Report

Methanol blending in gasoline
– some Swedish Experiences

A report for the Swedish Transport Administration

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Ecotraffic

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1. Sammanfattning (Swedish Summary)

Metanol kan produceras från olika typer av råvaror och skulle potentiellt kunna bli en universell energibärare i framtiden, en råvara för framställning av olika kemikalier och möjligen också ett fordonsbränsle. Emellertid noterades det senaste intresset för metanol som fordonsbränsle världen över under senare delen av 1990-talet och i början av 1980-talet. Endast ett mer närliggande projekt med flottförsök av metanolfordon har genomförts sedan dess i Sverige. I dag verkar Kina vara den marknad där metanol har rönt störst intresse men endast begränsat intresse finns i andra länder.

Den mesta dokumentationen från de svenska projekten som genomfördes under den nämnda perioden finns på svenska och är inte enkelt tillgänglig utanför Sverige. Som ett bidrag till det svenska deltagandet i IEA AMF överenskommelsen fick Ecotraffic i uppdrag av Trafikverket att samla in och summera kunskaperna från de projekt som utförts på låginblandning av metanol i bensin under den perioden.

Efter en snabb genomgång av projekt som genomförts i Sverige på låginblandning av metanol kunde två projekt av störst intresse identifieras. Dessa var:

- De svenska M15 flottförsöken under 1980-talet
- ”INTROMET” projektet med M3E3 inblandning som genomfördes mellan 2003 och 2006

Eftersom M15 projektet genomfördes för så länge sedan har personer som medverkat intervjuats och/eller medverkat i datainsamling och analys av resultaten. Eftersom INTROMET projektet genomfördes betydligt senare än M15 projektet finns dokumentationen från det lättare tillgänglig och dessutom deltog en av författarna av föreliggande rapport i INTROMET. Som tillägg till de svenska projekten hittades också ett intressant norskt projekt på M15 i litteratursökningen. Närhelst det varit nödvändigt för bedömningen av olika effekter och problemställningar har författarna också samlat information från andra källor för att stödja den diskussion som förts i rapporten.

Som förväntats redan före projektet inleddes kunde välkända effekter av metanolinblandning i bensin också konstateras i de svenska projekten. Till exempel kunde, avseende reglerade emissionskomponenter, lägre CO, marginell inverkan på HC och i några fall ökade NO_X emissioner ses i de svenska projekten, liksom också dokumenterats i många andra studier. Bland de icke-reglerade emissionskomponenterna var ökning av formaldehyd och motsvarande minskning av acetaldehyd trender som kunde noteras med ökande metanolinnehåll i drivmedlet. Några hälsofarliga föreningar, som t.ex. lätta aromater, var ofta lägre med metanolblandad bensin. En påtaglig minskning av partikelemissionerna sågs i ett projekt och minskningen var approximativt linjär med metanolinnehållet. Ingen klar trend har setts för polycykliska aromatiska kolväten (PAH) men det ska också noteras att provtagning och analys av PAH inte var så välutvecklad på den tiden. En annan faktor var att basbensinen inte alltid var densamma. Flera PAH föreningar är antingen mutagena eller carcinogena och utgör således en hälsofara. I ett relativt nyligen genomfört projekt på E85 bilar kunde väldigt höga PAH emissioner vid kallstart och låg temperatur ses, medan ingen ökning kunde konstateras vid normal temperatur. En liknande ökning som för PAH kunde också ses för cancerrisken från avgaserna. Eftersom inga liknande tester har utförts på metanolblandningar i moderna fordon är det svårt att säga om samma problem kunde förväntas för metanol som för etanol. Icke desto mindre är en stor brist på kunskap uppenbar här.

Tillförlitligheten i projekten med låginblandning av metanol måste konstateras vara god. Få problem har noterats. Till exempel har risken för fasseparation under normala förhållanden inte kunnat manifesteras. Materialkompatibiliteten har oftast inte varit något problem. Inspekterade komponenter i motorer och bränslesystem har oftast varit i god kondition. Emellertid kan inte uteslutas att problem av den här arten kan uppstå för moderna bilar och/eller vissa bilmodeller. Detta vore speciellt riskabelt om inblandningshalten skulle ökas från den i dag tillåtna nivån på 3 % i EU.

Ifall metanol skulle introduceras på marknaden i större skala har ett antal områden där brist på kunskap finns identifierats i studien. Det finns generellt en brist på erfarenheter för moderna bilar som körs på metanolblandningar. Inblandningen maximeras till 3 % i dag i EU men man känner inte till ifall denna gräns faktiskt skulle kunna ökas utan modifieringar av fordonen. Kunskapsbrister har också identifierats avseende icke-reglerade missioner som skulle kunna innebära hälsorisker. Till exempel borde PAH emissioner vid låg temperatur och kanhända också under flera andra körförhållanden som inte omfattas av dagens testcykler också karakteriseras för moderna fordon.

En generell kommentar om de äldre svenska projekten är att det inte tycks finnas mycket av systematiskt tillvägagångssätt för alla projekt som genomförts när man ser på dem som en helhet. Naturligtvis har fokuseringen skiftat mycket från tid till annan, vilket är en del av förklaringen till den uppenbara bristen på systematik. Olika intressenter har påverkat inriktningen över tiden och det ska inte förbises att också den internationella fokuseringen, med säkerhet, har haft en inverkan också på den policy som gällt i Sverige genom åren.

Den bästa introduktionsstrategin för metanol bör också diskuteras. Det kan till exempel bli möjligt att använda de unika egenskaperna för metanol i dedikerade eller bränsleflexibla fordon för att uppnå förbättringar av effektiviteten på ett sätt som låginblandning inte kan åstadkomma. Samtidigt kunde en del av de problem som finns när det gäller icke-reglerade emissioner lösas genom att använda ny teknik. Sådana fördelar bör vägas mot den uppenbara enkelheten i att distribuera ett låginblandat bränsle som skulle kunna användas i dagens fordonsflotta.

Den enda farhågan för att introducera en storskalig inblandning av 3 % metanol kan vara den potentiellt negativa responsen från bilindustrin och möjligen, viljan hos oljeindustrin att introducera drivmedelen under dessa förhållanden. Författarna av föreliggande rapport tror inte att högre inblandning än 3 % kan tänkas bli framgångsrik inom den närmaste framtiden. Det är faktiskt möjligt att den praktiska gränsen kan vara något högre än 3 % även när oro för materialkompatibilitet finns. Det finns emellertid en brist på underlag för tillfället för att föreslå en maximal koncentration som är högre än 3 %. Vi antar att det skulle handla om en lång process för att etablera ett sådant drivmedel. Ett bättre alternativ kunde vara att introducera dedikerade fordon som använder högre metanolinblandningar (M85/M100) och som har någon form av bränsleflexibilitet, t.ex. så att de kan köras på bensin när metanolbränslete inte finns tillgängligt[1]. Sådana fordon skulle också kunna optimeras för både låga emissioner och hög effektivitet. Det är troligt att detta skulle kunna

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[1] När sådana metanoloptimerade fordon körs på bensin antas att effekt och vridmoment kan behöva minskas. Detta är inte fallet för dagens bränsleflexibla fordon. Exempelvis har dessa motorer samma kompressionsförhållande som sina bensinmotsvarigheter, vilket är långt from det optimala när alkoholbränslen används.

åstadkommas genom användning av avancerad teknik som direktinsprutning med högt tryck, turboöverladdning och avsevärd nedskalning av motorn. Som ett alternativ för att överbrygga tidsperioden tills sådana fordon finns tillgängliga är användningen av blandbränslen innehållande bensin, etanol och metanol (GEM fuels) en option som bör undersökas mer detaljerat. Sådana fordon finns i stort antal i dagens fordonsflottor, t.ex. i USA och Brasilien men också i Sverige och andra Europeiska länder till i viss omfattning.

2. Summary

Methanol can be produced from a variety of resources and could potentially become a universal energy carrier of the future, a feedstock for production of various chemicals and perhaps also a motor fuel. However, the last recent major interest in methanol as a motor fuel worldwide was during the late 1990´s and early 1980’s. Only one more recent project on field tests with methanol vehicles has been carried out since then in Sweden. Today, China appears to the market where methanol has gained most interest but little interest is seen in other countries.

Most of the documentation from the Swedish projects carried out during the mentioned period was in Swedish and is not readily accessible outside Sweden. As a contribution to the Swedish participation in the IEA AMF agreement, Ecotraffic was commissioned by the Swedish Transport Authority to collect and summarize the knowledge gained from the projects carried out on low-level blending of methanol in gasoline during that period.

After a quick survey of projects carried out in Sweden with low-level blending of methanol, two projects of main interest in this context could be identified. These were:

- The Swedish M15 fleet test in the 1980’s
- The “INTROMET” project with M3E3 blending carried out in 2003 to 2006

Since the M15 project was carried out such a long time ago, persons directly involved have been interviewed and/or have participated in the data collection and analysis of the results. Since the INTROMET project is more recent than the M15 project, this documentation is readily available and, in addition, one of the authors of the present report participated in INTROMET. In addition to the Swedish projects an interesting Norwegian project on M15 was also found in the literature search. Whenever necessary for the assessment of various effects and issues, the authors have also collected information from other sources to support the discussion conducted in the report.

As expected already before the project started, well-known impacts of methanol blending in gasoline on emissions could be found also in the Swedish projects. For example, regarding regulated emission components, lower CO emissions, only marginal impact on HC and in some cases increased NO_X emissions seen in the Swedish projects have also been documented in many other studies. Among unregulated emission components, an increase in formaldehyde and a corresponding decrease in acetaldehyde emissions were trends seen with increasing methanol content in the fuel. Some air toxics, such as, e.g. light aromatics, were often somewhat lower for methanol blended gasoline. A substantial decrease in particulate emissions was seen in one project and the decrease was approximately linear with the methanol content. No clear trend has been seen for polycyclic aromatic hydrocarbons (PAH) but it should also be noted that sampling and analysis of PAH was not very well developed in those days. Another factor was that the base gasoline fuel was not always similar. Several PAH compounds are either mutagenic or carcinogenic and thus, pose a significant health hazard. In a relatively recent project on E85 cars, very high PAH emissions were seen during cold starts at low ambient conditions, whereas no increase was seen at normal temperature. PAH increased with increasing ethanol content. A similar increase as for PAH was also seen for the cancer potency from the exhaust. Since no similar tests have been conducted on methanol blends on modern vehicles, it is difficult to say if the same problem could be expected for methanol as for ethanol. Nevertheless, a significant gap in knowledge is apparent here.

The reliability in the projects with low-level blending on methanol should be considered good. Few problems have been experienced. For example, the fear for phase separation under normal conditions has not been manifested. Material compatibility has generally not been an issue. Inspected engine and fuel system components have mostly been in good condition. However, this does not exclude that problems of this kind would not occur on modern cars and/or at certain car models. This would be of particular concern if the blending level would be raised from the current level of 3 % allowed in the EU.

If methanol would be introduced on the market in a larger scale, a couple of areas where gaps in knowledge exist have been identified in this study. There is generally a lack of experience in running modern cars on methanol blends. Blending is maximised to 3 % in EU today but it is not known if the practical limit could, in fact, be raised without any vehicle modifications. Gaps in knowledge have also been identified regarding unregulated emissions that could pose a health hazard. For example, PAH emissions at low temperature and perhaps also in several other driving conditions not covered by current certification test cycles should be characterized on modern vehicles.

A general remark about the old Swedish projects is that there does not seem to be much of a systematic approach in all the projects carried out if these are looked at as a whole. Obviously, there has been much shift in focus from time to time, which is part of the explanation to the apparent lack of consistency. Various stakeholders have influenced the focus over time and it should not be neglected that also the international focus has, for sure, had an impact also on Swedish policies over the years.

The best introduction strategy of methanol should also be discussed. For example, it might be possible to utilize the unique properties of methanol in dedicated or flexible-fuel vehicles to gain significant improvements in efficiency in a way that low-level blending cannot achieve. At the same time, some of the problems regarding unregulated emissions could be solved by using new technology. Such benefits should be weighed against the apparent simplicity of distributing a blended fuel that could be used in current vehicle fleets.

The only concern for introducing blending with 3 % methanol on a large scale might be the potentially negative response from the auto industry and perhaps, the willingness of the oil industry to introduce this fuel under those conditions. The authors of this report do not believe that higher blending level than 3 % methanol would be likely to succeed in the near future. It is quite possible that the practical limit could be somewhat higher than 3 % even when material compatibility is of concern. However, there is lack of evidence for the moment to suggest a maximum possible concentration higher than 3 %. We presume that it would be a long process to establish such a fuel. A better alternative could be to introduce dedicated vehicles operating on high-level methanol blends (M85/M100), which possess some kind of fuel flexibility, i.e. that they could also run on gasoline when the methanol fuel is not available[2]. Such vehicles could also be optimized for both low emissions and high efficiency. It is likely that this could be accomplished via the use of advanced

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[2] When such methanol-optimized vehicles are operated on gasoline, it is anticipated that the power and torque may have to be reduced. For current fuel-flexible vehicles, this is not the case. For example, these engines usually have the same compression ratio as their gasoline counterparts, which is far from optimum when alcohol fuels are used.

technology such as high-pressure direct injection, turbocharging and significant downsizing. As an alternative to bridge the gap until such vehicles could be commercially available, gasoline/ethanol/methanol (GEM) fuels used in conventional E85 cars is an option that should be investigated in more detail. Large numbers of such vehicles are available in the current vehicle fleet, e.g. the USA and Brazil but also in Sweden and some other European countries to some extent.

3. Project information

Commissioned by:	The Swedish Tra	**Order No.**	
Date of commission	2012-12-05	**Due date**	2013-05-31
Ref. at commissioner	Magnus Lindgren	**Project No.**	6050
Respons. at Ecotraffic	Lars Eriksson	**Presentation**	
Discrepancies			
Linguistic approval		**Report approval**	Börje Gevert
Report No.	136050	**Date of report**	
Authors	Peter Ahlvik and Lars Eriksson		

4. Abbreviations and nomenclature

Some abbreviations and nomenclature used in the report or else, or relevant to the topics covered, is listed below.

1,3-C_4H_6	1,3-butadiene
A/F	Air/Fuel ratio
ACEA	European Automobile Manufacturers Association
AM	Artemis Motorway: the Artemis motorway driving cycle
AR	Artemis Road: the Artemis road, or “rural” driving cycle
AU	Artemis Urban: the Artemis urban driving cycle
B(a)P	Benzo(a)pyrene
BFV	Bi-Fuel Vehicle
BMEP	Brake mean effective pressure
C_2H_4	Ethene
C_3H_6	propene
C_6H_6	Benzene
C_7H_8	Toluene
CADC	Common Artemis Driving Cycle
CARB	California Air Resources Board
CH_4	Methane
CNC	Condensation Nuclei Counter (equivalent to CPC)
CNG	Compressed Natural Gas
CO_2	Carbon dioxide
CONCAWE	Conservation of Clean Air and Water in Europe, the oil companies’ European association for environment, health and safety in refining and distribution
CPC	Condensation Particle Counter (equivalent to CNC)
CVS	Constant Volume Sampler/Sampling, a dilution device used for dilution of engine/vehicle exhaust for emission measurements.
DI	Direct Injection
DISI	Direct Injection Spark Ignition
DMA	Differential Mobility Analyzer
DME	Di-methyl ether, the simplest ether
DMM	Dekati Mass Monitor, an instrument (Dekati Ltd. in Finland) for measuring (indirectly) particle mass in real time
DOE	U.S. Department of Energy
DPF	Diesel Particle Filter

E10	Gasoline blended with 10 % ethanol
E100	Pure ethanol fuel (possibly blended with some denaturant and small doses of other additives)
E15	Gasoline blended with 15 % ethanol
E20	Gasoline blended with 20 % ethanol
E3	Gasoline blended with 3 % ethanol
E5	Gasoline blended with 5 % ethanol
E70	Ethanol blended with 70 % gasoline
E75	Ethanol blended with 25 % gasoline
E85	Ethanol blended with 15 % gasoline
ECU	Electronic Control Unit
EGR	Exhaust Gas Recirculation
ELPI	Electrical Low Pressure Impactor, an instrument (Dekati Ltd. in Finland) that measures particle number and particle size distribution according to their aerodynamic size in real time
EPA	Environmental Protection Agency (USA)
ESFE	Energy-Specific Fuel Economy
EtOH	Short for ethanol
EUCAR	European Council for Automotive R&D, the automotive manufacturer's association for research and development in Europe
EUDC	Extra Urban Driving Cycle, the second part of the European driving cycle
Euro X	Emission limits in the EU, e.g. Euro 1, Euro 2, etc...
FAME	Fatty Acid Methyl Esters
FFV	Fuel-Flexible Vehicle
FSI	Fuel Stratified Injection, i.e. VW nomenclature for gasoline-fuelled engines with stratified air/fuel mixture using direct injection (DI) late in the compression stroke.
GC-MS	Gas Chromatography Mass Spectrometry
GEM	Gasoline, Ethanol and Methanol fuel blends.
GMP	GM Powertrain
HC	Hydrocarbon
HPLC	High Performance Liquid Chromatography
IDI	Indirect injection
JRC	The Joint Research Centre, a research based policy support organisation and an integral part of the European Commission.
LC-GC-MS	Liquid Chromatography- Gas chromatography Mass Spectrometry

LD	Light-duty
LPG	Liquefied Petroleum Gas
KLSA	Knock-Limited Spark-Advance
m.v.	Missing value
M100	Pure methanol fuel (possibly blended with some denaturant and small doses of other additives)
M15	Gasoline blended with 15 % methanol
M20	Gasoline blended with 20 % methanol
M3	Gasoline blended with 3 % methanol
M30	Gasoline blended with 30 % methanol
M3E3	Gasoline blended with 3 % methanol and 3 % ethanol
M85	Methanol blended with 15 % gasoline
MBT	Maximum Brake Torque: The spark advance that gives the highest torque for a given throttle position and speed.
MeOH	Short for methanol
MON	Motor Octane Number. The resistance to knock at high engine speeds. See also the abbreviation RON below.
MPG, mpg	Miles per gallon
MPI	Multi Point Injection
Mw	Molecular weight
n.r.	Not regulated
N_2O	Nitrous oxide
Nanoparticle	A particle smaller than 50 nm. Slightly different definitions (of size) are also used.
NEDC	New European Driving Cycle
NG	Natural Gas
NGV	Natural Gas Vehicle
NMHC	Non-Methane Hydrocarbon
NMHCE	Non-Methane Hydrocarbon Equivalent. When alcohol fuels are used, oxygenated compounds in the exhaust are present.
NMOG	Non-Methane Organic Gases
NO	Nitrogen monoxide (commonly referred to as nitrogen oxide)
NO_2	Nitrogen dioxide
NO_X	Oxides of nitrogen
OMHCE	Organic Matter Hydrocarbon Equivalent
PAH	Polycyclic Aromatic Hydrocarbons
PM	Particulate Matter
PMP	Particulate Measurement Program (the EU programme for developing new measurement methods for particle mass and number)

$\text{ppm}_{v/v}$	parts per million by volume
$\text{ppm}_{w/w}$	parts per million by weight
PUF	Poly Urethane Foam. Plugs of PUF are used for PAH sampling.
RFG	Reformulated Gasoline (petrol)
RON	Research Octane Number. Knock resistance of motor fuels at low engine speed. See also the abbreviation MON above.
RVP	Reid Vapour pressure
SAE	Society of Automotive Engineers
SHED	Sealed Housing for Evaporative Determination
SI	Spark Ignition
SIF	Soluble Inorganic Fraction
SDAB	Swedish Motor Fuel Technology Co.
SMAB	Swedish Methanol Development Co.
SMPS	Scanning Mobility Particle Sizer
SO_2	Sulphur dioxide
SO_3	Sulphur trioxide
SOF	Soluble Organic Fraction
SR	Specific Reactivity
TEF	Toxic Equivalence Factor
TFSI	VW nomenclature for gasoline-fuelled engines with turbocharger and direct injection (DI).
THC	Total HydroCarbon emissions. HydroCarbon (HC) emissions including methane
THCE	Similar as OMHCE, see above.
TWC	Three Way Catalyst
UDC	Urban Driving Cycle, the first part of the European driving cycle
ULEV	Ultra-Low Emission Vehicle, a nomenclature for vehicles that can fulfil very low emission limits within the California Low Emission Vehicle standards (LEV). The ULEV limits were updated (LEV II) in November 5, 1998. These standards cover the period from 2004 to 2010.
UN ECE	United Nations Economic Commission for Europe
US EPA	United States Environmental Protection Agency
VOF	Volatile Organic Fraction

5. Introduction

During recent years, there has been much debate about energy supply and energy security. It is obvious that the supply of oil and natural gas from conventional sources is diminishing. There might be some consensus about the limitation of the resources but there is yet no consensus about when this will happen. Several studies in this field have been carried out by a research group in the University of Uppsala in Sweden. Some researches from this group are also active in the Association for study of Peak Oil, ASPO (ASPO, 2012).

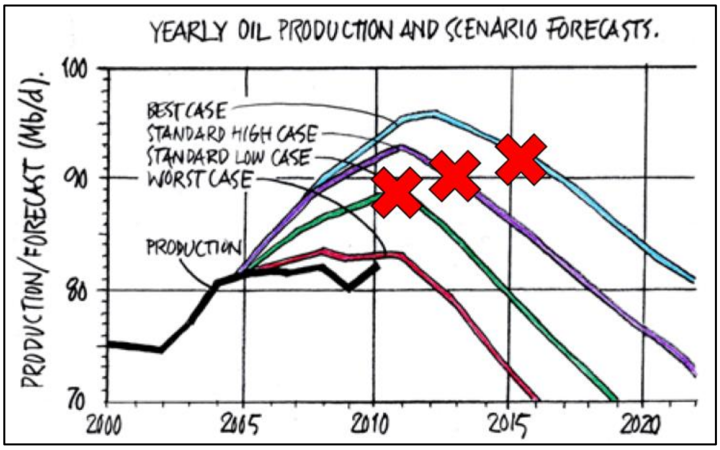

Figure 1. Peak oil scenarios according to ASPO (Aleklett, 2012)

In Figure 1, an example of a couple of scenarios for oil production is shown (Aleklett, 2012). As this is not the topic of this report, we will not comment on the results as such but we will just conclude that the findings of this research group, if they are valid, indicate that peak oil will occur very soon, or might even have occurred already. In view of this, alternatives to our conventional fuels have to be found.

As the supply of oil and gas might be decreasing in the future and, at the same time, the economy is booming in many countries in the Far East and Africa, a shortage in the supply of oil products could be an urgent situation in the near future. Substitutes would have to be found, since it is not likely that increased efficiency and curbing traffic growth would compensate for a decline in oil production. Several biofuels and alternative fossil fuel candidates have been suggested for this substitution. Methanol is one of these alternatives, albeit not the candidate of main interest worldwide for the moment. China is one of the exceptions in this case, since already a significant use of methanol has developed over the last couple of years.

Project background

While the increase in demand for automotive fuels in the West seem to be somewhat offset by improved efficiency, the increase in the booming markets in Asia and Africa appears to accelerate. China is one of the fastest growing markets in the world regarding transportation and fuels and it is already one of the largest in the world. An example of the growth of vehicle population and fuel use in China is shown in Figure 2 (CATARC, 2012).

With the discussion about Peak Oil in the previous section and the rapid growth in China in mind, it is not surprising that China has been looking for alternative fuels to substitute for conventional oil. Since a couple of years, the use of methanol has been gradually increasing on the Chinese market (Chi-Jen Yang et al., 2012). This development has been promoted by the Chinese government. In Figure 3, the growth of methanol production and demand in China is shown (Chi-Jen Yang et al., 2012).

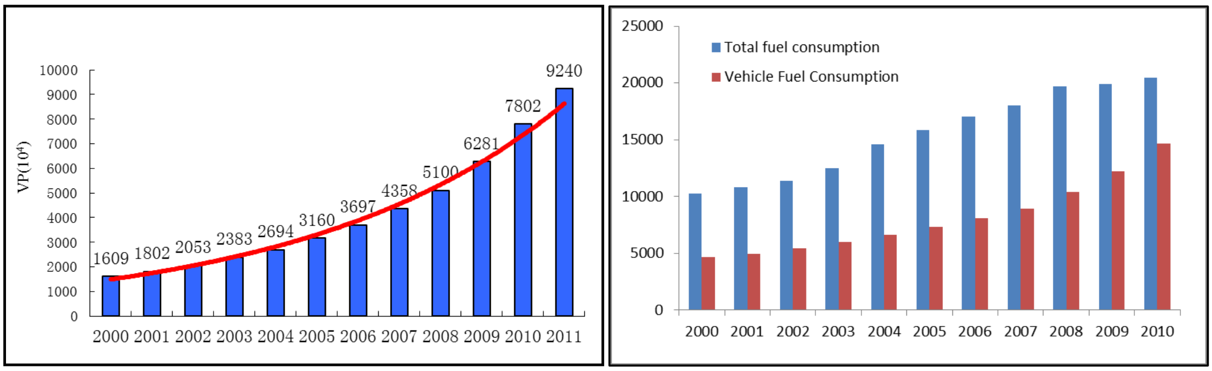

Figure 2. a) China´s vehicle population and b) Fuel consumption (CATARC, 2012)

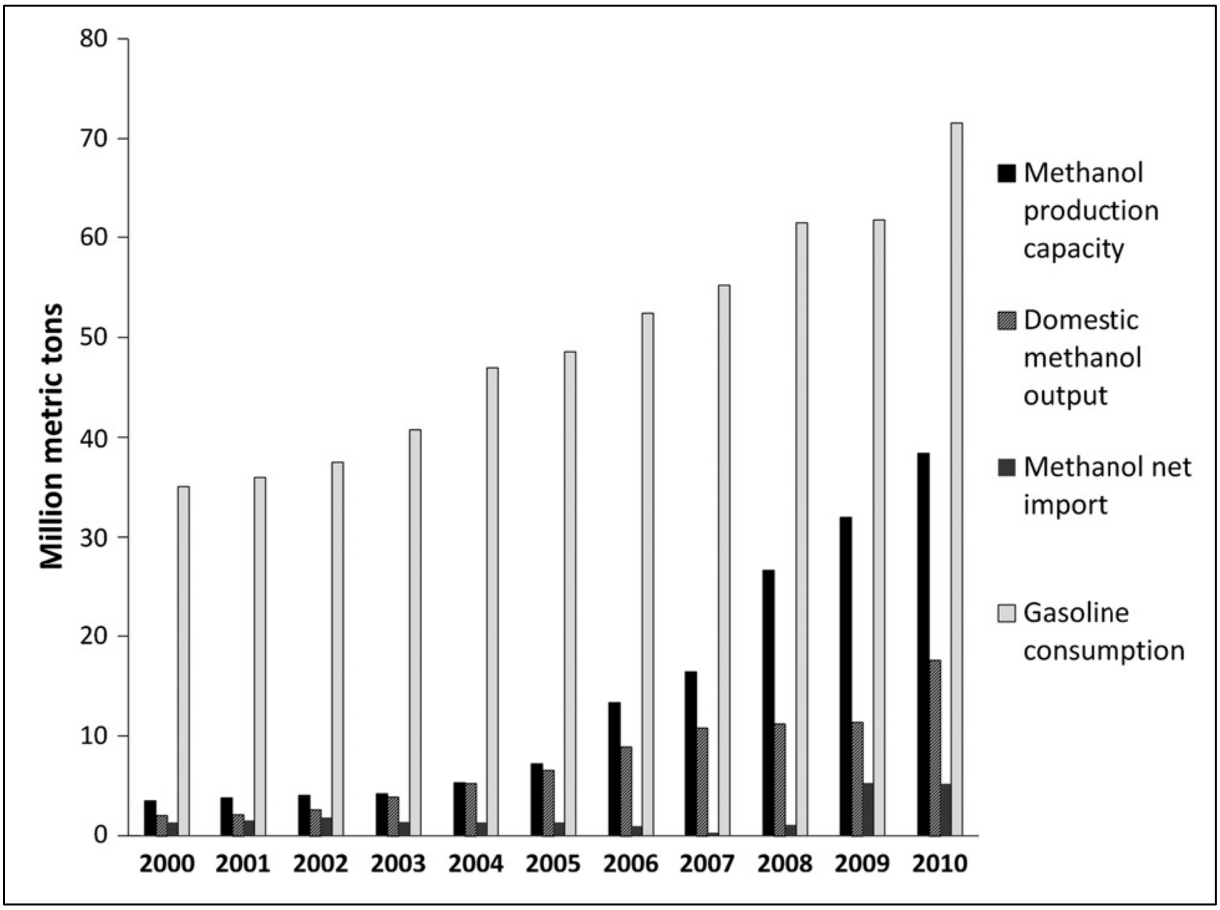

Figure 3. Growth of methanol production and demand in China (Chi-Jen Yang et al., 2012)

As Figure 3 shows, the growth of methanol production capacity in China has been rapid. Methanol from coal dominated the domestic production, which has several implications to be discussed in later sections of this report.

As a side note, it could be mentioned that one of the authors of this report (Ahlvik) visited China in 2008 for participation in the 17th ISAF Symposium (International Symposium on Alcohol Fuels) in Taiyuan. Within the framework of the ISAF Symposium, the use of methanol was discussed separately from the symposia topics in expert committees and visits to methanol fuelling stations was organised by ISAF. This “practical” experience of the mentioned author has been useful in the current work.

Within the framework of the International Energy Agency (IEA) co-operation, the Advanced Motor Fuel (AMF) is one of the Implementing Agreements in the field of transportation. The work within AMF is carried out in various Annexes (active projects). Annex 44 has the title: “Research on Unregulated Pollutants Emissions of Vehicles Fuelled with Alcohol Alternative Fuels.” Annex 44 is chaired by the China Automotive Technology & Research Center, CATARC (CATARC, 2012). Participation is via cost and/or task sharing. The work reported here is a task sharing contribution funded by the Swedish Transport Administration (STA). The main focus is on low-level blending of methanol in gasoline but other aspects of relevance to long-term introduction of methanol are also discussed. An objective is also that the work reported here should be of use for STA in other work, for example, regarding topics of relevance for the European Commission.

The main objective has been to collect and assess knowledge, mainly from projects in Sweden, regarding low-level blending of methanol in gasoline. To limit the scope of work, the focus has mainly been on the use of methanol in “pure” form, i.e. not as ethers (e.g. MTBE) but potentially with a co-solvent and other additives to avoid phase separation. A favoured co-solvent could be ethanol but other alternatives are also possible. Blending (or emulsion) of methanol in diesel fuel has not been studied.

Fuel-flexible vehicles (e.g. M85) or dedicated alcohol vehicles (e.g. M100) are not of major interest in the present study, although some conclusions might be drawn from experiences gained from such vehicles and their ethanol counterparts (E85/E100). The level of methanol blending considered in this project is quite wide. The starting point is at a few per cent with a maximum of up to some 25 %. The wide range – and the upper end in particular – is considered simply because an upper level has been considered in some countries, e.g. ethanol in Brazil and methanol in China (in fact, up to 30 % in this case). Another example is that raising the limit for ethanol blending in the USA up to 15 % is under discussion. Parallels between ethanol and methanol can sometimes be drawn but it is not obvious that such high blending levels could also be practical – or even possible with current or near-term vehicle fleets – with methanol as a blending component. Most likely, the technical and practical limit for methanol blending leads to considerably lower maximum levels than those mentioned. Many legislative barriers would also prevent this on the near-term horizon. However, an open mind is kept in this study and potential problems and barriers are noted with identification of potential solutions, wherever possible.

With few exceptions, the automotive and oil industry have mostly been sceptical to methanol during the last 2-3 decades. The current EU specification for gasoline fuel allows a maximum methanol content of 3%. This level has been present in the past as well. It is plausible that this option has been used by some oil companies in Europe from time to time when the price of methanol has been favourable compared to gasoline prices. However, this use of methanol has seldom been discussed in public and any documentation of the volumes used is not known to the authors of this report. If the interest in methanol as a motor fuel has been low among oil companies, the automotive industry has mostly been even more sceptical. One example is the so-called “World-Wide Fuel Charter, a proposed fuel specification by the organizations of automotive and engine manufacturers in EU, Japan and the USA. In the four versions of this document published so far, blending of methanol is dismissed via the footnote: “methanol is not permitted”. When the main body of this report was written (end of May 2013), the final version of the 5th edition was only available as a draft but it was released in September 2013 (ACEA, AAM, EMA and JAMA, 2013). Nevertheless, the same comments about methanol as in previous versions were still remaining in the 5th version. If the specification proposed in the mentioned documents would be implemented in the legislation worldwide, it would effectively ban the use of methanol as a blending component in gasoline. With this background it is also very difficult to envision that higher limits than the current 3 % would generally be permitted in gasoline – at least in the foreseeable future. However, it is not unlikely either that some markets – for example China – could go forward by allowing higher blending levels of methanol in the general gasoline specification. If this would also happen on other markets, we speculate that it would initially have to be through exemptions for field trials, via waivers or similar measures. In any case, both the auto and the oil industry would have to adapt to such mentioned changes and it will certainly be interesting to follow the debate about this and see how it would evolve in the future. For the time being, though, we have to admit that we do not see much of this development elsewhere and, besides China; it is not very likely to happen in any other region in the near future.

The commission

On the background of the IEA/AMF project mentioned and from a general interest in alternative fuels, STA commissioned Ecotraffic to carry out a study to collect and assess Swedish experiences in the field of low-level blending of methanol in gasoline fuel.

The overall scope of the project has been to address the following topics:

- Collect and compile knowledge about unregulated emissions
- Investigate available measurement methods for unregulated emission components
- Impact of various factors such as e.g.:
  - Measurement methods (GC-MS, HPLC, FTIR)
  - Engine technology
  - Ambient temperatures
  - Test cycles
  - etc…

After a quick survey of projects carried out in Sweden with low-level blending of methanol, two projects of main could be identified. These were:

- The Swedish M15 fleet test in the 1980’s
- The INTROMET project with M3E3 blending carried out in 2003 to 2006

It should be recognized that relatively little has been published in English from these projects. Thus, the results are probably not well-known and recognized by the technical/scientific community outside Sweden.

Since the M15 project was carried out such a long time ago, persons directly involved have been interviewed and/or have participated in the data collection and analysis of the results. In this context it should be mentioned that Anders Laveskog has been our best source of knowledge, help in finding these old reports and also in assessing the results from the projects (Laveskog A. , 2013). Laveskog has also been involved in many other similar projects in this field that we discuss below.

As the INTROMET project is more recent than the M15 project, this documentation is readily available and, in addition, one of the authors of this project participated in INTROMET.

In addition to the Swedish projects, an interesting Norwegian project on M15 was also found in the literature search.

In addition to the mentioned projects, some other Swedish projects of relevance have also been selected for discussion. These cover low-level blending of methanol and/or ethanol in gasoline or unregulated emissions from E85 vehicles. Although conclusions from ethanol blending or E85 cannot be directly applied on methanol, some general observations regarding unregulated emissions could be of interest and thus, some of these are commented in the present report. Likewise, indicative gaps of knowledge for methanol blending could be found by assessing these data.

Due to the scope and focus on Swedish projects, no comprehensive literature search was carried out in this project. However, a quick search in the database of the US SAE was nevertheless carried out to identify recent publications and some older ones of relevance to the project. Among these publications, the selection of publications to comment in this project has been very restrictive, implying that only very few of those found have been cited. In many cases, there are additional references with important information but the highlighted ones are exemplified just to illustrate a specific issue or since they can contribute with important knowledge on specific topics.

6. Historic development of methanol as a motor fuel

Early development

The potential use of alcohols as motor fuels has been recognized almost as long as the internal combustion engine (ICE) itself has been used. While coal was not as well-suited fuel for ICEs, as for steam engines that proceeded them, early development of ICEs such as by e.g. Jean Joseph Étienne Lenoir, Nikolaus August Otto and others, tested what we would consider as a gaseous fuels today (i.e. coal gas). Alcohols were also tried in ICEs in the early days, e.g. by N. Otto, until finally; gasoline became the preferred fuel for otto engines. Later, similar development of the diesel engine led to the use of another petroleum derivative, which today is referred to as “diesel fuel”, became the preferred fuel for diesel engines[3].

While ethanol was the most commonly used alcohol fuel in ICEs during the early days, methanol was also recognized for having similar properties. However, while ethanol could easily be produced via fermentation, the only production method for methanol in those days was via pyrolysis of wood, where methanol was one of the by-products of the process. Production volumes of methanol from these processes were generally low and so was the percentage of energy from the process represented by methanol. We could consider that the development of the market for methanol as a motor fuel worldwide started with the shortage of motor fuels during the First World War. Likewise, the use of methanol has received attention primarily during periods when shortage of fuel has been on the agenda. Two such periods besides WWI were the Second World War and the first oil crisis during the 1970´s. It remains to be seen if the anticipated future oil shortage due to Peak Oil will again spur the interest in methanol as a motor fuel and/or as a chemical feedstock (which is and additional use that is of greater importance today than in the past).

Methanol during the oil crisis and later

Besides the brief interest for methanol during WWI and WWII, the interest increased again during the oil crisis of the 1970’s. After the initial hype, one could say that the interest for methanol continued for a couple of years after the oil crisis but started to decline rapidly in the 1990´s. If we exclude Liquefied Petroleum Gas (LPG) that has been used extensively as an alternative fuel for a very long time, particularly on some specific markets and in niche applications (e.g. fork-lift trucks) on other markets, one could point out that methanol was the first alternative fuel to be seriously considered in modern times (i.e. during the last 50 years). Much of the activities in the 1970´s and 1980´s were in the form of blending, e.g. M15 (15 % methanol and 85 % gasoline). However, dedicated methanol vehicles, i.e. M100, but also high-level blends, such as M85, were of interest. For example, there was a considerable introduction of cars running on M85 in the USA and some other countries during late 1980´s and early 1990´s. Some 50 of these vehicles (i.e. Ford Taurus, gen 1)

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[3] In a wider definition, diesel fuel does not necessarily have to be a petroleum-based fuel intended for diesel engines. It is a common misconception that a diesel engine is defined as an engine running on diesel fuel. Rather the diesel engine was first conceived and later the denotation “diesel fuel” was given to the middle distillate fuel that was so well-suited for this engine. Using a wider definition of “diesel fuel”, e.g. methanol with an ignition improver could also be considered as a “diesel fuel”, since a diesel engine using compression ignition could run on this fuel with minor modifications.

were actually imported to Sweden as part of a common purchase but the vehicles were operated on E85 instead of M85[4].

Recent interest in methanol

While methanol has been of interest as a motor fuel from time to time during the last 100 years, there has been only one brief period of renewed interest since the early 1990´s. This was when the interest for fuel cells in vehicles started to increase in the late 1990's. However, the interest faded quickly at about the year 2000. Since then, hydrogen has been the favoured fuel option for fuel cell vehicles. In spite of this apparent lack of interest, methanol has some interesting properties for fuel cell vehicles. Methanol can be relatively easily reformed to hydrogen and since hydrogen distribution and storage poses so many practical problems, methanol could be a simpler solution. The fuel reformer could be mounted on-board the vehicle but also off-board solutions, such as at the refuelling station could be anticipated. In the latter case, hydrogen would still be the energy carrier in the vehicle, i.e. only the favourable properties of fuel distribution of methanol would be utilized. In addition, fuel cells using methanol directly (DMFC) could be an option on a more distant timeframe. Apparently, this mentioned renewed interest in methanol faded after only a few years due to relatively unclear reasons but some may be identified. First, the lack of interest could be linked to the fact that no large scale introduction of fuel cell vehicles has yet been made. Second, for local fleets, the issues of hydrogen distribution and re-fuelling can be handled. For a large-scale introduction, however, methanol could again be of interest. Third, for the DMFC option, the lack of interest is logical, since the necessary technical breakthroughs have not yet been made. Thus, this option is not competitive at all for the moment.

The interest in methanol as a motor fuel in China and the corresponding production of methanol was already discussed in the Introduction chapter and will not be commented again here. Besides these activities, there have been relatively few activities worldwide and only a handful in Europe. Project proposals for methanol (or methanol/di-methyl ether, DME) plants using forest residue or black liquor from pulp and paper production as feedstocks have been made by (Chemrec, 2013) and Värmlandsmetanol[5] (Värmlandsmetanol, 2013) in Sweden. So far, none of these projects have secured the necessary fundings for building a plant. Another example worth noting is the Dutch company BioMCN, who actually produces methanol from non-fossil feedstock today (BioMCN, 2013). The methanol produced is mainly used for low-level blending in gasoline. Plans for a considerable increase of the methanol production are discussed. Since production of methanol was beyond the scope of the three mentioned projects, they are not further commented on in this report. We can only conclude that if plants would be erected, potential issues regarding the utilization of methanol would have to be solved. On a smaller scale, blending up to the current EU limit of 3 % might provide an opportunity to launch considerable quantities of methanol on the market but on a longer term horizon, some kind of introduction strategy would be necessary. Companies that try to launch larger quantities of methanol on the market would sooner or later have to face these obstacles.

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[4] While these vehicles were optimized for M85, a later version of the car (Ford Taurus gen 2) was optimized for E85.

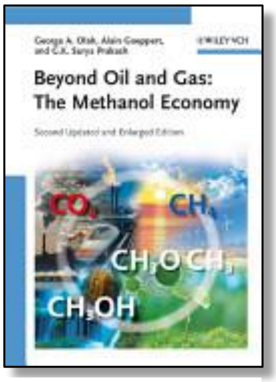
[5] The English translation of the Swedish project title would be: "Methanol in the county of Värmland".

In summary, there has been a great variation of the interest in methanol as a motor fuel in the Western World over the years. Obviously, the interest seems have been linked to fuel shortage in some way. The number of SAE papers from 1990 to 2006 found in the SAE GMD database indicates how the interest that has been manifested by the number of relevant SAE publications about methanol (Ahlvik & Eriksson, 2006). No update of this literature survey has been made in this study but a quick search in the SAE database has shown only a handful of papers during the last year were found, with one from CATARC and Tsinghua University among them (Fan Zhang et al., 2013). The low number of publications during the last couple of years clearly illustrates that the interest in methanol today is very low.

7. Fundamental properties of methanol as a motor fuel

This chapter cover some of the fundamental properties of methanol but also some of the topics that are the main scope of this project.

Methanol as an energy carrier



Picture 1

While the development during the last couple of years have shown little interest for methanol as a motor fuel, there are advocates for using methanol on a more distant future. One example is the 1994 Nobel-Prize winner George Olah, who has proposed the so-called “methanol economy”. This is in analogy with the “hydrogen economy” where hydrogen would be the main energy carrier of the future. In a thought-provoking book published in 2006, the pros and cons for a methanol economy (vs. a hydrogen economy) were outlined by Olah et al. (George A. Olah et al., 2006). The book does not only cover motor fuels but also the use of methanol as a feedstock for various chemicals that are currently derived from crude oil or natural gas. These chemicals would also have to be replaced somehow when oil and gas resources are diminishing and are almost as important for the society as motor fuels. Olah et al. points out the great feedstock and energy base for producing methanol. This includes the use of fission/fusion, albeit not via electricity generation but via a thermal/chemical cycle, and synthetizing methanol using CO_2 from power plants and the atmosphere.

While winning a Nobel Prize does not necessarily imply that a researcher is correct in all aspects of his opinions, it is still quite possible that methanol could become an important energy carrier and chemical feedstock in the long-term future. The first question is when and the second is if this would include methanol as a motor fuel? The logical follow-up question would be: how? As discussed in the Introduction chapter in the present report, there is currently only one major market for methanol as a motor fuel, i.e. China, and no apparent activities aim for a large-scale introduction on any other market. Today, methanol has a significant role as a chemical and as feedstock for producing polymers, glues, resins and many chemicals. This chemical industry is already largely based on methanol in China, whereas other feedstocks are mostly used outside China. It remains to be seen if methanol also could assume the role as a major energy carrier around the world and, as such, also a motor fuel.

While methanol could be produced from a variety of feedstocks and energy sources, this does not necessarily imply that all would have a small carbon footprint. In analysing the drawbacks, one obvious negative aspect concerning emissions of greenhouse gases would be if methanol is produced from coal. Some of these aspects were discussed in the paper by Chi-Jen Yang et al. (Chi-Jen Yang et al., 2012).

Methanol properties

General

Methanol is the simplest alcohol in its molecular structure and can be used in both pure form and as a blend with gasoline (e.g. M3 to M85).

Gasoline distributed to and sold at service stations normally contains 100 up to 200 ppm of water, dispersed and not visible (SMAB, 1976). Chemical grade of methanol transported on the sea is guaranteed to contain less than 350 ppm of water (SMAB, 1976).

In Table 1, the most important physical and chemical properties for M100/M85 and some other relevant fuels have been summarised and in Table 2 and Table 3, some additional properties for M85 and M100 are listed. Table 1 below has been compiled using a number of different sources. Some of them are national and/or corresponding EU standards (SIS (Swedish Standards Institute), 2001); (SIS (Swedish Standards Institute), 2000), a number of SAE papers (Machiele P. , 1987); (Machiele P. , 1990) and (R. H. Vaivads et al., 1995) and a report by the Methanol Fuel Cell Alliance (MFCA) (MFCA, 2003). Since the sources are of different origin, minor differences in comparison to the case for variation of fuel properties on a local base might exist. Note that the diesel fuel in Table 1 is Swedish Environmental Class 1 (EC 1) diesel fuel and not a diesel fuel corresponding to the European standard EN 590. Anyway, the fuel properties of interest in this case are not decisively different between the two diesel fuel qualities.

Table 1. Important physical and chemical properties for some fuels

Fuel property	Unit	Ethanol E100	E85[a]	Methanol M100	M85	Gasoline	Diesel EC 1
Density, liquid	Kg/m^3	794	765 - 785	795	780	720 – 775	800 – 820
Density (vapour)	Rel. air	1,6	> 1			3-4	5-6
Boiling point	°C	78,5	25 - 205	64,7	25 - 215	25 – 205	180 – ca305
Conductivity	cu	140 000	as E100	30 000 000	30 000 000	3 - 10	50 – 100
Vapour pressure	kPa	17	40 – 50[b]			45 - 95	0.4
Flash point	°C	12	< - 30	11	- 36	< - 40	56 (60)[c]
Flammability range fuel vapour in air	%	3,3 - 19	1,4 - < 19	6,0 – 36,5	2 – 34	1 - 8	0,6 – 7,5
Flammability range, sum[d] winter[d]	°C	12 to 40	-35 to +5 -35 to -5[e]	10 to 40	- 40 to + 23	- 40 to -10 -45 to -20	50 -
Autoignition temperature	°C	425	360	465	385 - 480	250 – 280	220 – 316
Stoichiometric air/fuel ratio	kg/kg	9,0	10			14,6	14,8
Heat of vaporisation	kJ/kg	910	850	1100	1044	335	251
Energy of combustion	kWh/lit	5,9	6,3			9,1	9,8
Energy of combustion, LHV	MJ/lit	21,2	22,7			32,8	35,3
Flame spread rate	m/s	2 - 4	3 - 5	2 - 4	3 – 5	4 - 6	0,02 – 0,08
Diffusion coefficient	cm^2/h	293		465	372	186	251
Pool burn rate	Mm/min			1,7		7,3	4,0
Energy of ignition[f]	mJ	0,14 – 0,24	~ gasoline	0,14 – 0,22	0,14 – 0,24	0,20 – 0,24	0,20 – 0,24

a) A new standard for E85 has just recently been enforced in Sweden. The data for a fuel corresponding to this standard might slightly deviate from the data presented here.

b) The interval is due to the difference between summer and winter qualities of E85 according to the Canadian study cited.

c) The demand for marine applications is 60°C

d) The values of the end points are dependent on a variety of factors as, tank fill level, changing fuel composition due to "tank breathing", etc.

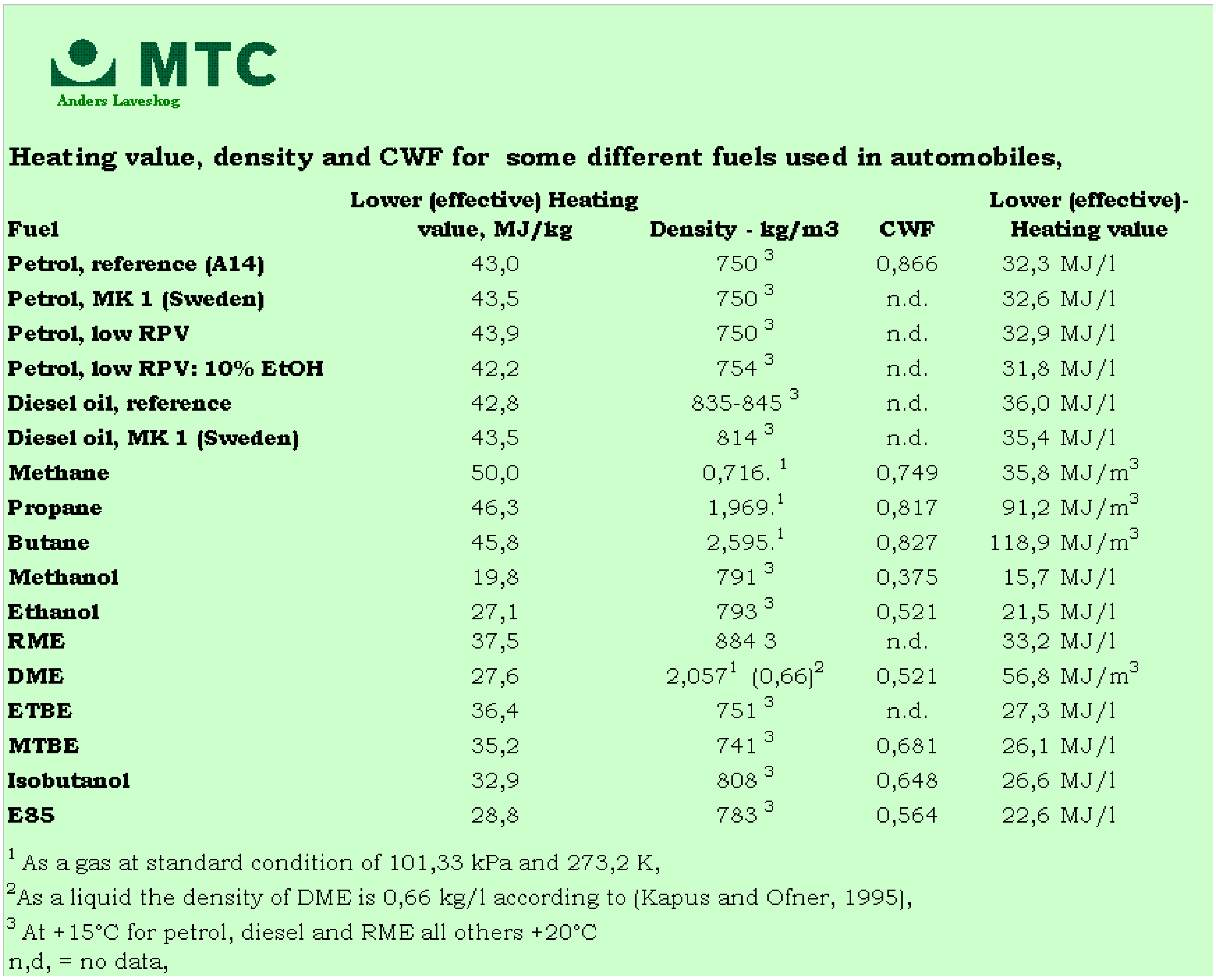
[e] The data for flammability range are taken from a Canadian study cited and might deviate slightly from Swedish and European E85 fuel.

[f] At the stoichiometric air/fuel ratio.

Table 2. Additional properties of biomethanol/M85

	VALUE	
PROPERTY (UNITS/CONDITIONS)	Methanol	M85
Relative molar mass	32	-
Carbon content (mass %)	49,9	43 – 45
Hydrogen content (mass %)	12,6	12 – 13
Oxygen content (mass %)	34,7	43 – 44
Relative density (@15°C/ 1 bar)	0,796	0,79 – 0,80
Boiling temperature (°C/ 1 bar)	65	49 – 66
Freezing temperature (°C)	-94	-
Autoignition temperature (°C)	464	> 257
Stoichiometric air/fuel ratio (mass)	6,45	7,7
Lower heating/calorific value (MJ/kg)	19,5	22 – 22,5
Flash point temperature (°C)	11	-
Vapour pressure @38°C (kPa)	32	48 – 103
Vapour flammability limits (volume %)	7,3 – 36	-
Research Octane number (RON)	120	108
Motor Octane number (MON)	88,6	89
Latent heat of vaporisation @ 1 bar (kJ/kg)	1178	1055
Specific heat (kJ/kg-k)	2,5	2,4
Cetane number	5	-

Table 3. Heading value, density and CWF for some different fuels used in automobiles



MTC
Anders Laveskog

Heating value, density and CWF for some different fuels used in automobiles,

Fuel	Lower (effective) Heating value, MJ/kg	Density - kg/m3	CWF	Lower (effective)-Heating value
Petrol, reference (A14)	43,0	750 [3]	0,866	32,3 MJ/l
Petrol, MK 1 (Sweden)	43,5	750 [3]	n.d.	32,6 MJ/l
Petrol, low RPV	43,9	750 [3]	n.d.	32,9 MJ/l
Petrol, low RPV: 10% EtOH	42,2	754 [3]	n.d.	31,8 MJ/l
Diesel oil, reference	42,8	835-845 [3]	n.d.	36,0 MJ/l
Diesel oil, MK 1 (Sweden)	43,5	814 [3]	n.d.	35,4 MJ/l
Methane	50,0	0,716. [1]	0,749	35,8 MJ/m^{3}
Propane	46,3	1,969.[1]	0,817	91,2 MJ/m^{3}
Butane	45,8	2,595.[1]	0,827	118,9 MJ/m^{3}
Methanol	19,8	791 [3]	0,375	15,7 MJ/l
Ethanol	27,1	793 [3]	0,521	21,5 MJ/l
RME	37,5	884 3	n.d.	33,2 MJ/l
DME	27,6	2,057[1] (0,66)[2]	0,521	56,8 MJ/m^{3}
ETBE	36,4	751 [3]	n.d.	27,3 MJ/l
MTBE	35,2	741 [3]	0,681	26,1 MJ/l
Isobutanol	32,9	808 [3]	0,648	26,6 MJ/l
E85	28,8	783 [3]	0,564	22,6 MJ/l

[1] As a gas at standard condition of 101,33 kPa and 273,2 K,

[2] As a liquid the density of DME is 0,66 kg/l according to (Kapus and Ofner, 1995),

[3] At +15°C for petrol, diesel and RME all others +20°C

n,d, = no data,

Properties of relevance to engine operation

In discussing the properties of methanol as motor fuel, some short notes can be made about the data in Table 1 and Table 2.

Methanol is per definition an excellent fuel for otto engines, i.e. the octane number (MON and RON) is high and cetane number is low. Thus, an otto engine could be operated on higher compression ratios when neat methanol, i.e. M100, or M85 fuel are used. For lower blending rates, the higher octane number could be used to some extent by compromising operation with gasoline by a small increase in compression ratio (probably realistic only for M30 or higher blends) or at very low blending rates by advancing the spark timing (this would be valid for e.g. M3 to M15). Since methanol has a low cetane number, it cannot be used directly in diesel engines without any kind of positive ignition or ignition improver (cetane-increasing additive). In both cases, extensive engine modifications might also be needed. The use of methanol in diesel engines is not of primary interest in the present study and is not commented further here.

The energy content of methanol is almost a factor of 2 lower than gasoline, implying that almost double the amount of fuel must be injected in the engine. Thus, the fuel system has to be adopted to accommodate this. In cases where the engine should be fuel flexible, such as e.g. an engine for M85, a compromise has to be made. Anticipating that the maximum capacity has to be chosen for M85 at rated engine speed, this indicates that engine operation in the other “extreme” point, i.e. low idle with gasoline, the injection nozzles would be larger than optimal. However, this compromise is not anticipated to be of major concern.

Blending methanol in gasoline increases the vapour pressure at low blending levels but is again reduced at higher blending levels (e.g. M85). The base gasoline must in most cases be adopted for blending with methanol. This can be a practical problem in some cases. Increased energy uses in the gasoline production and/or a decrease of the feedstocks for gasoline are some implications.

The heat of vaporisation is much higher for methanol than for gasoline and diesel fuels. This combined with the need for more fuel due to the lower energy content leads to that the necessary heat for evaporation is almost one order of magnitude higher than for gasoline. Furthermore, neat methanol has a fixed boiling point and not a distillation curve as gasoline, where the boiling temperature for the components with the lowest boiling point are far lower than for methanol. The lower heat content, and correspondingly larger nozzle holes of the fuel injector, may also lead to larger droplets in the air-fuel preparation. All-in-all, the mentioned properties lead to significant problems during cold starts, and particularly, at low-temperature ambient conditions. The result can be much higher emissions of several regulated and many unregulated emission components during cold starts.

Some properties that are positive for methanol can be the higher flame speed under realistic engine operation conditions, and the tendency for methanol to tolerate greater charge dilution (such as, exhaust gas recirculation) or a leaner mixture. In direct injection engines, the much higher heat of vaporization can also increase the volumetric efficiency and increase the tolerance for higher compression ratio due to the charge-cooling effect (this is additional to the higher octane number already due to the chemical properties of methanol). All these effects are of utmost importance and could provide conditions for a drastic increase in engine efficiency compared to the conventional gasoline-fuelled otto engine. However, these effects cannot necessarily be utilized (albeit perhaps to a limited extent) with low-level blending and in fuel-flexible engines. This would speak strongly in favour of using high-level blends or dedicated methanol engines on a longer term horizon.

Risk of fire and explosion

The physical properties of a fuel that affect fire hazards include its volatility, flashpoint, range of flammability, autoignition temperature and electrical conductivity. Other properties of fuels that influence the potential risk associated with a fuel fire include burn rate in liquid pool fires, the heating value of the fuel, flame temperature and thermal radiation emitted from the fire.

Fuel volatility is the vapour pressure exerted by a vapour over the liquid in a closed container. This is the key factor in determining a fire risk of a fuel, since it is (together with the latent heat of evaporation) a measure of the rate in which fuel vapour is produced from a container of fuel or a fuel spill. High vapour pressures tend to generate fuel vapour at a higher rate spreading the flammable vapour mixture through a wider area and therefore, increasing the probability for ignition from an ignition source.

Temperatures above the flammability limit give a too “rich” vapour for flame propagation. This means that, in a closed space, only if the temperature is within the flammability interval, the vapour is capable to sustain flame propagation.

Also diffusion coefficients and vapour density can be significant factors in determining fire risks, particularly in poorly ventilated areas. A fuel with a low diffusion coefficient will lead to high concentrations within a limited space more readily. If the fuel has a high vapour density relative to air, then the vapour will accumulate in low areas increasing the fire hazard.

Ignition energy of both gasoline and alcohol fuels are so low that potentially any ignition source will ignite either fuel.

Fuels that have low conductivity tend to accumulate static charge and release the charge through a spark. This has potential to become an ignition source for a fuel fire. The higher the conductivity of the fuel, the more quickly a static charge can dissipate and therefore it is less likely to cause ignition.

Flame spread rate is a factor of great importance for personal safety as it determines the time that a person has to move away from a spreading pool fire. It is also important for how fast a fire develops.

Fire fighting on different fuels has been performed by the Swedish Institute of Testing and the Gothenburg fire brigade. Tests were performed on fires in basins ranging from 0,25 m^2 to 50 m^2 . The largest size included 10 m^3 of fuels in every test and was used for methanol, M15 and gasoline. In all seven different foams were tested three alcohol resistant; AFFF (Aqueous Film Forming Foams); two alcohol resistant flour protein foams and two conventional detergent foams. The tests were then repeated in smaller scale to evaluate the possibilities to develop reliable laboratory test methods. The entire result is reported in reference (Statens Provningsanstalt and Göteborgs Brandförsvar, 1983).

The resultants were in short:

1. Fire in M15 is possible to extinguish with conventional foams. A synthetic alcohol foam gives however much safer effect.

2. Fire in polar solvents like methanol, acetone, isopropanol and others cannot be extinguished with conventional foams. Also the fluorine protein based foams are uncertain to use on polar liquids. The use of AFFF foams gives a good result.

A test method for a 4 m^2 large fire looks possible to be developed. Smaller fires should not be used for type approval of foams but could be used for quality control with the use of better methods of application.

A Twenty minutes film (on VHS?) was produced during the tests and may be recovered. Methanol burns with blue flames but in daylight and especially in sunlight, it is not visible. This can cause problem when wind changes direction. Otherwise, the much lower heat of radiation lowers the risk of secondary fires and makes it easier to approach the fire for fighting. Fires in cars are believed to be visible quite soon when plastics go on fire. The price of AFFF foams are 3 – 10 times higher than for conventional foams but they are more efficient.

For use on gas and methanol fires special powders, (BE), are available with up to 5 times better effect than standard powders. The effect on glowing fires in fibrous materials are however lower (Statens Provningsanstalt and Göteborgs Brandförsvar, 1983).

In fuel tanks, level indicators and fuel pumps could be sources for ignition of fuel vapours. Fuel gauges normally have low electric currents but fuel pumps are in the range of 10 amperes and above. In a simpler analogue fuel gauge, an instrument is connected in series with a variable resistance in the tank driven by a float. An indicator lamp for “soon empty” is connected to a contact in the fuel gauge assembly. Fuel pumps are often dc- permanent magnet motors with coal brushes lubricated and cooled by the fuel flow through the pump. Two fuel tanks equipped analogue fuel gauges and DC pumps have been tested by the Swedish testing institute. In normal operation, the fuel level measuring system will not give rise to ignition risks. The fuel pumps due to high currents can give rise to ignition of explosive air-fuel vapour mixtures. It is said in the report that no system can be regarded as safe since the fact that the gas mixture in the tank is over rich is not allowed as safe guard (Johnsson, 1983-01-03). Modern fuel pumps can be brushless and thus possess no risk for flashes during normal operation.

Material compatibility

Methanol and wet ethanol are corrosive to zinc, aluminium, magnesium and their alloys. Wet ethanol is also corrosive to iron and steel. Anodized aluminium fuel filter housing resists methanol (M100) well and no corrosion was observed after years of use (24). However, dry methanol (which is a normal condition) and dry ethanol are not corrosive to iron and steel and normal use keeps condensed water out of the system.

GM in the USA studied effects on polymers (rubber) of methanol in engine oil (Schwartz, 1986). Some plastic and rubber material are sensitive to the alcohols, others less than to gasoline and diesel oil. However, there is good knowledge about polymers that are compatible with alcohols as well as with the conventional fuels.

Problems encountered in the Swedish M15 and M100 projects.

Phase separation has occurred in the distribution of M15 fuel, once during the snow melting season in one filling station where the man hole lid wasn´t sealed perfectly. Another occasion was when sea transported lead free M15 was pumped to a refinery cistern. The pipeline had been flushed with unleaded gasoline but as the pipeline was going up and down before reaching the cistern a considerable amount of water was left in the lower parts of the pipe. This made some hundred cubic meters of M15 to completely separate in a bottom layer of water and methanol and on top the base gasoline.

In one filling station, M15 fuel was filled into a perfectly cleaned underground cistern where a “chain” of magnesium for corrosion protection had been left. The first car filled with the fuel worked well for 70 km but then there was no idle any longer. Dismantling of the carburettor revealed that the entire carburettor was coated in white metal salts from the evaporated fuel.

In the early tests of M100 buses and passenger cars a lot of problems with blocked fuel filters occurred. The reason for this was that tank trucks had not been cleaned from previous transports of fuel oils and other heavy petroleum products.

Also in the beginning of M100 tests there was a lot of fuel filter plugging with a jelly, which upon drying transformed into a white powder of aluminium, magnesium, silicon compounds. The reason in this case was found out to be filter cases of standard aluminium intended for gasoline use. It was also found that the M100 in filling stations contained particles with zinc, aluminium and silicon to a degree that could block the filters. All filling pumps were then supplied a 1 µm fiberglass filter in polypropylene filter housing. After this, filters in cars had a life of more than 20 000 litres of methanol (Laveskog A. , 2013).

SMAB started testing of M20 fuel in 1974 – 75 with standard equipped Volvo vehicles. Problems arouse quite soon with fuel gauges having broken wires. The potentiometer was a copper wire wound on phenol resin and coated with a lacquer that was dissolved in the test fuel and the copper wires corroded. In the mechanical fuel pump one make (APG) worked well but the SEV-pump had malfunctioning valves and a leaking packing.

In carburettors SU and Zenith floats have had increased tendency for leaks and swelling and membranes had higher incidence of perforations. Rubber tubing of NBR have swelled but tubing made of polyamide 11 (PA11) have worked well.

In early test cars (1970’s) in Sweden with fuel injection systems some problems with rubber tubing have occurred but PA11 worked well. The maker of fuel pumps indicated risks of short lifetime but no problems were found. The epoxy glue in fuel filters in part dissolved in many cases but caused no problem later on in the system. In some vehicles there have been camshaft problems due to inadequate formulation of the engine oil and/or incompatibility between oil and fuel. Some corrosion in fuel tanks (tern plated steel) has occurred. The lacquer inside jerry cans has flaked off (SMAB). Standard polyamide tubing for gasoline has worked well in Saab vehicles for 10 years with methanol and almost 20 years with E85 in long term tests. Some in tank fuel pumps have experienced galvanic corrosion on flat contacts but Walbro pumps have worked perfect in M100 (Laveskog A. , 2013; RV kemikonsult AB, 1982-08-03).

Health effects and emission toxicity

Leaks and spill

Toxicity to environment of methanol as well as ethanol is far less than for gasoline and diesel fuel when spilled on the ground and in the seawater. The toxicity of methanol is high to man but not so high to animals. Fish, for example, can survive 1 % of methanol in water for shorter periods.

Leaks of methanol and ethanol to the ground are probably less risky than that of gasoline and diesel oil. The alcohols are relatively rapidly broken down in the ground but aromatics and especially MTBE from the conventional fuels are not.

The effects in terrestrial and aquatic environments were studied in literature and performed on behalf of Swedish Motor Fuel Technology Co (SDAB) in 1982. Included are effects on vegetation, soil and aquatic environments as well as some studies in brackish water. The literature study also covered mobility and breakdown in soil. Ecological effects of methanol, ethanol, leaded gasoline and lead free M15 on soil and their organisms and on some brackish water organisms were studied in series of tests by scientists from zoological institute of the Stockholm University on the commission of the Swedish Motor fuel Technology Co. When the fuels were spread on vegetation a direct effect was shown for M15 and gasoline, in alcohol treated areas the more pronounced effects were seen after a week. After three to four weeks same re-colonisation was seen but it took until a year to get a new cover grass and herbs. The differences between the fuels are small. Soil samples show a relatively fast evaporation, microbiological decomposition and transport downwards after one month no concentrations above 3 ppm could be registered. Test in climate chambers on peas, rape and oats show that the alcohols are less toxic than M15 and Gasoline. The toxicity on seeds was less for the pure alcohols than for M15 and gasoline (Lindblad et al., 1982) and (Fondelius, 1982). The test on macro algae were performed with 360, 800 and 1 600 ppm in brackish water. The enteromorpha species were more sensitive than the focus vesiculosusa especially for M15 and gasoline, methanol and ethanol were less toxic. Blue mussels, (Mytilus edulis) were clearly stressed by M15 and gasoline while methanol and ethanol gave low effects. Acute toxicity test on Gammarus sp showed lethal and non-lethal effects at concentrations above 1 000 ppm. M15 and gasoline gave the highest mortality (Lindblad, 1983), (Lindblad et al., 1982) and (Fondelius, 1982)

If a large scale introduction of M15 or other methanol containing fuels for vehicles takes place there will be a great increase in sea transport of methanol. SDAB thus commissioned Studsvik Energi AB to simulate and calculate a tanker Wreckage in Swedish coastal waters. Experiments were performed in a test basin. The tests showed that the risk for explosion above the water surface was extremely small as the vapour concentration never reached the lower limit of explosion (Bertilsson B. , 1983). The most unfavourable case with no waves and methanol stratified in the surface gave 80 % of the lower limit of explosion. At a spill without waves and wind acute toxic effects could occur in the vicinity of the water surface. During an accident in the lake Vänern, when 50 m^3 of methanol was released into lake, less than 1 ppm of methanol could be detected in the water the day of spillage. In some weeks the water concentration was less than 0,5 ppm. No dead fish could be observed.

Water organisms typical of the Baltic have been tested in the brackish water laboratory of the Environment Protection Board. The toxic effect, LC 50 of methanol on bleak was > 28 g methanol/l of water at +10 °C and the nitocra specimen had a LC 50 value of 12 g/l tested at +20°C. According to simulations, measurements and calculations also initiated by SDAB, these levels of methanol concentration are found only in limited areas (E Linden et al., 1979).

General toxicity from methanol and some other gasoline blending component

In Table 4, an overview and classifications of the most common blending components for gasoline has been made (Laveskog A. , 2013). Health effects and emission toxicity are broadly classified in low, medium and high risk.

Table 4. General risk assessment of health effects and emission toxicity

Lower risk	Medium risk	Higher risk
Straight run gasoline	Heart cut reformate (without benzene and PAH)	Reformate
Isomerate	Cracked spirits	
Alkylate		
MTBE		
Other Ethers		
Methanol, Ethanol		

The use of the mentioned blending components could be as, e.g.:

- *Straight run gasoline* can be used only in very limited amounts due to low octane ratings.
- *Isomerate* is limited due to high volatility.
- *Alkylate* can be used in very high concentrations - in summertime, pure alkylate is the perfect fuel.
- *MTBE* is normally not used over 15 %.
- *Methanol and Ethanol* has substantially lower energy content than gasoline, however old vehicles running very rich can tolerate 10-15 % methanol and 15-25 % ethanol.
- *Heart cut reformate* is normally not used in gasoline but is much lower in toxicity than normal reformate and could be produced through simple distillation.

Both methanol and ethanol can produce more aldehyde than conventional gasoline in the exhaust from the engine (Laveskog A. , 2013). Methanol gives most formaldehyde and ethanol gives acetaldehyde and a minor amount of formaldehyde – but both of these aldehydes can rather easily be reduced with a catalyst. Malfunction of emission control is also easily detected by the nose due to the irritating smell.

Denaturation

Methanol as well as ethanol has to be denaturised to prohibit misuse or to be mistaken for drinking alcohols (Laveskog A. , 2013). A red dye addition to ethanol and a violet to methanol are also appropriate. Methanol has with success been denaturised with 1 ppm butyl mercaptane and ethanol with MTBE and isobutanol in combination 1+2 % or 2+1 % (Jansson, 1982-12).

Ethanol has high value on the black market and methanol is toxic, a poison. It was agreed upon by authorities and the ethanol project management to have a denaturation composition that made it more difficult and expensive to purify it for human consumption than to produce it via fermentation and distillation (illegal). After several tests rounds and analyses, as well as test on humans, a mixture of 2 % MTBE and 2 % isobutanol in ethanol was chosen, both having smell and taste far from ethanol. MTBE has a boiling point close to ethanol and isobutanol is soluble in water in all proportions as ethanol. The ethanol was also dyed with red dyes. This denaturation composition and dying made it possible to market high concentration ethanol fuels.

Methanol was not denatured in the M15 project but mostly mixed with gasoline and isobutanol in closed refinery areas. The methanol quality (chemical grade AA) however had a very faint smell, weak but a little like ethanol, so when it came to the M100 fuel project, denaturation was introduced. Several denaturants were tested that should be cost effective and not change the fuel significantly from 100 % methanol. Butyric aldehyde had a bad smell and 10 ppm was added to the methanol giving a distinct bad smell. However after the storage for some months in uncoated, maybe somewhat rusty jerry cans the aldehyde had oxidised to acid and then reacted with the methanol forming a fruit smelling ester. At last, butyric mercaptane was tested and found stable giving a bad smell already at the 1 ppm level. This increased the sulphur level in the fuel to less than 0,5 ppm. To further show that M100 fuel was not intended for other use than as a motor fuel, it was test dyed with some dyes from the BASF Flexoviolet® 600-series. A level of 1 ppm was sufficient to give a distinct violet colour, which also was stable for years in steel as well as plastic containers (Laveskog A. , 2013).

Response for Methanol in flame ionization instruments for emission testing.

Heated and non-heated instruments were tested in an inter calibration test performed by the Swedish Motor fuel Technology Co. during 1983-01-31 – 1983-06-02 in the laboratories of The Swedish Motor Vehicle Inspection Co., The Swedish Environment Protection Board, Volvo Co. and Saab development and production control. Seven different types of instruments were tested but minor differences may have been present in all ten instruments. The calibration gases were 203 ± 4 ppm and 1942 ± 46 ppm gas the latter could only be made at 10 bar pressure due to the risk for condensation and thus limited the number of instruments testable (Laveskog, 1983).

Table 5. Inter-calibration of emission instruments

Inter-calibration of emission instruments in Swedish auto emission laboratories 1983		
	Cal. Gas: 203±4 ppm C methanol in N_2	Cal. Gas: 1942±46 ppm C methanol in N_2
Instrument	Measured conc. (ppm)	Measured conc. (ppm)
IPM, RS5	145	1500
Horiba, OPE 412E	142	1380
Horiba, FIA-21	149	1494
Beckman 400	161	1563
JUM VE5, HFID	142,5	1335
Beckman 400	153,6	1485
Beckman 402 HFID	126,6	1213
Horiba Mexa 1620	165	1560
Horiba Mexa 1620	163	--

The detectors were non-heated and heated (H in the table). If divided into 2 groups the heated averaged 139 ± 8 ppm and 1360 ± 120 ppm respectively and the non-heated 157 ± 6 ppm and 1530 ± 40 ppm. An overall response factor for all the instruments was close to 0,75 for methanol in the FID-detectors calibrated with propane.

Calculation of fuel consumption

For all emissions tests not run on certification gasoline the relation C/H/O must be calculated in order to calculate the fuel consumption from emissions of CO_2, CO and HC. M15 comprising a mixture of unleaded gasoline (83 %), methanol (15 %) and isobutanol (2 %) has, depending on the gasoline used, a molecular weight of 15,3363 and a density of 0,7490 to a molecular weight 15,31 and density 0,760. Those factors were used for the vehicles in the Swedish M15-project (Hedbom, 1986).

8. The Swedish M15 project in the 1970’s and 1980’s

Background

After the oil crises in the beginning of 1970’s there was an interest from the Swedish government as well as the industry to find alternatives to gasoline and diesel as fuels for the transport sector as every litre of transportation fuel was imported. The text in the following contains comments from today, based on knowledge from experiences of emissions testing during the last decades.

Introduction

In the search for alternate fuels for the transportation sector, methanol was considered a competitive candidate in the late 1970’s. It was anticipated that methanol-gasoline blends may be used in the automobiles at that time with minor adjustments.

In the process of evaluating the environmental implications when gasoline is replaced by a methanol-gasoline blend, comparative emission data have been generated.

During 1975 – 76 two fuels were tested at the BP laboratories in Sunbury on Thames for Volvo and Swedish companies involved in introducing methanol as a component in gasoline. The main interest was to check the increase of octane requirement for a special blend of 16 % methanol and 4 % isobutanol in a mixture of reformate and straight run gasoline. Octane requirement increased for a test period of 30 000 km and had not stabilized. One fuel pump and one carburettor float malfunctioned due to the fuel. Nothing was said about cleaning additives in the reference or test fuel. There was a tendency for higher increase of octane number requirement for vehicles run on the methanol containing fuel compared to references run on a reference gasoline without methanol (BP, 1976).

Four vehicles of 1976 model, two Volvo 244 cars equipped with carburettors and two Volvo 264 cars with fuel injection without catalysts, were used for tests with gasoline followed by tests with a methanol-gasoline blend. No attempt was made to optimize the engine systems for best utilization of the methanol, for example, compression ratios and ignition timing. When running on gasoline, the vehicles were adjusted according to the manufacturer´s specifications. When running on methanol-gasoline blend the carbon monoxide content in the exhaust gas was used as a measure of the “leaning out effect” caused by methanol, which was compensated for. No other adjustments were made. Drivability was considered satisfactory with both fuels. However, no specific drivability tests were made.

Ordinary leaded gasoline and a methanol –gasoline blend consisting of 80 % (volume) of lead-free gasoline, 18 % methanol and 2 % isobutanol were used.

Tests were made on a chassis dynamometer according to the 1975 Federal Emission Test Procedure and also the European Test Procedure. Carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxides (NOx) sere measured and fuel consumption was calculated. In addition, total aldehydes, formaldehyde and polynuclear aromatic hydrocarbons (PAH) were analysed.

The following conclusions were drawn from the study of four Volvo cars where a methanol-gasoline blend was substituted for a standard gasoline:

- CO, HC and NO_X tended to slightly decrease (provided that the carburettor and fuel injection system are carefully maintained).
- Total aldehydes increased, formaldehyde being responsible for most of the increase.
- The amount of PAH seems to depend more on the driving cycle and driving pattern prior to the test than on the fuel. No significant difference could be detected between the two regarding PAH emissions.
- The fuel consumption was about the same on an energy basis.
- With widespread use, adjustment of the fuel system will be a critical point. Monitoring the carbon monoxide content at idling will not be sufficient to obtain optimal performance.

The experimental program was conducted by the Swedish Methanol Development Co. (SMAB), the group for Exhaust Gas Research, AB Atomenergi and the department of Analytical Chemistry, Arrhenius Laboratory, Stockholm University.

The tests in the project were run in the last quarter of 1977. The test was performed on chassis dynamometer and regulated emissions measured according to best available technique of that time for example measuring after CVS system and HC measured with FID for all driving cycles (Britt-Marie Bertilsson et al., 1978-02-01).

Fuel specification

Below, the analyses available for the test fuels are listed. The M20 was mixed to contain 18 % methanol and 2 % isobutanol in unleaded gasoline. The methanol fuel was thus like what was used in the early field test project and the regular (0,4 g/l leaded) gasoline was like a market gasoline quality. The data given for the M20 quality seems to contain figures for the base gasoline when it comes to the concentration of aromatics, olefins and paraffins, since they add up to 100 %.

Table 6. Fuel specifications in the tests run in 1977

Fuel specifications			
Property	**Unit**	**M20**	**Gasoline**
Density	g/ml	0,7721	0,7438
RON		99,5	93,2
MON calc.		89,7	
Lead	g of Pb/l	Nil	0,39
RVP	psig	9,8	8,5
V/L	°C	55	66
Aromatics	%vol	44,8	30-35
Olefines	%vol	1,5	
Paraffines	%vol	53,4	
C	%	78,8	86,7
H	%	12,6	12,3
O	%	10,6	1,2
N	%	<0,07	Nil
S	µg/ml	0,003	0,0084
Eff. heat value	kJ/Kg	38 350	43 500

Emissions

Emissions were tested according to the old ECE test procedure with four consecutive city cycles with a maximum speed of 50 km/h (Table 7). The US-73 test cycle was composed of one Y_{ht} and one Y_s cycle with maximum speeds around 90 and 55 km h (Bertilsson & Egebäck, 1978).

Table 7. Emission results, regulated emission components

Emissions US 73				
Average all vehicles		Gasoline	M20	M20/gasoline
	CO g/km	12,7	10,6	0,83
	HC g/km	1,54	1,48	0,96
	NO_x g/km	1,59	1,49	0,94
Emissions Y_{ht}				
Average all vehicles		Gasoline	M20	M20/gasoline
	CO g/km	8,7	6,3	0,73
	HC g/km	1,42	1,26	0,88
	NO_x g/km	2,14	2,1	0,98
Emissions ECE cold				
Average all vehicles		Gasoline	M20	M20/gasoline
	CO g/km	18,9	19,4	1,02
	HC g/km	2,42	2,58	1,06
	NO_x g/km	1,09	0,91	0,83
Emissions ECE warm				
Average all vehicles		Gasoline	M20	M20/gasoline
	CO g/km	15,9	14,1	0,89
	HC g/km	2,24	2,27	1,02
	NO_x g/km	0,97	0,89	0,92

The regulated emissions were very high, compared to what we demand today, but typical of well-maintained vehicles of that time. The two vehicles with carburettors had idle emissions of 3-4 % CO, the ones with fuel injection 1-2 %. As can be seen in the table below, the M20 has a leaning out effect on the emissions, especially the US cycles with their higher load.

In the

Table 8, the measured aldehyde emissions are shown.

For the ECE tests, formaldehyde was 35 to 45 % higher and total aldehydes were 10 to 30 % higher for M20 compared to gasoline. For the US tests, formaldehyde was 15 to 35 % higher and total aldehydes were 10 to 30 % higher. The increase of total aldehyde values were almost all the result of increased formaldehyde emissions when running on M20.

Table 8. Emission results, aldehydes

Aldehyde emissions mg/km, All vehicles					
Fuel	**Aldehyde**	**ECE**	**ECE warm**	**US-73**	**Yht**
Gasoline	Formaldehyde	29,82	25,94	24,88	29,26
M20	Formaldehyde	43,52	37,38	32,45	39,61
Gasoline	Total aldehydes	47,38	39,51	31,53	37,43
M20	Total aldehydes	61,48	47,8	39,76	41,42

Table 9. Emission results, regulated emission components

Tailpipe temperature.				
Vehicle/Reg. No.	**Carburettor 2,1 l.**		**Fuel injected 2,7 l**	
	ETG	**JAD**	**BAX**	**JBO**
	Approximate temp °C			
ECE :200 sec	60	50	50	60
ECE: 800 sec.	125	125	165	185
US 73: 200 sec.	120	120	120	130
US 73: 800 sec.	190	190	230	230

Temperature in the exhaust system is very much dependant on developed power from the engine and during start-up phase losses occurs via condensation of water and the deposition of combustion products in pipes and mufflers.

PAH emissions were sampled from undiluted exhaust with a constant flow system based on laminar flow elements in the engine air flow and after the sampling equipment. The volume sampled was about 7 % of the total flow. After cooling in all glass cooler, the gas was filtered in a 127 mm glass fibre filter 99,9 % effective on 0,3 µm particles. Acetone was used for rinsing the cooler after the test and added to the condensed water which was extracted and analysed separately.

Emissions of PAH were generally much higher in the US test cycles which could depend on the higher load and thus higher temperature rise and exhaust pipe/muffler temperature. This in turn will help to evaporate PAH from deposits in engine and exhaust system.

Table 10. **Emissions of PAH**

Emission of PAH µg/kg of fuel used when driving on gasoline All vehicles					Emission of PAH µg/kg of fuel Used when driving on M20 All vehicles				
	ECE cold	ECE warm	US Y_{ct}	USA -73		ECE cold	ECE warm	US Y_{ct}	USA -73
Cp(cd)P	49	36	117	459	Cp(cd)P	118	14	20	429
BaA	20	21	131	453	BaA	55	31	143	659
Chr/Trf	32	40	306	568	Chr/Trf	88	49	290	1000
B(bok)f	30	22	130	594	B(bok)f	36	10	161	908
BeP	22	40	99	342	BeP	29	7	133	530
BaP	20	15	78	310	BaP	42	5	145	598
Ind.P	12	5	25	151	Ind.P	17	2	34	244
B(ghi)P	75	37	142	621	B(ghi)P	142	15	173	878
Coronene	40	19	62	249	Coronene	73	7	43	166
Sum of PAH	287	234	1088	3745	Sum of PAH	581	139	1120	5411

Emissions of PAH were, as can be seen in the table below, on average 25 % higher for the M20 fuel. The cold started cycles however (ECE cold and US-73), has higher relative PAH emissions for the M20 fuel, which could be explained by cold start enrichment washing the inlet system and the cylinder walls thus dissolving deposited PAH in engine and exhaust system.

Table 11. **PAH for M20 in relation to gasoline**

Relation of M20 emissions of PAH in relation to emissions driving on gasoline.					
	ECE cold	ECE warm	USA -73	US Y_{ct}	**All tests**
Cp(cd)P	2,39	0,38	0,93	0,17	**1,24**
BaA	2,75	1,46	1,45	1,10	**1,89**
Chr/Trf	2,73	1,23	1,76	0,95	**1,91**
B(bok)f	1,23	0,47	1,53	1,24	**1,08**
BeP	1,31	0,16	1,55	1,34	**1,01**
BaP	2,07	0,36	1,93	1,86	**1,45**
Ind.P	1,47	0,47	1,61	1,34	**1,18**
B(ghi)P	1,89	0,39	1,41	1,22	**1,23**
Coronen	1,84	0,37	0,67	0,70	**0,96**
Sum of PAH	2,02	0,59	1,44	1,03	**1,35**

Concluding remarks about exhaust PAH

From this project much has been learned regarding results and methodology for emission measurements. Fuels used for blending M-fuels must be used also as the base for reference fuels in emission tests in order to have the “same” aromatic and polyaromatics content. All the fuels have to be analysed also for the content of polyaromatics compounds. Concerning the vehicle, the engine should be cleaned from combustion chamber deposits in the inlet system and valves. The exhaust system should be new and without a muffler. After change to new fully synthetic engine oil the vehicle must be conditioned with high speed driving in order to blow out deposits left and heat the exhaust system considerably to blow out oil from the manufacture.

In order to discriminate between fuels and show a worst case, no catalyst should be mounted; with a catalyst, emissions reflect vehicle-out emissions in normal use but the low emission levels may make some analyses of PAH difficult.

Since this project was completed, the methods for sampling polyaromatics have improved considerably. Sampling is now conducted in diluted exhausts from a dilution tunnel and after the filter, semivolatile compounds are absorbed in specially cleaned polyurethane foam (PUF) and there is no need for cooler any longer. To avoid “carry-over” effects from earlier tests, probably carried out on less “clean” fuels, the dilution tunnel and the rest of the sampling system should be cleaned prior to PAH sampling.

PAC in engine oil from one M15 passenger car

The only sensor-equipped vehicle in the Swedish M15 project was a Saab 900 i with K-jetronic fuel system made as a certification vehicle of the 1981 year model for the US-market. The engine oil of this vehicle was sampled during a long period of driving. The engine was tuned to run on $\lambda=1$ all the time after reaching a temperature with acceptable driveability. The fuel was the M15 quality used for the field test with high aromatic content and benzene concentration of 5 %. Oil and filter change was done every 15 000 km and samples taken then. The engine oil when new contained only trace quantities of PAC. The vehicle was driven 50 000 km per year mixed everyday short distances and up to 1 000 km/day for longer trips. Block heater was often used in winter time.

The method of clean up and analyses is described in the following. The oil samples were diluted 1:1 with n-hexane and internal standard added. The samples were then separated on silica columns deactivated to 10 %. Elution was first with n-hexane followed by the extraction of the aromatics fraction with benzene. The aromatic then were liquid-liquid extracted with nitro methane and n-hexane. The nitro methane phase was evaporated and then separated on Sephadex LH-20 coated with dimethyl formamid: water (85:15) as stationary phase. The PAC fraction was recovered and analysed on GC-capillary columns. Samples 1, 2, 5 and 7 also were analysed with capillary GC – MS (mass spectrometry) in order to ascertain the identification of PACs and to identify disturbing peaks in the chromatograms from some of the samples shown to be phthalates. Quantification was done with the aid of the internal standard, response factors on GC and correction for losses in the clean-up of samples.

GC instrument was Varian 3 700 with 10 m capillary column, stationary phase SE – 54. Programming: 2 min, split less injection at 70°C, temp increase 7°/min to 290 °C then isothermal 10 minutes, carrier gas: H_2.

In the table below sample 1 is new, not used oil and the others taken at oil and filter change every 15 000 km. As can be seen in the table and figure the concentration of PAC varies much but a tendency is seen that the concentration slowly increases with the mileage of the vehicle. Due to the long time, 2,5 years, many batches of fuel has been used. The last period an olefin-rich base gasoline was available with 8 % methanol, 11,2 % ethanol and 0,8 % isobutanol (M8E11). This quality was produced in another refining and may have contained lower concentrations of PAC in the fuel. The age of the reformer catalyst has also a strong impact on the PAC-content in the reformate with low concentrations when new and continuously higher when the catalyst ages and the severity in the reformer increases (Laveskog A. , 2013).

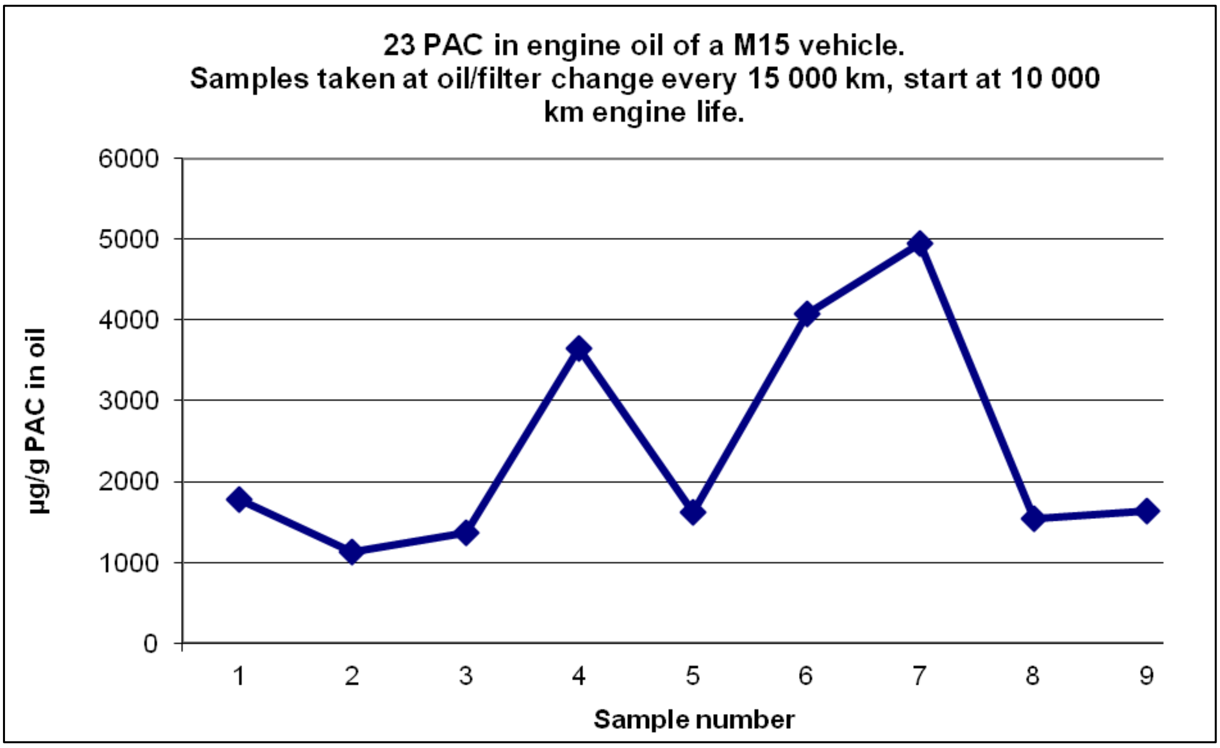


Figure 4. 23 PAC in engine oil of a M15 vehicle

Table 12. PAC concentration in new and used engine oil from a M15 vehicle

Concentration of PAC in new and used engine oils from a vehicle driven on M15 fuel. Concentration given as µg/g of oil.										
Sample number.	1	2	3	4	5	6	7	8	9	10
Approximate mileage km.	New oil	25 000	40 000	55 000	70 000	85 000	100 000	115 000	130 000	145 000
Compound										
Phenantrene	-	350	110	180	550	340	1100	690	260	190
Antracene	-	19	6,5	8,8	13	12	33	20	8,7	4,7
3-methylphenantrene	0,25	230	175	260	420	140	230	860	260	310
2-methylphenantrene	0,25	240	179	270	470	150	240	930	280	330
9-methylphenantrene	0,72	30	30	51	75	23	40	160	52	51
1-methylphenantrene	0,35	110	65	89	200	72	140	370	100	120
2-phenylantracene	-	34	23	110	88	21	72	130	30	62
Fluorantene	-	95	51	49	220	100	260	200	60	70

Concentration of PAC in new and used engine oils from a vehicle driven on M15 fuel. Concentration given as µg/g of oil. (cont.)										
Sample number.	1	2	3	4	5	6	7	8	9	10
Approximate mileage km.	New oil	25 000	40 000	55 000	70 000	85 000	100 000	115 000	130 000	145 000
Compound										
Pyrene	4,7	200	120	120	540	250	727	510	148	150
Benso(a)fluorene	-	91	25	43	120	62	210	150	26	58
4-methylpyrene	2,5	74	19	18	68	37	75	72	19	23
2-methylpyrene	3	59	35	33	120	42	120	130	30	45
1-methylpyrene	2,1	40	25	23	67	37	100	100	23	32
Benso(gih)fluorantene	-	3,8	-	-	6,4	-	3	-	-	-
Bens(a)antracene	0,1	18	17	11	42	26	56	36	8,2	13
Chrysene	0,6	25	25	25	84	42	70	67	21	22
Benso(j&k)fluorantene	-	23	27	9,6	120	40	94	79	31	24
Bens(e)pyrene	-	27	39	20	130	50	110	89	41	28
Bens(a)pyrene	-	17	17	*	47	28	46	43	14	12
Perylene	-	5,7	4,7	3,5	5,1	8,1	11	7	3,6	3,4
Indeno(1.2.3_cd)pyrene	-	6,4	6,8	2,9	19	9	22	21	8	7,8
benso(ghi)perylene	-	65	96	34	170	100	250	220	93	64
Coronene	-	19	29	7,1	71	35	63	69	28	15
Summ of 23 PAC:s	15	1782	1125	1368	3646	1624	4072	4953	1545	1635
Sum of 9 heaviest PAC	1	206	262	113	688	338	722	631	248	189

Evaporative emissions

The results on vapour pressure (Table 13) and evaporative emissions (Table 14) were used to evaluate the relative risk for benzene exposure. In the tables below are Reid vapour pressures and the relative benzene concentrations shown (Lindskog, 1981).

Table 13. Vapour pressure

Vapour pressure of base gasoline and corresponding M15	
Fuel / fuel component	Vapour pressure, kg/cm^2 at 38°C
High aromatic base gasoline	-
High aromatic base gasoline M15	0,86
Olefin rich base gasoline	-
Olefin rich base gasoline M15	0,73
Isoparaffine rich gasoline	0,36
Isoparaffine rich gasoline M15	0,53

Table 14. Benzene concentration

The relation of benzene concentration in vapours over M15 and gasoline			
Gasoline used for blending M15	**Temperature of fuel**		
	3°C	**25°C**	**50°C**
High aromatic base gasoline	0,75	1,8	6,0
Olefin rich base gasoline	0,86	0,75	5,8
Isoparaffine rich gasoline	0,75	0,93	2,0

In another project, emission measurements from a simulated tank filling of a car were performed with fuel filled from one 200 litre drum to another, while carrying personal samplers (Table 15) (R. Lindahl, 1982).

Table 15. Exposure from a simulated tank filling

Exposure at indoor filling of 200 l drums. Temp 17-21°C Average of 10-12 samples. Personal samplers			
Fuel	Methanol mg/m^3	Total HC mg/m^3	Benzene mg/m^3
M15	140 ±15%	780 ±27%	48 ±9%
M100	780 ±27%	Not analysed	Not analysed
Regular gasoline	Not analysed	600 ±16%	22 ±%
Benzene in gasoline: 4,5%, in M15 fuel: 5,8% . 15% methanol in M15. (GC analyses)			

In order to evaluate also the impact on the environment in areas close to gas stations, the emissions from the ventilation pipes in a gas station were measured at ordinary filling of underground storage tanks. Flows from the ventilation were not measured but can be approximated to the volume of the filled fuel. The temperature underground can be approximated to 10°C (Persson, 1982).

Road octane testing of 2 % oxygenate fuels

SDAB/Swedish Motor Fuel Technology Co was commissioned by the Swedish farmers' association to perform a test on fuels containing low-level of alcohols in gasoline with 10 % olefins. The blending and testing was performed at the BP Sunbury laboratories. All fuels were blended to give the same octane rating, one set of 4 unleaded regular qualities and one set of 4 leaded premium qualities. Five vehicles were then tested for borderline knock-limited spark-advance (KLSA) at WOT acceleration and full load at constant speeds.

Test fuels were blended to give the same RON and MON and then tested in passenger cars on chassis dynamometer in the laboratory. In the table below are shown the three ways to add 2% of oxygen to the fuel: 5,5 % ethanol (E5;5), 3 % methanol + 2 % butanol (MB3/2) and 3,5 % ethanol + 4 % MTBE (Emt 3,5/4).

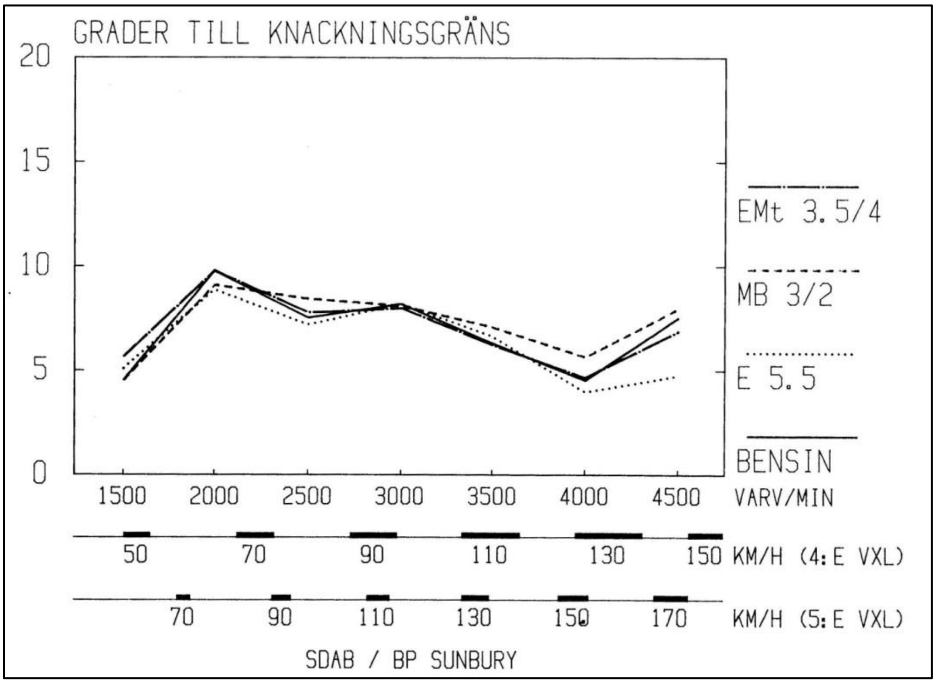
Table 16. Blend composition and inspection data of reference fuels

BLEND COMPOSITION AND INSPECTION DATA OF REFERENCE FUELS

			Gasoline-P resp. E	E5,5	MB2/2	Emt 3,3/4
Blend composition		%vol				
Butanes			2,0	2,0	1,0	1,0
Pentanes			12,0	8,0	6,0	8,0
Light Catalytic Cracked gasoline			33,0	33,0	33,0	33,0
Catalytic Reformate			53,0	48,0	55,0	45,5
Straight Run Products			-	3,5	-	4,0
Ethanol			-	5,5	-	3,5
Tertiary Butanol			-	-	2,0	-
Methanol			-	-	3,0	-
Methyl Tertiary Butyl Ether			-	-	-	4,0
Density			0,7505	0,7468	0,7542	0,7433
Distillation						
Recovered at 70°C		%vol	30,5	37,0	27,5	34,0
Recovered at 100°C		%vol	49,5	49,0	45,0	51,0
Reid Vapour Pressure		kPa	77,0	82,5	85,0	81,0
Octane Ratings						
Research Method	- Clear	(E)	95,5	95,5	95,5	95,2
	+ 0,15 gPb/l as TEL(P)		98,5	98,4	98,4	98,4
Research Method	- Clear		85,2	84,6	84,6	84,7
	+ 0,15 gPb/l as TEL(P)		89,9	87,6	88,2	87,9

The fuels had composition according to the table. The cars were in god condition with mileages of 5 000 to 30 000 km and before sent to the BP test centre checked in respect of compression, valve clearance, ignition position, idling speed and CO at idling speed. When necessary, adjustments were made according the manufacturers specification. All cars were found to be in good condition. Upon arrival at the BP Sunbury test site emissions were tested with the Swedish A10 test based upon the US federal CVS test procedure of 1978. All vehicles had emissions below the limits.

In Figure 5 trace knock at full load accelerations, in Figure 6 full load constant speed and in Figure 7 KLSA are shown (SDAB, 1984).



In the Figure 5, the full load knock limit at speeds from 1 500 to 4 500 rpm is shown. All the fuels perform well, the methanol/isobutanol being a little better in the high speed range and ethanol a little worse. Differences, however, are small (SDAB, 1984).

Figure 5. **Crank angle degrees to knock at constant vehicle speed**

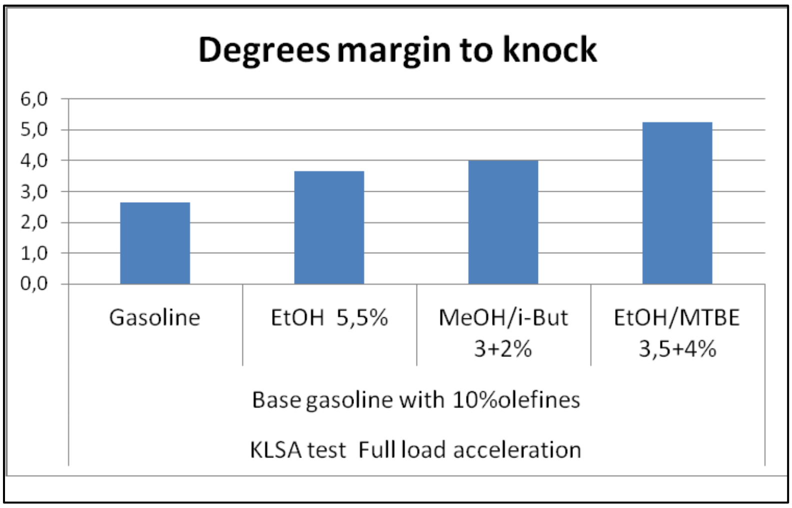


Figure 6. **Crank angle degrees margin to knock**

Under acceleration the fuels containing oxygenate showed a slightly better performance than the gasoline, at full load all fuels are considered to be equivalent (Figure 6 and Figure 7).

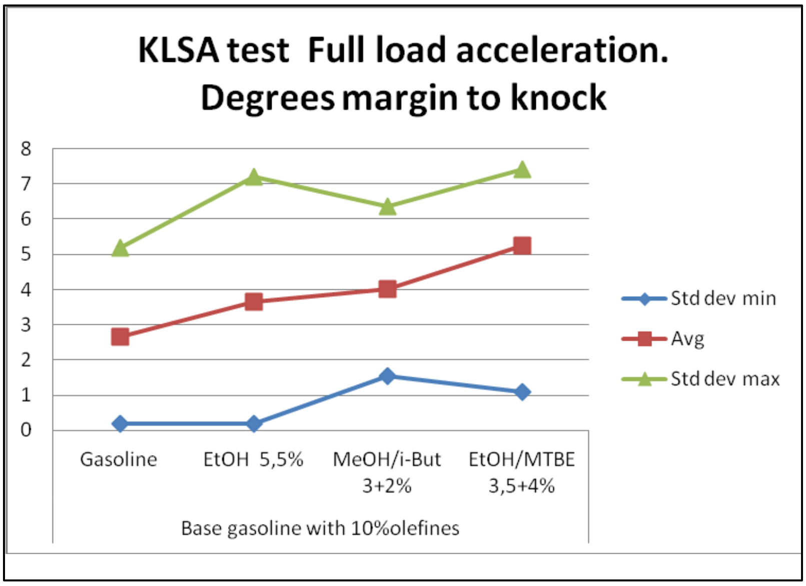


Figure 7. **KSLA test Full load acceleration. Crank angle degrees margin to knock.**

Evaporation of hydrocarbons and methanol from mixed fuels.

Already in 1980, a SAE-report gave results of evaporative emissions from vehicles with carbon canisters in the evaporative control systems. A blending level of 10 % ethanol increased evaporation 10 to 30 %, methanol about 90 %.Other test showed up to 100 % increased evaporative emissions for ethanol blends and up to 220 % for methanol with non-adjusted base gasoline. It was also shown in USA that the capacity of carbon canisters was lower when alcohols were present in the gasoline.

In Table 17, the vapour pressure of the base gasoline and the corresponding M15 blended fuel is shown.

Table 17. **Vapour pressure of base gasoline and corresponding M15**

Vapour pressure of base gasoline and corresponding M15	
	Vapor pressure, kg/cm² at 38°C
High aromatic base gasoline	-
High aromatic base gasoline M15	0,86
Olefine rich base gasoline	-
Olefine rich base gasoline M15	0,73
Isoparaffine rich gasoline	0,36
Isoparaffine rich gasoline M15	0,53

Due to these results, SDAB commissioned scientists in Sweden to perform tests on alcohol mixed gasoline. In one project IVL (The Swedish institute for water and air research) tested evaporation of M15-gasolines at +3°C, +25°C and + 50°C. The latter representing the carburettor temperature one hour after driving.

A mixture of 6 % of ethanol in non-vapour pressure adjusted regular gasoline the benzene in vapour phase was determined to increase 10 % at +3°C, 20 % at +25°C and 50 – 60 % at 50°C compared to the regular gasoline without ethanol (Lindskog et al., 1986).

9. The INTROMET project

The INTROMET (INTroduction of METhanol) project was started in 2003 with financial support from the Swedish Energy Administration (Ecotraffic, 2006). The objective was to study the introduction of methanol as a motor fuel, primarily via low-level blending in gasoline. In addition to low-level blending, many other aspects on the introduction on a long-term horizon were also discussed in the report.

The INTROMET project comprised field trials, emission measurements on vehicles and engines, literature surveys and oil and fuel analysis.

Since the INTROMET project is the only recent project in the field of methanol blending, it is of interest to summarize some of the results from this project. The project report is in Swedish, which makes it less accessible in the English-speaking community and therefore, of high interest to summarise in the present report.

Fuel and vehicles

The fuel composition used in the INTROMET project was 3 % methanol and 3 % ethanol, i.e. M3E3. A couple of reasons were listed as factors behind the choice of fuel composition but the most important was that it was anticipated that a co-solvent would be necessary besides the 3 % methanol that is permitted according to the EU specification. By adding a maximum of 3 % ethanol, the oxygen content was also below the maximum of 2,7 % allowed in the specification at that time. The fuel was supplied by Statoil, who was also responsible for the refuelling station.

In the INTROMET project, 10 vehicles were run in the field test between 2005 and 2006 in the city of Gothenburg. The vehicles and some data for mileage and fuel used are listed in Table 18.

Table 18. Vehicles in the field trial

Car brand / model	Distance (km)	Fuel tot. (litres)	Fuel cons (l/100 km)
Toyota Yaris	7026	499	7,1
Toyota Yaris	8247	546	6,6
Renault Clio	4786	377	7,9
Renault Clio	8232	534	6,5
Renault Clio	4193	299	7,1
Toyota Yaris Verso	7525	373	5,0
Toyota Yaris	3500	259	7,4
Toyota Yaris	3940	286	7,2
Toyota Yaris[6]	*3940*	*286*	*7,2*
VW Golf	4191	400	9,6
Sum	**55580**	**3859**	

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[6] The journal for this vehicle is missing. Same data as for the vehicle above has been anticipated.

Engine and fuel system inspection

One vehicle was subject to extensive inspection of the engine and fuel system. A Toyota Yaris with registration number UPE 255, environmental class 2005 (Euro 4), had at the occasion of the inspection accumulated 30 000 km, of which 7 000 km was on the M3E3 gasoline. Some of the findings are summarized below.

The cylinders were inspected using a borescope via the spark plug holes in the cylinder head and the fuel pump was dismounted from the fuel tank and disassembled in smaller components (Figure 8).

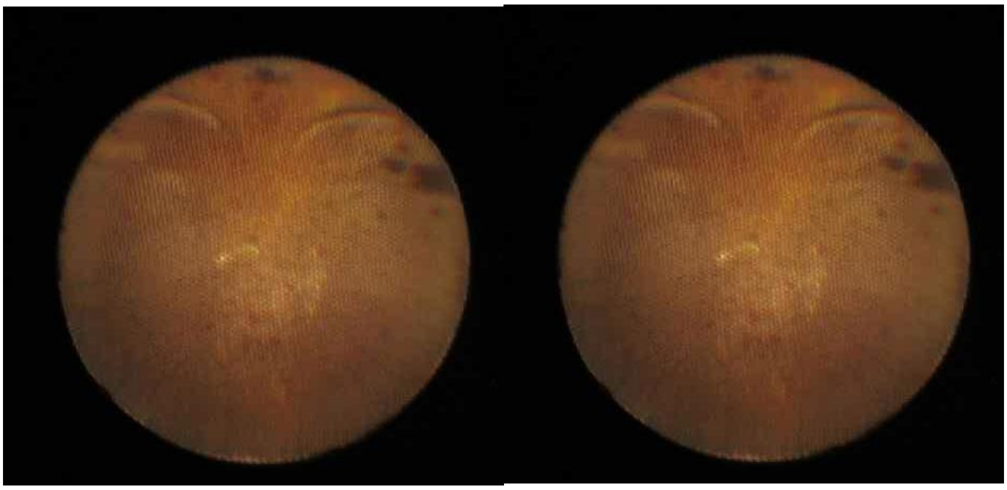


Figure 8. Borescope images of the cylinders

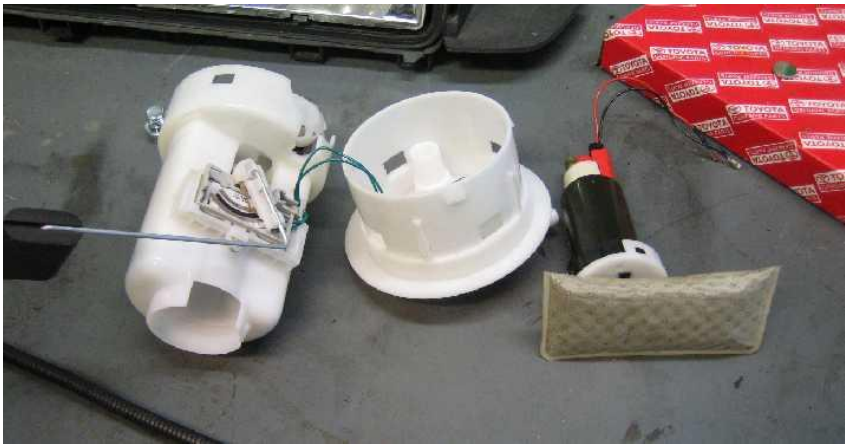
No degradation whatsoever could be seen on either the cylinders or on the fuel pump. The cylinder liner was clean and nice-looking (Figure 8). Some dark spots could be noted particularly on the left piston, which most likely is soot. For comparison, another Toyota Yaris that had not been part of the field trial and consequently had been running on 5 % ethanol-blended 95-octane standard gasoline was also inspected. This vehicle was newer and had lower mileage and somewhat cleaner cylinders but was in all other relevant aspects similar looking as the test vehicle.

The ignition plugs also looked normal (Figure 9).

Figure 9. Photo of the spark plugs

This particular car has a combined fuel supply pump and a filter but no additional separate filter. As seen in Figure 10, the filter, pump and other components were completely clean.

Figure 10. Photo of fuel pump and filter



In summary the workshop personnel confirmed that all inspected components looked normal.

Oil analysis showed impact of weather conditions (winter) and relatively short distances but no apparent negative impact of the blended fuel.

Emission results in chassis dynamometer tests

Before the field test started, one car, a Renault Clio of model year 2002, was tested at several fuel blends. The tests were conducted at a chassis dynamometer at AVL MTC in Jordbro. To isolate the effect of methanol on emissions, the base gasoline was ethanol free, and blended with 0 (baseline), 5, 10, 15 and 20 % methanol. The test cycle was the NEDC driving cycle and double tests at each fuel was conducted. The test temperature was 22°C.

Besides regulated emissions, also aldehydes (formaldehyde and acetaldehyde), particle mass, particle number and particle size distribution were measured. The latter components were measured with an electrical low-pressure impactor (ELPI™ by Dekati in Tampere, Finland).

Regulated emissions and fuel consumption

All the figures below show the weighted results for the whole NEDC test cycle (Swedish denotations “Totalt 1” and “Totalt 2”) from both duplicated tests and also the average of those tests (“Totalt M”).

The results for CO and HC emissions showed clear trends of decrease with higher content of methanol but in some cases, the measurement scatter was relatively large.

The measurement scatter for NO_X emissions was relatively high but the comparatively high level at the highest blending level suggests that the air-fuel ratio could have been too lean (Figure 11). This is a well-known phenomenon and also indicates that the blending limit for this particular car could lie at ~15 %. Modal emissions show the two phases of the driving cycle and the total weighted result.

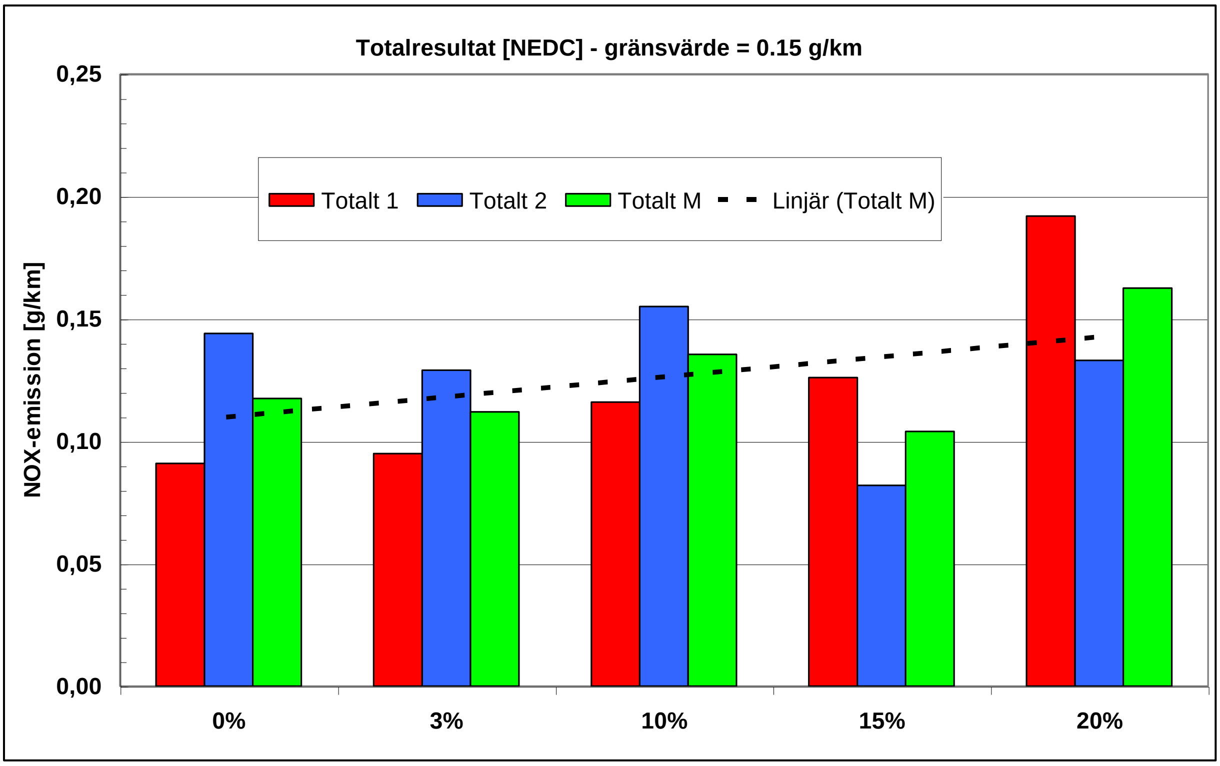


Figure 11. **NO$_X$ emissions**

Formaldehyde emissions showed an increasing trend (Figure 12) while the acetaldehyde emissions (not shown in a figure) were decreasing with increasing methanol content.

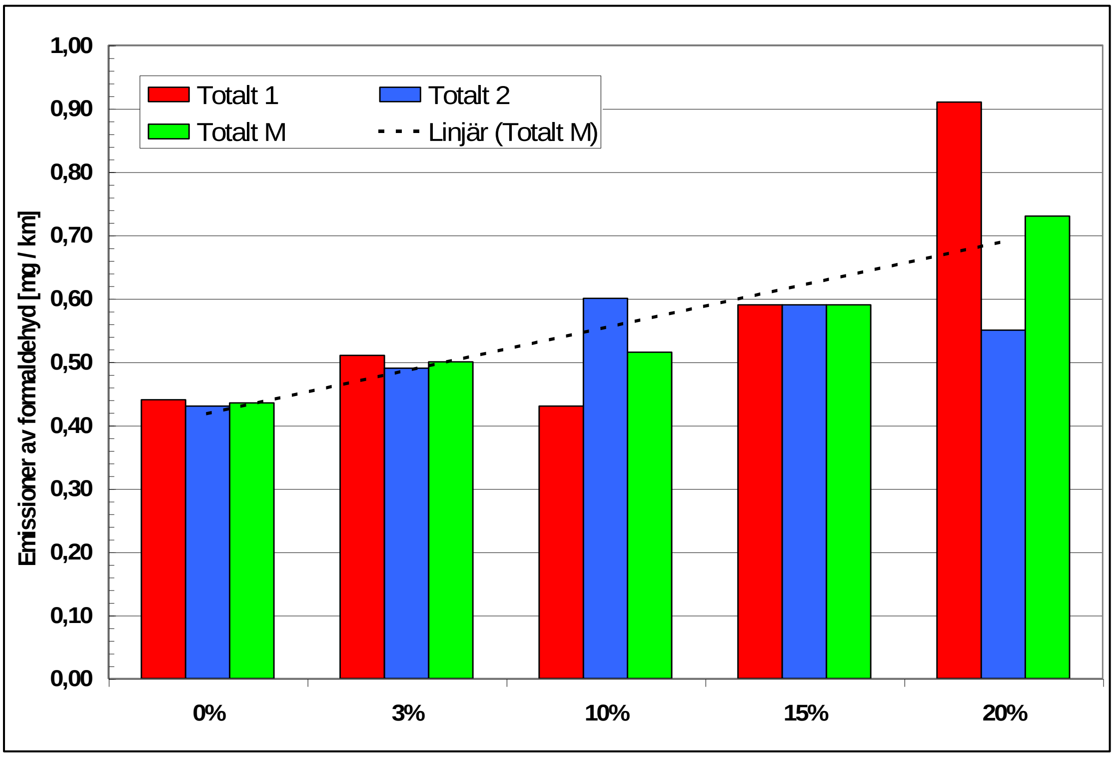


Figure 12. **Formaldehyde emissions**

Interestingly, the particle mass (PM) emissions decreased substantially with increasing methanol content (Figure 13). The decrease from baseline condition (0 % methanol) to the level for 20 % methanol content was as high as approximately a factor of 5. *Note that this was during test at normal ambient conditions, which was +22°C in this case. Therefore, it is not known if this very positive trend of PM vs. blending rate would also be valid at lower ambient temperatures.*

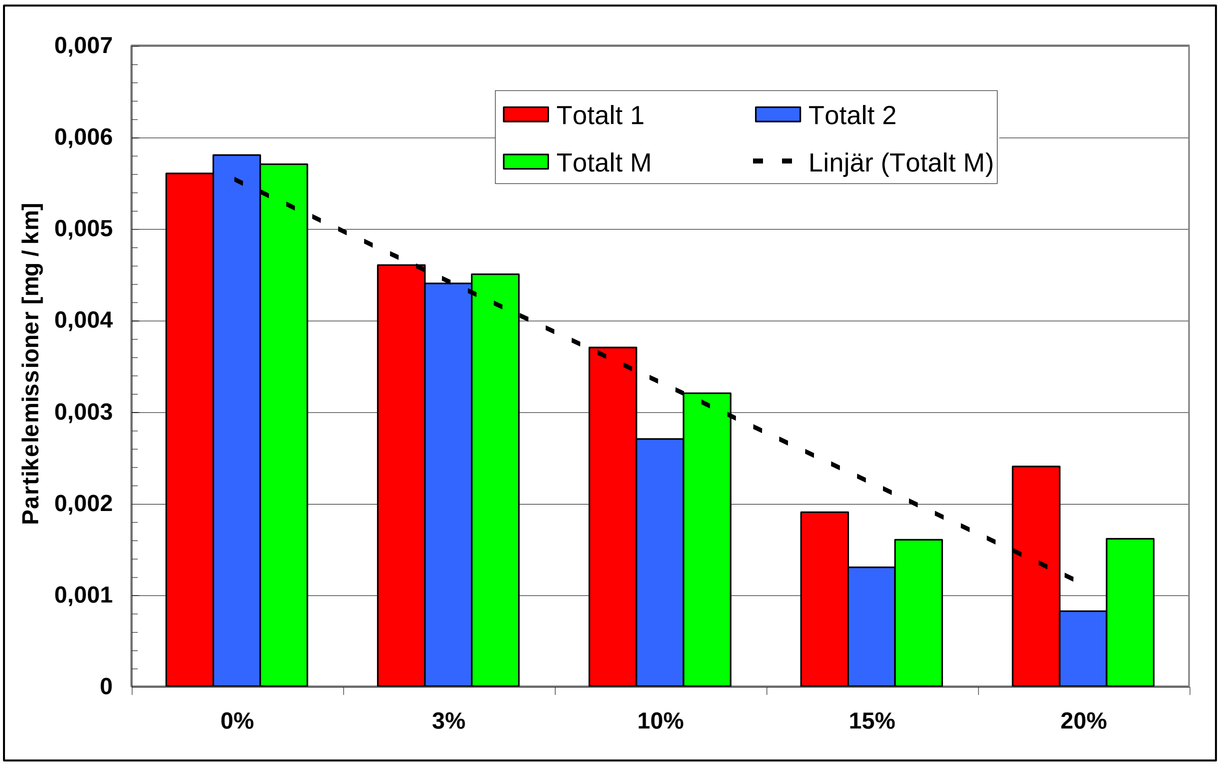


Figure 13. Particulate mass (PM) emissions

Extensive data on real-time emissions of particle number and size distribution were collected. One general observation was that significant levels of particles were emitted in the first acceleration with the cold engine and the acceleration in the highway part of the test cycle. The results for particle number and size distribution were not clear. Since the definition of solid particle number (SPN) was not conceived when these tests were carried out, it should be noted that the tests were not made with a sampling and dilution system that removes volatile particles. Thus, any firm conclusions from the results on particle number and size distribution should not be made.

A trend towards a marginal reduction of the CO_2 emissions could be seen. Since the ratio between hydrogen and coal is higher in methanol than in gasoline, this could explain the results for fuel consumption and CO_2 emissions.

Emission results in engine dynamometer tests

Emission tests on an engine dynamometer were carried out at the Chalmers Technical University in Gothenburg. The same fuel compositions as in the chassis dynamometer tests were used. Only regulated emission components were measured. A port-injected (Volvo) and a direct-injected engine (Mitsubishi) were used. Emissions were measured at various speed and load test points.

The extensive results were not always clear and are not discussed in detail here. Instead a short summary is made.

Methanol blending seems to have a certain positive impact on CO and energy efficiency. For HC and NO_X no clear impact could be seen. The trend was a small increase for HC for both engine types while NO_X decreased for the port-injected engine but increased marginally for the direct-injected engine. The exhaust content of methane, acetaldehyde, formaldehyde and methanol in the exhaust was very low. The catalyst will reduce these levels even further with the exception for methane. In summary, the authors concluded that no objections for blending methanol in gasoline could be found. Optimizing the engine and its injection system would give further improvements.

Concluding remarks

The authors of the INTROMET report concluded that blending of methanol in gasoline is viable today. The EU specification allows 3 % blending and emissions and driveability will not be affected at this blending level. A discussion was also made about introduction at a larger scale, if the fuel specifications of E10 and E85 fuels would allow a certain percentage (higher than 3 **%)** of methanol**.**

10. Some other Scandinavian projects of interest

Swedish tests on E4 gasoline

In this section, some results from a Swedish field trial on E4 gasoline are discussed. Although this was ethanol – not methanol – some of the results may be of general interest anyway and have some implications also on the use of methanol as a blending component. Thus, these results have been included and discussed here.

Evaporative and exhaust emissions from a market quality (base) gasoline and the same gasoline mixed with 4% of ethanol was performed on six passenger cars of 1982 to 1986 year model certified for the Swedish market according to the A10 regulation. Thus, the vehicles had no catalyst, λ-sensor or carbon canister.

The fuel specification is shown in Table 19 and the results from the evaporative emission tests are shown in Table 20.

Table 19. ***Evaporation of hydrocarbons from E4 fuel***

Specification of the base fuel		
Property	**Unit**	**Value**
Density @ 15°C	(g/ml)	0,759
IBP	°C	29
10% dest.	°C	45
50% dest.	°C	102
90% dest.	°C	155
FBP	°C	200
Colour	Pale yellow	
RVP	kPa	83
Lead content	g/l	0,0
RON		95,4
MON		94
Aromatics	% vol	38
Olefines	%vol	10

The evaporative emission test results, listed in Table 20, revealed 10 to 35 times higher HC levels in the SHED test compared to US limit value and the addition of ethanol increases the emission considerably (V. Grigoriades et al.). Total emissions as well as diurnal increase 40 % but hot soak emissions almost 80 %.

It could be noted that modern vehicles of the 2010’s with fuel injection systems and carbon canisters will have maybe 50-fold lower emissions but with faulty systems emissions may rise into the area shown here. It was also shown that it is important to use base gasoline adapted to the addition of even low additions of ethanol. Of the SHED test HC emissions, toluene increased 30 %, xylene 80 %, but benzene only 7 % when 4 % ethanol is added to the gasoline.

Table 20. Evaporative emissions

Evaporative emissions, SHED test (g/test).				
Vehicle/fuel combination		**Diurnal**	**Hot soak**	**Total**
Unleaded base gasoline	Toyota Corolla	41,3	15,9	57,2
	Saab 90	47,2	5,5	52,7
	Opel Ascona	65,1	8,4	73,5
	Volvo 245 DL	14,1	7,8	21,9
	Saab 900 GL	21,9	2,5	24,4
	VW Golf	23,5	4,6	28,1
	Average HC emiss.	35,5	7,5	43,0
	Benzene mg/phase	209,0	88,0	297
	Toluene mg/phase	88,0	104,0	192
	Xylene mg/phase	30,0	27,0	57
Unleaded base gasoline + 4% Ethanol	Toyota Corolla	54,7	24,5	79,2
	Saab 90	51,1	7,3	58,4
	Opel Ascona	69,1	8,1	77,2
	Volvo 245 DL	34,1	19,1	53,2
	Saab 900 GL	43,8	7,5	51,3
	VW Golf	?	?	35,9
	Average HC emiss.	50,6	13,3	59,2
	Benzene mg/phase	233	84	317
	Toluene mg/phase	151	101	252
	Xylene mg/phase	51	33	84
	HC % increase	42,4	78,5	37,8
	Benzene % increase	11,5	-4,5	6,7
	Toluene %increase	71,6	-2,9	31,3
	Xylene % increase	70,0	22,2	47,4

The results for regulated emissions are shown in Table 21.

Table 21. Regulated emissions

Exhaust gas emissions at US 73 test (A10)				
			Fuel	
			Unleaded base gasoline	**Unleaded base gasoline + 4% ethanol**
Average 6 vehicles	CO	g/km	21,1	19,3
	HC	g/km	1,57	1,53
	NOX	g/km	1,26	1,29
	Fuel cons.	l/10km	0,97	1,11
Volvo	Particulates	mg/km	26,6	21,5
Saab	Particulates	mg/km	6,9	6,1
Saab+Volvo	PAH total	µg/km	151	125
Average 3 vehicles	formal	mg/km	20,4	13,6
	acetal	mg/km	14,7	15,5
	acrolein	mg/km	3,3	4,1
	acetone	mg/km	1,3	1
	propanal	mg/km	2,3	2
	bensal	mg/km	28,6	25,9
	tolylal	mg/km	11,8	9,1
	Sum of aldehydes	mg/km	81,1	70,2

As is seen in Table 21, regulated emissions were almost unchanged when 4 % ethanol was blended in the gasoline but particulates and PAH as well as aldehydes were somewhat lower with the introduction of ethanol. The increase of fuel consumption is mysterious, maybe some error in the calculation formula has occurred.

In the following, a condensed review of some tests on evaporative and exhaust emissions dependence of gasoline and E4 is given (V. Grigoriades et al.). The vehicles tested were certified according to the Swedish A10 regulations that mean that they met the regulations without catalyst and evaporative control. The two gasoline qualities were one normal 98 octane leaded and one special unleaded 95 octane “base gasoline”. From the base gasoline an E4 quality was also made by mixing the gasoline with 4 % of dry ethanol. Only the results from base gasoline and E4 are shown here (Figure 21 and Table 23). The evaporative emissions increased almost 40 % when 4 % ethanol was blended into non-vapour pressure adapted gasoline. The toxic aromatics emissions increased in about the same range but for benzene which was only 7 % higher from the E4 fuel.

Table 22. Evaporative emissions, SHED test

Evaporative emissions, SHED test.				
		Diurnal	Hot soak	Total
Unleaded base gasoline	Toyota Corolla	41,3	15,9	57,2
	Saab 90	47,2	5,5	52,7
	Opel Ascona	65,1	8,4	73,5
	Volvo 245 DL	14,1	7,8	21,9
	Saab 900 GL	21,9	2,5	24,4
	VW Golf	23,5	4,6	28,1
	Average	*35,5*	*7,5*	*43,0*
Unleaded base gasoline + 4% Ethanol	Toyota Corolla	54,7	24,5	79,2
	Saab 90	51,1	7,3	58,4
	Opel Ascona	69,1	8,1	77,2
	Volvo 245 DL	34,1	19,1	53,2
	Saab 900 GL	43,8	7,5	51,3
	VW Golf	?	?	35,9
	Average	*50,6*	*13,3*	*59,2*
% increase with 4% ethanol		**42,4**	**78,5**	**37,8**

Table 23. Evaporative emissions of aromatic hydrocarbons

Evaporative emissions of aromatic hydrocarbons from gasoline versus E4, SHED test.				
		g Diurnal	**g Hot soak**	**g Total**
Unleaded base gasoline	Benzene mg/phase	209	88	297
	Toluene mg/phase	88	104	192
	Xylene mg/phase	30	27	57
Unleaded base gasoline + 4% Ethanol	Benzene mg/phase	233	84	317
	Toluene mg/phase	151	101	252
	Xylene mg/phase	51	33	84
Benzene	**% increase with E4**	**11,5**	**-4,5**	**6,7**
Toluene	**% increase with E4**	**71,6**	**-2,9**	**31,3**
Xylene	**% increase with E4**	**70,0**	**22,2**	**47,4**

When it comes to exhaust emissions they are quite the same regarding regulated emissions but the difference in fuel consumption was not acceptable and there is nothing said or primary figures given in the report to explain it (Table 24). Among the unregulated emissions particulates and PAH were somewhat lower for the E4 fuel and the same was true for aldehydes, except for acetaldehyde and acrolein.

Table 24. Exhaust gas emissions in US 73 test (A10)

Exhaust gas emissions at US 73 test (A10)				
			Unleaded base gasoline	**Unleaded base gasoline + 4% Ethanol**
Average 6 vehicles	**CO**	g/km	21,1	19,3
	HC	g/km	1,57	1,53
	NOX	g/km	1,26	1,29
	Fuel cons.	l/10km	0,97	1,11
Volvo	**Particulates**	mg/km	26,6	21,5
Saab	**Particulates**	mg/km	6,9	6,1
Saab+Volvo	**PAH total**	µg/km	151	125
Average 3 vehicles	**formal**	mg/km	20,4	13,6
	acetal	mg/km	14,7	15,5
	acrolein	mg/km	3,3	4,1
	acetone	mg/km	1,3	1
	propanal	mg/km	2,3	2
	bensal	mg/km	28,6	25,9
	tolylal	mg/km	11,8	9,1

Norwegian M15-test

During the period of 1980 – 1983, a test of gasoline-methanol fuel was performed in Norway (Norsk metanolgruppe, 1984). The responsible research and development organisation was founded by five oil and industrial companies. Grants were also received from the Norwegian oil and energy department. Technical support and emission testing was done at STI (The Government Technical Institute). After a pre-test of 6 vehicles, car importers were contacted and 9 of them proposed one or more models for testing. Around 100 vehicles took part in the project; some for shorter periods of time, others up to 3 years. In total 3 700 000 km was accumulated using M15 fuel. Most of the vehicles of 11 makes had carburettor engines and were slightly modified. The VW vehicles were more modified with new carburettors and inlet systems. All of the VW GTI injection engines were extensively rebuilt according to the instructions from VW in Germany.

All cars had to deliver monthly reports with fuelling data and problems noted. There were 94,2 % reports with no problems; 1,3 % had starting problems and 3,5 % had problems with uneven idling and engine stop. For vehicles that experienced running problems, 102 of the 108 were fixed at STI's workshops. No special starting problems were detected in wintertime even down to -35°C.

Norwegian M15 fuel

A special base gasoline was produced and after the admixture of 15 % methanol and 2 % isobutanol, the resulting super gasoline was 99 ROW minimum, max 0,15g/l Pb, water content max 250 ppm and RVP of 13,2 psi.

Storage and distribution

One batch of 400 m³ was unexplainably found to contain 1 400 ppm of water. However, it was decided to use the fuel. No material problems were seen in tank, piping or filling equipment. One distribution tank vehicle was used in Oslo for the entire period of time. The tank was made of aluminium and packing was made in Teflon. No problem could be seen in this system.

Two phase separations occurred in the project. One was during the snow melting period and the reason was that necessary packings were not in place. In the other case driveability problem in average temperatures of -18 °C was observed. In the storage tank, 3 300 ppm of water was found and 2 500 ppm in three of the cars. No explanation to the high water content was found.

One distribution pump experienced problem from corrosion of an aluminium plunger in a brass cylinder. Other than this, pumps worked as for gasoline.

Three underground storage tanks in the gasoline stations were emptied and inspected after the test. One tank was a new steel tank and was still looking as new after the test. One old steel tank earlier used for gasoline was rusty to the same extent as before the test. The third tank was coated with Derakane 470-36 from Dow Chemical before the test. At the end of the test the coating was completely unchanged.

During a 14-month period (two winters) M15 without isobutanol was distributed in one city. No problems with the vehicles or phase separation were detected.

Fuel consumption

The fuel consumption was measured for 7 cars on chassis dynamometer with M15 and gasoline. The theoretical increase in fuel consumption was 8 % with M15 fuel and it was found to be 9 % in the old ECE city test cycle and 8,5 % at constant speed of 80 km/h.

Materials problems from field test

Of the 100 vehicles, 16 experienced broken resistance of the fuel meters due to heavy corrosion of the wire and 17 had problems with corrosion of the fuel system giving blocked filters or nozzles. The blocking material consisted mainly of lead, zinc and iron compounds.

The inspection of 8 engines after the test revealed almost the same deposition of carbon and coke.

Wear of the engines was considered normal.

Oil change interval was 8 000 km and for 9 of the vehicles oil samples were drawn before oil change. All those samples were normal. One sample from 20 000 km oil life showed low base number and viscosity. Compared to gasoline, the M15 fuel showed normal values.

Emissions

Emissions were tested during the test period on M15 as well as gasoline for 4 vehicles according to the ECE 15-03 regulation. As the engines had the same tuning, emissions of CO were lower but also HC and NO (-22 %; -11 %; -7 %). Standard deviation in the tests was, however, high. After the test period 7 vehicles were tested on M15 according to ECE R15-03 and after recalibration to gasoline tested once more. M15 compared to gasoline gave CO: -27 ± 15 %, HC: -15±25% and NO: +3 ±6 %.

Conclusion and final remarks

The conclusion in 1983 from the project was that M15 fuel was a technically feasible alternative for Norway.

A comment of 2013 from the authors of the present report is that as gasoline engines in cars of today due to changes regarding emission regulations could have lower emissions in general but material problems still could emerge.

Norwegian M4 project

The Norwegian M4 project was run in Mongstad in a wet coastal climate. In the beginning, the fuel contained 4 % methanol and 2 % isobutanol but from summer 1980 to march 1982 only 4 % methanol was added to the super gasoline (Norsk metanolgruppe, 1984).

Around 40 vehicles of 1968 to 1981 model year were tested. No adjustments or change of parts were done. The vehicles were often driven short distances and engines thus often did not reach normal working temperature. No starting or driveability problems were experienced. The fuel consumption on chassis dynamometer at 80 km/h was about 0,5 % higher on M4-fuel, i.e. not significant. No problems with materials were found, except for rubber gasoline tubes being 5 % longer. No breakdowns were observed.

Low level of ethanol in gasoline

Ethanol added to gasoline is and has long been of interest for the Swedish farmer's association. And in following, results from tests on E0 to E25 fuels are presented (A. Laveskog, 1996).

A Swedish gasoline with 70 kPa RVP was used and mixed at the laboratory with four different levels of ethanol. The fuels were analysed as follows in Table 25. A four year old 1994 year model vehicle of 140 000 km mileage (no exchange of components) was tested for evaporative and exhaust emissions. The vehicle had a 2,4 l port fuel injected engine with λ-regulation, catalyst and activated carbon canister for evaporative emission control.

Table 25. **Fuel properties**

	Ref gasoline for evap. test	**Ethanol concentration in gasoline used for emission and fuel consumption test**				
Fuel property		**0%**	**10%**	**15%**	**20%**	**25%**
Density kg/m^3	758	770	772	773	774	775
Energy content MJ/kg	42,5	43,0	41,4	40,5	39,7	38,9
Energy content MJ/l	32,2	33,1	32,0	31,3	30,7	30,1
RVP, kPa	59,5	70	75,5	75,5	73	72,5
RON	96,6	97,5	99,5	100,3	101,1	101,4
MON	85,9	86,1	86,9	87,3	87,6	87,9

In the evaporative emission test (SHED test), the emissions increased with increasing vapour pressure; the highest emissions at 10 % ethanol in gasoline (Table 26). Not even with reference gasoline could the vehicle meet the certification limit for evaporative emissions due to the high mileage of the vehicle. It is shown that when ethanol is added to gasoline a, proper adjustment of the vapour pressure of the base gasoline must be made.

Table 26. Emissions in SHED test

Emissions at SHED test, g/test; Vehicle age 140 000 km						
	Ref gasoline	**Base gasoline 95 RON, 70 RVP, kPa**				
Ethanol concentration	**0%**	**0%**	**10%**	**15%**	**20%**	**25%**
RVP, kPa	59,5	70	75,5	75,5	73	72,5
Emissions	g	g	g	g	g	g
Diurnal	2,3	5,0	8,5	7,9	7,1	7,6
Hot Soak	0,7	2,1	3,0	3,1	2,9	2,6
Total	3,0	7,1	11,5	11,0	10,0	10,2

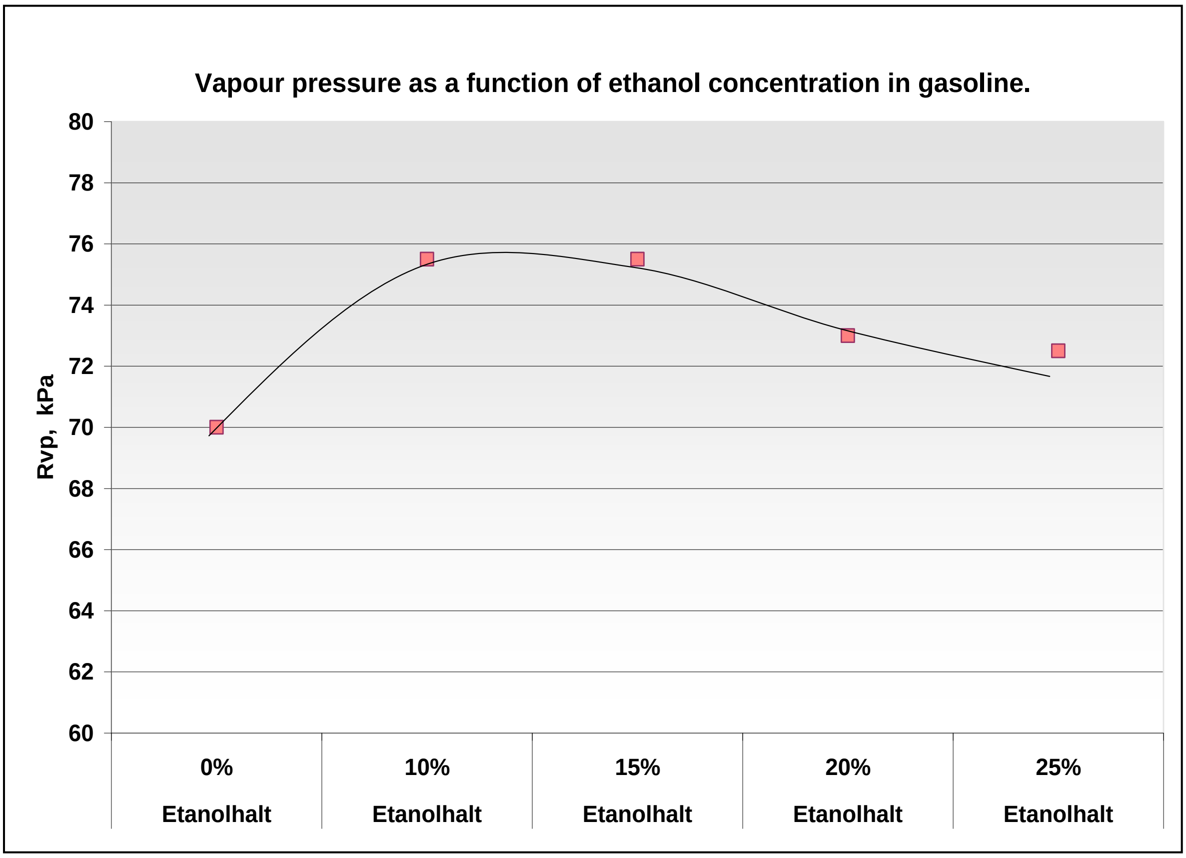


Figure 14. Vapour pressure as a function of ethanol content

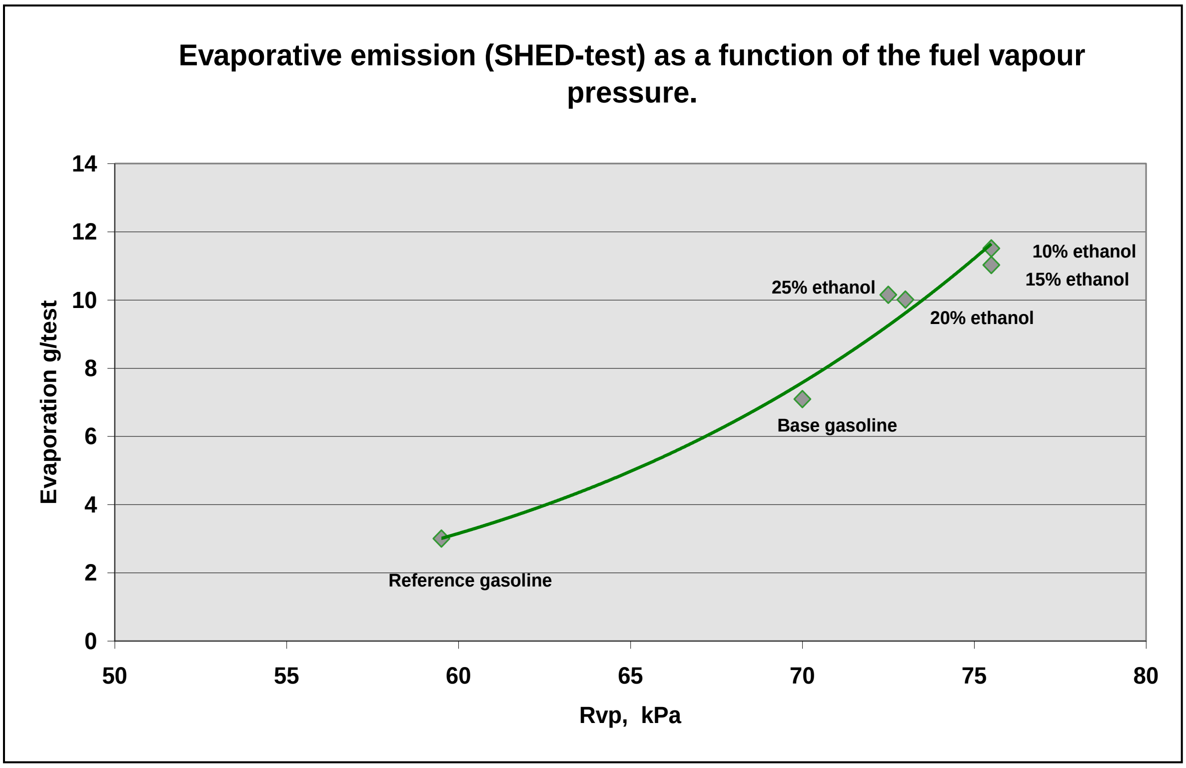


Figure 15. Evaporative emission (SHED test) as a function of vapour pressure

Exhaust emissions of regulated components (Table 27) were somewhat lower for CO and HC and higher for NO_X when ethanol was added to the gasoline, however all values were within the limits for which the vehicle was produced. Of high interest to note was that total CO_2 emissions as well as energy consumption was in the range of 1 % lower with 10 % of ethanol in the fuel without any adjustment to the vehicle.

Table 27. Exhaust emissions

<table>
<tr><th colspan="7">Exhaust emissions, US cycles. Different ethanol concentrations in gasoline.
2,4 l engine. Engine-out emissions. Vehicle mileage: 140 000 km</th></tr>
<tr><td></td><td>Ethanol concentration</td><td>0%</td><td>10%</td><td>15%</td><td>20%</td><td>25%</td></tr>
<tr><td rowspan="8">UDC</td><td>CO g/km</td><td>2,79</td><td>2,10</td><td>1,87</td><td>1,80</td><td>1,51</td></tr>
<tr><td>HC g/km</td><td>0,16</td><td>0,13</td><td>0,14</td><td>0,16</td><td>0,13</td></tr>
<tr><td>NOx g/km</td><td>0,16</td><td>0,18</td><td>0,21</td><td>0,23</td><td>0,30</td></tr>
<tr><td>Total CO_2 g/km</td><td>257</td><td>256</td><td>254</td><td>250</td><td>249</td></tr>
<tr><td>Fossil CO_2 g/km</td><td>257</td><td>256</td><td>254</td><td>250</td><td>249</td></tr>
<tr><td>NMHC g/km</td><td>0,15</td><td>0,12</td><td>0,12</td><td>0,14</td><td>0,12</td></tr>
<tr><td>Bf l/10km</td><td>1,07</td><td>1,11</td><td>1,12</td><td>1,12</td><td>1,14</td></tr>
<tr><td>Energy cons. MJ/100km</td><td>355</td><td>354</td><td>350</td><td>345</td><td>342</td></tr>
<tr><td colspan="7"></td></tr>
<tr><td rowspan="5">HDC</td><td>CO g/km</td><td>0,34</td><td>0,26</td><td>0,21</td><td>0,19</td><td>0,11</td></tr>
<tr><td>HC g/km</td><td>0,00</td><td>0,00</td><td>0,00</td><td>0,00</td><td>0,00</td></tr>
<tr><td>NOx g/km</td><td>0,17</td><td>0,24</td><td>0,24</td><td>0,28</td><td>0,29</td></tr>
<tr><td>Total CO_2 g/km</td><td>156</td><td>154</td><td>155</td><td>150</td><td>150</td></tr>
<tr><td>Fossil CO_2 g/km</td><td>156</td><td>154</td><td>155</td><td>150</td><td>150</td></tr>
</table>

	NMHC g/km	0,00	0,00	0,00	0,00	0,00
	Bf l/10km	0,64	0,66	0,67	0,66	0,69
	Energy cons. MJ/100km	213	209	211	204	207

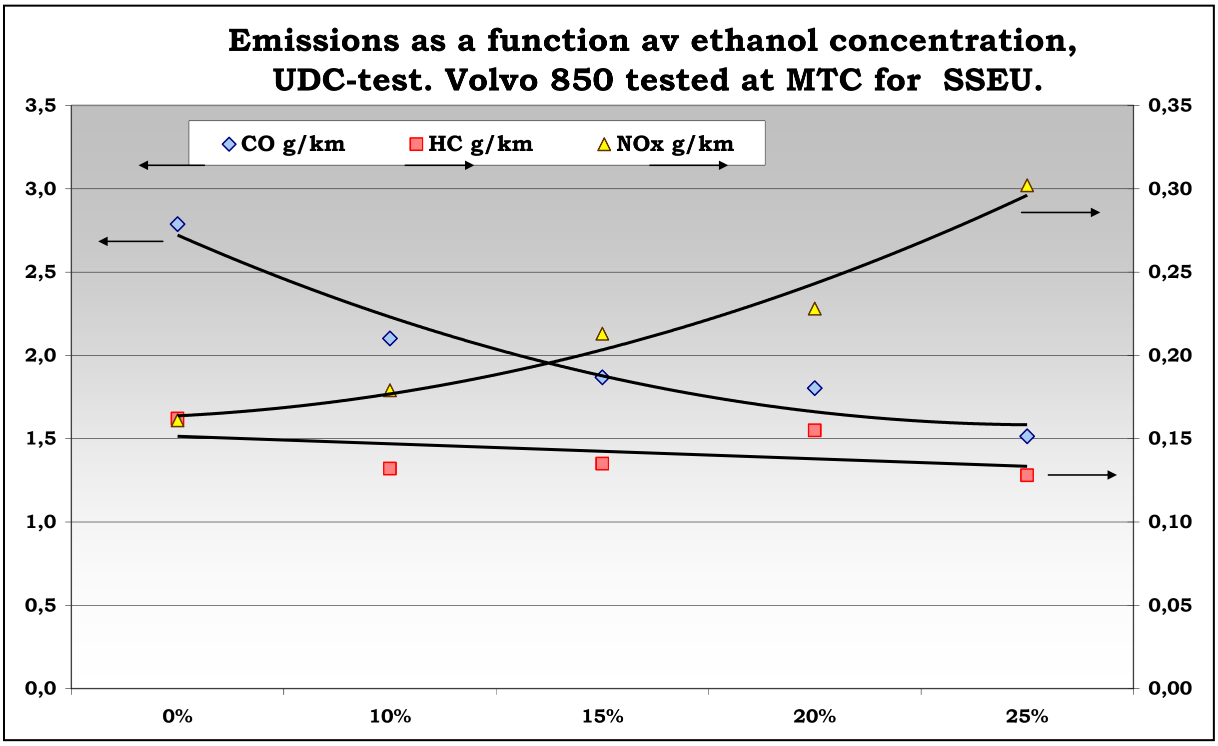


Figure 16. **Regulated emissions as function of ethanol concentration**

The emissions from vehicle 1 without feed-back regulation of the air-fuel ratio shows substantially lower CO and increased HC and NO_X with increasing ethanol concentration, due to the lean out effect. For all the tests but one for vehicle 3, CO_2 emissions and energy consumption are lower for the ethanol blends; the greatest reductions for the 25% blend. This means that ethanol to some degree seems to have improved the efficiency of the engines even with non-modified ignition and compression ratio.

In Figure 17 the energy consumption as a function of ethanol concentration in the fuel is shown.

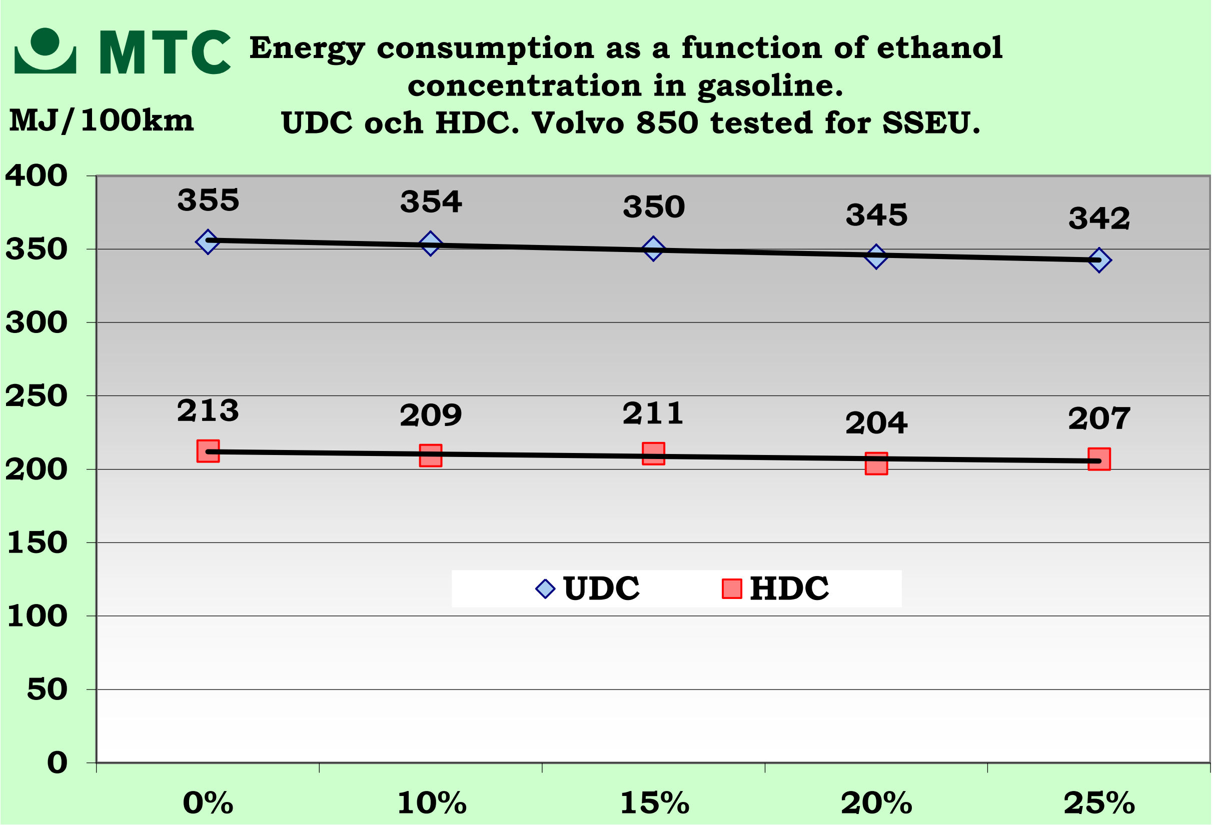


Figure 17. **Energy use with varying ethanol concentration**

Vapour pressure adjusted gasoline.

In another Swedish test two ethanol concentrations were used in standard (70 kPa RVP) and vapour pressure adjusted (63 kPa RVP) gasoline. All six resulting fuels were used for exhaust emission tests but only the 10 % ethanol concentration was used for evaporative emission test in a vehicle without evaporative emission control (Table 28). From the table it can be seen that a 10 % concentration of ethanol in the base gasoline quality required an RVP lowered with >5 kPa in order to keep the vapour pressure below the desired 70 kPa which is the Swedish standard for summer gasoline.

Table 28. **Vapour pressure**

Base gasoline, Intended	**Ethanol conc.**	**Ethanol conc.**	**Ethanol conc.**
	0%	10%	25%
RVP, kPa	Measured RVP, kPa (ASTM 5191)		
63	64	69	67
70	71,5	76	73

The fuels were tested in three vehicles representing three levels of emission control:

- Vehicle. 1: 2,4 l engine, Controllable jet carburettor engine repaired and adjusted to a level "as new".
- Vehicle. 2: 2,4 l engine, First generation emission control with Fuel injection, λ-sensor and catalyst, good condition.

- Vehicle. 3: 2,3 l engine, second generation adaptive emission control with Fuel injection, λ-sensor and catalyst , good condition.

Vehicle 1 had a carburettor similar to what is used in many motorcycles; the other represents emission control with lambda sensor and catalyst. Evaporative emissions were tested only in vehicle 1, which had no evaporative emission control; again like what is found in most motorcycles. The evaporative emissions were only tested for some of the fuels as shown in Table 29

Table 29. Evaporative emissions

Evaporative emissions, Vehicle 1 without emission control.						
	Diurnal			**Hot Soak**		
Base gasoline, Intended	**Ethanol conc.**	**Ethanol conc.**	**Ethanol conc.**	**Ethanol conc.**	**Ethanol conc.**	**Ethanol conc.**
RVP, kPa	0%	10%	25%	0%	10%	25%
63	-	25,7	-	-	13,2	-
70	26,5	26,5	-	10,7	15,9	-

The exhaust emissions and fuel consumption were as follows in Table 30 and Table 31.

Table 30. Regulated emissions, ”63 RVP”

Gasoline "63 RVP"	**Vehicle 1**			**Vehicle 2**			**Vehicle 3**		
UDC	**0%**	**10%**	**25%**	**0%**	**10%**	**25%**	**0%**	**10%**	**25%**
CO g/km	11,71	5,30	3,28	2,15	1,82	1,13	1,16	1,06	1,23
HC g/km	1,34	1,62	2,24	0,21	0,17	0,12	0,06	0,06	0,05
NOx g/km	1,25	1,44	1,35	0,17	0,18	0,23	0,14	0,14	0,13
CO2 g/km	237	237	232	243	240	235	242	253	250
NMHC g/km	1,31	1,59	2,22	0,18	0,15	0,10	0,05	0,05	0,04
F.C. l/100km	10,5	10,6	11,0	10,0	10,3	10,6	9,9	10,8	11,3
F.C. MJ/100km	349	338	330	331	328	320	327	345	342
HDC	**0%**	**10%**	**25%**	**0%**	**10%**	**25%**	**0%**	**10%**	**25%**
CO g/km	7,13	1,89	0,93	1,02	0,67	0,52	0,33	0,30	0,26
HC g/km	0,45	0,42	0,50	0,07	0,05	0,04	0,01	0,01	0,01
NOx g/km	1,25	1,52	1,43	0,07	0,06	0,08	0,02	0,01	0,01
CO2 g/km	149	150	145	179	178	175	150	148	149
NMHC g/km	0,43	0,41	0,49	0,06	0,03	0,02	0,01	0,00	0,00
F.C. l/100km	6,6	6,5	6,7	7,3	7,6	7,9	6,1	6,3	6,7
F.C. MJ/100km	217	208	201	243	241	238	202	201	202

Table 31. Regulated emissions, ”70 RVP”

Gasoline "70 RVP"	Vehicle 1			Vehicle 2			Vehicle 3		
UDC	**0%**	**10%**	**25%**	**0%**	**10%**	**25%**	**0%**	**10%**	**25%**
CO g/km	16,54	5,21	2,08	2,11	1,71	0,98	1,13	1,09	1,25
HC g/km	1,75	1,23	2,36	0,17	0,15	0,13	0,06	0,06	0,07
NOx g/km	1,73	1,36	1,05	0,19	0,17	0,30	0,16	0,15	0,12
CO2 g/km	238	240	229	243	240	238	251	244	238
NMHC g/km	1,00	1,20	2,35	0,14	0,13	0,11	0,05	0,05	0,06
F.C. l/100km	10,7	10,7	10,9	10,1	10,4	10,8	10,3	10,4	10,8
F.C. MJ/100km	355	342	327	335	331	327	342	334	327
HDC	**0%**	**10%**	**25%**	**0%**	**10%**	**25%**	**0%**	**10%**	**25%**
CO g/km	3,05	1,39	0,95	0,91	0,70	0,40	0,24	0,37	0,24
HC g/km	0,37	0,34	0,56	0,06	0,06	0,04	0,01	0,05	0,01
NOx g/km	1,33	1,41	1,32	0,06	0,07	0,09	0,02	0,02	0,03
CO2 g/km	153	150	147	179	176	173	152	148	147
NMHC g/km	0,36	0,33	0,55	0,04	0,04	0,02	0,00	0,04	0,01
F.C. l/100km	6,5	6,5	6,8	7,4	7,6	7,9	6,2	6,3	6,7
F.C. MJ/100km	216	209	205	244	241	237	206	202	200

Aldehyde emissions from fuel components

Concerning unregulated emissions a number of different fuels and fuel components were tested in a vehicle with adaptive lambda regulation but with the catalyst removed in order to get concentrations high enough for analyses. Here are shown the emissions of aldehydes (Figure 18). It is seen that many of the fuels gave rise to higher emissions of formaldehyde and acetaldehyde, however for example methanol was not worse than MTBE.

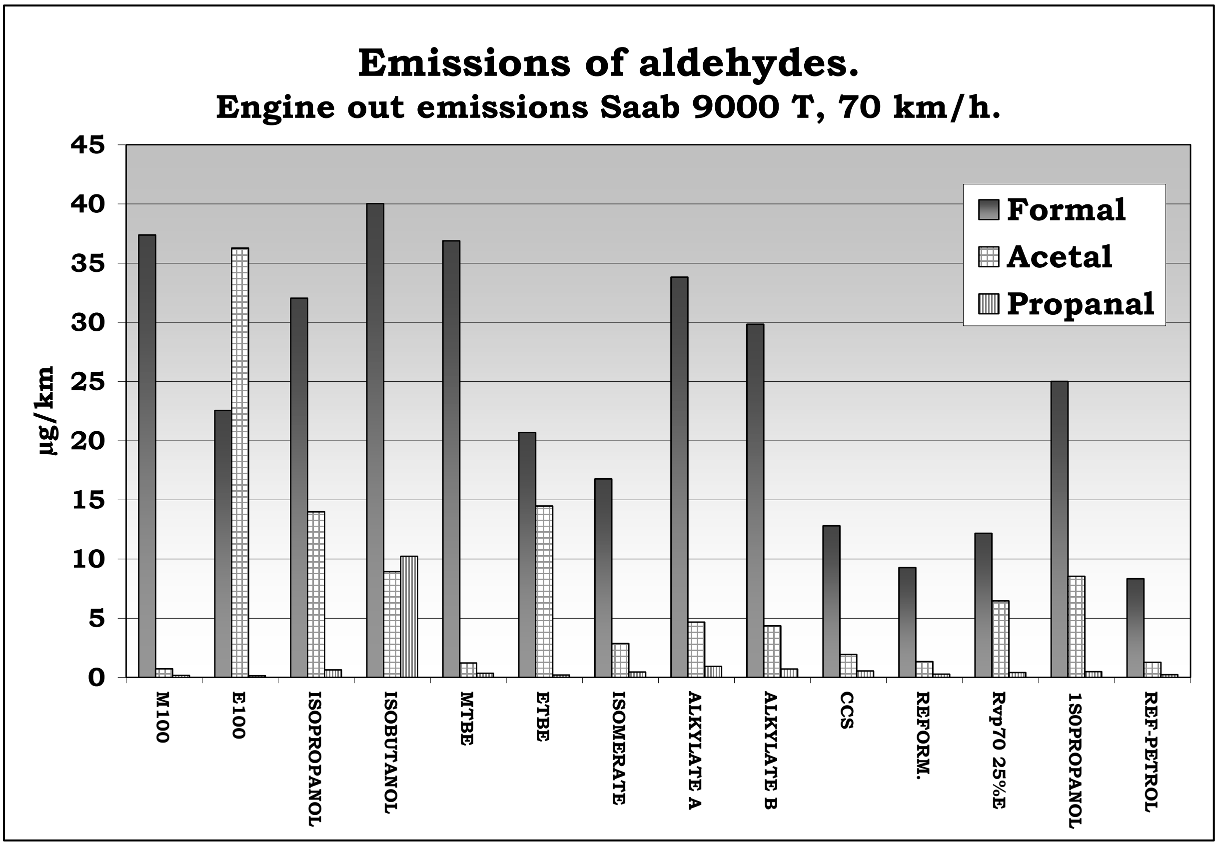


Figure 18. **Aldehyde emissions**

Swedish project on bioethanol (E70 & E85) and biogas

This project was included in the present study mainly since the results provide unique information about the emission of polycyclic aromatic hydrocarbons (PAH) at low ambient temperatures from two fuel-flexible cars running on ethanol fuel. In this short overview of the project, some data on emissions of regulated and several unregulated emission components are also shown and discussed.

Introduction and background

This Swedish research investigation was focused on the characterisation of exhaust emissions from vehicles operating on biofuels; one bi-fuel vehicle and two fuel-flexible (FFV) vehicles. The vehicles were run on bio-based fuels such as biogas and gasoline/ethanol fuel blends during different testing conditions (Roger Westerholm et al., 2008).

The aim of the project was to provide data and guidance to be used as basis for the future use of alternative fuels on the Swedish (and the European) market. The testing conditions investigated were two different driving cycles, i.e. the new European driving cycle (NEDC) and the Artemis driving cycles. Furthermore, two testing temperatures (+22 and -7°C) were used in the NEDC. The regulated as well as several unregulated emission components were investigated.

During wintertime, more gasoline is blended into the alcohol fuel to improve cold start properties. Thus, the cars were tested at the lower ambient temperature on both E70 and E85 fuels. No intermediate blends between E5 and E70 were tested.

Although the two fuel-flexible cars were run on ethanol blends, some of the results might also be relevant for methanol – or at least these topics should be investigated in future studies on methanol. Results on the biogas-fuelled vehicle are not specifically commented here, so the reader should refer to the source if such information is of interest.

In Table 32, some vehicle data on the two fuel-flexible vehicles are shown (a more comprehensive table, including also the biogas-fuelled car, is available in the source report).

Table 32. Vehicle specification of the two FFV cars (shortened compared to the table in the source)

Parameter / **Car**	**FFV1**	**FFV2**
Car, model	Saab 9-5 Biopower	Volvo V50 1.8 F
Model year, month	2005-12	2005-12
Certification	Euro 4	Euro 4
Odometer (km)	34 354	11 826
Inertia mass (kg)	1 670	1 420
Engine type	L4[a]	L4[a]
Displacement (cm^3)	1 985	1 798
Power (kW)[c]	110/132	92
Torque (Nm)	280	165
Max BMEP[c] (bar)	17,7	11,5
Compression ratio	8,8:1	10,8:1
Fuel	E5-E85	E5-E85

Notes:

[a.] In-line 4-cylinder engine (L4)

[b.] Higher numbers are for E85 (Saab) and lower for gasoline (Saab)

[c.] Brake mean effective pressure (BMEP)

Regulated emissions

For the regulated emission components of carbon monoxide (CO), hydrocarbons (HC) and oxides of nitrogen (NO_X), there was a relatively small impact of the fuels tested. In the Artemis motorway test cycle, the CO emissions were high for E5, whereas E70 and E85 had significantly lower levels. This trend was not seen for HC emissions.

As a general observation, CO and HC increased substantially at the low ambient temperature (-7°C). This was even more pronounced for the fuels with higher ethanol contents (E70 and E85). One of the fuel-flexible cars had very high NO_X emissions in the NEDC test cycle at -7°C.

Particulate emissions

In general, particle mass emissions (PM) were low at +22°C, except for the Artemis motorway test cycle where the level was relatively high for the two fuel-flexible cars running on E5, presumably due to fuel enrichment at the high engine loads. A reduction of the ambient temperature from +22°C to

-7°C generally increased the PM emissions for all fuels tested. PM emissions increased at the low temperature by increasing ethanol content of the fuels tested.

Particle number (PN) emissions were measured according to the (at that time) proposed particle measurement protocol (PMP) for Euro 5/6 emission regulations regarding this emission component. Compared to the +22°C NEDC tests, the -7°C tests showed higher PN emissions in general. The fuel dependence on PN emissions for the fuel-flexible cars was relatively small in most cases.

The particle size evaluation using an instrument (ELPI by Dekati Ltd. in Finland), which measures 12 size classes from 7 nm to 10 μm in real-time showed that the number of particles larger than 30 nm was usually lower for the E70, E85 and biogas fuels compared to the E5 fuel. However, in some cases, the number of the smallest size class of particles (7 to 30 nm) was higher in the E70 and E85 cases.

Aldehydes and some other speciated volatile emissions

Results on aldehyde emissions were more or less as expected when a fuel switch is made from gasoline to ethanol. The fuels with higher ethanol content gave somewhat increased formaldehyde levels and much higher levels of acetaldehyde.

Ethene was higher for the ethanol fuels but propene, 1,3-butadiene, benzene and toluene were lower.

PAH emissions and cancer potency

Sampling of both particle-associated and semivolatile-associated PAH was made in diluted exhaust using a CVS dilution tunnel, as previously described. Exhaust particulates were sampled on Teflon coated glass fibre filters (Pallflex Inc., USA) and semivolatile-associated compounds were sampled on Poly Urethane Foam Plugs (PUFs), as described in detail elsewhere (Westerholm R. et al., 1991). After sampling both filter and PUF samples was stored in a freezer until extraction and chemical analysis was made. PAH emissions are divided into two parts, i.e. particulate-associated and semivolatile-associated PAH emissions.

To limit this section only results from FFV1 are shown. However, the results for FFV2 were roughly similar and thus, the discussion and conclusions below apply to both vehicles and presumably, also to other vehicles that use similar technology. In Figure 19, results for particulate-associated PAH are shown and correspondingly, the results for PAH in the semivolatile phase are shown in Figure 20.

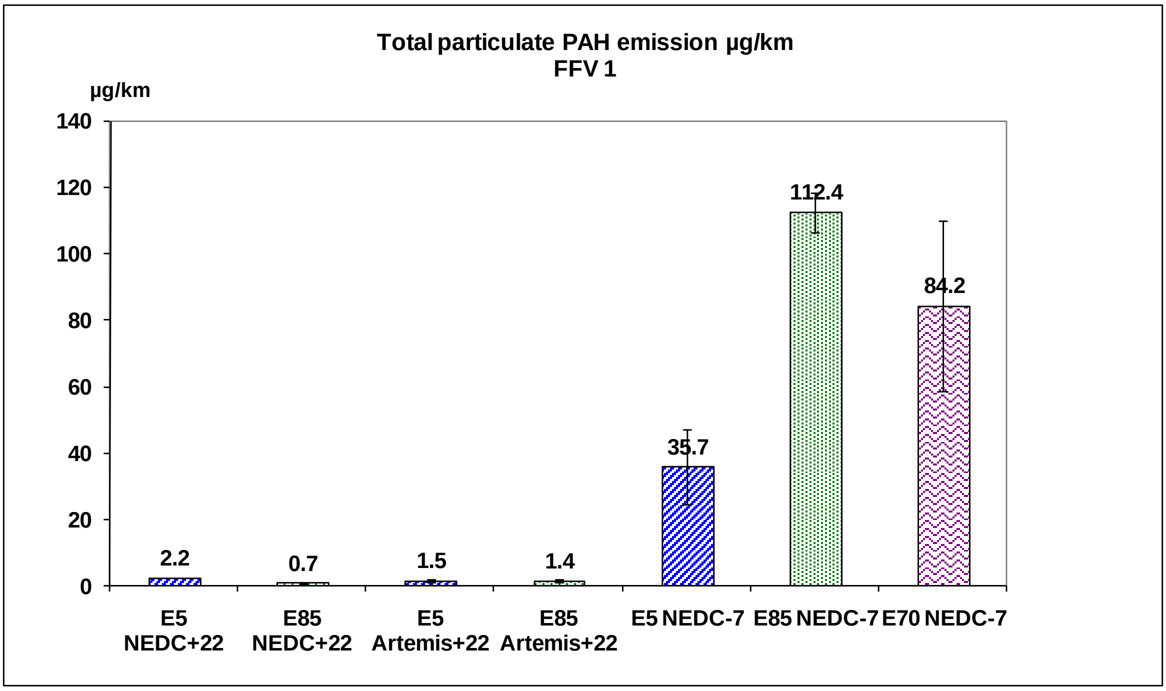


Figure 19. **Total PAH emissions in the particulate phase for FFV1**

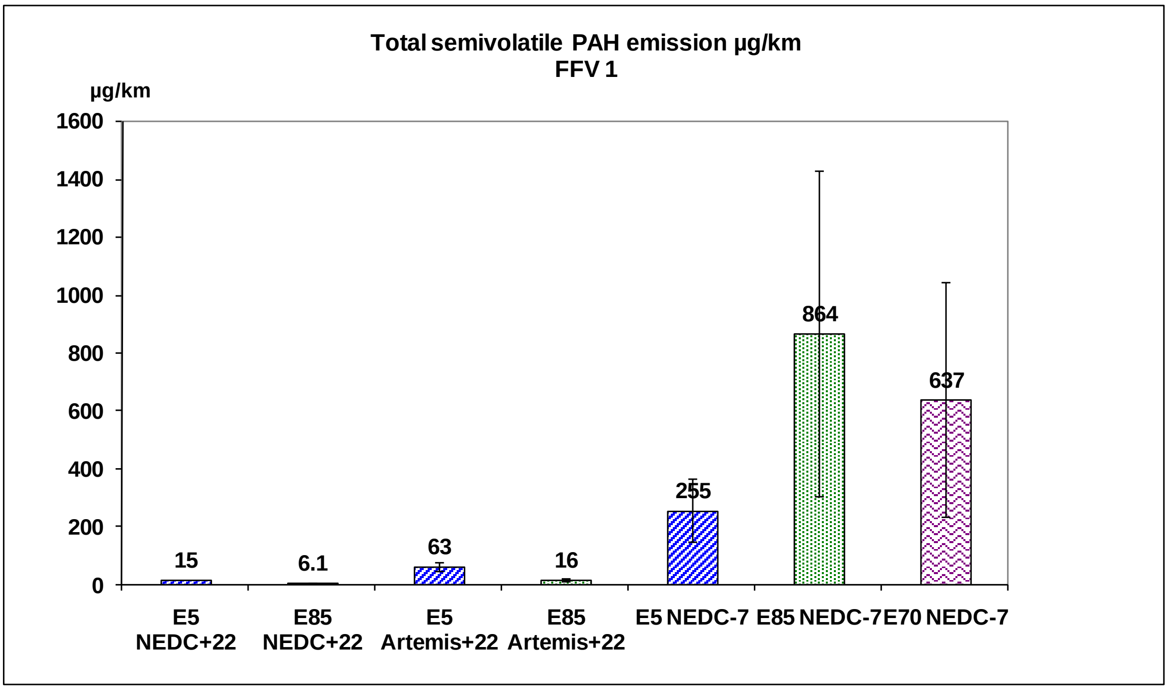


Figure 20. **Total PAH emissions in the semivolatile phase for FFV1**

While PAH in both the particulate (Figure 19) and semivolatile (Figure 20) phases appear marginally lower for E85 than E5 at high ambient temperature (+22°C), the result is totally reversed at the lower temperature (-7°C). Both the summer fuel (E85) and the winter fuel (E70) had higher PAH emissions than E5. Naturally, it should also be noted that PAH emissions increase considerably for the E5 fuel when the temperature decreases. The relative increase is greater than the corresponding increase of HC emissions.

The total carcinogenic potency was evaluated using the Toxic Equivalence Factor (TEF) concept. By this definition, relative cancer potency factors for each PAH compound are assigned using published data. By weighing the emissions of each compound, a total carcinogenic potency can be evaluated. Data for cancer potency resulting from both particulate and semivolatile phases are both shown separately and added together in Figure 21.

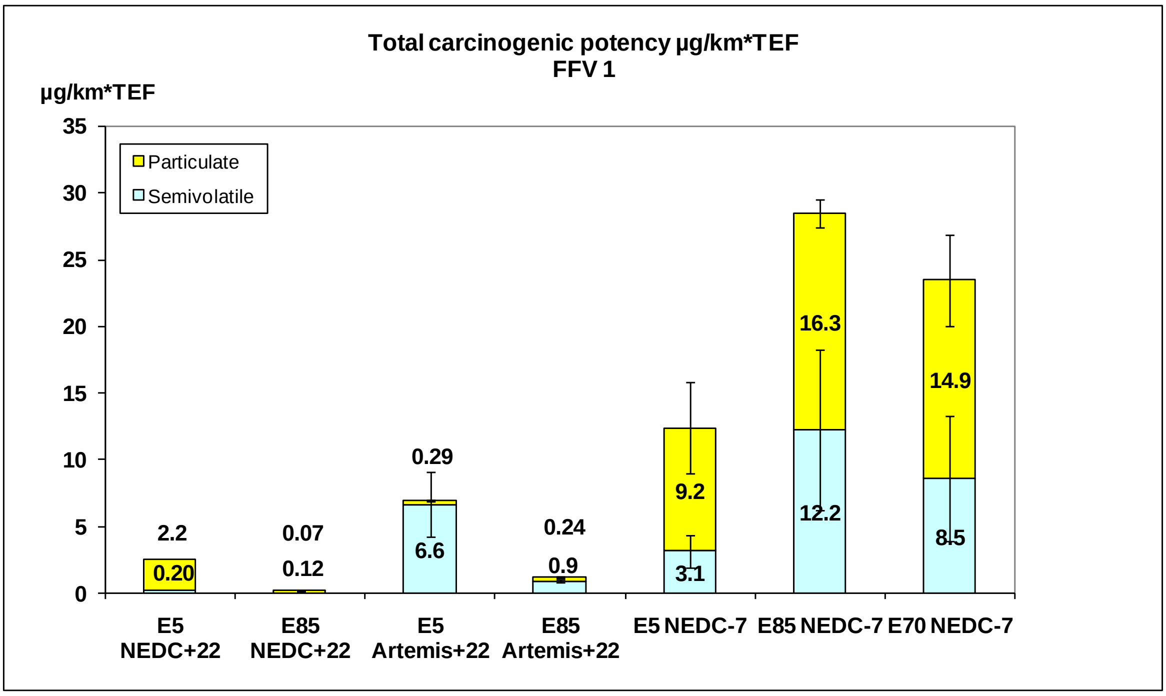


Figure 21. Total carcinogenic potency for FFV1

At the higher ambient temperature, E85 has an advantage over E5 but at the lower temperature, the cancer potency is higher for E85 and E70. Cancer potency increases with increasing ethanol content in the fuel. It is likely that a certain temperature in the interval between +22 and -7°C could result in similar cancer potency for both E5 and E85.

To put the results on PAH in some perspective, some comments in the following are added by the authors of the present report. It should be noted that the assessment presented above is only relative; it does not say, for example, how many cancer cases each fuel could result in due to exposure in, e.g. urban environment. Neither does this take into account that various emission components are transformed (e.g. oxidized) in a different way in the environment, which obviously may alter the composition of inhaled emission components and their effects on man. In line with the previous comment, this does not necessarily say that the total impact will be exactly the sum of particulate and semivolatile phases. Nevertheless, this way of assessing the data on cancer potency is both simple and provide the basis for a rough comparison of various fuels and engine/aftertreatment technologies. The general application of this methodology is, therefore, generally recommended in comparisons of cancer potency from various vehicle/fuel options.

Some general conclusions

With decreasing (ambient) temperatures, emissions of unwanted exhaust components during cold start at low ambient temperature (-7°C) increases substantially. At ambient temperatures lower than -7°C, cold start emissions of these exhaust components are expected to increase even more substantially. This is particularly important for the fuel-flexible cars regarding cold start emissions at low ambient temperatures. The use of E70 during wintertime instead of E85 provides some improvement of the exhaust emissions at the low temperatures. The authors of the study speculated that second generation of direct fuel injection would have a great potential to reduce these cold start emissions. A discussion about possible benefits of this technology can also be found in Chapter 12 in the present report.

Discussion – implications

The Swedish study on biogas and ethanol vehicles did not investigate the impact of low level blending. On the basis of the results shown and discussed above, it would have been interesting if also lower levels of blending would have included in the study. However, no funding for such investigations was available and the focus was different when the study was initiated. While the results on the two ethanol fuels (E70 and E85) indicated that the impact on emissions of blending level might be somewhat linear, this does not necessarily imply that this would be the case for lower levels of blending in conventional gasoline cars. However, if an increasing level of ethanol content, e.g. from E5 to E10, would imply that the PAH emissions and cancer potency increases, this could have negative impact on human health. Today, E10 is allowed in the European Union and it is already used in some EU member states, of which Finland has similar climatic conditions as Sweden. It has been proposed by the Swedish government that E10 could be introduced in Sweden from May 1, 2015[7]. Surprisingly, the impact on health has not been high up on the agenda in the discussions about E10 in Sweden and comprehensive results on E5/E10, such as in the study discussed here have not been generated.

The methodology of sampling and analysing PAH and their impact on human health should be further developed. Some of the work by Westerholm et al. at Stockholm University has already been mentioned above. Improvements of the extraction and analysis methods have enabled reducing the detection level. As the vehicles are becoming cleaner and cleaner, an increase of the sampling volume would most certainly also be welcome to facilitate investigating smaller differences between various fuels and engine technologies. A recent report, where two different diesel fuel qualities were investigated on a diesel car illustrates this problem (Ecotraffic, 2012-04-15). A special high-volume sampler was developed in order to increase sampling but a limitation of the sampling probe was also a bottleneck[8]. All-in-all, it was very difficult to distinguish between the two fuels regarding the selected unregulated emission compounds.

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[7] Actually E10 is currently allowed by the EU but the lack of economic incentives as, e.g. tax exemption for the whole quantity of ethanol, has made the introduction of E10 practically impossible. Currently, only E5 is available on the Swedish market.

[8] Due to limitations of the sampling probe, the high-volume sampler could not be utilized up to its maximum capacity in the test cell.

11. Short notes about some miscellaneous projects

Volkswagen AG has made extensive testing of unregulated emissions from different engine types and fuels. Test of methanol (M95 with 5 % pentanes) revealed lower HC and CO emissions compared to gasoline but much higher NO_X and aldehyde emissions. However the methanol vehicles were all prototypes, which was not the case for the gasoline fuelled ones. A richer tuning, to the same level as for the gasoline engines may have lowered NOx as well as formaldehyde emission (Volkswagen AG, 1989).

Startability of methanol vehicles, “M100”, at low temperatures was tested at the BP Sunbury laboratories. The best overall choices were found to be straight run gasoline (SRG) and light condensate, at 12 % concentration in methanol for summer and 16 % for winter. SRG had 70 % saturated hydrocarbons and a final boiling point FBP of 135°C. The condensate was 90 % saturated hydrocarbons with FBP of 125°C with descriptions in tables (SDAB, 1987) and (P. Beckwith et al, 1986).

ARCO chemical Co. tested 16 matched vehicles that ran on gasoline with multifunctional additives or gasoline with 5 % methanol and 5 % TBA (tertiary butyl alcohol). Driving distance was set to 50 000 miles in 24 months or less. SHED emissions were about 10 % higher for the gasoline-methanol blend but 10 % lower exhaust emissions for CO and HC and essentially the same NO_x emissions. Emissions in the SHED test comprised methanol to a sizeable part (30 %) at a RVP of 9,6 LB.

In as project commissioned by SDAB evaporation of gasoline components have been studied for two gasoline qualities, one regular and the other a different base with 5 % ethanol. (E5) The E5-fuel had a higher evaporation than gasoline, most due to butanes. There was also a tendency for a higher evaporation of aromatics (Lindskog et al., 1986).

12. Discussion

The main topic for discussion is without doubt exhaust emissions and, in particular, emissions at low ambient temperatures, where compounds posing health hazards can be formed. In this context, it has been necessary to extend the discussion beyond only low-level blending, since much experience and results from high-level blending are also of relevance to the topic. Potential technical solutions to overcome this problem are also discussed.

Besides emissions, the main barrier for the moment seems to be the lack of interest in methanol from automotive and oil industries. On the legislative side, the current EU limit of maximum 3 % is a barrier that will put a cap on the total volume of methanol that could be introduced on the market. Furthermore, the latest version of the Worldwide Fuel Charter September 2013, still retain the text "methanol is not permitted" as previous version, which indicates the negative attitude of the auto industry regarding methanol blending (ACEA, AAM, EMA and JAMA, 2013). Thus, it should be discussed if a higher blending rate would be a favourable route for large-scale introduction rather than the utilization of methanol via fuel-flexible and/or dedicated vehicles.

Cold start emissions and associated health effects

Without doubt, it can be concluded that the cold start emissions is one of the most significant problems for alcohol fuels. It should be pointed out that this is not mainly due to the lack of catalyst activity due to that the catalyst has not reached its light-off temperature early enough in the test cycle. In addition, there is not much difference between gasoline and alcohol fuels in this respect. The main problem is the fuel enrichment needed to start the engine and this has several reasons. First, alcohols have a specific boiling point and do not contain lower-boiling fuel components such as gasoline. E85 and M85 fuels contain such components to a certain extend and naturally the content of lower-boiling fuel components will be higher the lower ethanol content the fuel has. Second, the heat of evaporation for alcohol fuels is much higher than for gasoline. The two mentioned effects in combination necessitates that more fuel must be injected to facilitate a cold start when port-injection is used. This fuel enrichment causes elevated emissions of several emission components and health effects associated with these compounds. With increasing content of alcohol in the fuel it becomes more and more difficult to start the engine and with neat alcohols (E100 and M100), the engine does not start at all at low ambient temperatures without any starting aids.

It is likely that the problems with cold start emissions we see for E85/M85 vehicles, will also be present but to somewhat less extent also for lower blending levels. Although the increase in emissions for low-level blending is lower per vehicle, it should be recognized that if the same amount of alcohol is used for low or high-level blending, the increase in harmful emissions might be roughly similar regardless of how the alcohol is used. Thus, low-level blending of alcohols might not have any advantages over use of high-level blends in this respect.

Background

Substantial improvement of emissions at low ambient temperature could be achieved on alcohol-fuelled engines if air/fuel preparation could be drastically improved. In addition, the engine would also be easier to start at these low temperatures, which is of great concern for the driver.

An example of substantially improved air/fuel preparation is the high-pressure direct injection used on alcohol-fuelled diesel engines. Such engines are used in city buses in several cities in Sweden, e.g.

in Stockholm. These buses start without any specific starting aid down to very low ambient temperatures (~-30°C).

Direct injection using much higher pressure than port injection is also used on modern gasoline engines. Instead of the roughly 3-5 bar level for normal low-pressure port injection, the first generation direct injection had injection pressures up to ~120 bar. The second generation injection systems can reach up to ~200 bar. Still, this is not up to the levels used in the first generation of ethanol-fuelled diesel engines (~1 000 bar) or modern diesel-fuelled engines (up to 2 000 bar or even higher in some cases). Until recently, direct injection has not been used on E85 engines but the VW group now produces such engines. However, for the moment, no emission data for the emission components of interest in this context are available from these cars. A similar gap of knowledge exists for low-level blending of methanol (e.g. M3 to M30) in gasoline at low ambient temperatures and no car adapted for use of M85 is available on the Swedish market today.

It was demonstrated already in the 1980's by, e.g. Sievert and Groff at GM that an engine with high-pressure direct injection could have excellent cold start capabilities (Sievert & Groff, 1987). The test engine used by these researches could achieve unassisted cold starts down to -29°C by using direct injection of neat methanol (M100). This was the lowest temperature that that particular test cell could achieve, indicating that the real cold start limit could have been even lower. Thus, direct injection could be a very elegant way of overcoming the cold start problem. However, we do not know to what extent modern gasoline direct injection systems could improve – or perhaps even solve – the cold start problem. Thus, we can only use indicative data to test such a hypothesis. In this context, an overview of experiments with alcohol fuels used in gasoline direct injection engines in the past could be of interest.

Direct injection on gasoline engines is not new concept as a few examples below will show. For example, direct injection was used in aircraft engines already before WW I and gained popularity during WW II (Wikipedia, 2013). Adapting injection technology from stationary or marine diesel engines to on-road diesel engines was not an easy task in the early 1900. Thus, the so-called Hesselman engine by the Swedish inventor Jonas Hesselman was an appreciated option that was used by both Scania and Volvo in Sweden in heavy-duty vehicles in the 1930's. The Hesselman engine used direct injection and a spark plug. It started on gasoline and was then switched over to run on kerosene or diesel fuel, which at that time was much more economical than gasoline.

TCCS

A somewhat more recent direct-injection concept engine was the Texaco Controlled Combustion Concept (TCCS). As the Hesselman engine, this engine also used direct injection and a spark plug. Primarily, the TCCS engine was intended to use a broad-cut petroleum fuel, since it was not dependant on a high octane rating of the fuel, as conventional gasoline engines are[9], due to the late injection of the fuel that prevent knocking. Due to the lean-burn, it also had a potential for improved fuel consumption. The TCCS engine was considered a multi-fuel engine and was also tested on methanol by Kim et al. (C. Kim et al., 1985)and Lewis (Lewis, 1986). However, the tests by Kim et al. were not very successful, resulting in very high levels of unburned fuel and formaldehyde emissions.

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[9] This remark also includes contemporary direct-injection gasoline engines that are knock-limited albeit not quite to the extent that port injected engines are.

The authors speculated that substantial wall-wetting was one of the reasons for the high emissions. Lewis found relatively similar HC emissions at the lower test speed but greater HC emissions at high speed. No other emission components were reported from these tests.

Ford PROCO

The Ford PROCO (PROgrammed Combustion) concept engine was conceived in the 1970´s as an answer to the demand for lower fuel consumption due to the oil crises during that decade. This engine was considered a "gasoline version of the diesel engine" and, as such, it was also an alternative to the diesel engine[10]. Prototype engines demonstrated a potential for 20 % improvement of the fuel consumption (A. J. Scussel et al., 1978). The PROCO engine used direct injection with a central vertical injector, just as some of the second generation direct injection gasoline engines today (Figure 22). The maximum injection pressure at up to ~200 bar was on the same level as the highest level used today. In contrast, the injection system was derived from contemporary diesel injection systems and lacked the flexibility of modern direct injection systems. A specific feature of the PROCO engine was the twin spark plugs that were used to enhance ignition capabilities.

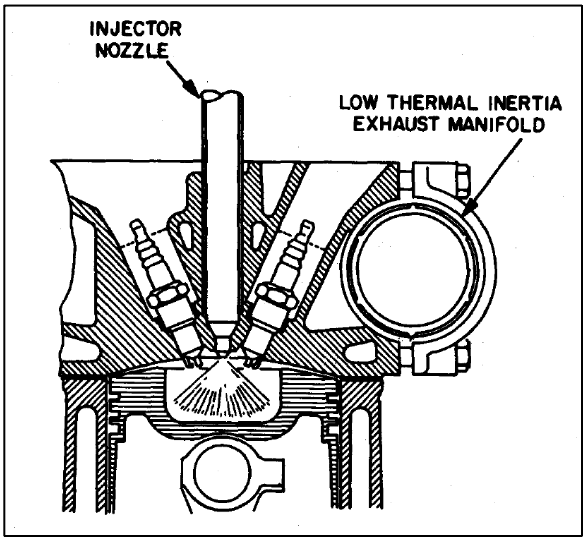

Figure 22. **Cross section of the PROCO engine**

At the end of its development, the PROCO engine was also tested on methanol (M100) fuel (M. A. Choma et al., 1981). No specific optimization was made; the injection system was just adapted for the higher flow needed to compensate for the lower energy content of M100 compared to gasoline. The emission results in the US FTP test cycle are shown in Table 33.

Table 33. **Vehicle tests with 100 % methanol**

	Emissions (g/mile)			**Fuel Econ. (MPG)**			**M/H MPG**	**BTU/Mix10^2**	
Fuel	CO	HC	NO$_X$	Urban	HWY	M/H	Gas equiv.	M/H	**Remarks**
Gasoline	0,5	0,33	0,70	16,7	21,5	18,6	N/A	62,3	4 test avg.
M100	0,7	0,39	0,41	7,8	11,2	9,0	18,5	63,7	1 test

In spite of the lack of optimization on the M100 fuel, the results in Table 33 are remarkable. No three-way catalyst was used; only an oxidation catalyst was implemented. The level for CO and HC was only marginally higher than for gasoline and the NO$_X$ level was considerably lower. The energy

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[10] Other US car manufacturers, such as GM, developed diesel engines as an option to reduce fuel consumption; a concept that was not a commercial success due to technical problems of the engines that were converted from engines initially running on gasoline. When Ford abandoned the PROCO project, they purchased diesel engines from BMW for a brief period but had to cancel this option as well due to low customer acceptance, probably due to the previous misfortune of the GM diesel engines.

use per mile was roughly similar. No cold starts at low ambient temperatures with this engine using M100 have been published, as far as the authors of the present report know of. However, it should be noted that low CO and HC emissions were achieved on neat methanol (M100), a feature that can only be achieved with blending with gasoline (M85) on port-injected engines. Thus, it is likely that results at low ambient temperature might also have been promising.

Other examples

Further insight in the potential for high-pressure direct injection can be derived from experiments on prototype methanol-fuelled (M100) diesel engines intended for passenger cars. The engine consultant companies FEV and AVL developed such engines in the 1990´s. The AVL engine (Kapus P. et al., 1990), (Zelenka & Kapus, 1992) is worth mentioning specifically, since it was tested at low ambient temperature’s and showed excellent startability and low emissions (Quissek F. et al., 1992). Very low emissions of formaldehyde were achieved on this engine. As mentioned above, the methanol-fuelled diesel engines used much higher injection pressures than currently is available for gasoline direct injection engines and the results on the diesel engine mentioned here may be indicative of the future potential if injection pressured would be increased also for direct injection gasoline engines.

Final remarks

The results on the TCCS engine demonstrated that direct injection alone will not be sufficient for achieving low emissions of unburned fuel in the exhaust and low level of formaldehyde emissions. The Ford PROCO engine achieved CO and HC emissions with neat methanol (M100) only slightly higher than with gasoline, so this concept worked well at the temperature tested. Sievert and Groff showed that an engine with high-pressure direct injection of M100 could achieve unassisted cold starts down to -29°C. Diesel engines running on M100 with high-pressure injection have also showed excellent cold start performance.

All-in-all, the indicative evidence points at the possibility that high-pressure injection might have a potential to improve cold start emissions considerably – potentially, even solve the cold start problem. However, we do not know exactly how high the injection pressure must be to achieve this task. The first logical approach would be to conduct an extensive test programme on direct-injected E85 cars using second generation of gasoline direct injection with injection pressures of ~200 bar. Different levels of blending, starting at e.g. E3, E10... and ending at E85 (possibly even E100), could be used to assess the potential for both low-level blending and the various mixtures that an E85 vehicle would be subject to. This would give an indication about the potential for methanol blends but the best approach would of course be if this particular vehicle also could tolerate the low levels of methanol under discussion here, e.g. M3 to M15 and possibly up to M30.

Potentials and options

In this section a few selected publications showing the potential for increased efficiency and reduced exhaust emissions are highlighted and discussed. This is not a full and comprehensive overview of the topic but just a few examples to show the potential.

Alcohol concept engine by MIT

In a couple of publications cited above, it has been demonstrated that blending of methanol and ethanol in gasoline often provides a small but significant improvement of engine efficiency. However, the potential for increasing efficiency might be much greater for a dedicated engine. This has been shown by, among others, a group of researchers at MIT in the USA, e.g. in a report by Bromberg and Cohn (Bromberg & Cohn, 2008). This concept uses the unique properties of alcohol fuels to boost efficiency and power density. The relatively high evaporation heat necessary to vaporize alcohol fuels was mentioned as a drawback for port-injected engines above. However, in direct injection engines, this can instead be used to an advantage for increasing efficiency. The so-called charge cooling effect by evaporation of alcohol fuels could reduce the temperature of the air/fuel charge so that the equivalent octane number can be as high as 160 for gasoline and 180 for methanol. Thus, the compression ratio could be increased and substantial downsizing could be enabled via a gain in specific power and torque with turbocharging. The authors of the mentioned report claim that an (relative) efficiency gain of 30-35 % could be achieved in comparison to port-injected engines, i.e. similar gain as turbocharged diesel engines have over port-injected gasoline engines. Due to considerable downsizing enabled by the concept, the alcohol engine would be much smaller than a corresponding gasoline engine.

Concept by Chalmers

The concept engine proposed by MIT has not been materialized yet in a production version but several other researchers have also adopted the ideas. One recent publication worth mentioning in this context is a paper from the Chalmers University of Technology in Sweden (J. Wärnberg et al., 2013). In this study, a direct-injected 2-litre BMW engine was used. The base engine was naturally-aspirated and had a combustion system laid out for stratified charge and exhaust gas recirculation (EGR). The compression ratio was increased to 13:1 albeit that very high boost pressure was used via two-stage turbocharging. Through direct injection at a pressure of up to 200 bar, the engine was able to operate on neat ethanol (i.e. not E100 but actually E98 where 2 % ethanol was substituted with MTBE for denaturation). The researchers mention a strategy with delayed first injection for cold starts but no actual cold start testing at low ambient conditions were carried out in the project.

Part load efficiency of 37% was demonstrated and modelling showed a predicted maximum efficiency of 39 %. Brake mean effective pressure (BMEP) of up to 31 bar over a wide range of engine speed was modelled. This resulted in maximum torque of 490 Nm and a power of 240 kW at 5 000 r/min. If the engine was downsized by 33 %, the maximum power would still be as high as ~210 hp and a further 11 % gain in efficiency would be enabled.

The reduction of particle number (PN) emissions by 85 % compared to gasoline was remarkable. PN was found to be dependent on injection pressure and other combustion parameters. It was speculated by the authors that the precursors for particle formation would not be present when neat ethanol fuel is used, which could explain the reduction of particulate emissions. An investigation of varying injection pressure showed relatively small difference between 130 and 200 bar (lower in the latter case), while 75 bar had much higher level. This would be an indicative answer to the question posed above about the minimum injection pressure, i.e. that 200 bar would be sufficient at these operating conditions. Still this does not answer the question how well this concept would work during cold start at low ambient temperatures. The authors of the Chalmers paper suggest this as future work.

NO_X emissions were anticipated to be handled via a lean-NO_X catalyst but no specific testing of such a concept was carried out within the project reported in the mentioned paper.

Material compatibility and fuel composition

The experience from the Swedish projects did not show many problems with material compatibility. Note that relatively minor modifications were made in the M15 projects and several of the issues noted are now considered well-known. No problems at all were seen at 3 % blending rate in the recent INTROMED project with M3E3 fuel. Most likely, problems could arise at higher blending rates.

A recommended practice for testing materials in the fuel system has been proposed by SAE International in the standard J1681 (SAE International, 2000). The last version is from 2000 and a new revision of this standard was initiated in 2008 but has not yet been published. Interestingly, a mixture containing 15 % methanol is a proposed fuel for gasoline testing, although methanol is rarely found in commercial gasoline (except China, as discussed above). Methanol is considered more aggressive than ethanol and should represent a “worst case” market place whether the fuel contain methanol or not. Thus, it could be speculated that the maximum blending rate could be higher than the current limit of 3 % in the EU. However, although this is a standard, it is only recommendations about how to test materials. It does not necessarily imply that all car manufacturers and their suppliers apply this standard in their work. A commercial fuel must work in essentially 100 % of all vehicles in operation, or else, it would have to be marketed as a special fuel quality and appropriately marked as such a fuel. Consequently, it is basically impossible to find out where the practical limit for methanol would be. Perhaps currently on-going research and field trials in China could provide more insight on this topic.

Although a comprehensive literature survey was beyond the scope of this project, one interesting recent paper on the topic in this section was found and should be mentioned for reference. This is an SAE Paper by Yuen et al. (P.K. Yuen et al., 2010). This is by the way, one of the few SAE Papers published on methanol during the last couple of years. In this paper, a comprehensive overview of all the relevant areas where material compatibility could be an issue with alcohol fuels. Several examples and references to other work are also made.

Phase separation has always been considered an issue with methanol fuels. However, this problem was encountered only in such cases when something wrong had happened in the fuel supply chain. Today, ethanol is an established blending component in gasoline and is extensively used in the EU. Ethanol is an excellent co-solvent that can be used in combination with methanol. Most likely, future production capacity in the EU will not be sufficient to provide ethanol for 10 % blending in all gasoline in the EU. Thus, there is a good opportunity to utilize both ethanol and methanol, i.e. in up to 3 % in the latter case and perhaps varying in the former case depending on supply and demand. This would also ensure that phase separation would not be an issue for methanol.

Global trends and future potential

One of the crucial factors that influence the potential use of methanol as a motor fuel is largely linked to the use of ethanol, including regulations and economic incentives. An apparent barrier was the maximum blending level of 5 % according to previous EU legislation. Today, this level has been raised to 10 %. E10 has been introduced in, e.g. Germany and Finland, and in both cases, consumers have expressed their concern about potential problems with the vehicles. In some countries, such as Sweden, lack of economic incentives, has not yet facilitated the use of E10 fuel. Most likely, this introduction will come in 2015. If E10 would be introduced on a larger scale by the oil companies, most of the additional ethanol needed would have to be imported to Sweden, since no major domestic production plants for ethanol are currently under construction.

Current production capacity of ethanol in Europe is not sufficient for blending 10 % ethanol in all gasoline in the EU. Further, by September 2013, the European Parliament voted to cap the use of biofuels produced from starch-rich crops, sugars, oil and other crops grown on land to 6 % (European Parliament, 2013). Still, according to current legislation, member states must ensure that renewable energy accounts for at least 10 % of energy consumption in transport by 2020. It is apparent that “advanced biofuels” that sometimes are referred to as “second generation” biofuels would have to fill this gap. It may of course be speculated that the 10 % target will be changed or not fulfilled by the member states. However, if this target would be upheld and potentially also increased in the long-term future, methanol might again have a chance on the market. With the lack of supply of ethanol on the market, the simplest and quickest introduction would be to blend the permitted level of 3 % methanol with ethanol and gasoline according to the limits (e.g. oxygen) in the current fuel regulations.

One option not discussed in this report is the use of ternary fuel blends comprising methanol, ethanol and gasoline. These blends are often referred to as GEM (gasoline, ethanol and methanol) fuels. This topic is actually beyond the scope of this report but nevertheless, some short comments might be of interest to include. The mentioned blending of 3% methanol with ethanol and gasoline mentioned above could be considered as a GEM fuel but mostly, higher blend levels are referred to as GEM fuels. One example was the use of methanol in Brazil in the 1990’s when production capacity of ethanol could not keep up with the demand. Then, a certain percentage of methanol substituted some of the ethanol in the fuel.

The main idea of GEM fuels is to provide a fuel with the same stoichiometric properties as the fuel it should replace. Thus, the GEM fuel could be considered as a “drop-in” fuel. Substituting some of the ethanol with 3 % methanol to replace E10 requires that the ethanol content is reduced so that the volumetric energy content in both fuels is similar. This is approximately achieved if the oxygen content is the same as in the E10.

Another option for a GEM fuel would be to substitute some of the ethanol in E85 with methanol. One particular problem in this case might be material compatibility, if all materials in contemporary E85 vehicles are not methanol-tolerant. This could, of course, be taken into account for new vehicles but it would be advantageous if also older vehicles could use the GEM fuel. Some aspects of using GEM fuels instead of E85 have been discussed in a recent paper by Turner et al. (Turner J. et al, 2012).

Concluding remarks

The scope of this study was to summarize old Swedish experiences from the use of low-level gasoline-methanol blends. For that purpose, a review of the publications on this topic has been carried out in the work reported here. A general remark is that there does not seem to be much of a systematic approach in all the projects carried out in Sweden if these are looked at as a whole. Obviously, there has been much shift in focus from time to time, which is part of the explanation to the apparent lack of consistency. Various stakeholders have influenced the focus from time to time and it should not be neglected that also the international focus has, for sure, had an impact also on Swedish policies over the years.

The results from projects where low-level methanol blends have been used in the past have not revealed any specific problems that could not be overcome. Relatively recently, this was also manifested in the INTROMET project on newer cars. There have, for example, been problems with phase separation, material compatibility and drivability in the past. However, all these problems can be overcome. Phase separation can be controlled via proper routines in fuel distribution and handling. The use of ethanol as a co-solvent will also make the fuel composition more “robust” regarding phase separation. There are no apparent problems with materials in modern vehicles at a 3 % blending level of methanol allowed in the current EU specification. Similarly, there are no problems with driveability in modern vehicles at the mentioned methanol concentration. The only concern for introducing blending with 3 % methanol on a large scale might be the potentially negative response from the auto industry and perhaps, the willingness of the oil industry to introduce this fuel under those conditions.

The authors of this report do not believe that higher blending level than 3 % methanol would be likely to succeed in the near future. It is quite possible that the practical limit could be somewhat higher than 3 % even when material compatibility is of concern. However, there is lack of evidence for the moment to suggest a maximum possible concentration higher than 3 %. We presume that it would be a long process to establish such a fuel. A better alternative could be to introduce dedicated vehicles operating on high-level methanol blends (M85/M100), which possess some kind of fuel flexibility, i.e. that they could also run on gasoline when the methanol fuel is not available[11]. Such vehicles could also be optimized for both low emissions and high efficiency. It is likely that this could be accomplished via the use of advanced technology such as high-pressure direct injection, turbocharging and significant downsizing. As an option to bridge the gap until such vehicles could be commercially available, GEM fuels used in conventional E85 cars is an option that should be investigated in more detail. Large numbers of such vehicles are available in the current vehicle fleet, e.g. the USA and Brazil but also in Sweden and some other European countries to some extent.

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[11] When such methanol-optimized vehicles are operated on gasoline, it is anticipated that the power and torque may have to be reduced. For current fuel-flexible vehicles, this is not the case. For example, these engines usually have the same compression ratio as their gasoline counterparts, which is far from optimum when alcohol fuels are used.

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Appendix 1 - Analysis of unregulated emissions in Sweden

The analysis of unregulated emissions in Sweden has a long tradition. Already 1967 a project was started on how to analyse and quantify the emissions of organolead compounds in auto emissions and in street air at the Institute of Analytical Chemistry of the Stockholm University. A method based on GC-mass fragmentography was developed and results presented at the second international conference of clean air in Washington DC 1970. (2Z) In the first half of the 1970:ies New projects were started at the institute concerning the analyses of PAH (Poly Aromatic Hydrocarbons), and soon cooperation was initiated with the emission laboratory at the Exhaust Gas Research, AB Atomenergi, in Studvik. Later on the emission laboratory was under the head of the Swedish EPA turned into a centre for testing and sampling of auto emissions. The analyses of specified organic compounds were done at the Stockholm University also in the institute for genetics and toxicology. Toxicology was also introduced in the testing at the Karolinska Institute. Both the emission laboratory and the university institutes have had frequent international contacts and published results in scientific magazines. All those efforts in characterizing auto emissions in Sweden made it possible for the authorities to demand testing and for developing companies and oil companies to secure that new fuels and additives did not impose new threats to human health or the environment. The demands from the authorities have stepwise included new tests and in the following is what can be demanded for liquid Otto engine fuels.

Recommended procedure for testing new Otto engine fuels and fuel additives

The producer (or importer) of a product is according to §7 in the 14th chapter of the Swedish Environmental Code, always formally responsible for a chemical product and has to evaluate its possible risks. In the following is presented general information from the products control board and environmental protection agency, but formally responsible person company always has to evaluate risks and measures.

When a new fuel is introduced on the market it is a prerequisite that emissions are not more toxic than from standard market fuels. It is also important that the fuel will not lead to increased wear of engines, corrosion problems, fuel system plugging due to partly dissolved old deposits or other fuel system related problems. Drivability problems must not occur and the emission performance is not allowed to deteriorate faster compared to driving on standard fuels. All of those possible vehicle-related problems can be studied in a well-designed fleet test. In such a test, a number of vehicles normally driven over long distances every day are chosen. Special pricing and control of fuel used has to be implemented in order to have close to 100 % use of the test fuel. Special failure reporting routines are to be followed and critical vehicle fuel system and engine components are to be inspected before and after the test period. When it comes to impact on the durability of emission control systems, two different cases can be seen. One is when a manufacturer has accepted the use the mixture of alcohols and ethers in gasoline fulfilling the European standards. In this case the responsibility is on the manufacturer. In other cases the applicant has to show either by own tests or certificates from manufacturers that the fuel under application is not impairing the durability of emission control systems.

The program proposed in the following should give a reasonable safe picture of how the introduction of the new fuel would affect exhausts from vehicles in Sweden and give rise to other impacts on the environment.

Control of impact on engines and emission control systems

Impact on engine oil and oil change intervals

Alternative fuels can produce more or less acid products and particulates. Some amount of those products and also unburned fuel will pass down into the crankcase and impair the function of the oil. Comparative studies must be performed so that adequate oil change intervals can be given, especially if they differ from what is recommended for standard gasoline and diesel fuels.

Risks from storage and distribution

Impact on the environment in comparison to ordinary fuels from evaporation and spills to water and soil should be investigated through literature studies and experiments if literature is not sufficient. The potential for ozone formation due to evaporation of the fuel should also be compared to ordinary fuels.

Emission testing of alternative fuels

Scope

This procedure specifies requirements and test methods for marketed and delivered environmentally classified alternative fuels and fuel components. It is applicable to liquid and gaseous fuels intended for use in vehicles on road as well as for non-road equipment. In the procedure, emission tests involving regulated as well as non-regulated emissions are the most important part.

1. Sampling

Samples for fuel analyses shall be taken as described in suitable EN ISO-standards. For example EN ISO 3170 or EN ISO 3171 can be used for many liquid fuels. The fuels sampled and used for emission testing should be typical for future deliveries to end-users.

2. Analyses

The fuel under test should be analysed for composition and other relevant parameters at accredited laboratories and the results presented.

3. Pump marking

Information about proposed marking on dispensing pumps used for the alternative fuels shall be given, and the dimensions of the mark shall be in accordance with the requirements of national standards or regulations for the marking of pumps for fuels.

4. Requirements on fuels

Dyes and markers

The use of dyes, denaturants, odorants and markers is allowed, but the compounds used must be evaluated to have no ill effect.

Additives

In order to improve the performance quality the use of additives is allowed. Suitable fuel additives without known harmful side-effects are recommended in the appropriate amount, to help to avoid corrosion, deterioration of driveability and emissions control durability.

Acidity

To adequately limit the acidity of the fuel the acidity of components used as fuels or as a blend stock shall not exceed 0,007% (m/m) (as acetic acid) when tested in accordance with ASTM D 1613:1991.

Emissions

Generally applicable requirements and test methods

When tested, the alternative fuel composition shall be in accordance with the specification for the fuel. The laboratories involved for emission should be accredited / certified for emission testing according to European emission test procedure.

Scope

This procedure specifies requirements and test methods for marketed and delivered alternative fuels and fuel components. It is applicable to liquid fuels intended for use in vehicles on road as well as for non-road equipment. Emission tests involving regulated as well as non-regulated emissions should be performed.

Background

Exhaust emissions from vehicles can be described as regulated and unregulated exhaust components. Non-regulated exhaust components comprise a large number of compounds and are defined as compounds that are not regulated by law. However, most of those belong to the group of unburned hydrocarbons (HC) or particles. The components selected for study depend on the fuel composition and are selected due to their impact on the environment and health. In addition different types of bio assays can be included. The extent of testing new fuels and fuel formulations is determined by the difference from existing fuels in respect of chemical composition. If for example low molecular weight alcohols are introduced into petrol, aldehyde emissions may increase. If for example the new fuel contains additives containing nitrogen there could be a risk for emissions of nitro-PAH and thus a need for testing those compounds and impact for example with a mutagenicity on the TA 98 NR strain in Ames test.

Reference and test fuels used for emission testing

The base test fuel used, reference fuel, is a fuel with a composition believed to be typical of today's gasoline. For special purposes, for example testing the effect of additives, ultra clean fuel should be used. The fuels should be analysed for relevant parameters depending on the composition. For example can the polyaromatic compounds (PAH) be analysed in the fuels if believed to have significant levels or if they are analysed in the exhausts.

Test car or test engine

All vehicles tested should be supplied with external fuel systems in order to change fuel quality entirely between tests. (To change fuel to 100 % in the vehicles fuel tank is very time consuming and not safe).

In the case of testing gasoline, the test object should be a passenger car, a vehicle with oxygen sensor controlled engine. As fuels have different energy content, a vehicle with adaptive fuel management system should be used. Before the test period starts, the vehicle should be serviced with adjustments needed. In order minimize the interference from previous fuels used the ventilation pipe from carbon canister to the engine inlet system should be plugged. In the test car the catalyst should be removed and replaced by a straight tube in order to ensure material enough especially for biological testing and safely discriminate between fuels. The silencer should be replaced by a straight pipe to avoid trapping of particulates, followed by a tail pipe with a welded flange for connection to the CVS. Normally the engine should be supplied with new air filter and oil filter, oil changed to a fully synthetic quality. New spark plugs mounted and worn details in the ignition system exchanged if needed. The entire exhaust system should be cleaned if there will be measured particulates, PAH or other compounds that can be trapped in the system and re emitted. Before the first test the car should for example be driven on chassis dynamometer with the reference fuel for 100 km and 100 km/h in order to thoroughly clean engine and exhaust system from previous driving. Then, finally, one test cycle is run for conditioning.

Emissions of regulated compounds

The emissions of regulated compounds are measured according to the regulations for test cycles earlier mentioned with the samples taken after dilution tunnel. The analyses of the regulated emissions will give important information about impact on emissions from the tested fuel as well as that there is a correct adaptation of the emission control and that the vehicle has acceptable drift. A small spread in energy consumption also can be a good indicator that the car is driven and functioning in the same manner from test to test. If the tests have to be driven by two drivers it should be planned so that every driver is driving two tests on every fuel, either morning or evening tests on all fuels. As the test car is driven alternately with and without additive it is believed that trends, if any, in driving manner, vehicle performance, sampling and analyses are minimized.

Emissions of particulates

The physical stage of organic compounds in both diesel and gasoline engine exhausts is strongly temperature and time dependent. To correctly sample what in street air is called "particulates", exhausts are sampled for particles as such as well as high molecular compounds still in the gaseous phase. The routine when analysing PAH and biologically active compounds on 250mm glass-fibre filter pollutants in the exhausts is to weigh the filters so that the mass of particulate emissions can be calculated.

Analyses of particulates and semi volatiles

The analyses of PAH, mutagenic effects and TCDD receptor binding effects are performed on extracts of particulates and of the semi volatile phase. Sampling is performed on 250mm glass-fibre filter and in a following polyurethane foam plug.

Although the temperature in the end of the dilution tunnel is only about 30°C, much of the polyaromatics and other heavy compounds are in the gas phase. Because of that, particles are sampled on filter and then the vapour phase is run through an absorbent. Compounds with boiling points above 200°C are well trapped in this system and not lost to significant degree during evaporation of the extracts from filter and absorbent. Filters and absorbent are acetone refluxed. Today normally the particulate and semi volatile phases are added to each other after the extraction and the sample is split so that 60 % of the extracts are sent for mutagenic testing, 10 % for TCDD receptor testing and the remaining 30 % are used for analysing PAH. In the extract for PAH analyses an internal standard should be added to compensate for losses during clean up and analyses. The samples are separated on a capillary gas chromatography column. Analyses are performed using mass fragmentography.

Components selected for analysis

Exhaust emissions from vehicles comprise regulated and unregulated exhaust components. Regulated exhaust components by law are: Carbon monoxide (CO), unburned fuel hydrocarbons (HC), nitrogen oxides (NO_X) and particles. Non-regulated pollutants are defined as compounds that are not regulated by law. However, these may well belong to the group of unburned hydrocarbons (HC) or particles. Unregulated exhaust components comprise a large number of compounds. The components selected for this type of study are the regulated components and six classes of unregulated components. These components are selected due to their impact on the environment and health. In addition two different types of bio assays are included.

Greenhouse gases.

Methane (CH_4) and nitrous oxide (N_2O) are two greenhouse gases that interact with the infrared radiation in the atmosphere in the same way as carbon dioxide. The increase in greenhouse gases is causing climatic changes and an increase in the average temperature of the earth.

Aldehydes.

Aldehydes are irritants to mucous membrane and they are known to give allergic reactions. Formaldehyde is also considered to be a carcinogen.

Alkenes

Alkenes such as ethene, propene and 1.3-butadiene are converted by metabolism in the human body to their corresponding epoxides which may react in the cells and thus initiate a mutagenic effect. These alkenes are also suspected of being carcinogenic to man.

Mono aromatic components.

Mono aromatic components to be measured in this study are benzene and toluene. Exposure to benzene is known to increase the risk of leukaemia.

Polycyclic Aromatic Hydrocarbons (PAH)

PAH are formed during incomplete combustion and are also emitted from unburned fuel. Some of them have been shown to be mutagenic in the Salmonella typhimurium bio assay (Ames test). Due to the fact that some of the PAH compounds are mutagenic in the Ames test and in some cases also give rise to cancer in animals in skin painting experiments it can be expected that these compounds may have the effect of causing cancer in humans. In studies a total of 27 individual PAH in both the semi-volatile as well as the particulate phase are measured.

Particulate size distribution.

The number and size distribution are important parameters when the health effects of exhaust particles are considered. For example can the Electrical Low Pressure Impactor (ELPI) be used which measures the particle number and size distribution of the emitted particles. It operates by charging the particles in a positive polarity charger with subsequent separation of the particles according to aerodynamic size in a low-pressure impactor. The charged particles deposited at each stage in the impactor produces an electrical current which is recorded with a time resolution of 1 s.

Bio assays.

Ames test.

Mutagenicity test can be carried out using the Salmonella typhimurium strains TA 98 and TA 100. Liver preparations (S9) from rats are used as the metabolising system. The exhaust extracts will be measured as the sum of both the particulate and the semi volatile phase. The mutagenic effect from the two tested fuels will be compared and expressed as number of revertants per km driving distance.

TCDD-receptor affinity test.

The TCDD affinity test is also performed on an extract taken from the sum of particulate and semi volatile phase. The test is carried out using the hydroxylapatite assay. To determine the binding affinities of samples competition experiments are carried out using increasing concentration of sample against a standard concentration of radio-labelled TCDD. The relative binding affinities of the samples are expressed indirectly as IC50 values. IC50 values are defined as the concentration of competitors required to reduce the binding of radio-labelled TCDD to its receptor by 50 %.

Determination of other unregulated pollutants.

In addition to the analyses of the particulate and semi volatile phase of the emissions, lower molecular weight compounds can be analysed if the additive or fuel component is believed to have an impact on such compounds. Especially if alcohols, ethers and the like are added to the fuel or the base composition is changed outside what is standard such circumstances prevail. Examples of compounds of environmental or health effects concern, measured under those conditions is: C_6 to C_8 aromatics, aldehydes and C_2 to C_4 olefins and di-olefins. If the combustion process or catalytic emission control is believed to influence the emissions, it is also possible to measure for example the NO-NO_2 relation and the N_2O content in the emissions; in this case catalysts are not removed (Laveskog A. , 2013)