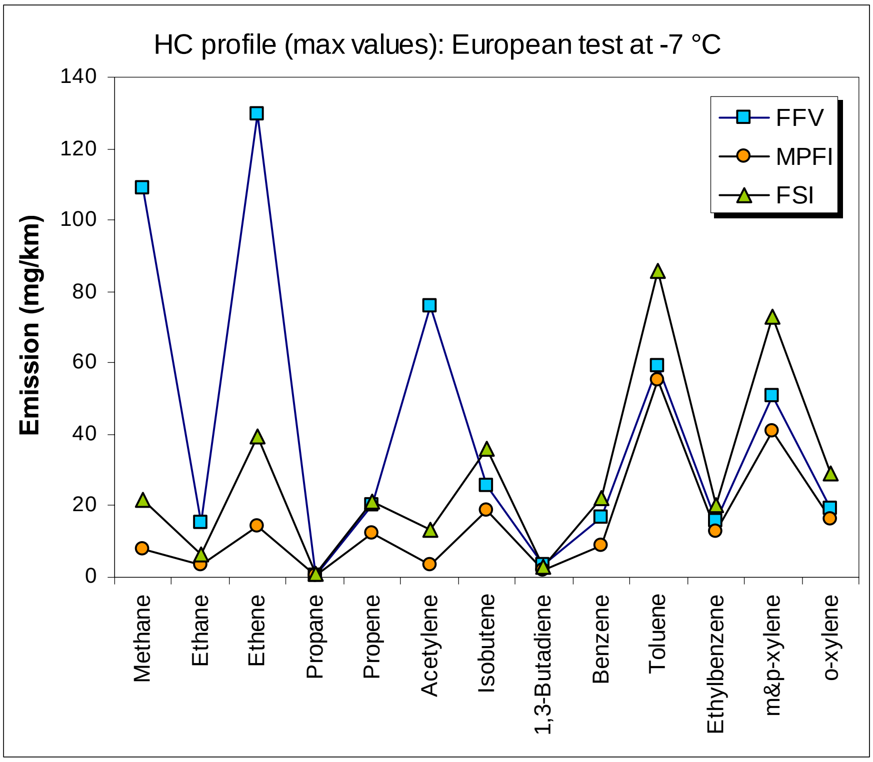

Figure 4.23. Hydrocarbon profiles as maximum emissions measured for each car, European test at -7 °C.

Emissions of 1,3-butadiene were below 3.6 mg/km for all fuels and cars over the European test cycle at -7 °C (Figure 4.24). Typically, 1,3-butadiene emissions for biofuels were lower than or at the same level as for the Fossil(0) fuel, but with some exceptions. Higher 1,3-butadiene emissions were observed for iB(14) fuel with the MPFI car, and nB(15) with the FSI and FFV cars. However, when the same amount of isobutanol as in the iB(14) fuel was blended with renewable hydrocarbon (R+iB(28)), 1,3-butadiene emissions reduced compared with Fossil(0) fuel in all three cars. As would be expected, this was also observed in the fuel risk factor calculations. The results indicate that the combination of the renewable gasoline component with oxygenates in gasoline had some beneficial effect on the formation of 1,3-butadiene in engines. However, taking into account the atmospheric conversion tendency of 1,3-butadiene, it is uncertain whether all changes in 1,3-butadiene emissions are fuel-related. For example, acrolein may be formed from 1,3-butadiene in the air (HEI 2007).

The FSI car had the highest benzene emissions at around 20 mg/km. With the MPFI and FFV cars, benzene emissions were below 10 mg/km with the exception of E85(56) fuel, which resulted in benzene emissions as high as 17 mg/km regardless of the low benzene content of the E85(56) fuel (0.07 v/v%) compared with the other test fuels (0.1–0.5 v/v%). The E85(56) fuel had an aromatics content of only 5 v/v%, while that of the other fuels was 16–35%.

Methane emissions were high with E85(56) fuel at 109 mg/km. When the ethanol content of the fuel was reduced to 30% (E30(20)), methane emissions fell to 21 mg/km for the FFV car. Methane emissions from the FSI car were 18–22 mg/km, and from the MPFI car below 10 mg/km. In the “hot” EUDC test, methane emissions were below 3 mg/km.

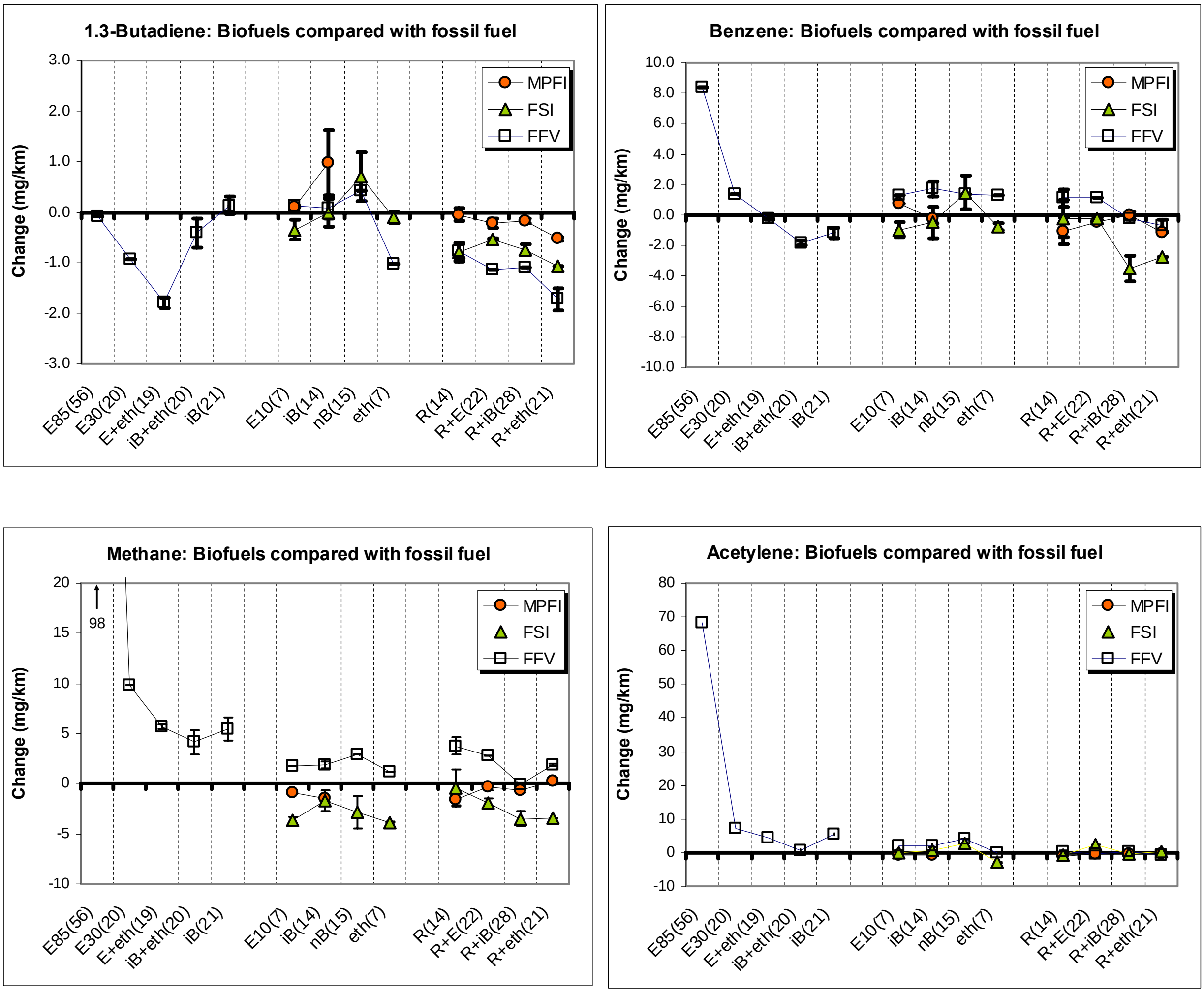

Figure 4.24. 1,3-Butadiene, benzene, methane and acetylene emissions: changes in absolute terms (mg/km) when biofuels are compared with Fossil(0) fuel. European test cycle at -7 °C.

4.4.6 Nitrogen dioxide, nitrous oxide and ammonia

Nitrogen dioxide (NO_2), nitrous oxide (N_2O) and ammonia (NH_3) emissions are shown in Figure 4.25 as concentrations over the European test cycle at -7 °C. Numerical results are shown in Appendix 2.

Nitrogen dioxide concentrations were below the detection limit with all cars, whereas nitrous oxide and ammonia concentrations exceeded the detection limit of the FTIR equipment. However, nitrous oxide emissions were mainly below the detection limit of the FTIR equipment (4 ppm). The detection limit of N_2O was exceeded only at the beginning of the test and occasionally during it.

Ammonia concentrations were substantial throughout the European test cycle. Amongst others, Mejia-Centeno et al. (2007) reported that formation of ammonia and nitrous oxide emissions increase in the TWC catalyst when sulphur content of fuel decreases. Decreasing fuel sulphur level activates formation of NH_3 as it increases NO conversion under rich conditions. N_2O is formed under lean conditions. Elevated ammonia emissions with decreasing fuel sulphur content was observed also in a study by Kytö et el. (1994).

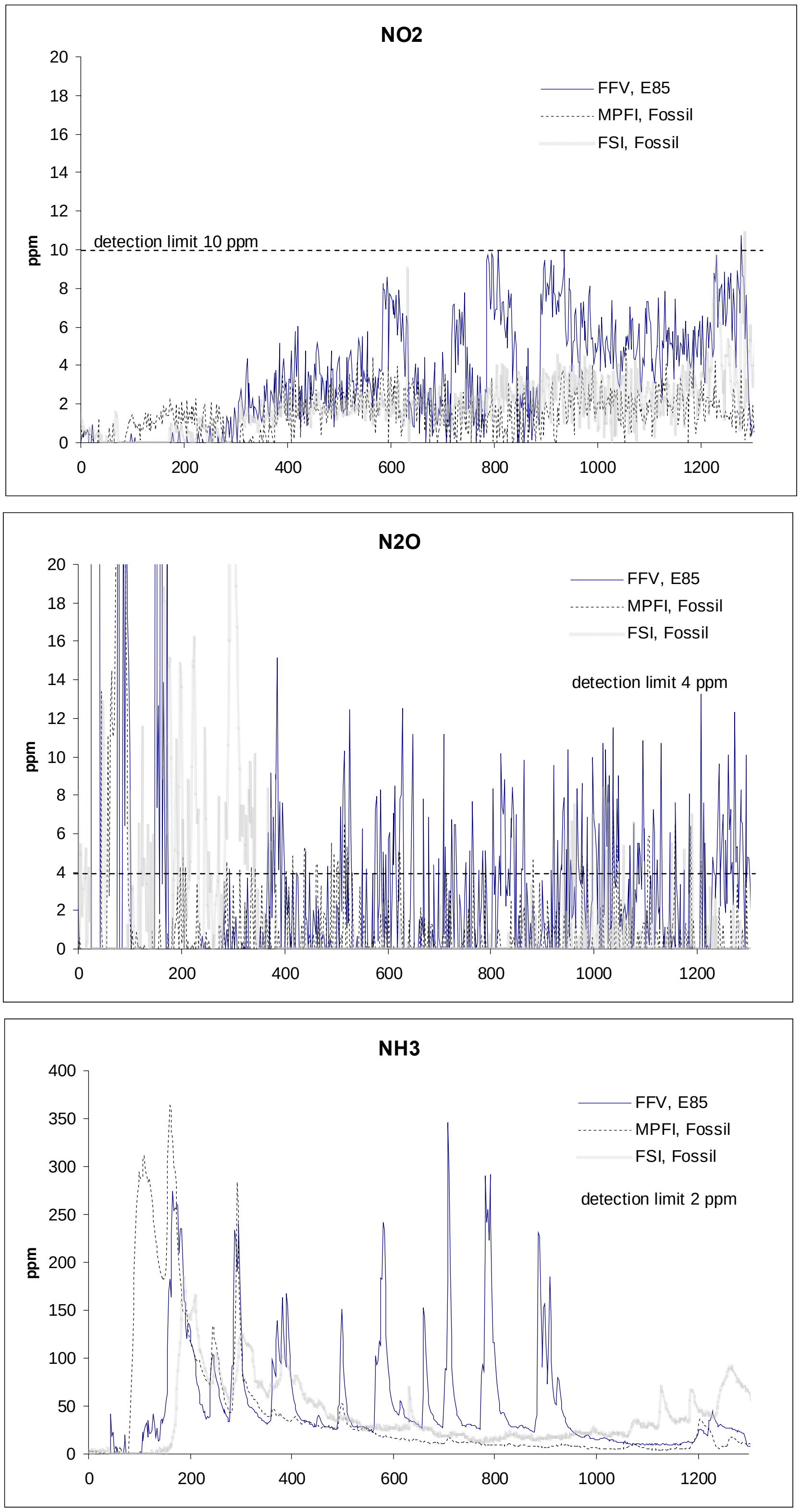

Figure 4.25. Nitrogen dioxide, nitrous oxide and ammonia concentrations.

4.4.7 PAH emissions and Ames mutagenicity results

4.4.7.1 Soluble organic fraction

Soluble organic fraction (SOF) results are only indicative when using fluoropore membrane filters for sampling of particulate matter (Chapter 4.2). However, it seems that particles from the MPFI and FFV cars contain higher share of soluble organic fraction than particles from the FSI car (Figure 4.26).

Mass of particulate matter on the filters was higher for the FSI car than for the MPFI and FFV cars. Therefore the SOF results may be more reliable for the FSI car than for the MPFI and FFV cars.

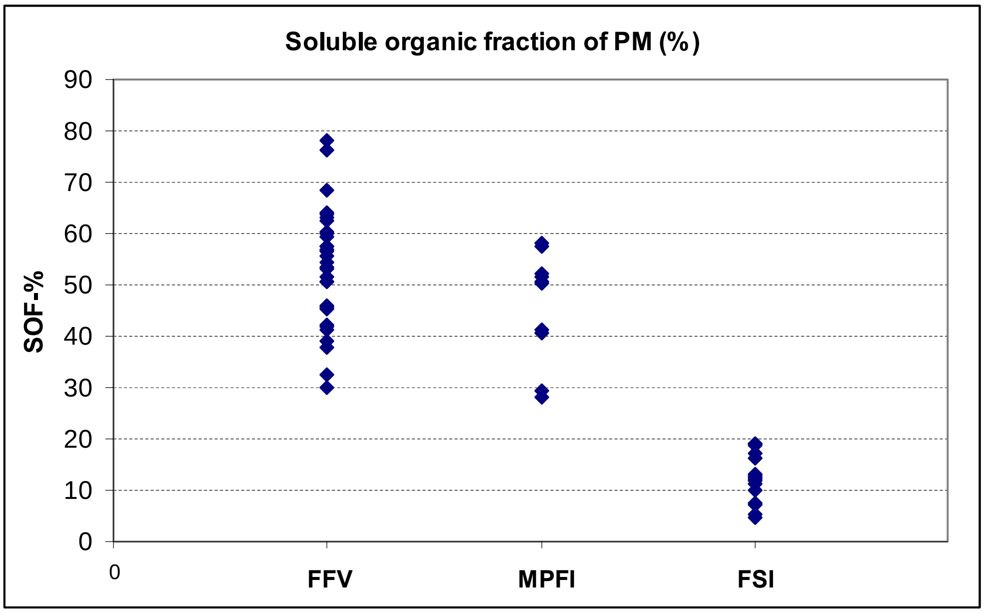

Figure 4.26. Soluble organic fraction of particulate matter with FFV, MPFI and FSI cars.

4.4.7.2 PAH emissions

Examples from the literature on PAH emissions from different engine technologies, together with emissions from this study, are collected in Table 4.18. A more detailed summary is presented by Aakko et al. (2006).

At normal temperature, PAH emissions are generally relatively low for the gasoline and diesel cars. For example, BaP emissions are below 1 mg/km for the MPFI gasoline cars, diesel cars and buses (Table 4.18).

Numerical PAH results are shown in Appendix 3.

In this study, BaP emissions in tests at -7 °C were below 2.5 µg/km for the MPFI car and 1.5–10 µg/km for the FFV car, but as high as 10–30 µg/km for the FSI car. The test temperature has a major impact on PAH emissions from gasoline-fuelled cars, particularly for direct-injection gasoline cars.

Table 4.18. Particle-associated PAHs from selected literature and from this study.

Car/vehicle, test temperature [a]	**PAH14 (µg/km)**	**BaP (µg/km)**	**Reference**
Conventional gasoline cars			
MPFI at +22 °C	0.2–5.5	0.01–1	Kokko et al. 2000 Pentikäinen et al. 2004
MPFI at -7 °C	10–35 (5–10[c])	1–2.5	This study
Direct-injection gasoline cars			
GDI +22 °C	15–55	1–4	Kokko et al. 2000
GDI at -7 °C	180–300	30–35	Kokko et al. 2000
FSI car at -7 °C	80–150 (45–90[c])	10–30	This study
FFV cars			
FFV cars at +22 °C	0.3–1.2 [b]		Westerholm et al. 2008
FFV cars at -7 °C	16–100 [b]		Westerholm et al. 2008
FFV car at -7 °C	20–75 (5–35[c])	1.5–10	This study
Diesel cars			
IDI, ox. cat., +22 °C	15–90	0.1–1	Rantanen et al. 1996, 2005
IDI, ox. cat., -7 °C	100–125	0.7–1.2	
Diesel buses, heavy-duty Euro IV and EEV			
Diesel buses, Euro IV	20–45 (1–4[c])	0.2–0.7	Murtonen et al. 2009
Diesel buses, EEV	0–8 (0–0.2[c])	<0.1	Murtonen et al. 2009

a Cars are tested with the cold-start European driving cycle. Heavy-duty buses are tested with the hot-start cycle.
b Sum of undefined PAHs.
c Sum of seven PAHs.

Gasoline cars emit substantial amounts of heavy PAHs at the -7 °C test temperature (Figure 4.27). For three cars representing different gasoline car technologies, the profiles for the 14 PAHs are quite similar. Substantial emissions were observed for phenanthrene (Phe), fluoranthene (F), pyrene (P), benz(a)anthracene (BaA), chrysene (Chr), benz(b,k,j)fluoranthene (BbF, BkF, BjF), benzo(e,a)pyrene (BeP, BaP), indeno(1,2,3-cd)pyrene (IP) and benz(g,h,i)pyrene (BghiP).

It is exceptional to find emissions of heavy PAHs from car exhaust emissions as high as those shown in Figure 4.27. This indicates that PAH emissions from gasoline cars warrent further attention, particularly at cold ambient temperatures. BaP emissions from gasoline cars in this study were generally higher than those from diesel passenger cars at -7 °C (Table 4.18). PAH emissions from modern diesel buses are extremely low. However, buses are measured only with hot-start tests.

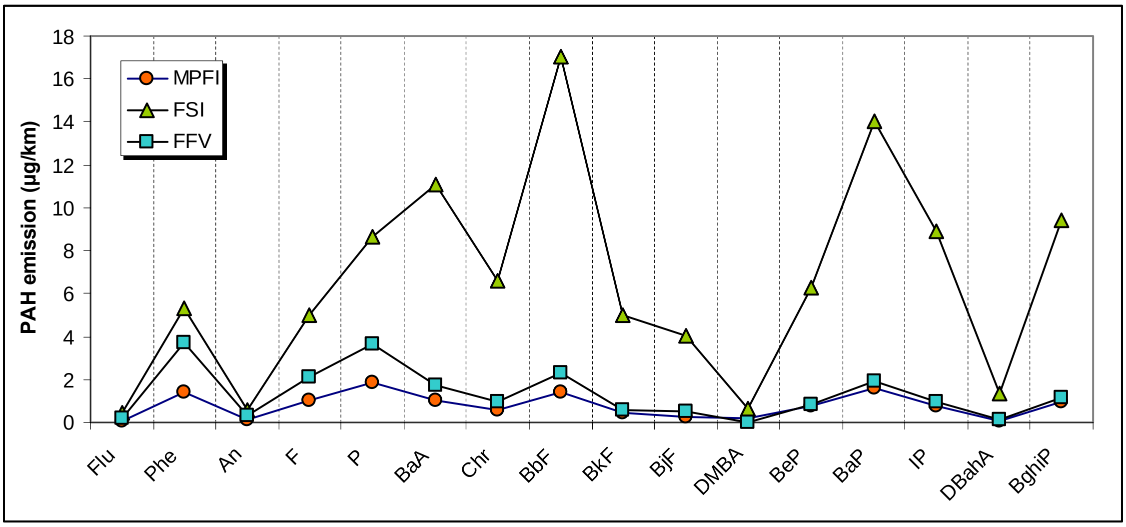

Figure 4.27. PAH profile from gasoline car particles using current market fuel (E10) fuel. European test at -7 °C.

In this study, particle-associated priority PAH emissions were highest for the FSI car, next highest for the FFV car, and lowest for the MPFI car. This was clearly evident as PAH concentrations (per mg particles) and as PAH mass emissions (per km) (Figure 4.28).

With the FSI car, the priority PAH emissions were highest with the hydrocarbon fuels, and lower for the oxygen-containing fuels. This was evident as a lower PAH concentration in particles (per mg), and particularly in the PAH mass emissions results (per km).

With the FFV car, the highest PAH emissions were observed for the Fossil-b fuel. PAH emissions for the other hydrocarbon fuel, R(14), were substantially lower. The E85(56) fuel resulted in an elevated PAH emissions level as mass emissions per km due to elevated PM emissions, but the PAH concentration per mg particles was at the same level as for the other fuels.

With the MPFI car, only minor differences in PAH emissions between fuels were observed. PAH emissions with the iB(14) fuel seemed to be higher than those with the other fuels, but the significance of this result is uncertain due to the low PAH emissions level of the MPFI car. In two cases, ETBE-containing fuels resulted in lower PAH emissions levels than did the other fuels.

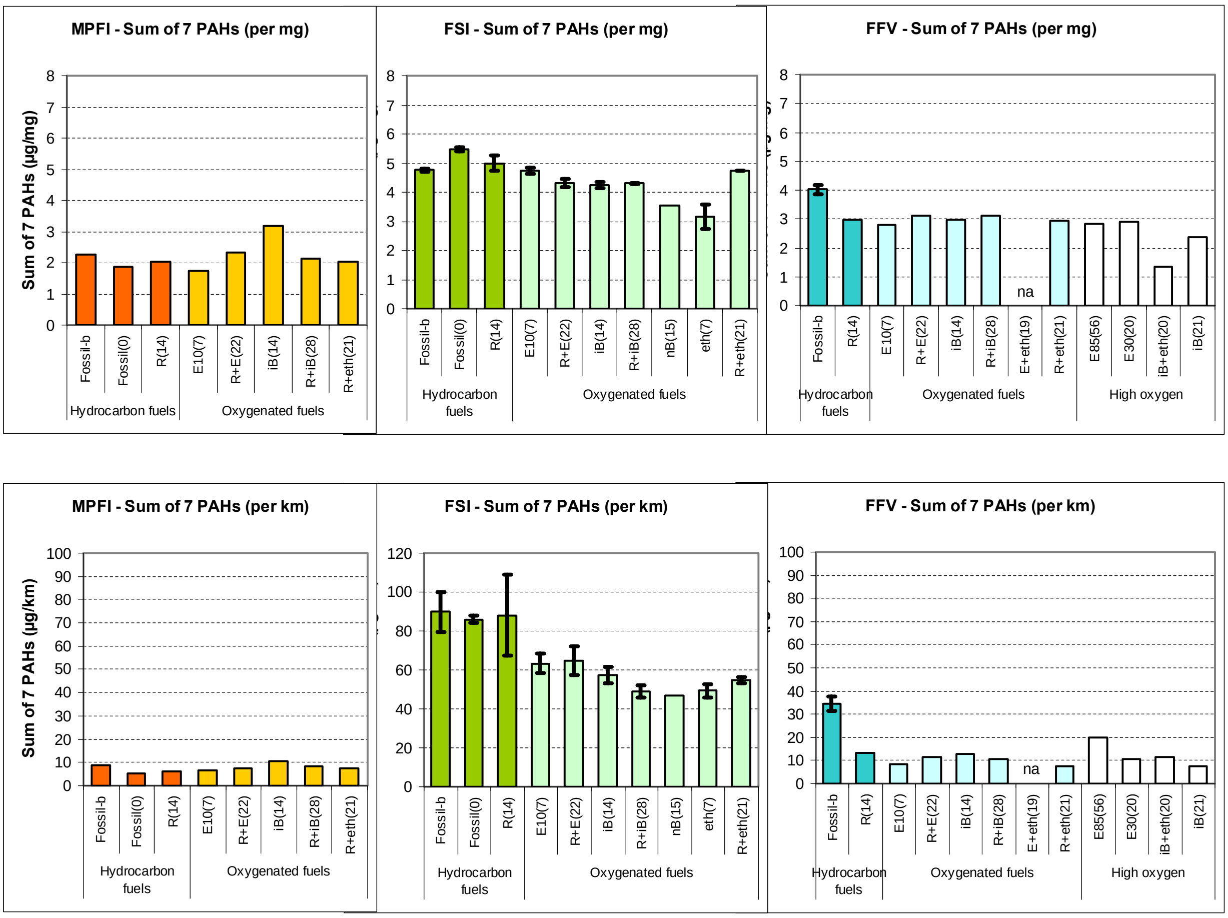

Figure 4.28. Sum of 7 priority PAHs as concentration (µg/mg) and mass emissions (µg/km). European test at -7 °C.

4.4.7.3 Ames tests

The numerical results of the Ames tests are shown in Appendix 3.

The mutagenicity of particle extracts from three gasoline-fuelled cars reported here was substantial at -7 °C (Table 4.19). At normal temperature, direct mutagenicity tested with the TA98 strain without metabolic activation (-S9) has been typically below 5 krev/km with MPFI gasoline cars and EEV diesel buses. In this study, indirect mutagenic activity after metabolic activation (TA98+S9) was 1–10 krev/km for the MPFI car and 2–25 krev/km for the FFV car at -7 °C. However, the highest mutagenic activity was observed in particle extracts from the FSI car: 20–100 krev/km. Rantanen et al. (1996) observed direct mutagenic activity of 44–112 krev/km with the IDI diesel car equipped with an oxidation catalyst at -7 °C. The mutagenicity aspects of the gasoline-fuelled cars are considerable and warrant further attention, particularly at low test temperatures.

Table 4.19. Ames test results from selected literature and from this study.

Car/vehicle, test temperature [a]	**TA98+S9/ TA98-S9 (krev/km)**	**Reference**
Conventional gasoline cars		
MPFI at +22 °C	/0.1–5	Kokko et al. 2000 Pentikäinen et al. 2004
MPFI at -7 °C	1–10/	This study
Gasoline direct-injection cars		
GDI +22 °C	/40–200	Kokko et al. 2000
GDI at -7 °C	/50–65	Kokko et al. 2000
FSI car at -7 °C	20–100/	This study
FFV cars		
FFV car at -7 °C	2–25/	This study
Diesel cars		
Diesel Euro 3, +22 °C	<10	Rantanen et al. 2005
IDI, ox. catalyst, +22 °C	/6–51	Rantanen et al. 1996
IDI, ox. catalyst, -7 °C	/44–112	
Diesel buses		
Diesel buses, Euro III	16–60	Nylund et al. 2004
Diesel buses, Euro IV	/0–12	Murtonen et al. 2009
Diesel buses, EEV	/0–5	Murtonen et al. 2009

A Cars are tested with the cold-start European driving cycle. The heavy-duty buses are tested with the hot-start driving cycle.

In some studies, a clear relationship has been observed between PAH emissions and the Ames test results (for example, Rantanen et al. (1996)). In this study, the Pearson's correlation factors between PAH and the Ames results were mainly weak or not significant. Correlations were stronger for mass emissions (per km) than for concentrations (per mg). When all cars are considered, the Ames test results correlated to some extent with the benz[a]pyrene emissions (Figure 4.29).

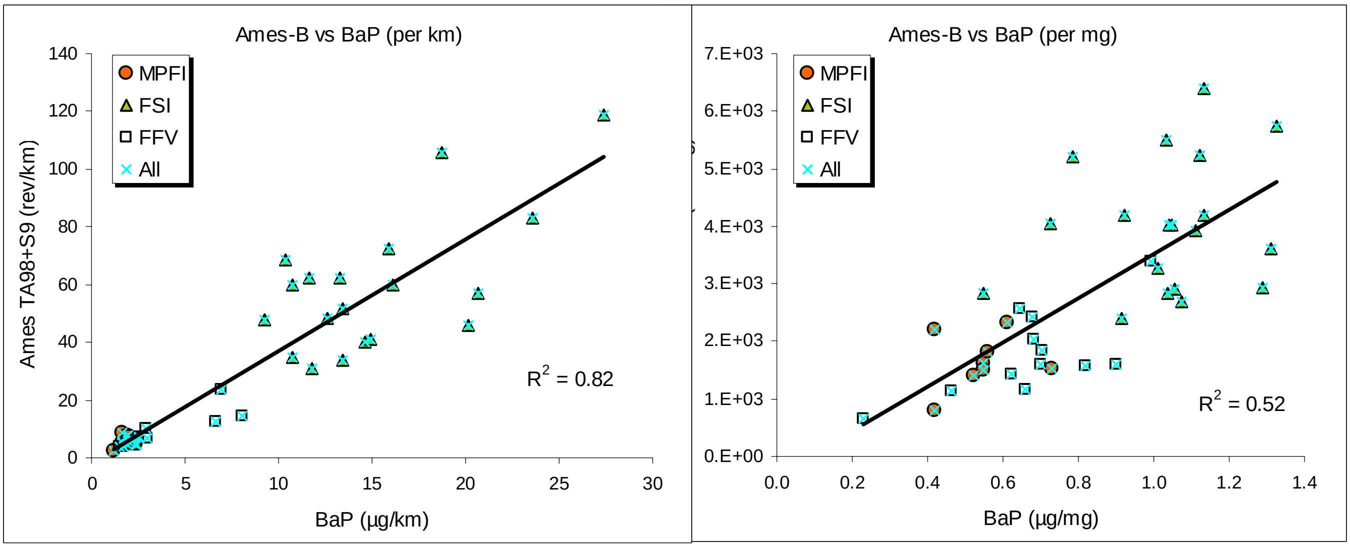

Figure 4.29. Correlations between Ames test (TA98+S9) and benzo[a]pyrene results for two units (per km and per mg).

In the preliminary assays (Table 4.20), the particle extracts from three cars tested exhibited strong, indirect mutagenicity against tester strain TA98 after metabolic activation. The results obtained demonstrate the presence of frameshift-type mutagens, for example polycyclic aromatic hydrocarbons (PAH). In particular, the sample from the FSI car was extremely mutagenic without being toxic to the tester strain at the dose levels tested. The mutagenic activity of the sample from the FFV car was also very strong, while the mutagenicity of the sample from the MPFI car was somewhat lower. The sample was to some extent inhibitory to the test organism at higher dose levels, and this may have an effect on the magnitude of the mutagenic response reported.

In the preliminary tests, the particle extract from the FSI car was tested using two tester strains, TA98 (+/-S9 mix) and TA98NR. The highest response was observed with tester strain TA98 after metabolic activation (+S9 mix). The same observation was reported by Kokko et al. (2000). Direct mutagenicity (-S9 mix) demonstrated in the sample from the FSI car by tester strain TA98 was substantially lower, and probably not due to nitro-PAH-type compounds because the response remained when the sample was assessed using the nitroreductase-deficient tester strain TA98NR.

The results obtained from the assessment of the actual samples produced with different fuels are illustrated in Tables 4.21 and 4.22 and in Figures 4.30 and 4.31.

Particle extracts from three cars tested exhibited strong, indirect mutagenicity against tester strain TA98 after metabolic activation. In particular, the sample from the FSI car was extremely mutagenic. The mutagenicity detected was clearly higher than in the particle extracts from the MPFI and FFV cars, in terms of both concentration- and emissions-based results. This is in line with the results from the preliminary tests. The mutagenic activity of the sample from the FFV car was also very high. The mutagenicity of the sample from the MPFI car was somewhat lower.

With the FSI car, the highest mutagenicity of particle extracts (per mg) was produced by the Fossil-b and R(14) fuels. Fossil(0) fuel exhibited lower mutagenic activity than did the other two hydrocarbon fuels.

The particle extracts for the FFV car exhibited elevated mutagenic activity when E85(56) fuel was used. It is difficult to conclude whether the differences between the other fuels would be significant. The same applies to the MPFI car.

Table 4.20. Mutagenic activity in the preliminary tests (revertants per mg particle mass extracted).

	MPFI iB(14) (rev/mg)	FSI iB(14) (rev/mg)	FFV E85 (rev/mg)
TA98, -S9	not tested	286	not tested
TA98,+S9	255	2129	952
TA98NR, -S9	not tested	319	not tested

Table 4.21. Mutagenic activity with Ames test (TA98+S9) over the European test cycle at -7 °C. The results are calculated at the dose level of 0.1 mg particles at plate.

	TA98+S9 (rev/mg)			TA98+S9 (rev/km)		
	MPFI	FSI	FFV	MPFI	FSI	FFV
E85(56)			3380			24
E30(20)			1840			6.7
E+eth(19)			na			5.9
iB+eth(20)			650			5.6
iB(21)			1130			3.7
Fossil(0)	810	3270	1830	2.3	51	5.9
R(14)	1820	4970	2420	5.3	89	10
Fossil-b		5160	1590	6.4	95	14
E10(7)	2210	2765	2560	8.6	37	7.6
iB(14)	1520	2655	1590	5.0	36	6.9
nB(15)	na	5200	na	na	69	na
eth(7)	na	3440	600	na	54	3.5
R+E(22)	2320	4115	2420	7.5	62	7.5
R+eth(21)	1400	5370	1780	5.0	62	3.9
R+iB(28)	1490	3640	2030	6.0	42	4.3

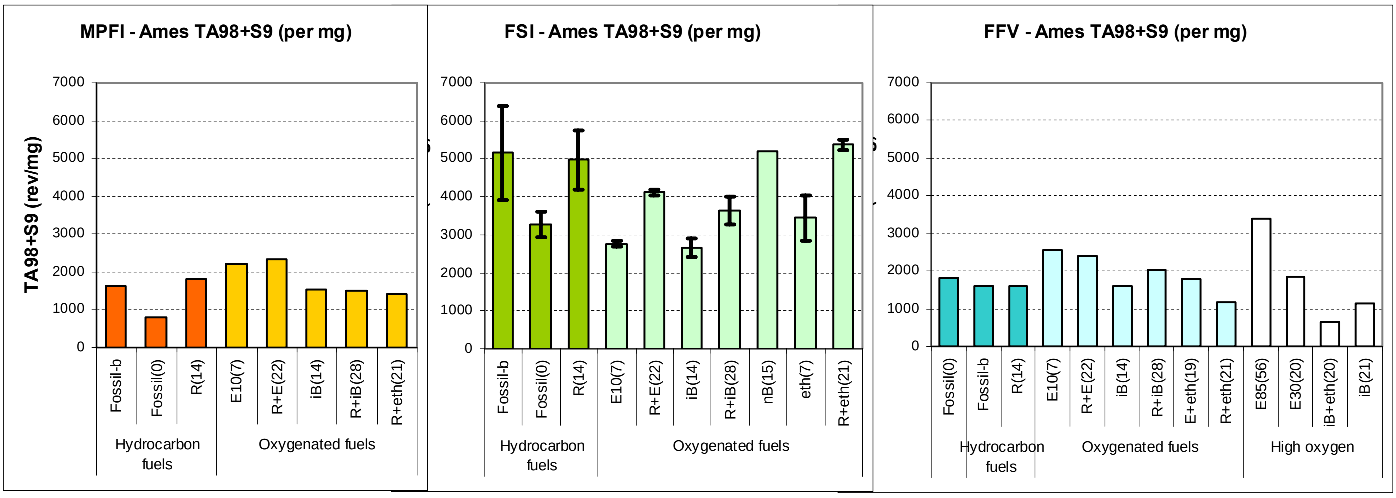

Figure 4.30. Ames test results as revertants per mg particles. European test at -7 °C.

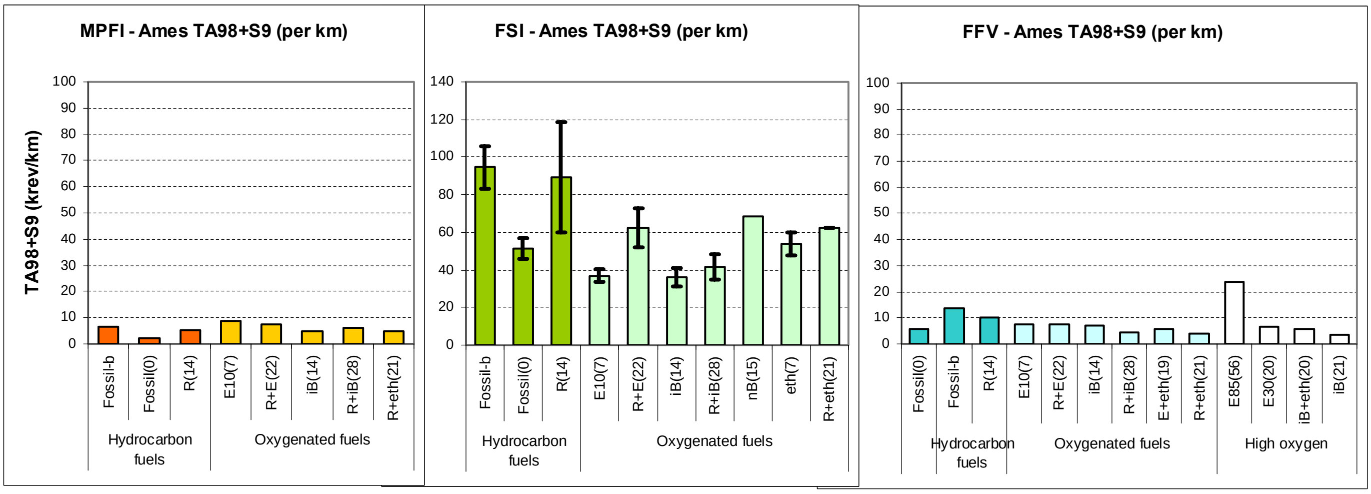

Figure 4.31. Ames test results as concentrations (per mg particles) and emissions-based results (per km). European test at -7 °C.

4.5 Fuel groups

4.5.1 General

Selected exhaust emissions of different fuel groups are compared with the exhaust emissions of Fossil(0) fuel. Factors are used to set exhaust emissions of Fossil(0) fuel to 1. Exhaust emissions presented are carbon monoxide (CO), total hydrocarbons (HC), nitrogen oxides (NOx), particulate matter (PM), formaldehyde (FA), acetaldehyde (AA), total aldehydes (Ald), 1,3-butadiene (1.3BD), benzene (Bz), sum of benzene, toluene, ethyl benzene and xylenes (BTEX) and Risk factor (Risk).

4.5.2 Hydrocarbon fuels

Three hydrocarbon fuels were included in the test fuel matrix. Fossil(0) and R(14) renewable fuels were closer to each other than to the Fossil-b fuel, which was a commercial reference gasoline from Haltermann (RF-02-03). The octane numbers of Fossil-b were higher than those of the Fossil(0) and R(14) fuels. The vapour pressure of Fossil-b was lower than those of the other hydrocarbon fuels. Distillation indicated that Fossil-b contained more front-end and heavy-end hydrocarbons than did the other hydrocarbon fuels.

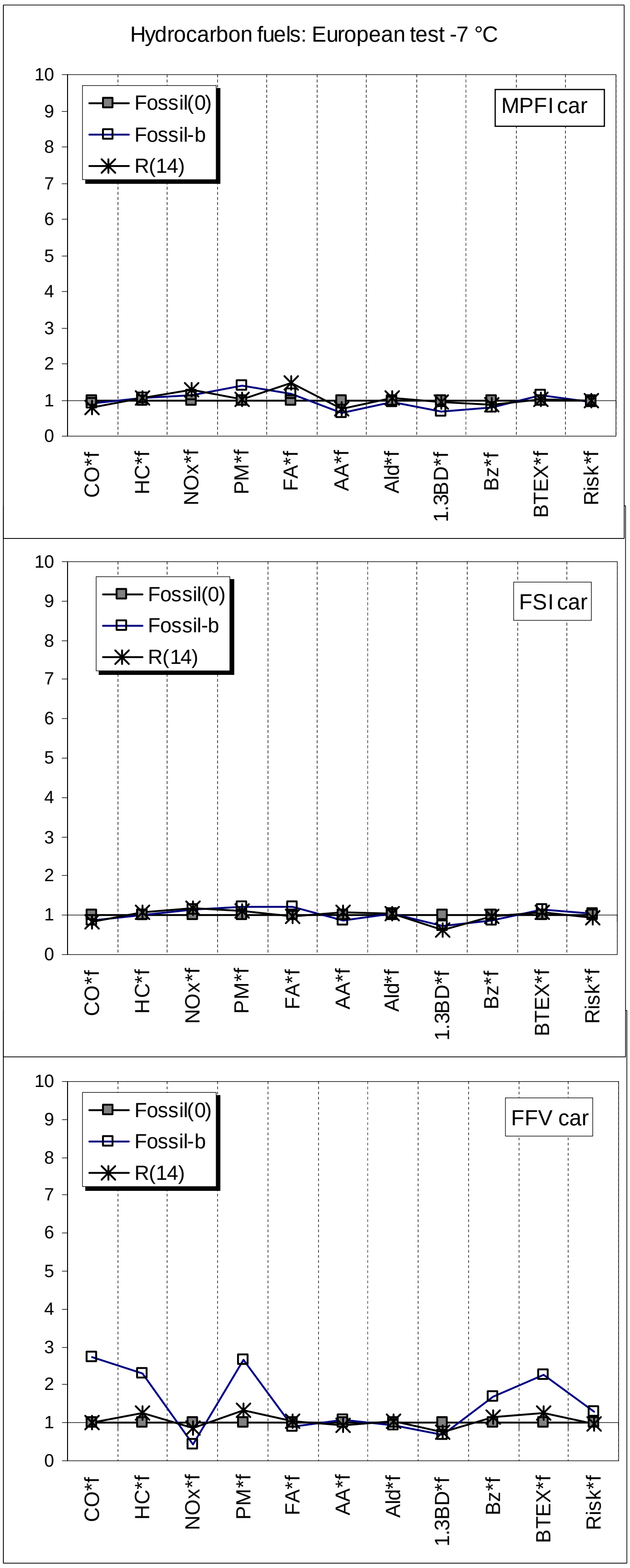

Figure 4.32. Selected exhaust emissions with hydrocarbon fuels, European test at -7 °C. Fossil(0) = 1.

Emissions with three hydrocarbon fuels, Fossil(0), R(14) and Fossil-b, were quite close to each other with the MPFI and FSI cars (Figure 4.32). CO, 1,3-butadiene and benzene emissions were slightly lower, but NO_x and PM emissions slightly higher with other fuels compared with Fossil(0) fuel. Fossil-b fuel generated high emissions of xylene, which are observed in the BTEX group.

With the FFV car, emissions from Fossil-b fuel differed substantially from those from the other hydrocarbon fuels. CO, HC and aromatic BTEX emissions were high, whereas NO_x emissions were low with the FFV car using the Fossil-b fuel. The main differences in the properties of hydrocarbon fuels concern their octane numbers, volatility and distillation characteristics. Adjustments of the FFV may be changed for the high-octane, non-oxygenated fuel, and the volatility of the fuel may also play a role.

4.5.3 Ethanol-containing fuels

Ethanol-containing fuels have major impacts on acetaldehyde emissions (Figure 4.33). With the three cars tested, ethanol-containing fuels increased acetaldehyde emissions substantially, something also observed for the total aldehyde emissions (Ald.). Extremely high

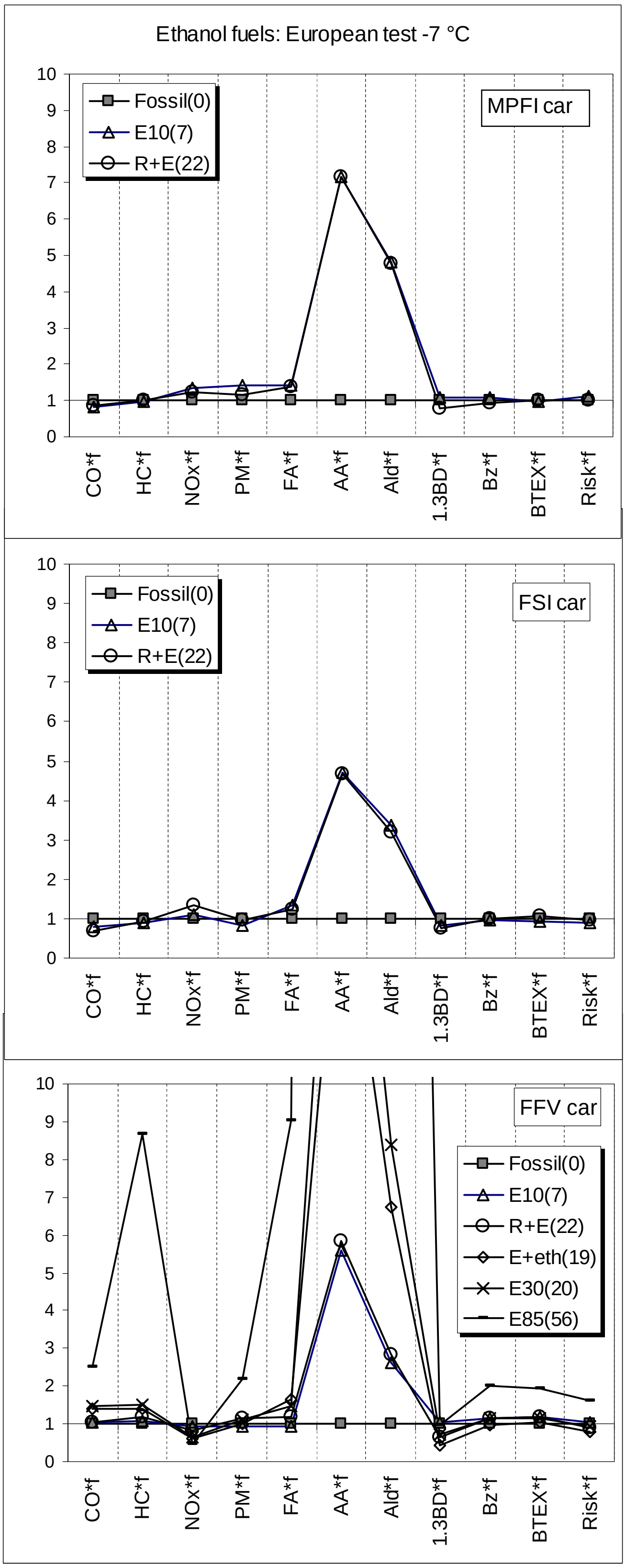

Figure 4.33. Selected exhaust emissions with ethanol-containing fuels, European test at -7 °C. Fossil(0) = 1.

acetaldehyde emissions were generated by E85(56) fuel with the FFV car.

With the MPFI and FSI cars, ethanol in fuel reduced CO and 1,3-butadiene emissions, but increased NO_x emissions. With the FFV car, ethanol reduced NO_x emissions and also 1,3-butadiene emissions in most cases.

E85(56) fuel with the FFV car was a special case with regard to exhaust emissions. NO_x emissions were low compared with Fossil(0) fuel, but most other emissions were substantially higher than those with Fossil(0) fuel.

4.5.4 Butanol-containing fuels

CO emissions were lower, but NO_x emissions higher, for butanol-containing fuels than for Fossil(0) fuel with the MPFI and FSI cars, but not with the FFV car (Figure 4.34). PM emissions were lower for butanol-containing fuels than for Fossil(0) fuel with the FSI car, but not with the MPFI or FFV cars.

Isobutanol or n-butanol, when blended with fossil fuel, resulted in 1,3-butadiene emissions higher than or at a similar level to those from Fossil(0). On the other hand, isobutanol blended with a renewable component or ETBE resulted in 1,3-butadiene emissions lower than those of Fossil(0) fuel.

Butanol-containing fuels increased emissions of formaldehyde, acrole-

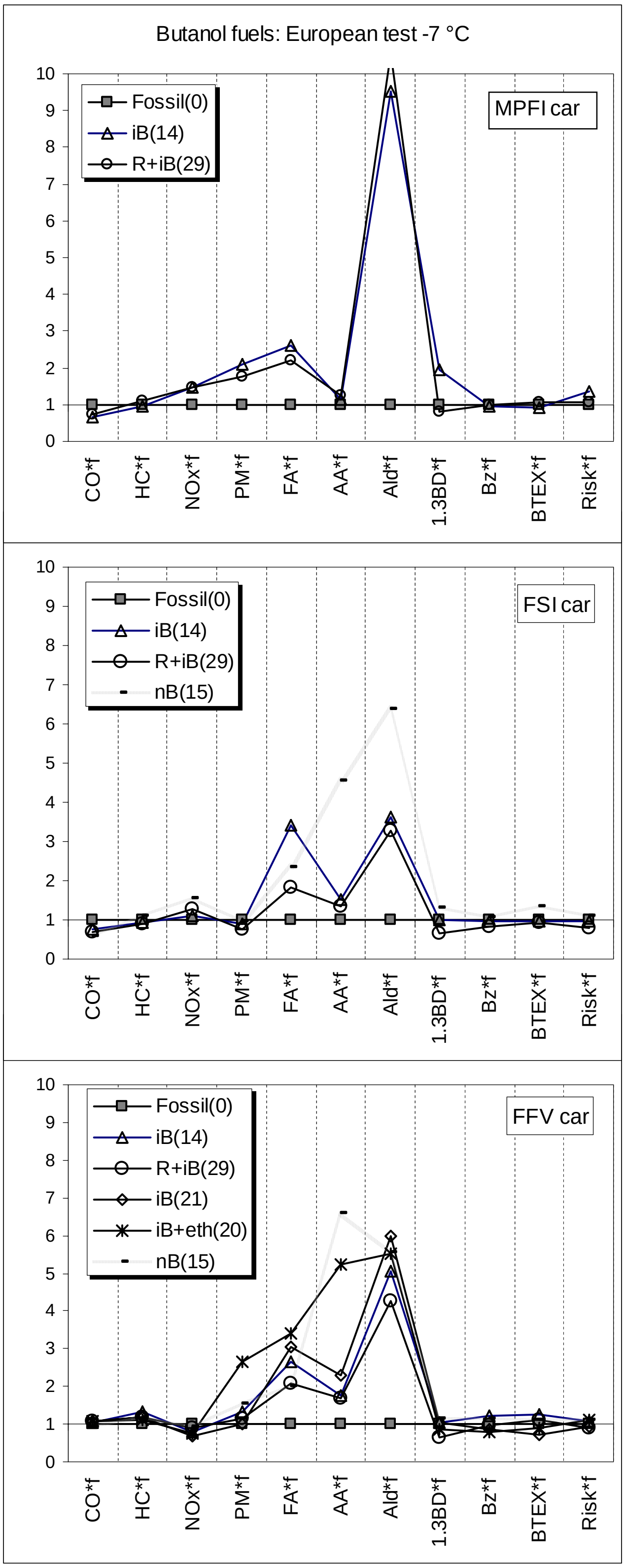

Figure 4.34. Selected exhaust emissions with butanol-containing fuels, European test at -7 °C. Fossil(0) = 1.

in, butyraldehyde, methacrolein and propionaldehyde. However, total aldehyde emissions with butanol-containing fuels (around 10 mg/km) are substantially lower than those for E85(56) fuel (over 100 mg/km) in the European test at -7 °C.

Overall, emissions with n-butanol were worse than those with isobutanol.

4.5.5 ETBE-containing fuels

ETBE-containing fuels have major impacts on acetaldehyde emissions, which are increasing with increasing ETBE content of fuel (Figure 4.35). However, acetaldehyde emissions are slightly lower with ETBE-containing fuels compared with ethanol-containing fuels at the same bio-energy level.

When ETBE was combined with a renewable hydrocarbon component, emissions of CO, HC, PM, NO_x, 1,3-butadiene and benzene were lower than for the Fossil(0) fuel in most cases with the MPFI and FSI cars.

Ether also seemed to be a beneficial fuel component in many respects for the FFV car compared with Fossil(0) fuel.

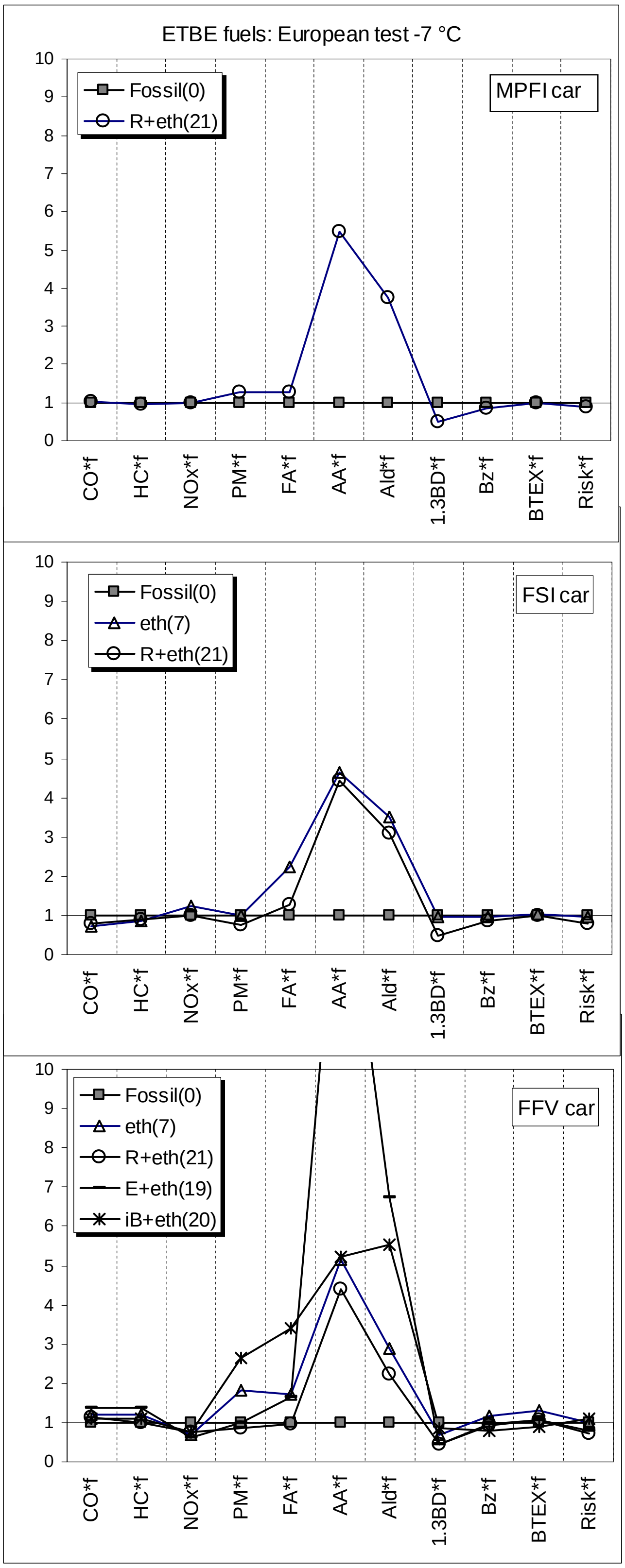

Figure 4.35. Selected exhaust emissions with ETBE-containing fuels, European test at -7 °C. Fossil(0) = 1.

4.6 Risk factors

4.6.1 Risk factors – CO, HC, NO_x, PM, formaldehyde, acetaldehyde, 1,3-butadiene and benzene emissions

The risk factors for exhaust toxicity were calculated separately using regulated and unregulated emissions as described in the methods section.

Particulate matter, non-methane hydrocarbons (NMHC) and NO_x emissions were the most significant species affecting the regulated risk factor (Figure 4.36).

The risk factor based on unregulated exhaust emissions was evaluated by calculating the weighted sum of the 1,3-butadiene, benzene, formaldehyde and acetaldehyde emissions. The unit risk toxicity factors, defined by OEHHA (2009), give 1,3-butadiene the highest unit risk among the unregulated compounds measured in this study. For benzene, the unit risk is lower than for 1,3-butadiene, but higher than for the aldehyde species. When the levels of emissions of these compounds in exhaust gases are taken into account, 1,3-butadiene and benzene become the priority compounds in the evaluation of the unregulated gaseous emissions risk factors in this study. When E85 fuel is used, acetaldehyde is also a significant contributor to the unregulated risk factor (Figure 4.37).

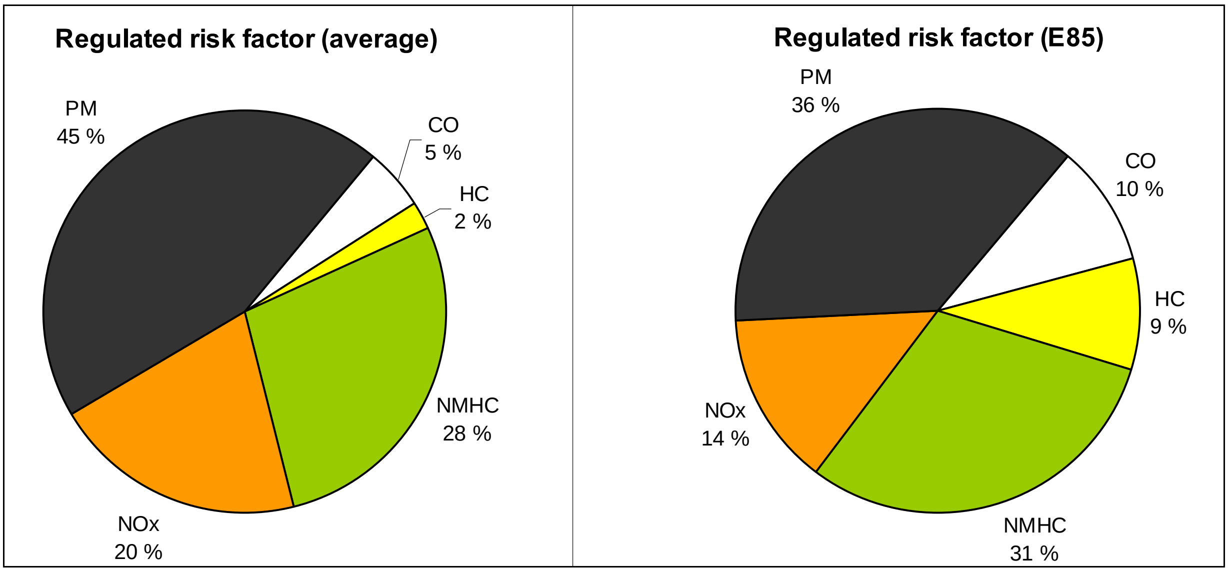

Figure 4.36. Average contributions to the regulated risk factor as an average of car/fuel combinations (left) and with E85(56) fuel (right).

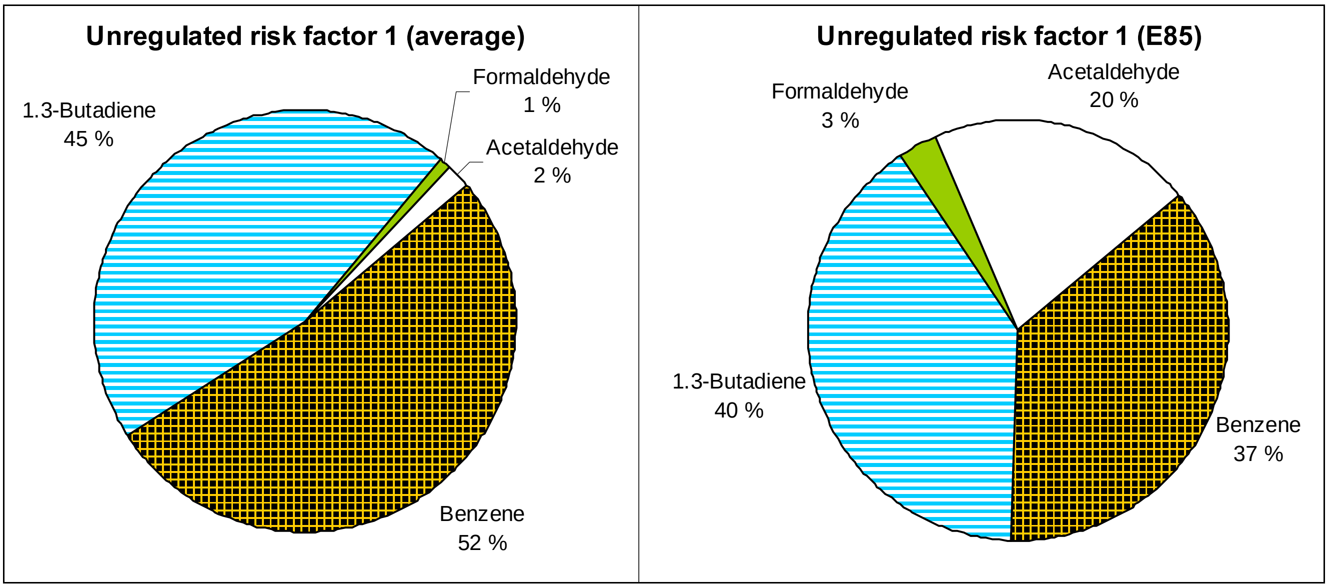

Figure 4.37. Average contributions to the unregulated risk factor as an average of car/fuel combinations (left) and with E85(56) fuel (right).

The risk factor calculated using regulated emissions was less sensitive to emissions changes between fuels than was the unregulated toxicity risk factor. The normalized risk factors calculated using regulated emissions ranged from 0.8–1.6, and the risk factors for unregulated emissions from 0.6–1.7 (Appendix 4). The summarized risk factors were less sensitive to emissions changes between fuels than was the regulated or unregulated emissions toxicity risk factor alone. In some cases, the regulated and unregulated risk factors were contradictory when biofuels were compared with Fossil(0) fuel.

Most biofuels had total exhaust toxicity risk factors lower than or similar to those of fossil fuel for all cars tested (Figure 4.38). This applies to fuels containing ethanol, isobutanol, ETBE and/or renewable components.

Exhaust gas with E85(56) fuel was clearly more noxious than with fossil gasoline, with a significantly higher overall exhaust toxicity risk factor (3.2 vs. 2.0). This was mainly due to acetaldehyde, benzene and particulate matter emissions. Reducing the ethanol content of the fuel from 85 to 30 v/v% reduced the exhaust toxicity risk factor.

The second-highest overall risk factor for exhaust toxicity compared with fossil fuel was observed for the isobutanol-containing fuel iB(14) with the MPFI car (3.0 vs. 2.0). This was mainly due to the formation of 1,3-butadiene in the exhaust gases. The significance of this result is uncertain: first, the standard deviation across the replicate tests was high for 1,3-butadiene; second, a similar result was not observed with the FSI or FFV cars; and third, the phenomenon was not observed with the other isobutanol-containing fuels (iB+eth(20), iB(21) and R+iB(28)). n-Butanol-containing fuel (nB(15)) resulted in a slightly higher risk factor for exhaust toxicity compared with fossil fuel with the FSI and FFV cars, mainly due to elevated 1,3-butadiene and benzene emissions.

Two fuels were better than the others in diminishing toxicity calculated using the emissions risk factor. On the one hand, fuel containing a renewable gasoline component and ETBE (R+eth(21)) had a lower risk factor than did fossil fuel (0.6–0.7 vs. 1.0) in all cars, mainly due to the lower 1,3-butadiene and benzene emissions. On the other, the high-oxygen containing fuel E+eth(19) resulted in a lower risk factor (0.6 vs. 1.0) in the FFV car mainly due to the low 1,3-butadiene emissions.

All other fuels resulted in quite small changes in risk factors for exhaust toxicity (<0.5). These kinds of small changes should be evaluated further before conclusions are reached on their significance.

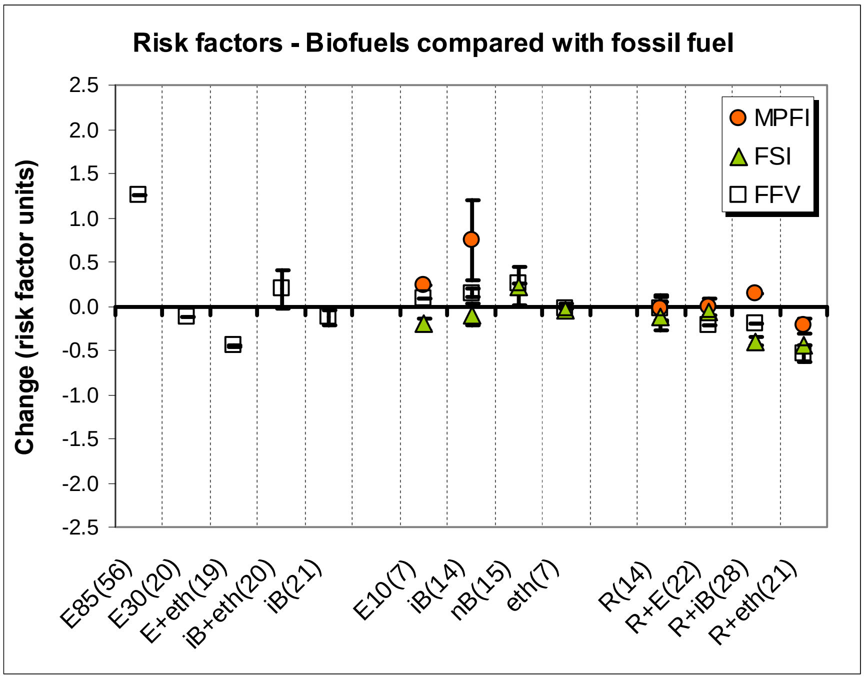

Figure 4.38. Risk factors for exhaust toxicity calculated from the regulated and unregulated emissions with biofuels in comparison with Fossil(0) fuel. European test cycle at -7 °C.

4.6.2 The effect of PAH emissions on the risk factors

The effects on the risk factors of the polyaromatic hydrocarbons of particle extracts were evaluated. The polyaromatic hydrocarbons can be taken into account using defined toxic equivalency factors (TEFs) relative to benzo(a)pyrene, as explained in Chapter 4.2.5. Furthermore, the Nordic Ecolabelling method also takes into account ethene and propene emissions.

Benzo(a)pyrene equivalent (BaP_{eq}) PAH emissions show a significant contribution on the unregulated risk factor alongside benzene and 1,3-butadiene (Figure 4.39). For E85 fuel, acetaldehyde is also a significant contributor to the unregulated risk factor. Formaldehyde emissions make a relatively small contribution to the risk factors evaluated.

In the Nordic Ecolabelling method, the most significant contributors to the risk factor were ethene, particulate matter, BaP_{eq}, and 1,3-butadiene emissions (Figure 4.40).

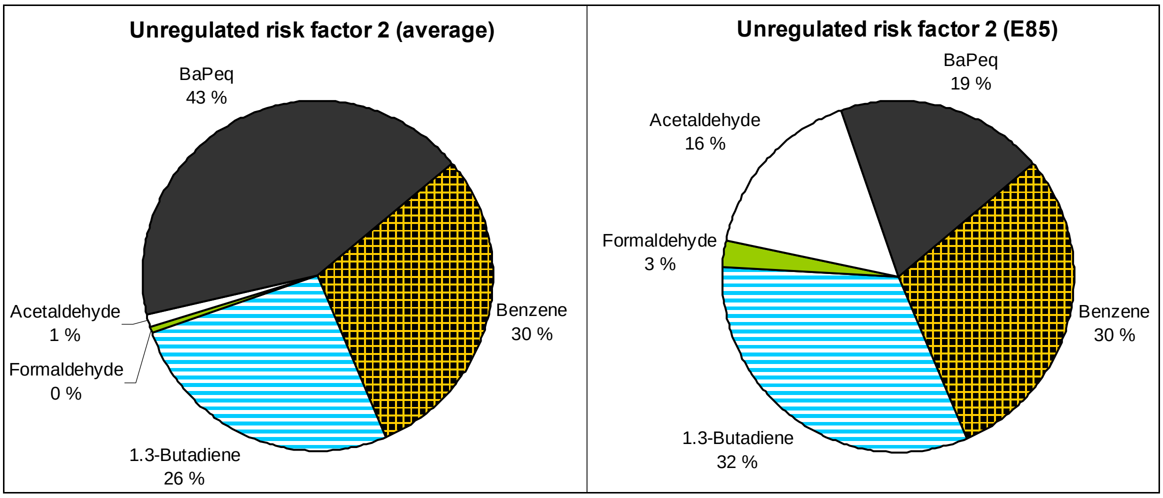

Figure 4.39. Average contributions to the unregulated risk factor including PAHs as benzo(a)pyrene equivalent (BaP_{eq}). An average of car/fuel combinations (left) and with E85 fuel (right).

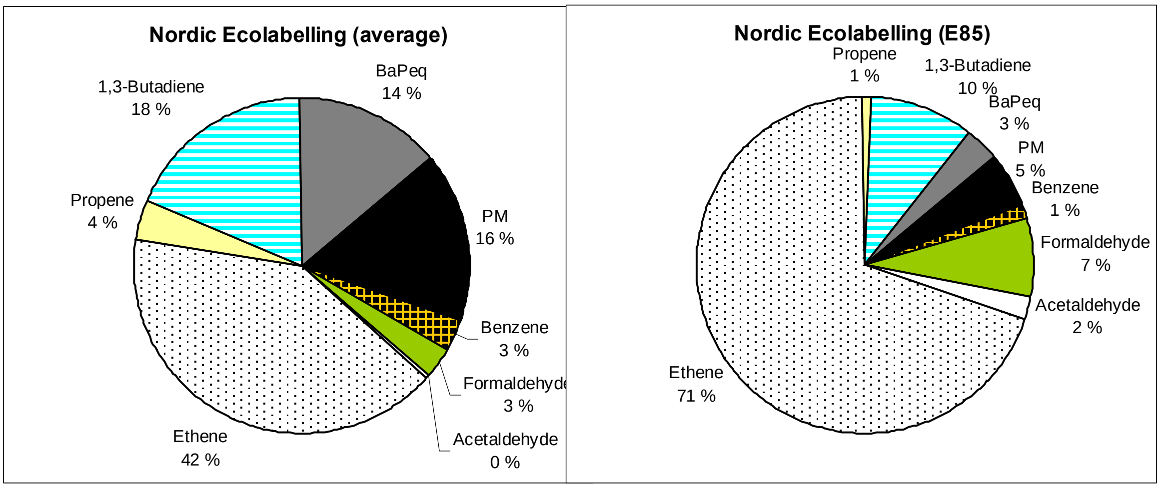

Figure 4.40. Average contributions to the Nordic Ecolabelling risk factor as an average of car/fuel combinations (left) and with E85 fuel (right).

Unregulated risk factors calculated with PAH compounds (BaP_{eq}) and Nordic Ecolablelling methods show rather similar trends for fuel comparisons with a few exceptions compared with the unregulated risk factors presented in Chapter 4.6.

With the MPFI car, no significant changes between fuels are observed for the unregulated risk factors when PAH compounds (BaP_{eq}) are included in the evaluation or when the Nordic Ecolabelling method is compared with the original risk factors (Figure 4.41).

With the FSI car, the risk factors for hydrocarbon fuels (Fossil(0), Fossil-b and R(14)) converged due to the elevated PAH emissions with these fuels.

The unregulated risk factor for E85(56) fuel is very high using the Nordic Ecolabelling method for the FFV car, particularly due to high ethene emission with E85 fuel. PAH emissions did not significantly affect the risk factor trends for the FFV car.

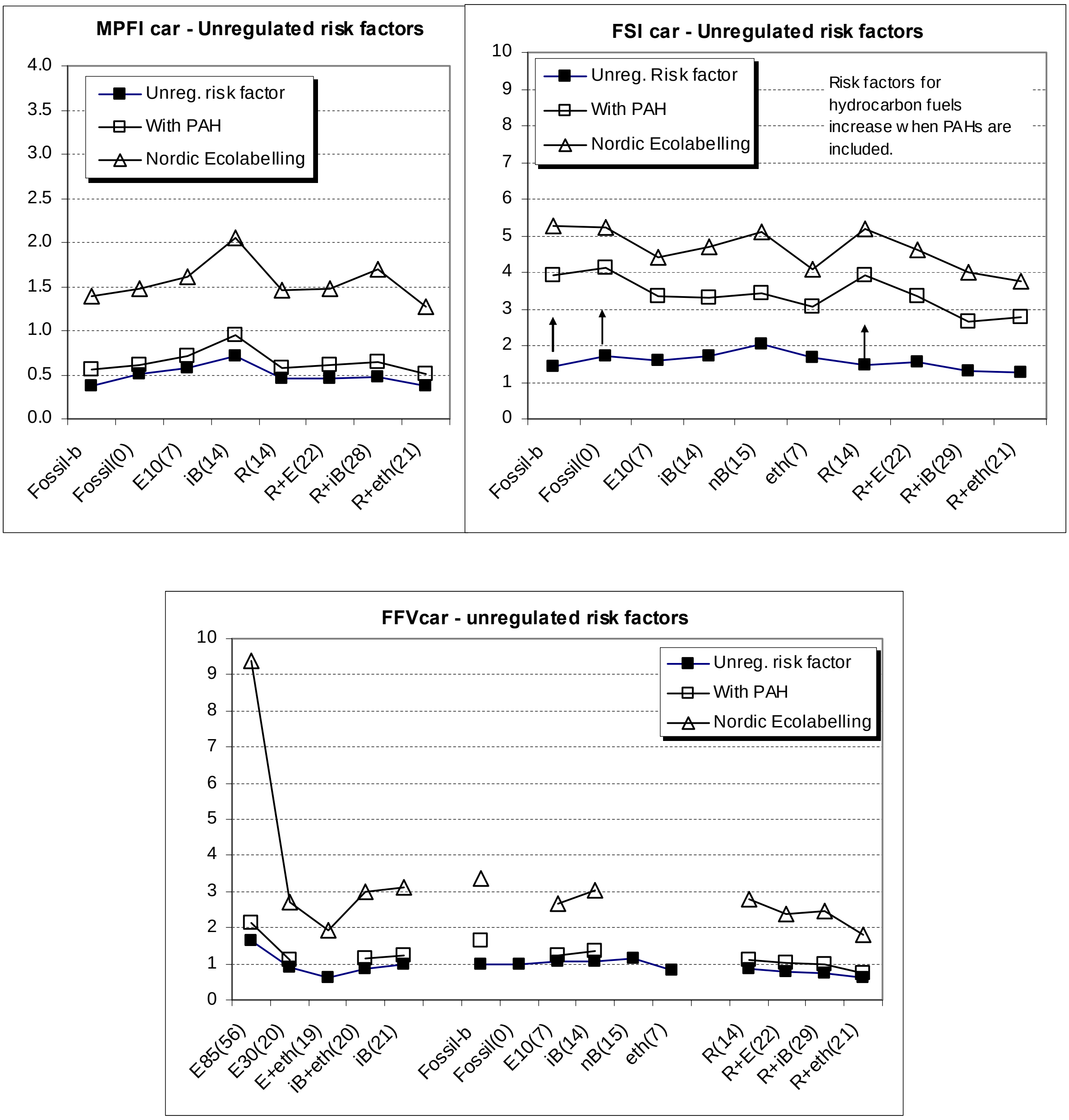

Figure 4.41. Unregulated risk factors based on benzene, 1,3-butadiene, formaldehyde and acetaldehyde emissions (Chapter 4.6) and with PAH emissions as benzo(a)pyrene equivalent (BaP_{eq}). Nordic Ecolabelling method also takes into account ethene and propene emissions.

4.7 Ozone-forming potential

The ozone-forming potential (OFP) factor was calculated using the MIR factors descrybed in Chapter 4.2.5. For E85(56) fuel, ethanol emissions are clearly the dominant contributor to the OFP factor (Figure 4.42).

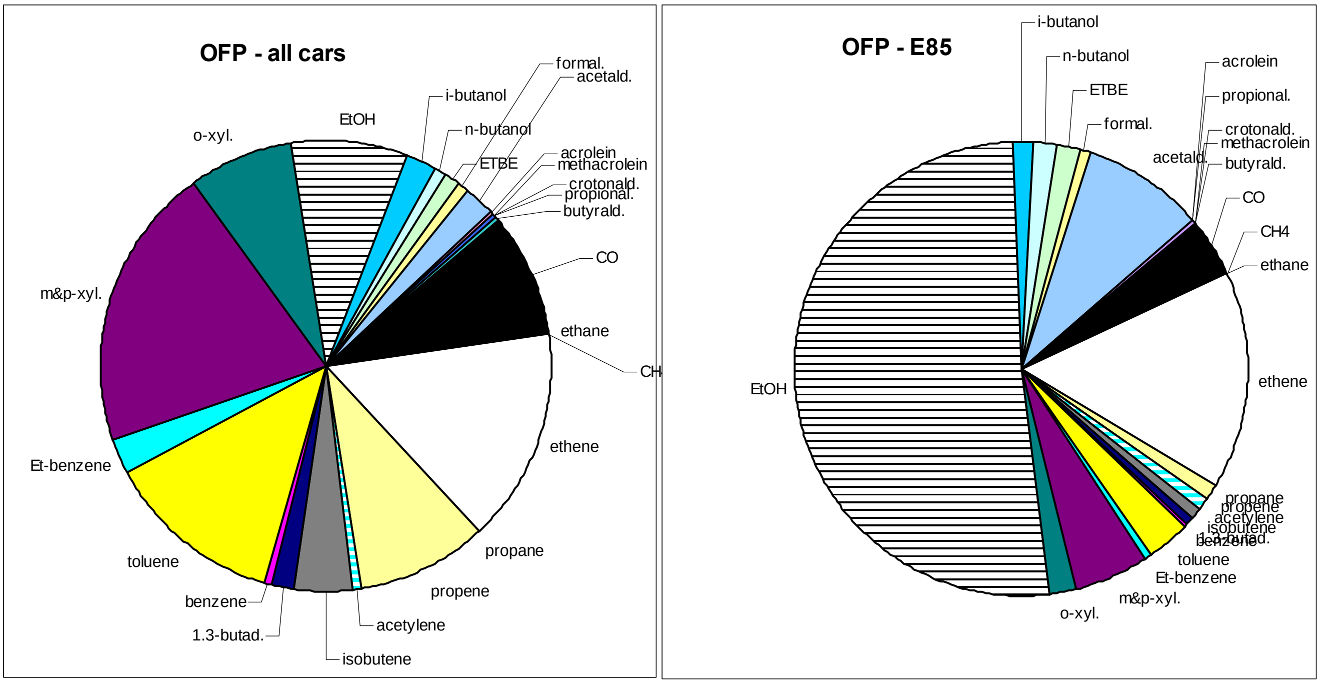

Figure 4.42. Contributions to the ozone-forming potential as an average of car/fuel combinations (left) and with E85 fuel (right).

The ozone-forming potential of Fossil-b fuel was higher than that of the two other hydrocarbon fuels (Figure 4.43). Detailed analysis showed that this was due to increased xylene emissions with Fossil-b fuel.

The OFP for E85(56) fuel was very high. This was due to ethanol emissions, but ethene (MIR 9 g ozone/g VOC) and acetaldehyde (MIR 6.5 g ozone/g VOC) emissions also played a significant role.

High-oxygen ethanol-containing fuels other than E85(56) fuel elevated also the OFP of exhaust gases to some extent. In some cases, the addition of butanols led to a slight increase in the OFP compared with Fossil(0) fuel. The MIR factor for ethanol is lower (1.5 g ozone/g VOC) than that for butanols (2.5 and 2.9 g ozone/g VOC).

ETBE also seemed to slightly increase the OFP, due to the formation of isobutene (MIR 6.3 g ozone/g VOC).

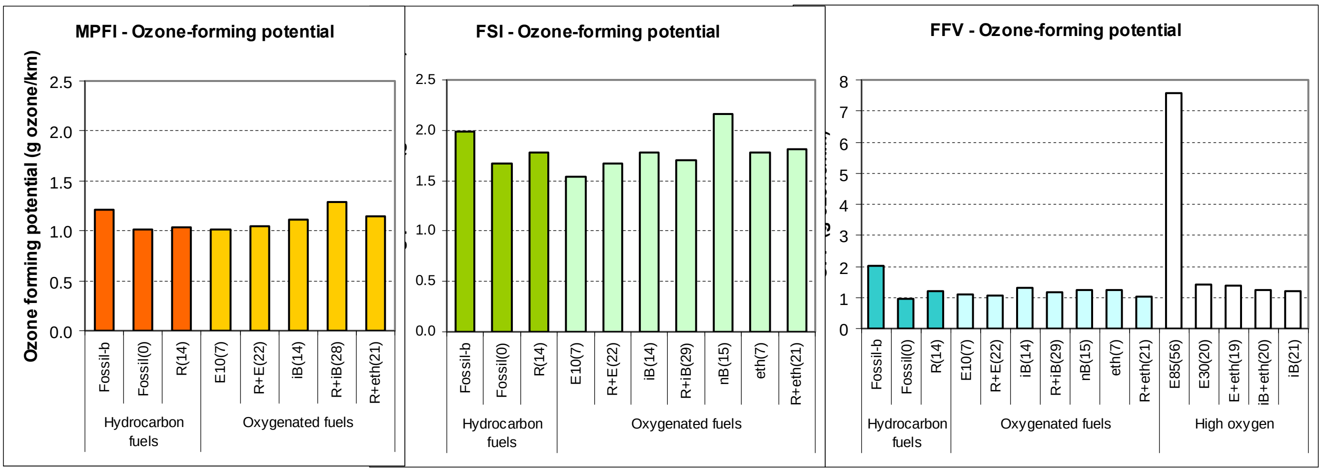

Figure 4.43. Ozone-forming potential results, European test at -7 °C.

5. Conclusions

The purpose of this study was to explore feasible gasoline biocomponents alternative or supplementary to ethanol, and to assess their exhaust emissions performance. When evaluating new fuel components, it is important to ensure that their performance is acceptable throughout the well-to-wheel chain, including production and end-use aspects such as infrastructure, car compatibility, health and environmental effects.

There are limitations in the use of ethanol as a gasoline biocomponent…

Ethanol is the dominant liquid biofuel globally, either as such or as feedstock for ETBE. However, technical restrictions limit the use of ethanol in conventional gasoline cars to 10–15 v/v%. Higher ethanol blending ratios are possible with flexible fuel vehicle (FFV) technology.

The biofuel targets for transport energy are challenging. Therefore, biocomponents alternative or supplementary to ethanol are desired for the gasoline pool to *achieve high bio-share fuels compatible with conventional cars*.

There are many biocomponent options…

Ethanol is produced traditionally by fermenting sugars and starches. However, the use of ligno-cellulosic feedstocks requires an advanced enzymatic or acid hydrolysis step[29]. Alcohols could also be produced by gasification followed by fermentation or alcohol synthesis. Biobutanol and higher alcohols can be produced using processes resembling those for ethanol. Alcohols can be converted into ethers, which are preferred to alcohols as gasoline components.

There are pathways for producing gasoline-range hydrocarbons from biomass. Gasoline can be produced via gasification and a "*methanol to gasoline, MTG*" liquefaction route, such as Exxon-Mobil's MTG and Haldor Topsøe's TIGAS processes. Lurgi's

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[29] The conversion of cellulosic biomass into biomethanol is a known process.

MtSynthesis is one option to produce hydrocarbons from methanol, gasoline as a side product.

Gasification and *Fischer-Tropsch liquefaction* are used in diesel production, with a gasoline fraction formed as a side product. Alternatively, the process can be optimized for gasoline production. An example is Sasol's coal-based production line, which is specially designed for gasoline production. Virent Energy Systems Inc. has developed a *"BioForming" process* for producing gasoline from biomass.

Biofuels can be produced in *petroleum refineries*. For example, natural oils and fats, tall oil, FT crude or processed pyrolysis oil could be used as co-feeds in refineries, or in units specifically developed for those feedstocks. Currently oils and fats are hydrotreated commercially by several companies to produce renewable diesel (HVO). As a side product, an *renewable gasoline fraction* is formed.

End-use aspects must be taken into consideration…

Technical reasons limit blending ratio of ethanol in gasoline. Butanol isomers have many benefits compared with ethanol as a gasoline component. The conversion of bio-alcohols to ethers produces preferred gasoline components with excellent fuel properties. However, the oxygen tolerance of conventional gasoline cars limits the blending ratio for all oxygenates.

Gasoline-range biohydrocarbons are advantageous because they are fully compatible with gasoline, cars and current infrastructure. However, biohydrocarbons are not consistent with each other. Their properties depend on the production processes and feedstocks used.

High bio-energy gasoline options compatible with conventional cars…

Combinations of bio-oxygenates and biohydrocarbons in gasoline were studied experimentally. Biocomponents included *isobutanol, n-butanol, ETBE,* and *a renewable hydrocarbon component* as alternatives or supplementary to ethanol. The results emphasize car emissions at low temperatures (-7 °C).

The results show that there are many options for **increasing the bio-energy content of gasoline to 20% or more without increasing the gasoline oxygen content to a higher level than can be tolerated by E10-compatible gasoline cars** (Figure 5.1). This means that various fuels with high bio-energy contents and different chemistries can be used with conventional gasoline-fuelled cars. In most cases, using ethanol, isobutanol, n-butanol, ETBE or blends of these together with renewable hydrocarbon components in gasoline **does not significantly or harmfully impact emissions from conventional cars**. The preferred combination of a renewable component with oxygenates indicated a reduced exhaust toxicity compared with fossil fuel.

E85 fuel with the FFV car clearly had the most harmful exhaust emissions and the highest ozone-forming potential. These adverse effects can be substantially reduced by using a lower ethanol content, for example 30 v/v%. In this case, the bio-energy content of gasoline could be increased by using biohydrocarbon components. Improved engine and emissions control technology is expected to reduce the exhaust emissions of FFV cars.

The toxicity of gasoline car exhaust particles at low ambient temperatures increases health concerns in general, though this is not primarily a fuel-related problem. In addition, ammonia emissions were high for the cars and fuels studied.

Renewable hydrocarbons for gasoline already exist, for example as a side product from renewable HVO diesel production in Finland. There are also promising pathways towards gasoline biohydrocarbons from cellulosic feedstocks. These processes and products warrant further studies to evaluate aspects such as economy and well-to-wheel greenhouse gas emissions.

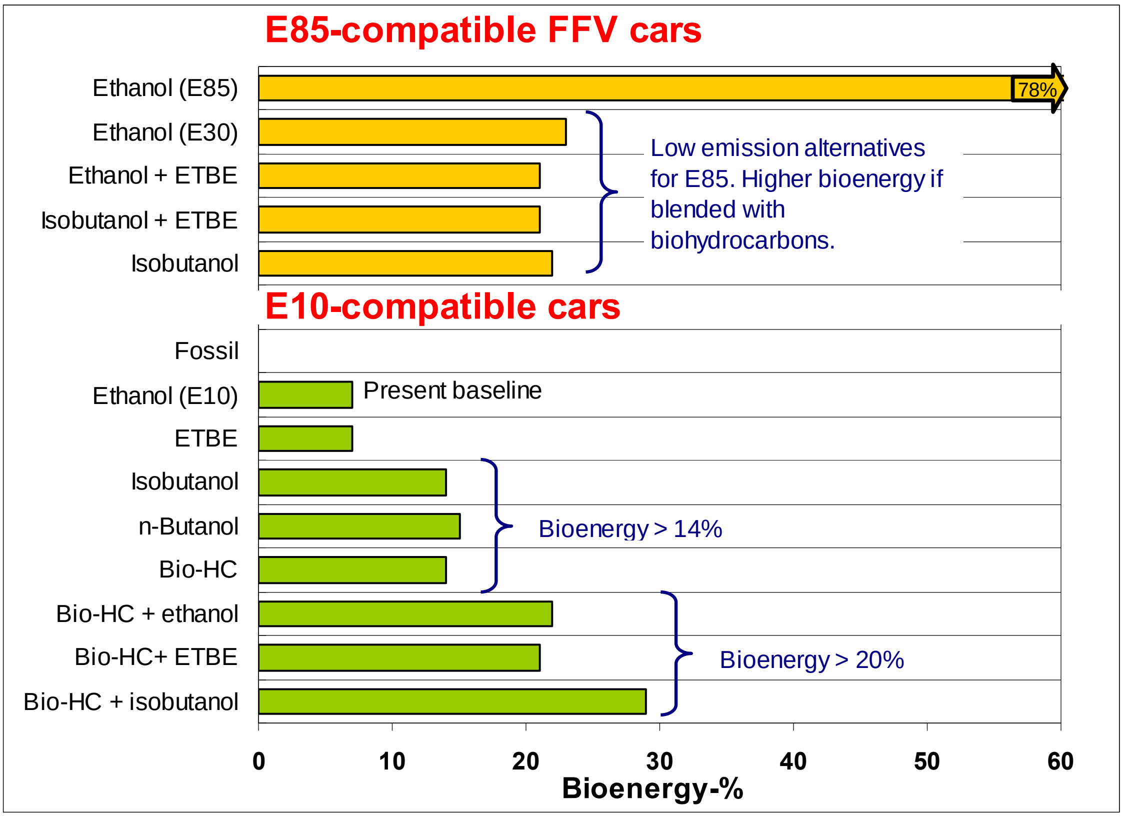

Figure 5.1. High bio-share fuels for E10-compatible cars are available.

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Appendix 1: Regulated emissions, CO_2 and fuel consumption. European test at -7 °C

Average results.

	CO	HC	NMHC	NOx	PM	CO_2	Fuel consumption	
	g/km	g/km	g/km	g/km	g/km	g/km	l/100km	kg/100km
MPFI car								
Fossil(0b)	1.2	0.42	0.41	0.03	0.004	204.6	8.7	6.6
Fossil(0)	1.3	0.39	0.38	0.02	0.003	204.0	8.8	6.5
E10(7)	1.0	0.39	0.37	0.03	0.004	202.7	8.9	6.7
iB(14)	0.8	0.38	0.35	0.04	0.006	201.5	8.9	6.7
R(14)	1.0	0.42	0.41	0.03	0.003	204.2	8.8	6.5
R+E(22)	1.1	0.40	0.38	0.03	0.003	205.3	9.1	6.8
R+iB(28)	1.0	0.44	0.40	0.04	0.005	204.8	9.1	6.8
R+eth(21)	1.3	0.38	0.36	0.02	0.004	205.5	9.2	6.8
FSI car								
Fossil(0b)	3.4	0.59	0.61	0.07	0.019	169.1	7.5	5.6
Fossil(0)	3.9	0.59	0.56	0.06	0.016	169.0	7.5	5.6
E10(7)	3.1	0.52	0.49	0.07	0.013	170.0	7.7	5.8
iB(14)	2.9	0.55	0.50	0.07	0.014	169.6	7.6	5.8
nB(15)	2.3	0.66	0.62	0.09	0.015	171.4	7.7	5.8
eth(7)	2.8	0.51	0.49	0.07	0.016	175.2	7.9	5.9
R(14)	3.3	0.63	0.58	0.07	0.017	170.4	7.6	5.6
R+E(22)	2.7	0.55	0.52	0.08	0.015	170.8	7.7	5.8
R+iB(29)	2.7	0.53	0.48	0.08	0.012	168.4	7.6	5.7
R+eth(21)	3.1	0.52	0.48	0.06	0.012	170.8	7.8	5.8
FFV car								
E85(56)	5.5	2.40	0.51	0.05	0.007	247.4	15.8	12.5
E30(20)	3.2	0.42	0.34	0.07	0.004	248.5	12.0	9.1
E+eth(19)	3.1	0.39	0.32	0.07	0.003	245.9	11.9	9.0
iB+eth(20)	2.4	0.31	0.27	0.08	0.009	251.8	11.7	8.8
iB(21)	2.4	0.32	0.27	0.07	0.003	250.1	11.4	8.6
Fossil(0b)	6.1	0.64	0.61	0.05	0.009	257.9	11.3	8.5
Fossil(0)	2.2	0.28	0.26	0.11	0.003	251.0	10.9	8.1
E10(7)	2.3	0.30	0.29	0.10	0.003	255.0	11.3	8.5
iB(14)	2.3	0.36	0.34	0.08	0.004	251.4	11.1	8.4
nB(15)	2.0	0.32	0.30	0.10	0.005	261.1	11.5	8.7
eth(7)	2.6	0.34	0.31	0.07	0.006	260.7	11.5	8.7
R(14)	2.3	0.35	0.33	0.10	0.004	255.0	11.1	8.2
R+E(22)	2.3	0.32	0.29	0.09	0.004	254.1	11.3	8.5
R+iB(29)	2.4	0.32	0.29	0.10	0.004	255.0	11.3	8.5
R+eth(21)	2.5	0.28	0.26	0.08	0.003	255.5	11.4	8.5

Appendix 1: Regulated emissions, CO2 and fuel consumption. European test at -7 C

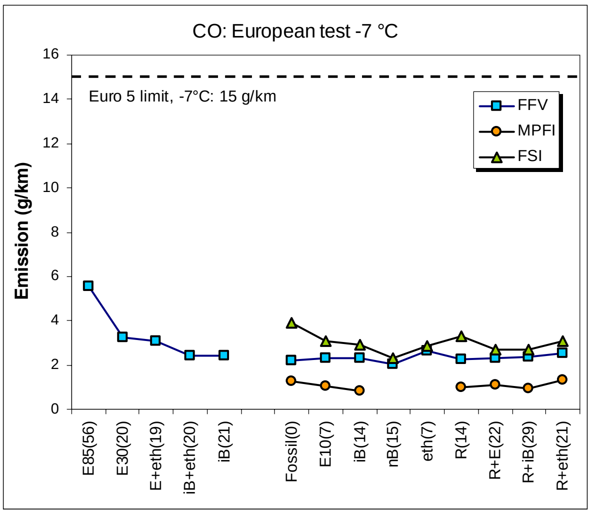
Change-% when biofuels are compared with Fossil(0) fuel.

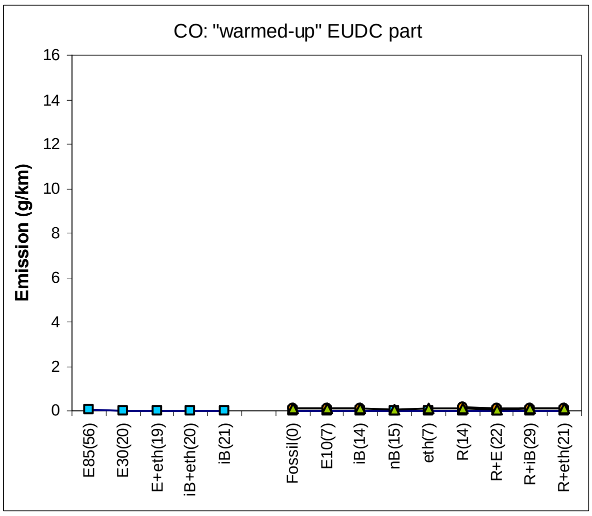
	CO change-%		**HC change-%**		**NOx change-%**		**PM change-%**		**CO_2 change-%**		**FC(vol) change-%**	
MPFI car												
E10(7)	**-19.4**	±2	-1.5	±3	**32.7**	±6	40.7	±8	-0.7	±0.6	**1.2**	±0.6
iB(14)	**-34.8**	±12	-3.6	±7	**48.0**	±12	110.1	±46	**-1.2**	±0.7	0.4	±0.7
R(14)	**-20.8**	±17	6.1	±9	**28.1**	±15	3.3	±10	0.1	±0.5	0.1	±0.7
R+E(22)	**-14.0**	±1	1.2	±3	**23.7**	±12	14.5	±4	0.6	±0.1	**3.2**	±0.1
R+iB(29)	**-24.8**	±10	**11.5**	±3	**47.5**	±6	75.7	±27	0.4	±0.7	**2.7**	±0.6
R+eth(21)	1.9	±3	-3.1	±3	-2.2	±9	26.4	±13	0.7	±0.1	**3.8**	±0.2
FSI car												
E10(7)	**-21.4**	±5	**-11.2**	±4	**11.5**	±3	-16.2	±5	0.6	±0.4	**1.8**	±0.3
iB(14)	**-25.2**	±2	-5.8	±8	**10.7**	±3	-10.4	±7	0.3	±0.5	**1.4**	±0.6
nB(15)	**-40.6**	±2	**11.9**	±8	**53.6**	±5	-4.5	±12	**1.4**	±0.4	**1.6**	±0.2
eth(7)	**-26.8**	±3	**-12.5**	±0	**22.7**	±14	0.6	±6	**3.7**	±0.2	**4.4**	±0.1
R(14)	**-15.0**	±2	8.0	±7	**17.0**	±12	11.1	±15	0.8	±0.7	0.5	±0.8
R+E(22)	**-30.3**	±5	-7.1	±2	**33.2**	±9	-5.2	±12	**1.0**	±0.5	**2.6**	±0.5
R+iB(29)	**-30.8**	±2	**-10.4**	±4	**29.2**	±5	-25.8	±6	-0.3	±0.3	0.8	±0.4
R+eth(21)	**-21.6**	±2	**-11.5**	±1	-1.7	±4	-26.0	±2	**1.0**	±0.5	**3.2**	±0.5
FFV car												
E85(60)	**150.6**	±5	**765.6**	±9	**-52.3**	±12	118.2	±0	**-1.4**	±0.5	**45.3**	±0.5
E30(23)	**46.2**	±5	**51.6**	±2	**-35.6**	±1	12.5	±0	**-1.0**	±0.3	**10.8**	±0.2
E+eth(21)	**38.4**	±4	**39.0**	±1	**-39.6**	±4	1.4	±3	**-2.0**	±0.2	**9.3**	±0.2
iB+eth(22)	8.6	±5	**10.9**	±2	**-23.9**	±2	166.2	±22	0.3	±0.9	**7.5**	±0.9
iB(22)	8.4	±8	**16.5**	±5	**-33.5**	±2	0.8	±6	-0.3	±0.4	**5.1**	±0.3
E10(7)	4.9	±5	6.4	±8	-5.8	±1	-7.4	±3	**1.6**	±0.4	**3.8**	±0.4
iB(14)	4.5	±4	**31.0**	±8	**-22.6**	±15	33.5	±8	0.2	±0.6	**2.3**	±0.7
nB(15)	-8.2	±11	**16.9**	±2	-5.4	±1	55.7	±15	**4.1**	±0.9	**5.6**	±1.0
eth(7)	**18.9**	*	**20.8**	*	**-32.2**	*	83.0	*	**3.9**	*	**6.9**	*
R(14)	2.0	±5	**26.4**	±5	-12.8	±20	31.7	±9	**1.6**	±0.1	**1.8**	±0.2
R+E(22)	4.1	±9	**16.8**	±1	**-17.7**	±7	13.9	±4	**1.3**	±0.2	**4.1**	±0.2
R+iB(29)	7.7	±1	**16.7**	±2	**-11.5**	±9	13.4	±6	**1.6**	±0.1	**4.1**	±0.1
R+eth(21)	**13.2**	±1	0.3	±6	**-25.5**	±2	-15.5	±5	**1.8**	±1.1	**5.1**	±1.1

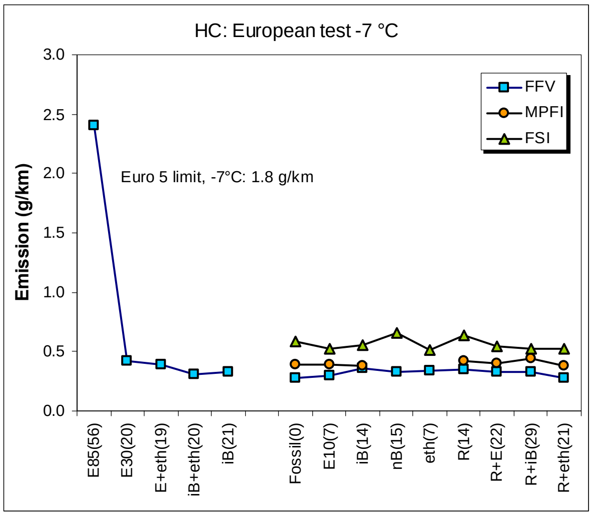
*) one measurement

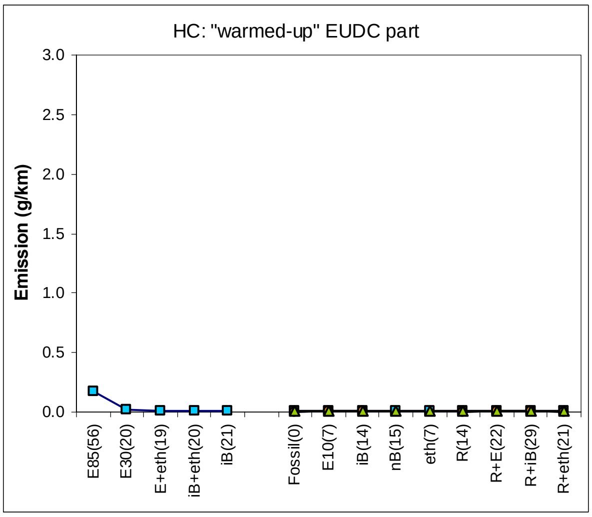
Appendix 1: Regulated emissions, CO2 and fuel consumption. European test at -7 C

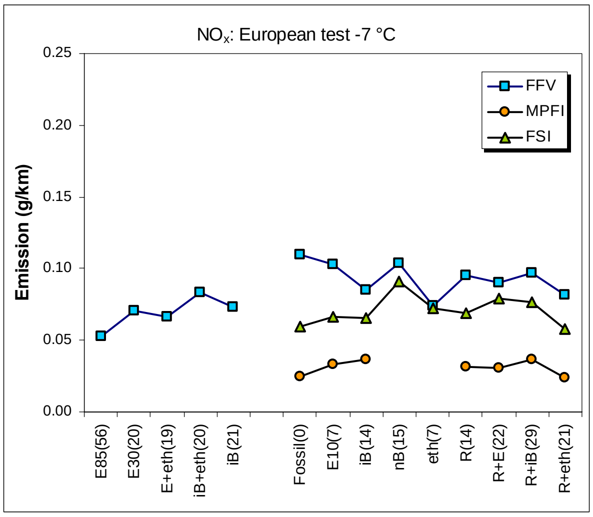
Emissions over the European test cycle at -7 °C (left) and over the warm EUDC part of the test (right).

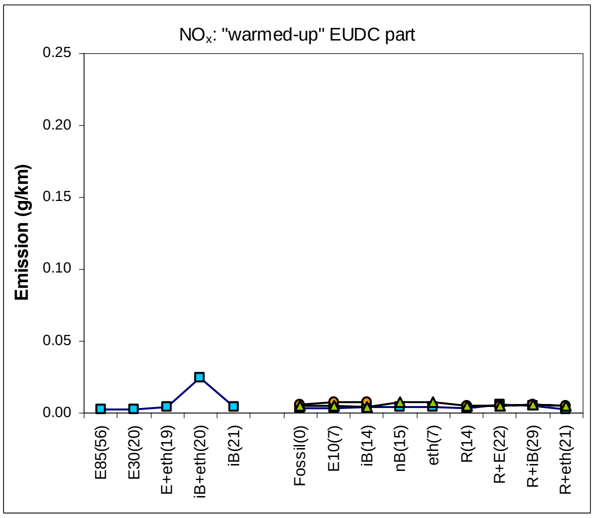












Appendix 2: Aldehydes, C_1-C_8 hydrocarbons and FTIR results. European test at -7 °C

Average aldehyde results. European test at -7 °C.

	Formaldehyde mg/km	Acetaldehyde mg/km	Acrolein mg/km	Propionaldehyde mg/km	Crotonaldehyde mg/km	Methacroleine mg/km	Butyraldehyde mg/km	Benzaldehyde mg/km	Valeraldehyde mg/km	m-Tolualdehyde mg/km	Hexaldehyde mg/km
MPFI car											
Fossil-B	0.3	0.4	0.05	0.11	0.00	0.06	0.00	0.05	0.00	0.00	0.00
Fossil(0)	0.3	0.6	0.00	0.04	0.00	0.03	0.00	0.09	0.00	0.00	0.00
E10(7)	0.4	4.0	0.02	0.03	0.00	0.07	0.04	0.09	0.00	0.00	0.00
iB(14)	0.7	0.6	0.11	0.80	0.00	2.15	4.76	0.12	0.00	0.00	0.00
R(14)	0.4	0.4	0.00	0.03	0.00	0.06	0.00	0.12	0.00	0.00	0.00
R+E(22)	0.4	4.1	0.02	0.04	0.00	0.04	0.00	0.12	0.00	0.00	0.00
R+iB(28)	0.6	0.7	0.07	0.80	0.00	2.50	5.41	0.19	0.00	0.00	0.00
R+eth(21)	0.3	3.1	0.01	0.03	0.00	0.10	0.03	0.07	0.00	0.00	0.00
FSI car											
Fossil(0b)	0.4	0.92	0.11	0.17	0.00	0.16	0.00	0.14	0.00	0.00	0.00
Fossil(0)	0.3	1.07	0.02	0.12	0.00	0.17	0.00	0.14	0.00	0.00	0.00
E10(7)	0.4	5.05	0.08	0.17	0.00	0.17	0.08	0.19	0.00	0.00	0.00
iB(14)	1.0	1.64	0.16	1.04	0.00	1.53	0.98	0.23	0.00	0.00	0.00
nB(15)	0.7	4.87	0.25	0.55	0.09	0.70	4.18	0.27	0.00	0.00	0.00
eth(7)	0.7	4.96	0.07	0.09	0.00	0.21	0.17	0.21	0.00	0.00	0.00
R(14)	0.3	1.15	0.04	0.09	0.00	0.15	0.00	0.19	0.00	0.00	0.00
R+E(22)	0.4	4.99	0.07	0.09	0.00	0.13	0.00	0.21	0.00	0.00	0.00
R+iB(29)	0.5	1.45	0.13	0.91	0.00	1.53	1.16	0.23	0.00	0.00	0.00
R+eth(21)	0.4	4.73	0.05	0.11	0.00	0.18	0.00	0.17	0.00	0.00	0.00
FFV car											
E85(56)	6.9	99.3	1.23	0.82	0.40	0.30	0.26	0.35	0.00	0.00	0.00
E30(20)	1.1	13.0	0.14	0.02	0.04	0.15	0.06	0.21	0.00	0.00	0.00
E+eth(19)	1.3	10.0	0.08	0.00	0.02	0.20	0.00	0.20	0.00	0.00	0.00
iB+eth(20)	2.6	3.3	0.18	0.81	0.00	1.75	0.83	0.30	0.00	0.00	0.00
iB(21)	2.3	1.4	0.23	1.85	0.00	3.52	0.94	0.23	0.00	0.00	0.00
Fossil-b	0.7	0.7	0.02	0.00	0.00	0.09	0.00	0.19	0.00	0.00	0.00
Fossil(0)	0.8	0.6	0.03	0.00	0.00	0.10	0.00	0.24	0.00	0.00	0.00
E10(7)	0.7	3.5	0.06	0.00	0.00	0.09	0.00	0.26	0.00	0.00	0.00
iB(14)	2.0	1.1	0.22	1.02	0.00	3.48	0.61	0.39	0.00	0.00	0.00
nB(15)	1.5	4.1	0.13	0.19	0.10	0.52	2.85	0.34	0.00	0.00	0.00
eth(7)	1.3	3.2	0.03	0.00	0.00	0.16	0.00	0.36	0.00	0.00	0.00
R(14)	0.8	0.6	0.02	0.00	0.00	0.10	0.00	0.33	0.00	0.00	0.00
R+E(22)	0.9	3.6	0.05	0.00	0.00	0.06	0.00	0.32	0.00	0.00	0.00
R+iB(29)	1.6	1.1	0.14	0.83	0.00	3.05	0.45	0.36	0.00	0.00	0.00
R+eth(21)	0.7	2.7	0.04	0.00	0.00	0.13	0.00	0.25	0.00	0.00	0.00

Detection limit corresponds to approximately 0.01 mg/km.

Average results for C_1-C_8 hydrocarbons. European test at -7 °C.

	Methane mg/km	Ethane mg/km	Ethene mg/km	Propane mg/km	Propene mg/km	Acetylene mg/km	Isobutene mg/km	1,3-Butadiene mg/km	Benzene mg/km	Toluene mg/km	Ethylbenzene mg/km	m,p-xylene mg/km	o-xylene mg/km
MPFI car													
Fossil-B	7.0	2.4	12.1	0.0	8.3	3.0	8.0	0.7	6.3	24.2	20.0	69.4	20.9
Fossil(0)	7.8	2.7	14.2	0.3	8.0	3.5	3.9	1.0	7.9	51.4	13.0	38.3	14.7
E10(7)	6.8	2.1	14.1	0.0	6.7	2.6	2.5	1.1	8.7	51.5	11.8	36.7	14.6
iB(14)	6.3	2.5	12.2	0.3	11.2	2.8	4.1	2.0	7.7	45.4	11.3	36.2	14.1
R(14)	6.2	3.6	13.6	0.3	9.3	2.3	5.8	1.0	6.9	51.9	12.7	38.9	15.4
R+E(22)	7.5	2.1	14.1	0.2	6.7	3.2	2.8	0.8	7.5	53.1	12.5	39.0	15.1
R+iB(28)	7.2	2.7	14.3	0.4	12.5	3.1	4.4	0.8	7.9	55.3	12.4	40.8	16.2
R+eth(21)	8.0	1.6	12.3	0.2	5.1	3.1	18.8	0.5	6.8	52.9	12.0	38.6	15.3
FSI car													
Fossil-B	18.8	5.8	34.4	0.1	17.6	12.4	15.7	1.6	17.9	40.0	23.6	87.8	25.7
Fossil(0)	21.7	5.5	35.7	0.5	15.5	10.2	7.0	2.1	20.6	71.3	15.2	45.9	17.0
E10(7)	18.1	4.7	32.9	0.5	12.4	10.4	4.4	1.8	19.6	65.8	14.1	42.5	16.6
iB(14)	20.1	5.5	33.6	0.9	20.8	10.9	9.8	2.1	20.1	66.8	14.3	44.2	16.8
nB(15)	18.9	5.5	39.6	1.2	18.6	13.1	5.0	2.8	22.1	85.6	20.2	73.0	29.3
eth(7)	17.9	3.8	25.1	0.5	9.7	7.3	35.9	2.0	19.8	73.0	15.1	49.0	18.4
R(14)	21.3	6.5	36.5	0.5	18.7	9.6	10.3	1.3	20.4	79.1	16.5	50.3	19.4
R+E(22)	19.8	4.6	34.5	0.7	13.8	12.6	5.4	1.6	20.3	75.7	14.8	48.9	18.6
R+iB(29)	18.3	5.3	32.5	1.0	21.0	9.9	8.6	1.4	17.1	66.8	13.4	43.2	16.6
R+eth(21)	18.4	4.5	29.9	0.4	11.2	10.7	34.5	1.1	17.8	73.7	14.2	47.1	18.4
FFV car													
E85(56)	109.0	15.0	129.8	0.5	7.5	76.1	10.1	3.1	16.7	59.3	15.6	50.8	19.1
E30(20)	21.1	4.8	25.1	0.3	12.7	14.9	8.9	2.3	9.7	38.7	8.8	27.2	10.5
E+eth(19)	16.9	4.3	18.8	0.0	10.4	12.2	25.8	1.4	8.1	35.9	8.3	25.9	9.9
iB+eth(20)	15.3	4.5	18.2	0.2	12.3	8.5	20.8	2.8	6.5	27.3	7.6	24.5	9.2
iB(21)	16.6	6.3	24.2	0.4	20.1	13.0	10.2	3.3	7.1	23.4	5.9	17.3	6.9
Fossil(0b)	28.0	4.7	24.4	0.0	15.9	25.0	15.1	2.2	14.1	36.4	24.1	87.6	26.0
Fossil(0)	11.2	5.0	17.7	0.7	11.9	7.7	5.6	3.2	8.3	33.1	7.6	25.4	9.2
E10(7)	13.0	3.7	21.4	0.5	10.9	9.6	3.8	3.3	9.6	40.8	9.0	29.1	11.1
iB(14)	13.1	5.2	21.9	0.4	16.7	9.9	6.8	3.3	10.0	41.1	10.4	32.0	12.2
nB(15)	14.1	5.5	31.3	0.5	14.0	11.9	3.8	3.6	9.7	36.4	9.3	26.2	10.1
eth(7)	12.4	2.9	16.3	0.0	7.5	7.7	21.6	2.2	9.6	46.7	9.9	32.0	12.2
R(14)	15.0	7.1	24.4	0.5	17.9	7.9	9.8	2.4	9.4	44.2	9.9	30.2	11.7
R+E(22)	14.0	4.0	20.5	0.3	10.4	7.2	3.8	2.1	9.4	40.6	8.9	29.3	11.3
R+iB(29)	11.1	4.9	20.9	0.4	14.4	8.0	5.5	2.1	8.1	37.5	8.7	27.7	11.2
R+eth(21)	13.0	2.7	16.9	0.4	7.6	6.9	16.5	1.5	7.6	37.0	7.9	25.7	10.1

Detection limit corresponds to approximately 0.5 mg/km for 1,3-butadiene, 0.7 mg/km for benzene and 0.1 mg/km for methane.

Average results for alcohols, ETBE and nitrogen-containing compounds analyzed by FTIR. European test at -7 °C.

	Ethanol mg/km	n-Butanol mg/km	Isobutanol mg/km	ETBE mg/km	NO_2 mg/km	N_2O mg/km	NH_3 mg/km
MPFI car							
Fossil-b	0.2	0.7	3.0	1.1	3.9	3.8	18.9
Fossil(0)	0.7	1.0	3.7	0.1	2.4	2.8	24.0
E10(7)	18.4	2.0	4.0	0.1	2.5	5.5	21.9
iB(14)	0.0	0.1	36.8	6.7	2.3	6.5	18.9
R(14)	0.3	0.8	3.7	0.2	3.4	4.1	19.9
R+E(22)	18.3	2.3	4.2	0.3	2.6	3.3	18.0
R+iB(28)	0.1	0.4	56.7	4.2	2.9	1.3	17.5
R+eth(21)	7.7	1.6	2.5	29.7	3.2	3.1	16.5
FSI car							
Fossil-b	0.2	0.4	4.4	2.3	2.5	3.6	19.9
Fossil(0)	0.0	0.8	5.3	0.5	2.9	3.5	21.2
E10(7)	13.7	2.2	6.5	0.9	1.7	4.7	15.5
iB(14)	0.4	0.1	46.8	6.6	2.2	3.2	5.1
nB(15)	0.0	24.0	6.5	3.9	1.8	5.4	22.5
eth(7)	8.6	0.8	3.0	41.2	1.8	5.4	10.7
R(14)	0.1	0.9	5.9	0.2	2.4	2.7	20.2
R+E(22)	16.7	5.0	5.4	0.4	2.6	4.0	19.8
R+iB(29)	0.3	0.3	39.9	5.2	2.6	2.8	19.4
R+eth(21)	11.2	3.0	2.5	34.2	1.9	3.4	18.9
FFV car							
E85(56)	2539.2	45.8	45.6	58.9	6.4	11.4	39.0
E30(20)	93.6	7.5	5.1	0.7	3.0	5.6	5.4
E+eth(19)	70.7	5.0	4.5	36.6	3.4	5.3	7.7
iB+eth(20)	5.6	2.2	29.3	28.2	3.0	15.7	3.1
iB(21)	0.2	0.2	47.3	4.0	3.4	6.9	4.8
Fossil-b	0.7	0.8	4.2	1.4	1.4	5.0	29.4
Fossil(0)	0.1	0.3	1.9	0.4	4.7	5.9	5.6
E10(7)	11.3	3.5	3.6	0.2	3.1	6.5	5.0
iB(14)	0.3	0.4	29.3	3.6	4.6	7.2	6.5
nB(15)	0.0	19.8	4.1	0.7	2.7	9.5	10.1
eth(7)	7.0	2.5	3.2	22.3	3.3	11.6	3.9
R(14)	0.4	0.4	3.1	0.5	3.7	4.8	8.0
R+E(22)	10.6	3.5	4.0	0.9	3.3	4.9	7.9
R+iB(29)	0.0	0.5	26.8	2.1	4.4	6.0	7.4
R+eth(21)	5.2	2.0	2.8	15.4	4.0	5.4	6.3

Appendix 2: Aldehydes, C1-C8 hydrocarbons and FTIR results. European test at -7 C

Unregulated emissions. Change-% when biofuels are compared with Fossil(0) fuel.

	Formaldehyde change-%		Acetaldehyde change-%		Methane change-%		1,3-Butadiene change-%		Benzene change-%	
MPFI car										
E10(7)	41	±5	616	±6	-12	*	10	*	9	*
iB(14)	162	±17	13	±13	-19	±4	95	±33	-3	±4
R(14)	48	±7	-25	±14	-20	±11	-5	±13	-13	±13
R+E(22)	38	±8	618	±0	-4	±5	-20	±11	-5	±1
R+iB(28)	122	±15	25	±16	-8	±4	-18	±6	0	±4
R+eth(21)	26	±9	448	±8	3	±4	-51	±7	-14	±1
FSI car										
E10(7)	34	±8	372	±10	-17	±2	-16	±11	-5	±3
iB(14)	242	±13	53	±3	-8	±5	-1	±13	-2	±5
nB(15)	133	±2	355	±1	-13	±9	33	±17	7	±5
eth(7)	124	±0	364	±1	-18	±0	-5	±6	-4	±1
R(14)	-4	±15	7	±5	-2	±8	-37	±13	-1	±6
R+E(22)	23	±4	366	±5	-9	±3	-25	±1	-1	±0
R+iB(28)	81	±6	35	±5	-16	±4	-35	±8	-17	±5
R+eth(21)	28	±2	342	±5	-16	*	-50	*	-13	*
FFV car										
E85(56)	802	±26	15812	±9	875	*	-2	*	101	*
E30(20)	47	±4	1984	±7	88	*	-29	*	16	*
E+eth(19)	66	±2	1510	±4	51	±1	-56	±7	-3	±0
iB+eth(20)	240	±5	423	±1	37	±8	-13	±10	-22	±2
iB(21)	204	±19	130	±12	49	±7	4	±5	-14	±5
E10(7)	-5	±21	460	±4	16	*	4	*	16	*
iB(14)	165	±0	77	±5	17	±3	2	±6	21	±5
nB(15)	101	±6	559	±24	26	*	14	*	16	*
eth(7)	72	*	417	*	11	*	-32	*	16	*
R(14)	5	±9	-5	±6	34	±6	-24	±7	14	±6
R+E(22)	19	±11	484	±1	26	*	-36	*	14	*
R+iB(28)	109	±8	68	±4	-1	*	-34	*	-3	*
R+eth(21)	-3	±6	339	±1	17	±1	-54	±15	-8	±6

* One measurement. Hard disk of gas chromatograph failed and data from replicate measurements were lost.

Appendix 3: Results from PAH analysis. Average results. European test at -7 °C

	Flu µg/km	Phe µg/km	An µg/km	F µg/km	P µg/km	BaA µg/km	Chr µg/km	BbF µg/km	BkF µg/km	BjF µg/km	DMBA µg/km	BeP µg/km	BaP µg/km	IP µg/km	DBahA µg/km	BghiP µg/km	PAH14 µg/km	PAH9 µg/km	PAH7 µg/km	Other PA µg/km	All PAHs µg/km	BaPeq µg/km
Fossil(0b)	0.1	1.0	0.1	1.1	2.2	1.5	0.9	2.2	0.7	0.5	0.2	1.0	2.2	1.2	0.2	1.4	15.8	9.6	8.9	4.0	20.5	5.0
Fossil(0)	0.1	1.7	0.1	1.2	2.3	1.1	0.5	1.2	0.4	0.2	0.3	0.6	1.2	0.6	0.1	0.9	11.9	5.5	5.2	3.8	16.2	2.9
R(14)	0.0	1.4	0.1	1.0	1.8	1.0	0.5	1.4	0.4	0.3	0.2	0.8	1.6	0.8	0.1	0.9	12.0	6.3	6.0	3.4	15.8	3.4
E10(7)	0.1	1.7	0.2	1.8	3.8	1.4	0.8	1.5	0.4	0.3	0.2	0.8	1.6	0.9	0.1	1.0	15.9	7.1	6.7	4.1	20.5	4.0
R+E(22)	0.1	2.0	0.2	1.4	2.4	1.3	0.7	1.9	0.5	0.4	0.2	1.0	2.0	0.9	0.1	1.1	15.4	8.0	7.5	4.7	20.8	4.2
iBi(14)	0.1	2.0	0.3	5.6	12.7	2.1	1.3	2.6	0.7	0.5	0.3	1.3	2.4	1.0	0.1	1.1	33.4	11.0	10.4	7.1	41.3	6.6
R+iB(28)	0.1	2.4	0.2	1.4	2.7	1.6	0.8	2.1	0.6	0.5	0.3	1.0	2.2	1.0	0.1	1.1	17.3	9.2	8.6	5.5	23.6	4.8
R+eth(21)	0.1	1.7	0.1	1.3	2.4	1.3	0.7	1.8	0.5	0.4	0.2	1.0	1.9	0.9	0.1	1.0	14.7	7.8	7.3	4.7	20.1	4.0
Fossil(0b)	0.7	7.8	1.0	9.8	17.2	16.8	9.5	23.5	6.5	6.0	0.0	9.2	21.2	12.3	1.8	12.7	149.8	97.5	89.7	47.5	203.3	50.5
Fossil(0)	0.5	6.0	0.8	8.4	14.6	16.1	9.2	22.3	6.1	5.2	0.4	8.9	20.4	11.5	1.6	12.5	139.0	92.9	86.0	43.3	187.9	47.8
R(14)	0.6	7.6	0.8	9.3	17.1	15.9	9.4	22.7	6.5	4.8	0.7	9.3	21.7	11.1	1.4	12.2	145.8	94.3	88.1	42.0	193.4	48.8
E10(7)	0.4	5.3	0.6	5.0	8.6	11.1	6.6	17.0	5.0	4.0	0.7	6.2	14.1	8.9	1.4	9.4	99.6	68.7	63.3	31.6	136.0	34.9
R+E(22)	0.7	6.8	0.7	6.4	11.0	11.4	6.7	18.0	4.7	4.1	0.7	7.0	14.7	8.4	1.3	8.9	106.9	70.2	64.8	35.8	147.5	35.8
iBi(14)	0.6	5.0	0.5	5.5	10.4	10.2	5.8	15.1	4.0	3.3	0.6	6.0	13.4	8.4	1.2	8.9	95.0	61.9	57.4	32.3	131.2	32.1
R+iB(28)	0.6	6.4	0.5	4.9	8.9	8.0	4.6	13.5	3.6	2.9	0.7	5.2	11.7	6.9	0.9	8.1	83.8	52.8	49.0	26.9	114.3	26.9
nB(15)	0.4	6.3	1.1	10.9	21.4	9.3	5.6	10.9	3.0	2.4	0.6	4.7	10.4	7.1	1.0	7.7	99.6	50.1	46.8	27.8	130.3	27.8
eth(7)	0.5	6.6	0.6	7.3	13.2	10.3	5.9	12.6	3.0	2.7	0.6	4.7	10.0	7.0	1.0	7.3	90.0	53.0	49.3	32.1	125.4	27.6
R+eth(21)	0.4	5.5	0.5	5.5	9.7	9.7	5.8	14.5	4.2	3.5	0.7	5.7	12.5	7.4	1.0	8.4	91.0	59.3	54.8	26.3	121.5	30.0
Fossil(0)	na																					
Fossil(0b)	0.5	10.8	1.3	6.4	10.8	7.0	4.2	8.7	2.7	2.0	0.0	3.7	7.4	4.4	0.6	5.5	74.1	37.0	34.4	17.8	93.9	19.2
R(14)	0.2	4.9	0.4	2.6	4.0	2.9	1.5	3.6	1.0	0.8	0.0	1.4	2.9	1.4	0.2	1.6	28.5	14.2	13.2	8.5	37.8	7.4
E10(7)	0.2	3.7	0.3	2.1	3.6	1.7	0.9	2.3	0.6	0.5	0.0	0.8	1.9	0.9	0.2	1.2	20.5	9.0	8.4	6.3	27.3	4.9
R+E(22)	0.2	4.8	0.3	2.4	3.8	2.3	1.3	3.1	0.8	0.7	0.0	1.4	2.5	1.3	0.2	1.5	26.1	12.3	11.4	7.5	34.3	6.4
iBi(14)	0.2	4.2	0.4	2.4	3.8	2.7	1.4	3.4	1.0	0.8	0.0	1.4	3.0	1.3	0.2	1.8	27.4	13.8	12.9	7.2	35.4	7.3
R+iB(28)	0.2	5.4	0.3	2.6	4.0	2.4	1.2	2.8	0.7	0.6	0.0	1.1	2.4	1.2	0.2	1.5	26.1	11.6	10.7	7.1	33.8	6.1
E+eth(21)	na																					
R+eth(21)	0.2	3.5	0.2	1.8	2.9	1.6	0.8	2.0	0.5	0.4	0.0	0.9	1.7	0.9	0.1	1.1	18.3	8.2	7.6	5.2	24.0	4.4
E85(56)	0.3	3.6	0.4	3.4	10.2	2.7	1.4	4.0	1.1	0.7	0.7	3.6	7.0	2.9	0.4	6.9	48.0	21.0	19.8	11.1	60.5	13.5
E30(20)	0.1	3.8	0.3	2.4	4.7	2.2	1.1	2.5	0.7	0.5	0.0	1.2	2.6	1.4	0.2	2.1	25.3	11.2	10.5	6.0	31.7	6.1
iB+eth(20)	0.2	5.8	1.0	10.5	20.8	3.5	2.1	2.6	0.6	0.4	0.0	1.2	2.0	0.8	0.1	1.1	52.4	12.1	11.6	10.3	63.2	7.8
iB(21)	0.3	5.0	0.7	9.8	20.1	2.2	1.9	1.1	0.6	0.2	0.0	0.8	1.5	0.5	0.0	0.8	45.2	8.0	7.7	7.8	53.2	6.3

Detection limit corresponds to approximately 0.04 µg/km for the MPFI car and 0.08 µg/km for the FSI and FFV cars.

Appendix 4: Risk factors. Average results. European test at 7 °C

	Regulated risk factors before normalization					REG Risk	REG Risk	Unregulated risk factors before normalization.				UNREG Risk	UNREG Risk	Risk factor
	CO x 10^{-4}	HC x 10^{-4}	NMHC x 10^{-4}	NO_x x 10^{-4}	PM x 10^{-4}	Before norm	Normalized	Benzene	1.3-Butadiene	Formaldehyde	Acetaldehyde	Before norm	Normalized	Sum
MPFI car														
Fossil-b	0.34	0.26	4.09	1.22	3.4	9.3	1.2	0.23	0.15	0.00	0.00	0.4	0.7	1.9
Fossil(0)	0.37	0.24	3.81	1.09	2.5	8.0	1.0	0.29	0.22	0.00	0.00	0.5	1.0	2.0
E10(7)	0.30	0.24	3.74	1.44	3.5	9.2	1.2	0.31	0.24	0.00	0.01	0.6	1.1	2.2
iB(14)	0.24	0.23	3.54	1.61	5.2	10.8	1.4	0.28	0.42	0.01	0.00	0.7	1.4	2.7
R(14)	0.29	0.26	4.07	1.39	2.5	8.5	1.1	0.25	0.21	0.00	0.00	0.5	0.9	2.0
R+E(22)	0.32	0.25	3.78	1.35	2.8	8.5	1.1	0.27	0.17	0.00	0.01	0.5	0.9	2.0
R+iB(28)	0.28	0.18	4.00	1.61	4.3	10.4	1.3	0.29	0.18	0.00	0.00	0.5	0.9	2.1
R+eth(21)	0.38	0.24	3.64	1.06	3.1	8.4	1.1	0.25	0.11	0.00	0.01	0.4	0.7	1.8
FSI car														
Fossil-b	0.99	0.37	4.07	2.98	11.0	19.4	1.0	0.93	0.48	0.00	0.00	1.4	0.8	2.1
Fossil(0)	1.13	0.36	5.60	2.61	13.7	23.4	1.0	1.07	0.65	0.00	0.01	1.7	1.0	2.0
E10(7)	0.89	0.32	4.92	2.90	11.5	20.5	0.9	1.02	0.54	0.00	0.02	1.6	0.9	1.8
iB(14)	0.85	0.34	5.01	2.88	12.2	21.3	0.9	1.04	0.64	0.01	0.01	1.7	1.0	1.9
nB(15)	0.67	0.41	6.17	4.00	13.0	24.3	1.0	1.14	0.86	0.00	0.02	2.0	1.2	2.2
eth(7)	0.83	0.32	4.87	3.20	13.7	22.9	1.0	1.03	0.62	0.00	0.02	1.7	1.0	2.0
R(14)	0.96	0.39	5.83	3.05	15.2	25.4	1.1	1.06	0.41	0.00	0.01	1.5	0.9	1.9
R+E(22)	0.79	0.34	5.15	3.47	13.0	22.7	1.0	1.05	0.49	0.00	0.02	1.6	0.9	1.9
R+iB(29)	0.78	0.33	4.80	3.37	10.1	19.4	0.8	0.88	0.42	0.00	0.01	1.3	0.8	1.6
R+eth(21)	0.89	0.32	4.84	2.56	10.1	18.7	0.8	0.92	0.32	0.00	0.02	1.3	0.7	1.5
FFV car														
E85(56)	1.61	1.49	5.10	2.30	6.1	16.6	1.5	0.61	0.66	0.05	0.33	1.7	1.7	3.2
E30(20)	0.94	0.26	3.36	3.11	3.2	10.8	1.0	0.35	0.48	0.01	0.04	0.9	0.9	1.9
E+eth(19)	0.89	0.24	3.16	2.91	2.8	10.0	0.9	0.29	0.30	0.01	0.03	0.6	0.6	1.5
iB+eth(20)	0.70	0.19	2.68	3.67	7.5	14.7	1.3	0.23	0.59	0.02	0.01	0.9	0.9	2.2
iB(21)	0.70	0.20	2.75	3.21	2.8	9.7	0.9	0.26	0.71	0.02	0.00	1.0	1.0	1.9
Fossil-b	1.77	0.40	6.06	2.06	7.4	17.7	1.6	0.51	0.46	0.01	0.00	1.0	1.0	2.6
Fossil(0)	0.64	0.17	2.65	4.82	2.8	11.1	1.0	0.30	0.68	0.01	0.00	1.0	1.0	2.0
E10(7)	0.67	0.18	2.89	4.55	2.6	10.9	1.0	0.35	0.71	0.01	0.01	1.1	1.1	2.1
iB(14)	0.67	0.23	3.37	3.73	3.7	11.7	1.1	0.36	0.69	0.02	0.00	1.1	1.1	2.1
nB(15)	0.59	0.20	3.04	4.56	4.4	12.8	1.2	0.35	0.77	0.01	0.01	1.1	1.2	2.3
eth(7)	0.76	0.21	3.14	3.27	5.1	12.5	1.1	0.35	0.46	0.01	0.01	0.8	0.8	2.0
R(14)	0.66	0.22	3.33	4.20	3.7	12.1	1.1	0.34	0.51	0.01	0.00	0.9	0.9	2.0
R+E(22)	0.67	0.20	2.93	3.97	3.2	11.0	1.0	0.34	0.44	0.01	0.01	0.8	0.8	1.8
R+iB(29)	0.69	0.20	2.86	4.27	3.2	11.2	1.0	0.29	0.45	0.01	0.00	0.8	0.8	1.8
R+eth(21)	0.73	0.17	2.58	3.59	2.4	9.4	0.9	0.28	0.31	0.01	0.01	0.6	0.6	1.5

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