

Fuel vapour composition and flammability properties of E85

Henry Persson, Peter Bremer, Lars Rosell, Karine Arrhenius och Kent Lindström

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Abstract

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A series of experiments have been conducted to study the flammability characteristics and determine the flammable temperature range of E85 fuel vapours. E85 is a mixture of ethanol and petrol the composition varies depending on time of the year. According to the Swedish standard, SS 155480:2006, the ethanol content may not be below 70 %/75 % (winter/summer) and may not exceed 86%.

E85 of summer and winter qualities were conditioned in sealed vessels at various temperatures and the composition and concentration of the fuel vapours were determined. Fuel vapours from conditioned vessels were also used for ignition tests in an explosion chamber (the bomb). The tests shows that the fuel vapours mainly consist of petrol fractions despite the high content of ethanol in the liquid phase. The bomb tests indicate a flammable range of the fuel vapours from about -18 °C up to about +2 °C to +5 °C for E85 of summer quality. Some tests with E85 of winter quality and petrol were conducted as well. These tests indicated a flammable range up to -8 °C to -9 °C for the winter E85 and up to about -20 °C for petrol. The lower limit of the flammable range was not investigated for these fuels.

The consequences of ignition of fuel vapours inside some fuel tanks for cars have also been studied. Electrical sparks were generated inside the tank or at the filling opening. In addition, a spill fire below the tank was used as an ignition scenario. When the ignition occurred inside the tanks, the overpressure caused a rupture and generated a short duration flame outside the tank.

Tests have also been conducted to study the fuel vapour concentration and composition around the filling pipe during filling of the tank. The measurements indicate that vapours in the flammable range might be present around the filling opening, especially if the vapour recovery system at the fuel pump is not activated. One test with a fuel tank equipped with an Onboard Refuelling Vapour Recovery (ORVR) system, indicated that the fuel vapour emission was very low, probably reducing the risk for ignition of fuel vapours significant during filling.

Key words: E85, ethanol, petrol, fuel vapour composition, flammable characteristics, explosion point, ignition properties, risk, fire, fuel tank, car

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Foreword

Interest in and the use of the fuel Ethanol E85 (normally called simply E85) has increased markedly in recent years. E85 is a mixture of ethanol and petrol where the composition varies depending on the time of year. The ethanol concentration may be 70%/75% (winter/summer) at the lowest and 86% at the highest. Questions concerning the risk for fires and explosions connected to this increased use have, however, not been fully investigated which was clear from an inquiry conducted by Stockholm City. Issues concerning the risks can be found in all parts of the distribution chain for E85, i.e., from production (mixing), transport to filling stations, filling of tanks, storage in tanks, pump systems, refuelling of cars and storage of the fuel in the vehicle fuel tanks. In the case of petrol, gas recovery systems are also a part of the distribution of the fuel, both between the road tanker and the fuel tank (stage 1) and between the vehicle's filling opening and the fuel pump system/bulk fuel tank (stage 2).

The Swedish Road Authority has been tasked by the Swedish government to investigate the possibility to convert cars to accommodate alternative fuels. In light of the uncertainties associated with this issue the Swedish Road Authority proposed an initiative to investigate the issues in hand and invited other interested parties to participate in this work. A first meeting was held 2006 with representation from the Swedish Road Authority, the Swedish Rescue Services Agency, Swedish Petroleum Institute, the Swedish Environmental Protection Agency, SAAB, Volvo and SP Technical Research Institute of Sweden.

Based on these initial discussions, SP developed a proposal for an evaluation scene that resulted in the project reported here. In connection with this work, further interested parties and funding organisations joined the project.

The following organisations have participated in the funding of this project and the persons listed below have participated in a reference group that has been connected to the project:

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Alice Kempe Swedish Energy Agency (STEM)

SP has participated with representatives from the following departments: Fire Technology, Electronics, Chemistry and Material Technology, and Weights and Measures. All SP participants would like to take this opportunity to thanks the reference group for their active participation and input throughout the whole of the project.

Henry Persson Project Leader

Executive Summary

Interest for renewable fuels is increasing rapidly and Ethanol E85 (traditionally called simply E85) is the fuel that has reached the greatest market penetration in Sweden. There have, however, been a significant number of issues associated with the fact that our knowledge of the fuels fire and explosion characteristics has been limited. This has, in turn, limited our ability to assess which risks may exist along the whole logistical chain from the refinery or depot to tanking and use of the fuel in a variety of vehicles. A set of primary issues associated with E85, has been compiled together with various interested parties to better identify and evaluate risks and suggest suitable measures to increase safety during use.

A project has been conducted against this lack of knowledge. The project has been divided into five different Work Packages. The first two Work Packages were intended to provide fundamental information concerning the characteristics of E85. The first Work Package entailed determination of the concentration and composition of fuel vapours in a closed vessel at different temperatures. The second Work Package investigated which temperature window the fuel vapours were flammable and what their combustion characteristics were. The combustion experiments were comprised of ignition tests conducted in an explosion chamber (the bomb).

The ensuing three Work Packages were more applied than the first two. Work Package 3 and 4 were primarily focussed on studying the consequences of the ignition of fuel vapours in fuel tanks for cars. Work Package 5 focussed on the determination of gas composition around the filling tube in conjunction with filling of the vehicle. This was in part to determine the risk for ignition and in part to provide basic data to assess the need for a gas recovery system for E85 from an environmental perspective.

This project has resulted in an increased understanding of the basic differences between E85 and standard petrol. The more applied part of the project have also provided a great deal of information but these results, provide guidance rather than fundamental data due to their limited extent relative to the number of car makes and models and potential ignition sources and fire scenarios.

Amongst other things, the results from the project show that fuel vapours in a closed vessel containing E85 are mainly comprised of petrol fractions, i.e. approximately 70-90 % of the vapour phase is petrol despite the fact that petrol is only approximately 15% of the liquid phase. The high percentage of petrol fractions in the fuel vapours means that the flammable zone is significantly different from that one would expect for pure ethanol.

The vapours that are formed in the closed vessel or in a fuel tank containing E85 of summer quality are flammable within the temperature interval from approximately -18 °C up to approximately +2-5 °C. This temperature interval varies depending on the fuel quality and how much fuel is present in the tank, i.e., to what extent the tank is filled. For winter quality E85 (E85W) the upper temperature is judged to be approximately -8 °C till -9 °C while for lead-free 95-octane petrol of summer quality (LF95S), the upper flammability temperature is judged to be approximately -20 °C. The experiments illustrated that E85 can be placed in explosion group IIA, i.e., the same explosion classification as petrol.

Experiments conducted with a number of different types of fuel tanks show that ignition of fuel vapours at the filling tube or inside the fuel tank can lead to high pressures inside the tank under worst case conditions. Such a pressure increase could potential cause deformation or rupture of the fuel tank. Under such conditions the underbody of the vehicle could also be deformed. Transient flames from the filling tube and/or cracks in the tank are to be expected. Under extremely unfavourable temperature conditions a pool fire under the fuel tank could lead to ignition inside the tank, transient flames and burning droplets of fuel. It should be noted,

however, that the same conditions could occur for petrol as well. When filling the fuel tank of a vehicle fuel vapours immediately outside the filling tube may be flammable, in particular when the gas recycling system is not connected. This risk is probably significantly reduced in vehicles which contain a functioning Onboard Refuelling Vapour Recovery (ORVR) system.

List of Abbreviations

A number of abbreviations are used in this report. A list of these is provided in the table below together with an explanation of their meaning.

Abbeviation	Explanation
E85	The full name is "Ethanol E85". The fuel specification is provided in
	SS 155480:2006. This standard also specifies acceptable ethanol
	concentrations for summer or winter qualities, see below.
E85S	This is the E85 quality that is sold during the summertime. E85S contains at
	least 75% ethanol and an allowed volume percentage of petrol of 14-25 %,
	and partial pressure of 35-70 kPa
E85W	This is the E85 quality that is sold wintertime. E85W contains at least 70 %
	ethanol, and an allowed volume percentage of petrol of 14-30 %, and partial
	pressure of 50-95 kPa (designated E85 V in figures and diagram's)
LF95S	Lead free, 95-octane petrol of summer quality. (Designated BF95S in figures
	and diagram's)
Bomb	Explosion chamber for ignition tests (The term "bomb" is used in e.g. EN
	1839:2003, having the meaning "a container capable of withstanding high
	internal pressure".)
UEP *)	Upper Explosion Point, given in °C.
LEP *)	Lower Explosion Point, given in °C
MESG	Maximum Experimental Safe Gap
AIT	Auto Ignition Temperature, given in °C
ORVR	Onboard Refuelling Vapour Recovery system
SHED-test	Sealed Housing for Evaporative Determinations
VRS-system	Vapour Recovery System. Stage 1 concerns the system between the tanker
	and the fuel cistern at a filling station. Stage 2 concerns the system between
	the vehicles filling tube and the fuel pump system/fuel cistern.
P_{fp}	Pressure at First Peak (bar, over pressure)
$t_{ m fp}$	Time to First Peak (ms)
V_{fp}	Velocity to First Peak (bar/s)

^{*)} The terms UEP and LEP are used in this report independent of which test method has been used to determine the temperature limits.

1 Background

1.1 The fundamental issues

The number of ethanol driven cars has increased significantly in recent years. The number of registered vehicles as of July 2007 was approximately 66 000 in Sweden. The rate of sales for the first 6 months of 2007 has been 2000 new vehicles per month [1].

Data from the Swedish Petroleum Institute (SPI) indicate that in 2004 approximately 6 500 m³ of E85 were sold, while in 2005 approximately 20 000 m³ were sold and in 2006 approximately 63 000 m³ were sold. The forecast for 2007 indicate that approximately 80 000 -100 000 m³ will be sold in 2007. By the end of August 2007 there were approximately 1000 filling stations that sold bio fuels, and 938 of these sold E85. Monthly updates of this data are published on the SPI website (www.spi.se) [2].

In other words, the increase in use of bio fuels is proceeding very quickly and E85 is the single bio fuel with the greatest market penetration. The main issue associated with this increase is, however, that our knowledge of the fuel's fire and explosion characteristics is limited. This means that we have only limited ability to determine the risks and opportunities that exist throughout the distribution chain from the refinery/depot to refuelling and use in different types of vehicles. In light of this there is a large interest concerning the characteristics of E85 from a variety of organisations with responsibility for different parts of the distribution chain.

The Swedish Road Authority has been tasked by the Swedish government to investigate the possibility to convert existing cars for the use of e.g. ethanol in the fuel. The issue of the risk for a fire or explosion, in particular the risk for ignition when refuelling a vehicle with E85, is however not included in the task from the Swedish Government. This issue is also more general in nature as it affects even factory built vehicles, which means that the need for more detailed knowledge is pressing, both for relevant regulatory organisations and car manufacturers.

SPI sees the safety aspects as central as they need knowledge of such issues to be able to design suitable safety measures within the distribution of E85, and its storage and use on site at filling stations. SPI is therefore working to define industry guidelines for handling, storage and transportation of E85.

The aim of the Swedish Rescue Services Agency is that the risks associated with the use and distribution of E85 shall not be greater than those associated with the use and distribution of petrol. Therefore, the Swedish Rescue Services Agency and SPI have defined preliminary guidelines for safety measures concerning E85 filling stations.

1.2 Aim and scope of the project

Based on discussions with various interested parties, five main issues were defined which should be answered in order to better evaluate the potential risks associated with E85 and to propose possible safety measures associated with the use and distribution of E85. These issues were:

- What are the flammability limits for those qualities of E85 that are sold in Sweden?
- What petrol/ethanol concentrations are found in the fuel vapours inside a closed vessel and within what temperature range are these fuel vapours flammable?
- What are the consequences should a gaseous mixture ignite in the fuel tank of a vehicle or at the filling opening of the vehicle?

- Is there any significant difference in the fire development if a pool fire occurs below a fuel tank filled with petrol or a fuel tank filled with E85? What difference can be discerned between fuel tanks constructed from plastic or metal?
- What concentrations of fuel vapours are found around the filling opening of the vehicle during refuelling of the vehicle and what is the composition of this vapour mixture? This is important both from a safety and an environmental point of view. Further, what effect do different technical solutions, such as an Onboard Refuelling Vapour Recovery (ORVR) system, have?

Both petrol and E85 are generally seen to be highly flammable, i.e., they are easy to ignite at room temperature and burn intensely. From a labelling and classification point of view there is, however, a small difference between E85 and petrol as petrol is classified as "extremely flammable" while E85 is classified as "highly flammable". These classes are based on the initial boiling point of the two fluids. As society has a long history of handling petrol, one of the aims of this project was also to provide a comparison between petrol and E85 wherever possible to allow an assessment of the risk of E85 relative to that of petrol.

1.3 Experimental planning

The project was divided up into five separate Work Packages in order to maximise the use of information obtained early in the project in other parts of the project and thereby simplify the overall evaluation of the results. The Work Packages were defined as follows:

- 1. Determination of the composition and concentration of fuel vapours in a closed vessel at different temperatures
- 2. Determination of the range of temperatures for which E85 vapours are flammable
- 3. Investigation of the consequences of ignition of a flammable gas mixture in a car fuel tank
- 4. Investigation of the difference in fire development for a pool fire under a fuel tank filled with petrol or E85
- 5. Determination of the fuel concentrations and fuel composition around the filling opening of a vehicle during refuelling.

The first two Work Packages were related to fundamental information concerning the characteristics of E85. These were conducted based on fuel vapours extracted from a closed vessel at different temperatures. The ignitability of these vapours was then tested in an explosion chamber (or so called bomb). The second Work Package also aimed to determine whether E85-vapours could be represented using a test gas mixture in the ignition tests to be conducted in the car fuel tanks in Work Package 3.

The final three Work Packages were more applied in nature. In particular Work Packages 3 and 4 were primarily aimed towards studying the consequences of a more or less forced ignition. Work Package 5 determined the fuel concentration and gas composition around the filling opening of a vehicle when refuelling in order to assess the risk for ignition and provide details for assessment of the need for a gas recycling system for E85.

One should note that probability assessments were not conducted as part of Work Packages 3 and 4. In other words, one has not taken the risk for ignition into account but merely investigated the consequences should ignition occur through a "worst case" scenario.

The majority of the analyses and experiments were conducted on E85 of summer quality (E85S). This has been seen to be the "worst case" from a flammability perspective as this quality normally contains the maximum allowed amount of ethanol. The summer quality also has a lower partial pressure which means E85S would be expected to remain flammable at the

highest temperatures. In order to obtain some knowledge concerning the difference in performance between winter and summer qualities of E85 a limited number of comparative experiments have been conducted with E85W. There is also a potential risk that the characteristics of E85 could change due to ageing, i.e., when the most volatile fractions have evaporated. This has been investigated in a small number of experiments. In order to have a good basis for comparison with petrol, some comparative experiments have also been conducted using 95-octane lead-free petrol of summer quality (LF95S). The various fuel specifications are given in Appendix 1.

An account of the various Work Packages is given in chapters 3-7. The experimental equipment, procedures and results are presented in these chapters. Chapter 8 discusses the results from the Work Packages and chapter 9 gives a summary of the most important lessons to be learned from this project.

During the course of this project a large amount of literature has been collected and studied. The results of this literature review are presented in chapter 2.

2 Literature review and ongoing activities

The aim of this work has not been to conduct a systematic and exhaustive literature review. During the planning and realisation of this project, however, a number of investigations and experimental studies that are relevant for the project in hand have been collected. The following chapter gives a short summary of these activities. In some cases investigations and recommendations of relevance to this work have also been summarised.

2.1 Experimental studies

The single piece of work that is most referred to concerning the ignition characteristics and flammability limits of different mixtures of petrol and ethanol was conducted in Canada by Vaivads *et al.* [3] in the mid-1990's. This report is often referred to simply as the "SAE-report". This report summarises a combined experimental and theoretical analysis of the ignition characteristics of six different qualities of fuel: petrol, ethanol (E100), methanol (M100) and three mixtures of these: M85, E85 and E10. The ethanol that was used in the experiments was comprised of 92 % ethanol, 5 % methanol, 1 % 4 methyl-2 pentanone, 1 % ethylacetate and 1 % aliphatic hydrocarbons (vol-%). The petrol that was used was originally winter quality but has been "aged" to attain the same partial pressure as the corresponding summer quality.

The investigation was based in part on ignition experiments and in part on measurements of the fuels partial pressure. Based on this data the flammability limits were calculated for the different fuel mixtures. The ignition experiments were conducted in a 570 ml plastic bottle which was filled up to 1/30 (19 ml) with fuel. The bottle was equipped with two different ignition systems: a low energy system, approximately 70 mJ; and a high energy system, approximately 250 mJ.

The bottles were conditioned to the specific experimental temperature, which varied between - 30°C and +40°C. During the conditioning process a shaking mechanism was used to ensure equilibration inside the bottle. In each test series a set of 10 separate test bottles were used. Thus a statistical data set could be obtained to assess the probability of ignition for each test situation.

The partial pressure was measured as a complement to the ignitions tests. Further, the composition of the gas phase was measured once equilibration had been achieved. Based on this data, a mathematical model was developed to calculate the flammability limits for the different mixtures which could then be compared to the experimental results. Using this model one could then study the influence of different parameters, e.g.: other fuel mixtures, different temperature, different degrees of filling etc.

The SAE-report shows that the flammability limits for the E85-fuel used in this study lie between +3 °C (UEP-upper explosion point) and approximately -35 °C (LEP-lower explosion point). If the degree of filling is below approximately 20 % the UEP is shifted upward and at e.g. approximately 10 % degree of filling the UEP is calculated to be approximately 10 °C, while at 1 % it is approximately 20 °C. Even the LEP is shifted upwards somewhat, but not as significant.

Towards the end of the 1990's the National Renewable Energy Laboratory (NREL) commissioned a similar study in the USA by South West Research Institute (SWRI) [4]. The aim of the SWRI study was to develop a vehicle designed for ethanol power that could comply with the emissions requirements as defined in California for an "Ultra Low Emission Vehicle" (ULEV). As a part of this project, different types of ethanol fuels were studied and a small part of that study involved the running of certain experiments to determine the ignition characteristics of the fuels and flammability limits. The fuel mixtures that were studied could

not, however, be seen to be commercial mixtures but were mixtures of ethanol and other types of specific additives to vary the octane, partial pressure etc.

The experiments were conducted in much the same manner as in the SAE-report [3] and the results exhibit a very clear relation between the flammability limits and the partial pressure of the fuel mixture for most mixtures.

In Germany, PTB (Physikalisch-Technische Bundesanstalt) has recently published an investigation of the safety aspects concerning the handling of different petrol-ethanol mixtures [5-7]. This investigation includes, amongst other things, determination of: UEP, MESG (maximum experimental safe gap) and AIT (auto ignition temperature), all of which are necessary to define safety requirements for petrol stations and other similar locations. Even the flash point and flammability limits (%-vol) have been determined.

As it was unclear which types of petrol-ethanol mixtures could be most relevant in Germany, experiments were conducted for several different fuel mixtures, including ordinary 95-octane petrol, E50, E60, E65, E70, E75 and E85. In some cases the mixtures were tested using both winter and summer qualities.

A summary of how to determine UEP and MESG is given below as these parameters have a significant effect on how the petrol-ethanol mixture is classified.

The upper explosion point (UEP) is determined using a method that was developed at PTB. The fluid that is to be evaluated is placed in a cylindrical glass vessel covered with a tightly fitting lid allowing for pressure relief. The vessel containing the liquid should be pre-conditioned in a climate cabinet until the contents have reached temperature equilibrium. Once equilibrium has been reached an ignition test is conducted of the vapours above the liquid surface. Whether ignition has been obtained or not depends on a visual assessment of the vessel in combination with a temperature measurement inside the vessel.

Depending on the results of the test, the temperature is raised or lowered stepwise until the temperature boundary for ignition/non-ignition has been established according to the predetermined ignition criteria. The experiments can be conducted with varying degree of filling of the vessel to investigate how this parameter affects the UEP.

The methodology is presently described in a draft EN-standard, "Determination of explosion points of combustible liquids" which is under development within CEN TC 305 [8].

MESG is used to characterize the explosion characteristics of fuel vapours, related to gaps in e.g. flame arresters and flameproof enclosures designed to stop a flame from penetrating from one volume to another. This value is used to determine which explosion classification the gas or gas mixture obtains, e.g., IIA, IIB, IIB1, etc. The test is conducted according to IEC 60079-1-1 in which an explosion chamber is filled with the gas mixture to be evaluated. Inside the chambers centre is a smaller test volume, which is also filled with the fuel mixture and provided with an ignition system. The smaller test volume is comprised of two half spheres made from steel with a gap between the halves that can be regulated accurately with a micrometer. During the test, the gas inside the small test volume is ignited and one studies whether the flame produced by the ignition propagate through the slit and ignites the gases in the large explosion chamber. The maximum gap which does not allow propagation of the flame is the MESG-value for that specific gas. As the gas mixture in a closed vessel does not have the same composition as the fluid phase, an analysis was made of the gas composition inside a closed vessel under equilibrium conditions. Based on these measurements, a similar composition was produced by vaporising petrol and ethanol in corresponding proportions to reconstruct the test gas as closely

as possible. The determination was made at 50 °C as this gives a certain safety margin relative to normal temperature levels as the MESG decreases with increasing temperature.

Table 1 gives a summary of the results for UEP from two different E85-qualities (winter and summer quality) that were tests at PTB. Other fuel qualities were tested at PTB and we refer you to PTB's reports for full information [5, 6].

Table 1 The results from the determination of UEP for two different qualities of E85 at different degrees of filling obtained at PTB [6].

Fuel designation*)	20 %	10 %	3 %	1 %
E85 ROZ 95 Summer	3,5 °C	4,5 °C	8,5 °C	18,0 °C
E85 ROZ 95 Winter	**)	-6 °C	2 °C	17 °C

^{*)} Both E85 summer and winter qualities contained 85 % ethanol.

Determination of the MESG-value has been used as the basis for the classification of E85 in different explosion classes. Petrol is classified as IIA which implies that the MESG-value should be greater than 0,90 mm. If the value of MESG is 0,90 mm or less the fuel is classified as IIB (IIB1 for flame arrestors). Tests that have been conducted to determine the MESG of E85-vapours from petrol/ethanol mixtures show that those with an ethanol concentration in the liquid phase of \leq 97 %-vol can be classified as IIA while those with a higher ethanol content fall into IIB1 [7].

Concerning the ignition temperature PTB's measurements show that E85 attains a temperature classification of T3 which is the same as petrol.

2.2 Other investigations and recommendations

A survey of safety aspects associated with E85 as a vehicle fuel has been conducted in Sweden by Ecotraffic ERD³ AB [9]. The survey was commissioned by the Environmental and Health Administration of the City of Stockholm and gives an assembled overview of different safety aspects such as general fire risks, safety improvement measures, risks and procedures in the case of a fire, regulations for the handling of vehicle fuels, experience of handling ethanol and material compatibility.

The report was published in 2006 and contains a collation of chemical and physical data where the uncertainly in certain data is clearly presented, e.g. the flammability limits for E85 based on the results presented in the SAE-report [3]. Even other characteristics, e.g., how E85 performs under fire conditions, have been the subject of discussion. The collective assessment is, however, that E85 does not represent an increased risk relative to that associated with the distribution and handling of petrol and diesel fuel.

The Swedish Petroleum Institute (SPI) has been working on these issues and developed their own recommendations concerning the handling of E85 since it first began to be marketed. This work has been conducted in consultation with the Swedish Rescue Services Agency (SRSA) and a preliminary issue was released in the beginning of 2007 [10]. These recommendations contain certain results from this project but SPI has also commissioned additional investigations.

One such issue concerns how the fire characteristics of E85 are compared to petrol in a pool fire scenario [11]. Two comparative experiments were conducted using a pool fire approximately 1,7 m² which corresponds approximately to the size of the fuel spill tray at a filling station. The tests showed that E85 burns with a lower burning rate and gives lower radiation compared to petrol. The flame from E85 is, however, fully visible. In a second investigation the risks for and

^{**)} Temperature not determined.

consequences of an ignition of E85-vapours inside a 6 m³ underground steel tank were studied [12]. Tests were conducted on two separate occasions. In the first set of tests conducted in October 2006, the temperature in the tank was approximately 11°C, the degree of filling was approximately 20 %. Under these conditions the fuel vapours inside the tank could not be ignited, despite efforts to dilute the vapours with pressurised air. During these ignition tests, a small "puff" was created at the filling pipe but this was self-extinguishing due to the fuel rich nature of the mixture inside the tank. The second set of tests were conducted in April 2007 when the temperature in the tank was lower, approximately 4 °C. Further, the tank had been essentially emptied so that only approximately 50 l of fuel remained, i.e. a degree of filling of less than 1 %. Despite this fact the tank could not be ignited. The fuel vapours inside the tank were therefore diluted with fresh air (40-50 % of the tank volume) after which ignition was achieved. The ignition gave rise to a rapid pressure increase, followed by a forceful exhaust of the combustion gases at a high velocity via the tank ventilation pipe during several seconds. Some parts from the P/V-vent were blown off their connections due to this, but apart from this minor damage, no other visual effect of the explosion could be seen above ground. After the tank had been removed from the ground it was inspected and no visual damage could be seen. The main conclusion of this study was that if one applies these results to a filling station scenario, one would expect potential damage to confine itself to property damage on the tank and a possibly associated equipment but that the risk for damage to people or other equipment. e.g. through fire spread to nearby objects, would be minimal.

A final version of the SPI recommendations is expected to be finished in December 2007.

The Swedish Rescue Services Agency is the regulatory body that issues regulations based on the law concerning flammable and explosive goods (1998:868). A handbook concerning the transport of flammable liquids and gases at filling stations is under development and will also include E85 [13].

The US Department of Energy (DoE) has in consultation with the National Ethanol Vehicle Coalition (NEVC) developed a handbook concerning the distribution, storage and sales of E85 [14]. This handbook contains certain basic data concerning E85 but is not particularly detailed concerning the safety data that has been the focus of this project. The handbook gives more general information concerning E85 compared to petrol and in some parts is more of a "marketing" brochure for E85 than a handbook.

General regulations concerning filling stations are already available in Germany, TRbF 40 [15]. Based on the results from the project run by PTB concerning E85 and referred to above, a series of recommendations have been developed concerning interpretation of these regulations in terms of handling of E85 [16]. The regulations specify that fuels with an upper explosion point (UEP) above minus 4 °C shall be equipped with a Class IIA flame arrester. In the case of ethanol mixtures this is applied to mixtures containing more than 60 % ethanol. In cases where the ethanol content is greater than 90 % in the liquid phase a Class IIB1 flame arrester should be used. According to PTB's results Class IIA should be sufficient up to 97 % ethanol in the liquid phase, but this limit has been reduced to 90 % to introduce a certain margin of safety. Commercially available E85 qualities are well within those specifications.

It should, however, be noted that an exception should be made concerning the requirement of a flame arrester on the tank ventilation pipe for underground tanks constructed out of steel. Experiments conducted by PTB on such fuel tanks show that these can withstand an internal explosion without substantial damage. As the consequences of an explosion were small, the additional cost of installation of a flame arrester was not considered justified relative to the risk [17].

A flame arrester which is installed in the end of a pipe (so called end-of line protection), e.g. in the top of a tank ventilation pipe, may be subject to an additional requirement for "endurance burning". In this case the flame arrester should be able to prevent penetration of a transient flame and continue to protect against flame penetration should the fuel vapours continue to burn on the outside of the flame arrester. In such situations, the MESG-value of the gases is not the most important parameter as other factors dominate. In those cases where the flame arrester also needs to be approved for "endurance burning", the approvals test [18] should be conducted with ethanol as fuel as the choice of fuel is known to effect the results and final classification. The standard allows the allocation of different classes of "endurance burning" relative to the time that the flame arrester is required to withstand flame penetration.

Whether there should be a requirement for a flame arrester (e.g. in the case of underground tanks, whether their should be exceptions to their exemption), and in that case, which requirements should be made, is not presently regulated but is determined based on a specific risk analysis depending on the layout of the a specific filling station [17].

One point that should be noted concerning the German regulations and applications is that there are no provisions concerning the use of vapour recovery systems for the E85 but in practice, vapour recovery is also used for E85 as such systems are already available at existing filling stations [17]. Further, a latch-open device is allowed on the fuel nozzle. There are, however, no requirements for a break-away coupling on the pumps. The risk of generation of static electricity when filling is not considered to be so great as to require special provisions to reduce the risk. It is not acceptable to use plastic piping for the pumping of petrol in German filling stations. The question of whether the pipes are conductive or not, has therefore not been an issue.

In Sweden there is a standard specifically for E85, SS 155480:2006 which states the technical specifications for E85 in winter and summer qualities [19]. There is no such corresponding ENstandard presently. The main difference between summer and winter qualities is the vapour pressure of the fuel. The summer quality has a vapour pressure of between 35 kPa and 70 kPa while that for winter quality lies between 50 kPa and 95 kPa. The vapour pressure is regulated using the amount of petrol in the E85 mixture. This means that the percentage of petrol in the winter quality is normally higher than that in the summer quality. The minimum allowable amount of ethanol in E85 is 75% for the summer quality and 70 % for the winter quality. The minimum allowable amount of petrol is 14%, i.e. the volume percentage of ethanol can vary between 70 % and 86 % at the most.

It should also be noted that in the UN regulations for the transport of hazardous goods, there is presently a separate UN-number for petrol/ethanol mixtures with an ethanol concentration of over 10 % (e.g. E85), UN 3475. The formal introduction of the UN-number in the UN regulations will probably occur during late 2007 or early 2008 [17].

2.3 Risk for ignition through static electricity during vehicle refuelling

One of the potential ignition sources that is often mentioned is the building up of electrostatic charge while filling a vehicle. In Sweden there are no assembled statistics concerning how frequent such incidents are in conjunction with filling a vehicle but the UK Petroleum Industry Association, Society of Motor Manufacturers and Traders Ltd and the Institute of Petroleum in England published a report in 2001 where this phenomenon had been studied [20]. In this investigation, data concerning fires at filling stations in conjunction with filling a vehicle in Germany, France, the USA and England during the middle of the 1990's, were collated.

The collation concerning actual fires is probably not complete but it does give a good picture of the types of fires that can occur. In total, this material is comprised of 36 fires in Germany (for the period 1992-1995), 100 fires in France (for the periods 24/3-24/4 and 1/9-31/10, 1997), 4 fires in Ireland (reported during 1997), an average of 2 fires per year in England, and 26 fires in the US (for the period 1993-2000). Considering the large number of vehicles filled during this time period, the general conclusion is that the probability of ignition while refuelling a vehicle is very small.

These results do show large differences between the various countries, however. The reason for the extremely low frequency in England is thought to be the fact that no snagging mechanism is allowed there. The analysis of the fires which occurred in Germany, France and the US show there are several dominant reasons. Also the design of the fuel nozzle can affect its ability to dissipate a potential difference between the vehicle and the nozzle. Other factors that have been identified as potentially important include: use of tyres with poor conductivity and whether the surface on the ground around the pumps has poor conductivity. Also dry conditions, with low relative moisture content in the surrounding air, have been identified as raising the risk of ignition.

Work Package 1: Composition of fuel vapours in a closed vessel at different temperatures

The aim of Work Package 1 has been to determine the composition and concentrations of the fuel vapours (i.e. relative ethanol and petrol fractions) which can be obtained in a closed vessel at equilibrium at different temperatures. E85 of both summer (E85S) and winter (E85W) qualities and 95-octane lead free petrol (LF95S) have been analysed to provide a sound basis for comparison. The analyses have been conducted by filling small glass bottles with a predefined amount of fuel. These have been closed and conditioned to the required temperature, after which a gas sample has been extracted from the bottle and analysed.

The analyses have been conducted by SP Chemical and Material Technology.

3.1 Experimental equipment and procedure

The various fuel samples have been stored in a freezer in closed 250 ml or 500 ml bottles. A sample of 30 ml was extracted from these bottles for each temperature and introduced in a 120 ml sealed bottle, in order to reach a 25 % degree of filling.

This bottle was conditioned to the pre-determined temperature in a water bath for the temperatures +20 °C and +10 °C, while an ethylene glycol/water bath was used for the temperature from 0 °C down to -25 °C, see Figure 1.

After 2-6 hours and 24 hours, respectively of conditioning, a 50 μ L gas sample was extracted using a sealed syringe. This sample was injected directly into a gas chromatograph equipped with a flame ionisation detector (GC-FID). The analyses were conducted using a Varian Star 3400Cx gas chromatograph, equipped with a Poraplot-Q capillary column (Chrompack, 25 m long, 0,32 mm internal diameter, 10 μ m consistent thickness). The column temperature was programmed from 35 °C (for 6 min) to 250 °C (for 10 min) with a temperature gradient of 10 °C/min. The injection temperature was constant at 200 °C and the flame ionisation detector temperature was constant at 200 °C.

3.1.1 Calibration of analysis equipment

Calibration of the gas chromatograph and FID-detector was conducted using a known amount of ethanol and the various petrol fractions. These were injected into a 120 ml glass bottle and after vaporisation, the gas sample was analysed from the bottle in the same way as described above. The relative response factors were determined for 20 species, relatively to ethanol. The calibration also provides information concerning the retention time for each species which is useful in identifying the species from the test. The species that were analysed as part of the calibration were: methanol, ethanol, propanol, MTBE, pentane, 2-methylpentane, 3-methylpentane, hexane, 1-hexene, 2,2-dimethylbutane, 2,3-dimethylbutane, heptane, trimethylpentane, bensene, toluene, xylenes, cyclopentane, cyclohexane, methylcyclopentane, methylcyclohexane.

To facilitate the identification of these species a GC-MS (gas chromatography/mass spectrometry) analysis was performed in one case (gas phase at 0 °C). A gas sample of 0,5 ml was extracted from the sample bottle and transferred to an adsorbent tube packed with Carbotrap/Carbosieve III. The tube was thermally desorbed and analysed using a gas chromatograph equipped with both a flame ionisation detector and a mass selective detector (GC-FID/MS). This GC was a Hewlett Packard gas chromatograph HP5890 series II, with a mass spectrometer detector HP5972 operating in "electron impact mode" with ionisation energy

of 70 eV and mass scanning range of 29 to 300 amu. Individual species can be identified using their fragmentation pattern ("mass spectra") which every species which exits the column produces in the mass detector. The resulting mass spectra are compared to a computerised library containing many thousand species. This analysis is performed on a similar column as used during the FID-analysis for concentration determinations as described above.

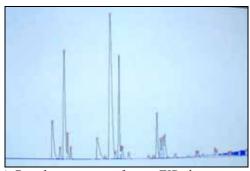
Concerning the uncertainty of the measurements, the 95 % confidence interval has been estimated to correspond to approximately \pm 20 % of the measured values.





a) Conditioning in a water bath.

b) Injection into the GC



c) Gas chromatogram from a FID-detector

Figure 1 Photos of a) the test bottle in a water bath, b) analysis equipment, c) a gas chromatogram.

3.1.2 Ageing of E85

One aspect that has been suspected to affect the properties of E85 is the "ageing" which can occur due to the evaporation of the fuel or diffusion through the walls of a fuel tank. This can affect the partial pressure of the fuel and therefore also the composition of the fuel vapours. The allowed emissions of fuel from a complete vehicle was used as a basis for the assessment of what could be a reasonable level of evaporation. This requirement means that a car is allowed to emit no more than 2 g/day (24 hour period) in a so called SHED-test.

Our estimation assumed that a car containing 15 litre E85 in the fuel tank will emit the maximum allowed amount for 10 days, i.e. a total of 20 g (2 g \times 10 days), and that all these

emissions will stem from the fuel tank. This corresponds to a weight loss of approximately 0,15 wt %.

Based on this assumption ageing of E85 was conducted by placing an open 120 ml container with 30 ml E85 at room temperature and allow approximately 0,15 % of the weight to evaporate. The desired weight loss was achieved after approximately 25 minutes, at which point the container was sealed and conditioned.

3.2 Results from gas analyses

The gas analyses have primarily focused on E85 summer quality (E85S) and analyses have been conducted at six temperature levels within the temperature interval from -25 $^{\circ}$ C to +20 $^{\circ}$ C (i.e., -25, -20, -10, 0, 10, 20 $^{\circ}$ C). E85 winter quality (E85W) has only been analysed at 0 $^{\circ}$ C to enable a comparison with E85S. Also the aged E85S was analysed at 0 $^{\circ}$ C only, for the sake of comparison.

Petrol is more volatile than ethanol. Therefore the analyses were reduced to four temperature levels for petrol in the temperature interval from -25 °C to 0 °C (-25, -20, -10, 0 °C).

The following chapter contains the first summary of the analysis data obtained presented according to type of fuel. In chapter 3.2.4, a comparison is given between the different qualities of E85 and petrol.

3.2.1 E85 Sommer quality

Table 2 provides a collation of the analysis results obtain for E85S at the different temperatures studied. The concentrations are expressed as g/m³ while those in Table 3 have been expressed as vol-%. The tables contain two sets of analysis data for each temperature level: one after 3-5 hours conditioning, the other after 24 hours conditioning.

A visual summary of the analysis results is also given in Figure 2.

Table 2 Collati	on of ar	nalysis (data (g/	m³) for	E85S a	t differe	nt temp	eratur	es.			
Temperature (°C)	-25	-25	-20	-20	-10	-10	0	0	10	10	20	20
Conditioning												İ
time (h)	5	24	5	24	5	24	6	24	3	24	3	24
Alkenes C3												İ
(Propene)	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
Propane	0,1	0,1	0,1	0,1	0,2	0,2	0,2	0,2	0,2	0,2	0,3	0,3
Total C3	0,1	0,1	0,1	0,1	0,2	0,2	0,2	0,2	0,3	0,3	0,3	0,3
Branched alkanes												İ
C4 (Isobutane)	3,9	3,7	5,8	5,4	8,9	8,4	12,2	12,2	15,5	15,0	18,8	18,8
Alkenes C4	1,9	1,8	2,9	2,6	4,9	4,8	6,6	6,7	8,8	8,7	11,2	11,3
Butane	8,9	8,6	13,3	12,5	21,3	19,5	29,6	30,8	39,1	37,6	49,0	49,3
Total C4	14,8	14,1	22,0	20,5	35,1	32,7	48,4	49,7	63,4	61,3	79,0	79,4
Branched alkanes												
C5 (Isopentane)	16,0	15,5	24,6	22,5	42,0	38,3	61,2	64,5	85,4	84,8	117,7	117,4
Alkenes C5	1,4	1,4	2,3	1,9	4,1	4,9	5,4	5,7	8,5	8,3	12,0	11,6
Pentane	3,9	3,8	6,2	5,6	10,9	9,9	16,0	16,9	23,3	22,2	31,8	31,6
Cyclic C5	0,4	0,4	0,3	0,2	1,2	1,0	1,7	1,8	2,5	2,4	2,5	3,5
Total C5	21,7	21,1	33,4	30,2	58,1	54,1	84,3	88,9	119,7	117,7	163,9	164,0
Branched alkanes												
C6	3,0	3,1	5,3	4,7	10,0	8,6	14,7	14,6	22,5	21,3	30,6	31,4
Alkenes C6	0,2	2,4	0,5	0,5	1,0	0,8	1,3	1,3	1,9	1,8	2,6	2,6
Hexane	0,5	0,5	1,0	1,0	2,0	1,7	2,0	2,8	4,9	4,6	6,9	7,1
Cyclic C6	0,5	0,6	1,2	1,2	2,5	2,1	2,7	3,4	5,9	5,6	8,3	8,6
Total C6	4,2	6,7	7,9	7,3	15,5	13,2	20,7	22,1	35,3	33,3	48,4	49,7
Branched alkanes												
C7	0,4	0,6	1,0	0,8	2,2	1,7	2,9	3,1	5,1	4,9	7,1	7,7
Heptane	0,1	0,1	0,1	0,1	0,3	0,2	0,4	0,4	0,7	0,7	1,0	1,7
Total C7	0,5	0,7	1,2	0,9	2,5	1,9	3,3	3,5	5,8	5,5	8,1	9,4
Branched alkanes												İ
C8	0,2	0,2	0,5	0,4	1,0	0,9	1,9	1,5	2,9	3,2	3,7	3,9
Total C8	0,2	0,2	0,5	0,4	1,0	0,9	1,9	1,5	2,9	3,2	3,7	3,9
Benzene	0,0	0,1	0,2	0,2	0,5	0,4	0,6	0,6	1,0	1,0	1,5	1,4
Toluene	0,2	0,3	0,5	0,4	1,2	0,9	1,7	1,7	3,6	3,0	4,2	4,5
Xylenes	0,0	0,0	0,1	0,1	0,4	0,2	0,7	0,6	1,8	2,0	2,4	2,7
Ethanol	2,4	2,3	6,6	5,0	17,2	16,2	31,5	34,9	60,1	57,8	95,0	96,2
MTBE	2,2	2,2	3,7	3,5	7,5	6,5	7,5	15,0	14,9	14,7	25,1	24,2
Total	46	46	76	69	139	127	201	219	309	300	432	436

Table 3 Collation of analysis data (%-vol) for E85 at different temperatures.

Temperature (°C)	-25	-25	-20	-20	-10	-10	0	0	10	10	20	20
Conditioning time												
(h)	5	24	5	24	5	24	6	24	3	24	3	24
Total C3 *)	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
Total C4 *)	0,6	0,6	0,9	0,9	1,5	1,4	2,0	2,1	2,7	2,6	3,3	3,4
Total C5 *)	0,7	0,7	1,15	1,0	2,0	1,9	2,9	3,1	4,1	4,0	5,6	5,6
Total C6 *)	0,1	0,1	0,2	0,2	0,4	0,4	0,6	0,6	1,0	0,9	1,3	1,4
Total C7 *)	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	0,01	0,1	0,1	0,1	0,2	0,2
Total C8 *)	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	0,1	0,1	0,1	0,1
Total aromatics												
(C6 + C7 + C8)	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	0,2	0,2	0,2	0,2
Ethanol	0,1	0,1	0,3	0,3	0,9	0,9	1,7	1,9	3,2	3,1	5,0	5,1
MTBE	0,1	0,1	0,1	0,1	0,2	0,2	0,2	0,4	0,4	0,4	0,7	0,7
Total	1,7	1,7	2,8	2,5	5,2	4,8	7,6	8,2	11,8	11,4	16,6	16,7

^{*)} Sum of alkanes and alkenes

Figure 2 presents a summary of the analysis results as a diagram. The results are presented as a function of temperature after 24 h conditioning. The diagram shows that the highest concentrations were registered for C5 species which account for approximately 5,5 % at 20 °C. Also C4 och C6 species have significant concentrations while the concentrations of C3, C7 och C8 hydrocarbons are very low. The concentration of ethanol varies from about 0 % at -25 °C to approximately 5 % at +20 °C while the concentration of MTBE is approximately 0,7 % at +20 °C. The total fuel concentration varies between approximately 1,7 % to approximately 16,5 % at +20 °C.

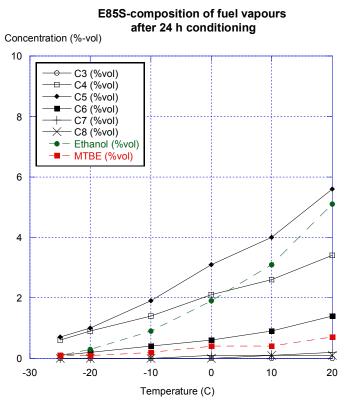


Figure 2 Concentration of different hydrocarbon fractions relative to MTBE and ethanol as a function of temperature for E85S.

3.2.2 E85 winter quality and aged E85

Table 4 contains a compilation of the analysis results for E85W and aged E85S. The concentrations are expressed as g/m^3 while those values in Table 5 have been expressed as vol-%. All analyses have been conducted at 0 °C.

Table 4 Collation of the analysis data (g/m³) for aged E85S and E85W at 0 °C.

	Aged 1	E85	E85 W			
Temperature (°C)	0	0	0	0		
Conditioning time (h)	4	24	6	24		
Alkenes C3 (Propene)	0,0	0,0	0,0	0,0		
Propane	0,1	0,1	1,0	0,9		
Total C3	0,1	0,2	1,0	0,9		
Branched alkanes C4 (Isobutane)	10,0	10,1	23,2	21,5		
Alkenes C4	6,0	6,0	10,6	9,7		
Butane	26,1	26,8	77,1	74,4		
Total C4	42,1	42,8	110,8	105,6		
Branched alkanes C5 (Isopentane)	59,5	59,6	64,3	58,7		
Alkenes C5	5,5	5,8	5,7	5,2		
Pentane	16,2	15,9	14,0	12,6		
Cyclic C5	1,8	1,7	2,2	1,9		
Total C5	83,0	83,0	86,2	78,4		
Branched alkanes C6	15,2	14,5	17,8	18,0		
Alkenes C6	1,2	1,3	9,7	12,7		
Hexane	3,1	2,9	3,2	4,4		
Cyclic C6	4,2	3,6	3,8	4,9		
Total C6	23,7	22,3	34,5	40,0		
Branched alkanes C7	3,4	2,7	3,2	2,6		
Heptane	0,5	0,5	0,5	0,3		
Total C7	4,0	3,2	3,7	3,0		
Branched alkanes C8	1,9	1,4	1,3	1,6		
Total C8	1,9	1,4	1,3	1,6		
Benzene	1,0	0,7	0,7	0,5		
Toluene	2,3	1,4	2,0	1,5		
Xylenes	0,6	0,6	1,2	1,5		
Ethanol	38,8	35,4	22,4	19,5		
MTBE	13,1	13,1	8,5	11,5		
Total	211	204	264	252		

Table 5	Collation of the a	nalysis data i	(vol-%) for aged l	E85S and E85W at 0°C.

	Aged	E85	E85W		
Temperature (°C)	0	0	0	0	
Conditioning time (h)	4	24	6	24	
Total C3 *)	< 0,1	< 0,1	< 0,1	< 0,1	
Total C4 *)	1,8	1,8	4,7	4,5	
Total C5 *)	2,9	2,9	3,0	2,7	
Total C6 *)	0,7	0,6	0,7	0,8	
Total C7 *)	< 0,1	< 0,1	< 0,1	< 0,1	
Total C8 *)	< 0,1	< 0,1	< 0,1	< 0,1	
Total aromatics $(C6 + C7 + C8)$	0,1	0,1	0,1	0,1	
Ethanol	2,1	1,9	1,2	1,0	
MTBE	0,4	0,4	0,2	0,3	
Total	8,0	7,7	10,1	9,5	

^{*)} Sum of alkanes and alkenes

If one compares the results after 24 hours conditioning of the aged and unaged E85S fuel (see Table 3) it is clear that evaporation reduces the concentration of C4 and C5 species while the other species are unchanged. The total concentration at 0 °C was reduced by 0,5 %, from 8,2 % to 7,7 %.

The composition of E85W contains a relatively high proportion of C4-species compared to E85S. This is probably a consequence of the increased content of petrol in order to increase the partial pressure of the fuel. This causes the concentration of ethanol to be almost halved, from approximately 1,9 % to 1,0 %.

3.2.3 Lead-free 95-octane petrol

Table 6 provides a collation of the analysis results for petrol, LF85S, at different temperature levels. The concentrations are expressed in g/m³ while those in Table 7 have been recalculated and expressed as vol-%. A summation of analysis results are also presented in Figure 3 below.

Table 6 Collation of the analysis data (g/m³) for petrol, LF85S, at four different temperature levels.

levels.	2.5	25	20	20	10	10		0
Temperature (°C)	-25	-25	-20	-20	-10	-10	0	0
Conditioning time (h)	4	24	5	24	5	24	3	24
A 11 (C2 (D	0.1	0.1	0.1	0.1	0.0	0.0	0.1	0.2
Alkenes C3 (Propene)	0,1	0,1	0,1	0,1	0,0	0,0	0,1	0,2
Propane	1,2	1,2	1,6	1,5	1,9	1,9	2,6	2,8
Total C3	1,3	1,3	1,7	1,7	1,9	1,9	2,8	3,0
Branched alkanes C4 (Isobutane)	17,6	17,6	23,9	22,1	29,8	31,3	46,1	48,7
Alkenes C4	8,4	8,4	11,8	10,8	16,0	15,9	25,0	26,7
Butane	40,7	40,6	55,5	51,3	70,4	74,8	116,9	118,5
Total C4	66,7	66,5	91,2	84,2	116,2	122,1	188,0	193,8
D 1 1 11 05								
Branched alkanes C5	12.5	42.6	(0.0	55.2	02.0	07.6	126.0	1.42.1
(Isopentane)	42,5	42,6	60,9	55,3	83,0	87,6	136,9	143,1
Alkenes C5	4,3	4,3	6,9	5,8	10,6	9,3	16,2	18,4
Pentane	9,1	9,2	13,6	12,1	19,5	19,9	33,2	34,0
Cyclic alkanes C5	1,1	1,1	1,7	1,5	3,8	2,5	4,4	5,5
Summa C5	57,0	57,1	83,1	74,6	117,1	119,4	190,7	201,0
Branched alkanes C6	7,1	7,2	12,6	10,6	19,4	17,8	31,5	35,8
Alkenes C6	1,8	2,5	3,2	2,4	6,1	3,9	8,1	10,5
Hexane	1,0	1,0	2,0	1,5	3,4	2,6	5,5	6,3
Cyclic alkanes C6	1,4	1,4	3,3	2,0	5,1	3,7	7,6	8,6
Total C6	11,3	12,2	21,0	16,5	34,0	28,0	52,7	61,2
Branched alkanes C7	1,0	1,0	2,4	1,5	4,8	2,7	5,8	6,0
Heptane	0,1	0,1	0,2	0,2	0,8	0,3	0,7	0,7
Total C7	1,1	1,1	2,6	1,7	5,6	3,0	6,5	6,7
Branched alkanes C8	0,4	0,4	1,4	0,6	2,8	1,1	2,4	2,8
Total C8	0,4	0,4	1,4	0,6	2,8	1,1	2,4	2,8
1000	٠,٠	,,,	1,1	0,0	_,0	1,1	_,.	_,0
Benzene (C6)	0,4	0,4	1,3	0,5	1,7	1,1	2,1	2,3
Toluene (C7)	1,1	1,1	2,8	1,5	4,5	2,3	6,3	5,9
Xylenes (C8)	0,2	0,2	0,8	0,6	1,0	0,3	2,9	1,6
Ethanol	1,8	2,1	4,5	3,7	10,5	7,5	19,0	23,2
MTBE	<1	<1	<1	<1	<1	<1	<1	<1
				-1	· •	-1	'.	
Total	141	142	210	186	295	287	473	501

levels.								
Temperature (°C)	-25	-25	-20	-20	-10	-10	0	0
Conditioning time (h)	4	24	5	24	5	24	3	24
Total C3 *)	0,1	0,1	0,1	0,1	0,1	0,1	0,2	0,2
Total C4 *)	2,8	2,8	3,9	3,6	4,9	5,2	8,0	8,2
Total C5 *)	2,0	2,0	2,9	2,6	4,1	4,1	6,6	7,0
Total C6 *)	0,3	0,3	0,5	0,4	0,8	0,7	1,3	1,5
Total C7 *)	< 0,1	< 0,1	< 0,1	< 0,1	0,1	0,1	0,1	0,1
Total C8 *)	< 0,1	< 0,1	< 0,1	< 0,1	0,1	< 0,1	0,1	0,1
Total aromatics $(C6 + C7 + C8)$	< 0,1	< 0,1	0,1	0,1	0,2	0,1	0,3	0,3
Ethanol	0,1	0,1	0,2	0,2	0,6	0,4	1,0	1,2
MTBE	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1

Table 7 Collation of analysis data (vol-%) for petrol (95 octane) at four different temperature levels.

Total

Figure 3 present a summary of the analysis results as a function of temperature after 24 hours of conditioning. As shown in the diagram the highest concentrations consists of C4 and C5 species which correspond to approximately 8,2 % and 7,0 % respectively at 0 °C. The concentration of C6 species corresponds to approximately 1,5 % while the ethanol concentration is 1,2 %. The concentrations of C3, C7 and C8 species are very low. Traces of MTBE were noted but these were under the quantification level.

7,9

7,0

10,9

10,7

17,6

18,7

5,3

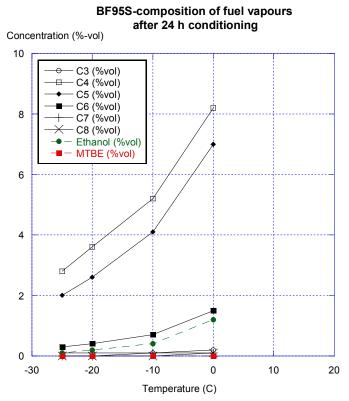


Figure 3 Concentration of different hydrocarbon fractions and ethanol as a function of the temperature for petrol (LF95S).

^{*)} Sum of alkanes and alkenes

3.2.4 Comparison between E85 and petrol

Figure 4 provides a summary of the analysis results for the different E85 qualities and LF95S. The diagram shows the sum of C3-C8 species, ethanol and MTBE plus the total fuel concentration, i.e., the sum of these three groups. In the case of MTBE, the concentration was under the minimum quantification level in LF95S. Therefore, MTBE is not presented in the diagram for LF95S.

There is a strong temperature dependence of the fuel vapour concentration for both E85 and LF95S. Comparing the various E85 qualities at 0 °C one can see that the E85S quality has a total concentration of 8,2 % while E85W has a slightly higher total concentration (9,5 %) while the aged E85S shows a marginally lower concentration (7,7 %). In the case of LF95S, the total concentration is twice as high at 0 °C, approximately 18,5 vol-%.

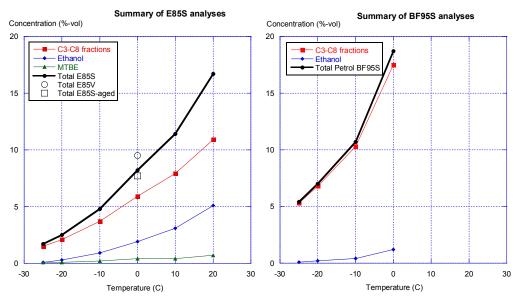


Figure 4 Comparison between the fuel vapour composition of E85 and LF95S (BF95S in the figure) at different temperatures.

The analyses clearly show that the difference between the fuel compositions in liquid and gas phase. Figure 5 shows the ratio between the sum of C3-C8 species and ethanol versus temperature. Despite the fact that E85S contains 85 % ethanol in the liquid phase the fraction of ethanol in the gas phase varies between 5 % (0,05) and 30 % (0,3). This indicates that, despite the low concentration of petrol in E85, the petrol fractions (C3-C8) dominate in the gas phase. As shown in the diagram, the difference is even greater for E85W, where the ratio at 0 °C is approximately 10 % ethanol and 90 % petrol fractions in the gas phase.

Temp (C)

Figure 5 Relationship between the fraction of ethanol and the fraction of C3-C8 species as a function of temperature for E85S (excluding MTBE).

4 Work Package 2: Temperature range for flammable fuel vapours

The aim of Work Package 2, was to determine the temperature range when a closed vessel or tank would contain a flammable mixture of fuel vapours and air, i.e., the temperature range between UEP and LEP. The fuels that were testes were E85S, E85W and petrol LF95S.

Another aspect was to determine the explosion characteristics of E85-vapours, in order to confirm which explosion group (IIA or IIB) that could be seen as most representative for E85 vapours. Two test gas mixtures were therefore used in the tests. Those gas mixtures are normally used for, e.g. the type approval and certification of explosion tight enclosures, as representative gases for these two explosion groups.

The tests were conducted in SP's explosion laboratory at SP Electronics. The laboratory is equipped with an ignition system, pressure measurement equipment and equipment for the generation and control of the test gas mixtures.

4.1 Experimental equipment

The tests were conducted in an explosion chamber ("bomb") which was filled with fuel vapours of different qualities from a sealed, conditioned vessel. After each filling, an electric spark was generated inside the bomb and signs of ignition were studied. Registration of ignition was made visually, through glass windows in the bomb, and through the measurement of pressure changes inside the bomb.

4.1.1 Generation of fuel vapours

In order to ensure that the gas mixture tested in the bomb was as close as possible to that which would be found in a closed vessel, in equilibrium with the contained liquid at a specific temperature, a closed vessel was conditioned at the specific temperature with the correct liquid content. The fuel vapours inside the vessel were then transferred to the bomb via a gas sampling bag, after which the ignition tests took place.

A 60 l metal drum filled with 15 l of the specific fuel being tested (25 % degree of filling) was used to condition the fuel being tested, see Figure 6. The drum was equipped with three connections through the lid, one for the introduction of air (1), one for the extraction of fuel vapours (2), and one for pressure equalisation (3). The connection for pressure equalisation was connected to a 40 l Tedlar gas sampling bag which was placed inside the drum and which acted as a "lung" when the fuel vapours were extracted out of the drum. This prevented the fuel vapours from mixing with incoming air during the extraction process.

The drum was placed in a large freezer where the temperature would be regulated between - 30 °C and +20 °C. The fuel was allowed to temperature equilibrate for approximately 24 hours or more between each temperature level to ensure stable temperature conditions.

Type K shielded (diameter 1 mm) thermocouples were used to measure the temperature both in the liquid phase and in the gas phase inside the drum. Further, a thermocouple was placed inside the freezer to register the gas temperature surrounding the drum. The temperatures were measured manually by connecting each thermocouple to a hand held measurement device of type: Terma 1. The connections to the thermocouples were located outside of the freezer to enable measurements without opening the freezer.

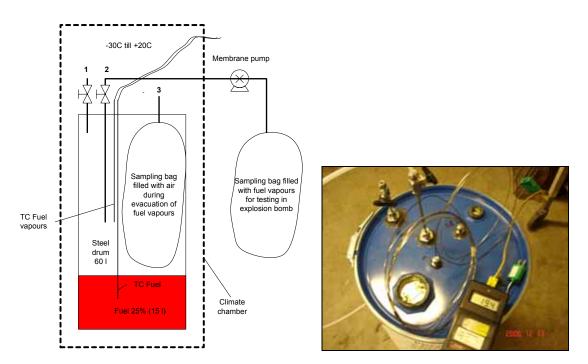


Figure 6 Equipment for the conditioning of fuel and extraction of fuel vapour samples.

When equilibrium had been reached the fuel vapours were extracted from the drum into a 40 l Tedlar gas sampling bag using a membrane pump. The bag was filled with approximately 30 l of fuel vapours which was sufficient for three separate bomb tests. The bag was transported to the bomb equipment where the vapours were injected into the bomb for testing, see chapter 4.2 for more information.

4.1.2 Generation of test gas mixture

Determination of the reference pressure is part of the type testing that is conducted for flameproof enclosures which are to be certified for explosive environments. Flammable species in explosive environments are usually classified as explosion group IIA, IIB or IIC (where IIC is the most severe explosion group). Which explosion group a certain flammable species is included in depends on the ignition characteristics of the species which is determined based on the MESG according to IEC 60079-1-1:2002 [21].

An explosion safe enclosure should be constructed, tested and certified for the explosion group that is relevant for that particular environment. In an environment that is classified as IIB, for example, it is suitable to use a IIB (or IIC) classified enclosure, but not a IIA. In the case of flame arresters in process pipes etc, there is a further division of explosion group IIB (IIB1, IIB2, IIB3), according to a special standard for such equipment (EN 12874:2001) [18].

The two test gas mixtures that were used, propane/air and ethane/air, represent flammable vapours and gases from explosion group IIA and IIB respectively, when determining the highest explosive pressure (reference pressure) in an enclosure, according to IEC 60079-1:2007 [22].

The test gas mixtures that were used in the tests had the following composition (according to 15.1.2.1 in IEC 60079-1):

IIA: 4.6 ± 0.3) % propane in air IIB: (8 ± 0.5) % ethylene in air

The flow of flammable gases (propane and ethylene, N 35 = 99,95 % purity) were mixed with a flow of air so that the above compositions were obtained. The flow was regulated using valves and measured using a rotameter. The test mixture was introduced (via a flame arrester) into the explosion chamber and back in a return pipe (again, via a flame arrester) to an interferometer (SP inv.nr 501069), where the concentration was measured, see Figure 7. The test gas mixture flow to and from the explosion chamber was turned off before each ignition test. Before and after every test the surrounding air pressure, air moisture content and temperature, were registered.



Figure 7 Laboratory equipment for the mixture and analysis of test gas mixtures.

4.1.3 Explosion chamber ("bomb")

The tests were conducted in an explosion chamber similar to that described in SS-EN 1839, "Determination of explosion limits of gases and vapours" [23] and SS-EN 13673-2, "Determination of maximum explosion pressure and the maximum rate of pressure rise of gases and vapours" [24]. These standards prescribe the use of a spherical or cylindrical explosion chamber ("bomb") with a minimum volume of 0,005 m³.

A cubic bomb has been used in this project with dimensions: $0.2m \times 0.2m \times 0.2m$ and a volume of $0.008~m^3$, see Figure 8. The cubic shape can affect the results to a certain degree which means that the results are not immediately comparable to similar results from a spherical or cylindrical bomb. Even the volume of the bomb has an effect which means that direct comparisons cannot be made between various types of equipment. In EN 13673-2, Annex A [24], guidance is provided concerning verification of test bombs with volumes between 0,005 m^3 and 2 m^3 and how the test volume effects the pressure increase rate.

The tests in this project have had the primary goal of determining the temperature range for flammable mixtures of E85 (i.e., UEP and LEP), and to provide information concerning the relative explosive characteristics compared to petrol and the test gases. Against this background, the effect of the physical design of the bomb has been deemed to be of minor importance.





Figure 8 Explosion chamber ("bomb"), volume of 8 dm³, which was used for the explosion tests.

The ignition source was comprised of two electrodes placed centrically inside the bomb, connected to the ignition system. The ignition system was composed of a conventional inductive ignition system for cars, where the ignition coil was connected to the electrodes and the primary coil was connected to a battery via an electronic ignition unit with a semiconductor switch. The ignition system corresponded to that described in IEC 60079-1-1:2002 [21] which is used for the determination of MESG where it is described as "...normal automotive ignition coil for the voltage supply".

The spark energy for the car ignition system is normally approximately 30-50 mJ. The necessary ignition energy for a stoichiometric fuel mixture in a traditional, petrol powered, internal combustion engine is approximately 0,2 mJ; but, in order to reliably start a cold engine with a fuel rich mixture, dirty spark plugs, moisture, poor contact etc, the car ignition system is constructed to produce significantly higher energy.

By way of comparison it is worth noting that in the case of an electrostatic discharge from a person, the energy from a barely audible or visible spark is approximately 2 mJ. A person who has been sitting in a vehicle seat can produce a spark of approximately 30 mJ, if one assumes that the person is conductive with a capacitance of 150 pF and very low air moisture content. If one takes into account the transition resistance of a person, this energy of 30 mJ corresponds to an effective energy of approximately 10-15 mJ. Under very unfavourable conditions (i.e., major electrostatic build-up due to e.g. carpet, low air moisture etc) the energy can be up to 100 mJ, which corresponds to an effective energy of approximately 25-50 mJ due to the transition resistance of a person.

The pressure in the bomb is registered using a pressure guage connected to a signal amplifier and computer logging system. The pressure guage was a piezo-resistance type manufactured by American Sensor Technologies (SP inv.nr 502615, serial nr 01A01A09-D07), with a pressure measurement range up to 35 bar and a band width of (-3 dB) 5 kHz. The pressure guage was mounted on a short pipe which was connected to an outlet in the base of the bomb. The measurement system had a time resolution of $10~\mu s$.

As a complement to the pressure measurements, the course of the ignition was studied visually through the two glass windows in the bomb. All tests were also video recorded using a digital camera.

A vacuum pump was used to evacuate the bomb to an absolute pressure of approximately 6-8 mbar which corresponds to less that 1 % of the air mixture remains in the bomb. In order to measure the under pressure in the bomb, a pressure gauge manufactured by Special Instruments,"Digima FP", was used. In order to ensure a homogeneous mixture inside the bomb, it was also equipped with a stirrer located in the bottom of the bomb.

4.2 Test procedure

4.2.1 Conditioning and sample extraction of fuel vapours

15 liters of the fuel quality in question was introduced into the drum which thereafter was closed air tight. The drum was placed in the freezer for conditioning to the temperature in question. During the conditioning time, the temperature was checked regularly in the liquid and gas phases to ensure that equilibrium conditions had been achieved before extraction of the fuel vapours.

When the fuel vapours were extracted a tube was connected to outlet nr 2 on the drum (see Figure 6) and the valve was opened. The tube was connected to a membrane pump which was placed outside the freezer. The gas was led from the pump to a 40 l Tedlar gas sampling bag via a rotameter. The pump capacity was approximately 5 l/min which meant that it took approximately 6-7 min to fill 30-35 l of fuel vapours into the Tedlar bag. At the same time as the fuel vapours were lead out of the drum, atmospheric air was able to flow into the drum in a gas bag that was placed inside the drum to ensure that the pressure inside the drum was maintained without effecting the composition of the fuel vapours. After the Tedlar bag was filled it was closed and transported to the explosion laboratory for the subsequent bomb test.

After the extraction of fuel vapours was completed, outlet 1 was opened. The membrane pump was then connected to the gas bag placed inside the drum and emptied so that air could flow into the drum through outlet 1. When the gas bag had been emptied, outlets 1 and 2 were closed and the fuel was reconditioned for the next temperature level.

4.2.2 Bomb tests

Prior to every ignition test, the bomb was evacuated down to approximately 6-8 mbar (absolute pressure). The valve between the vacuum pump and the bomb was then closed and the leak integrity of the bomb was checked by monitoring the pressure inside the bomb for a few minutes to ensure that this did not change. The Tedlar gas sampling bag containing the fuel vapours was connected using a tube connected to the bottom of the bomb. The valve to this connection was opened slowly so that the gas was sucked into the bomb slowly. When the bomb was filled with fuel vapours and the vacuum pressure gauge measured zero (i.e. atmospheric pressure) the valve was closed again and the bag was disconnected. The valve to the vacuum pressure gauge was closed and the valve to the pressure gauge used to measure the explosion pressure was opened. The stirrer inside the bomb was run for approximately 1 minute to ensure a homogeneous mixture inside the bomb. The video camera was placed in front of one of the bomb windows and the camera started.

The pressure measurement system was started and a total measurement time for the pressure registration was defined. The ignition system and pressure measurement system were activated

as soon as the pressure exceeded a pre-defined value, normally 0,2-0,5 bar. The registered pressure was saved for the defined measurement time, normally: -100 ms to +500 ms calculated from the start of the measurement, see for example Figure 9. In some tests, the measurement time was extended to +1000 ms, +2000 ms or +3000 ms. The measurement system generated two measurement files from each test, a filtered and an unfiltered pressure signal. For the filtered signal, a low passage filter, with 3 dB at 5 kHz ± 10 %, according to section 15.1.2 in IEC 60079-1 [22], was used.

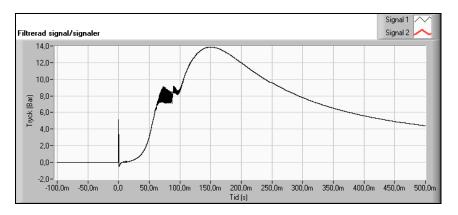


Figure 9 Filtered pressure curve as a result of a bomb test (E85S test #7).

After the test, the filling outlet to the bomb was opened and the stirrer and vacuum pump were started. The valve to the pressure gauge measuring the explosive pressure was closed and the vacuum pressure gauge was re-connected. The bomb was ventilated for several minutes to ensure that all the combustion gases had been evacuated at which point a new filling process could be started.

In the case of tests using the test gas mixture, the bomb was not evacuated but the bomb was flushed with the specific test gas in question through an inlet and an outlet as described in section 4.1.2. The outgoing gas was led to an interferometer to check the gas composition. When the exiting gas corresponded to the pre-defined composition the flushing process was stopped and all connections were closed to allow the ignition test to be started as described above.

Typically, three full ignition tests were conducted for each gas mixture.

4.2.3 Tests using temperature conditioned equipment

In the normal procedure, described in 4.1.1, the fuel mixture was extracted from a conditioned container but the fuel vapours in the gas sampling bag rapidly assumed the surrounding temperature, which was approximately 17-20°C at the time of the tests. The bomb equipment had the same temperature initially but after each ignition a small increase in temperature could be seen inside the bomb due to the heat generated by the combustion.

It is clear that the gas composition expressed in vol-% is unchanged by this methodology, but the composition expressed as, e.g., g/m^3 is reduced due to the expansion of the gas and gas bag. For an ideal gas a temperature change from -10 °C till +20 °C corresponds to a volume increase of just over 10 %.

In order to study the potential effect of the method described above, two tests (#25-26) were conducted where both the bomb and the fuel were conditioned to a low temperature and the fuel vapours were introduced to the bomb directly from the drum.

As the freezer was not positioned in the immediate vicinity of the explosion laboratory both the bomb and the drum containing the fuel were transported to the explosion laboratory immediately prior to the tests. In order to minimise the increase in temperature of the fuel and the bomb itself, these were insulated from the surroundings during transport. Unfortunately, it proved to be difficult to obtain perfect insulation and it was found that the temperature of the fuel increased rather rapidly. Further, when ignition occurred in the bomb energy was generated which added to the successive heating of the bomb after each test. The tests results showed, despite these difficulties, a general agreement between these test data and the other test data obtained with the bomb at room temperature.

4.2.4 Evaluation of pressure measurements

Zero time on the x-axis (see Figure 9) corresponds to the point in time that the measurement system is activated. The measurement system was programmed to active at approximately 0,2-0,5 bar. Typically this activation occurred at the same time as the ignition spark, but in those cases where this was not the case, zero time has been adjusted to correspond to the moment of ignition.

Based on the pressure curve obtained from the tests, the maximum pressure at the first peak, P_{fp} , and the time from ignition until the first peak, t_{fp} , was determined (see Figure 10). Based on this information, the average rate of pressure increase (v_{fp}) was calculated by dividing the pressure, P_{fp} , by the time, t_{fp} .

In several of the tests subsequent peaks were seen, see Figure 10, with a higher pressure than the first peak. The reason for these pressure peaks has not been fully investigated but is probably due to the placement of the pressure gauge and the shape of the explosion chamber where the internal geometry is significant for the spread and pressure build-up in the chamber. The subsequent peaks have not been deemed to be of primary interest and they have not been used in the evaluation of the results from the tests.

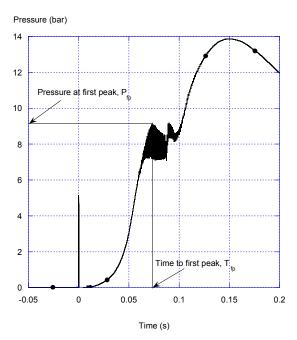


Figure 10 Detailed analysed of measurement data for the determination of over pressure at the first pressure peak (P_{fp}) and the time until this maximum pressure (t_{fp}) (E85S test #7).

In total 26 test series were conducted, normally with three separate ignition tests in each test series. These tests included the following fuel types: E85S, E85W, LF95 and the test gases comprised of a propane and ethylene in air.

4.3 Results from bomb tests

As E85S has been assumed to present the highest risk of ignition of fuel vapours, the tests have focused primarily on this fuel. In order to compare the results to known conditions a small number of tests were also conducted using petrol, i.e., LF95S. Further, a small number of tests have been conducted with E85W and some test gases comprised of propane and ethylene in air. The results are provided in sections 4.3.1 to 4.3.4.

4.3.1 E85 Sommer vs winter quality

As shown in Table 8, a total of 11 test series have been conducted with E85 of summer quality (E85S) while three test series have been conducted with E85 of winter quality (E85 V). Further, two test series (#25-26) have been conducted with pre-conditioned instruments.

As shown in Table 8, the tests with E85S cover a temperature range from approximately -25 °C to +20 °C. Within this temperature interval ignition was obtained from +1,5 °C down to - 16,0 °C. Figure 11 shows the recorded pressure increase in these tests. It is difficult to provide the exact temperature range for flammable mixtures, in part due to the fact that there is some variability in the test results, partly due to the fact that the temperature interval used in the tests is finite, especially close to the upper temperature boundary. The tests conducted at both +1,5 °C and +0,2 °C show a very slow combustion reaction which implies that this is close to the upper explosion point (UEP). The lower explosion point (LEP) tends to be more distinct, ignition was obtained without a problem at -16,0 °C while it was not possible to ignite the fuel vapours at -18,4 °C.

Table 8 Collation of the test data for E85S and E85W. If not otherwise specified, the pressure and pressure increase times are averaged based on single ignition tests.

Test	Date	Fuel	$T_{\mathbf{f}}$	Tg	P_{fp}	$t_{ m fp}$	V_{fp}	n_{ex}/n_{tot}	Note
nr			(°C)	(°C)	(bar)	(ms)	(bar/s)		
3	070117	E85S	+21,1	+21,2	-	ı	1	0/3	
4	070118	E85S	+10,9	+10,8	-	-	-	0/3	
5	070119	E85S	+1,5	+1,5	1,45	800	1,8	2/3	
20	070221	E85S	+0,2	-0,5	2,9	1230	2,4	3/4	1, 2)
22	070223	E85S	-5,0	-5,5	6,8	73	93	3/3	1)
7	070122	E85S	-8,3	-8,4	9,1	74	123	2/4	3)
17	070131	E85S	-12,0	-12,2	7,7	86	89	2/3	
9	070123	E85S	-16,0	-16,4	7,4	126	59	3/3	
15	070129	E85S	-18,4	-17,9	-	ı	1	0/3	
13	070125	E85S	-21,9	-22,7	-	-	1	0/3	
11	070124	E85S	-24,8	-26,0	-	ı	1	0/3	
21	070221	E85W	+0,5	+0,4	-	ı	1	0/3	
23	070223	E85W	-3,8	-2,3	-	1	1	0/3	
24	070612	E85W	-9,1	-11,0	0,45	805	0,6	2/3	4)
								_	
25	070613	E85S	-3,9	-	4,8	732	6,6	2/2	5)
26	070613	E85W	-0,3	-	-	-	-	0/2	6)

$T_f = Temperature fuel (°C)$	t_{fp} = Time to first pressure peak (ms)
T _g = Temperature gas (°C)	v _{fp} =Average pressure increase rate until the first
P_{fp} = Pressure at first peak (bar)	peak (bar/s)
(over pressure)	$n_{ex}/n_{tot} = Number$ of detected ignitions relative to the
	number of ignition tests

- 1) Retest with "fresh" fuel to study the possible effect of "ageing".
- 2) The gas was ignited after the second spark in the first bomb test (thus no pressure increase was registered). In the second bomb test, a "slow" explosion with increasing pressure for the whole measurement period (500 ms). The third bomb test was conducted at approximately 80 mbar under pressure in the bomb due to the fact that there was insufficient fuel vapour remaining in the Tedlar bag. Despite this, a "slow" explosion was seen in this case as well. The specified values are for the third bomb test.
- 3) A supplementary bomb test was conducted due to problems with the pressure recordings. The specified values correspond to the supplementary test (fourth bomb test) where the pressure development was recorded.
- 4) In the first bomb test the gas was ignited on the second spark and in the third bomb test the gas was ignited after 5-6 sparks (due to this a very low pressure was measured and there was no pressure recordings in this test). In the second bomb test no ignition was obtained.
- 5) Fuel vapour introduced direct from the conditioned drum into the cooled bomb. The fuel temperature in the drum was -4.0° C in bomb test 1 and -3.7° C in bomb test 2. The gas temperature in the conditioned drum was not measured. The bomb's outer surface temperature was 0° C in the first bomb test and $+3.0^{\circ}$ C in the second test.
- 6) Fuel vapour introduced direct from the conditioned drum into the cooled bomb. The bombs outer surface temperature was +5,6°C. No ignition was obtained.

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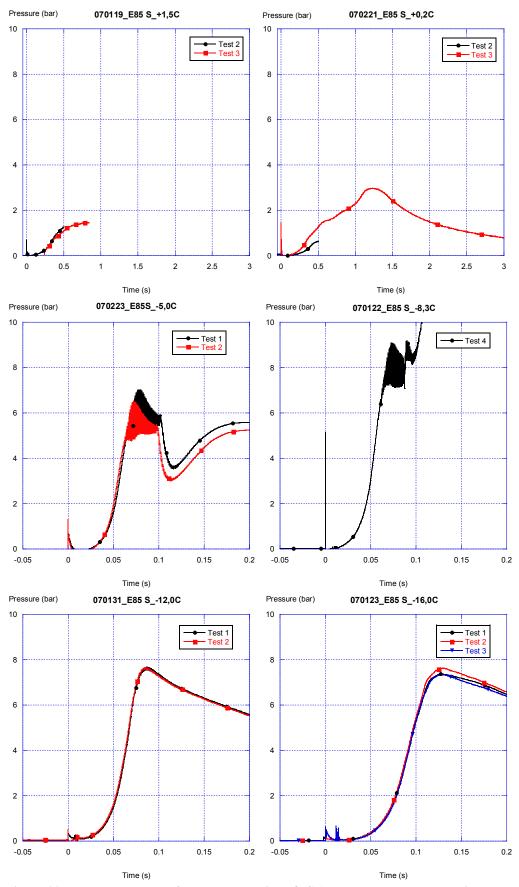


Figure 11 Pressure curves from the tests with E85S (note the scale on the x-axis on the top two diagrams)

The pressure curve from the test conducted with extraction of fuel vapours direct from the conditioned drum into the cold bomb is shown in Figure 12. The aim of this test, as described in section 4.2.3, was to confirm that the sample extraction methodology where the fuel vapours were extracted into a Tedlar gas sampling bag did not significantly affect the results. The pressure increase that was seen was relatively slow which agrees with the trend from the other tests conducted in this specific temperature range (see also Figure 17).

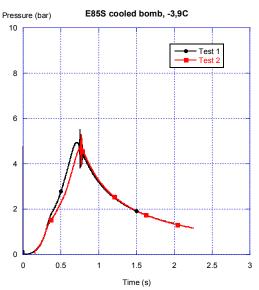


Figure 12 Pressure curves from the test with E85S where the sampling of fuel vapours was made directly from the conditioned drum (fuel temperature -3,9 °C) into the cooled bomb.

The results from the only test series where ignition was obtained with E85W is shown in Figure 13. Two ignition tests were conducted but as one of the tests required several sparks to cause ignition, only one pressure measurement was obtained. Visually the experiments were identical. Due to the slow combustion and the low pressure, the tests indicate that the fuel temperature, -9,1 °C, is very close to the upper explosion point (UEP).

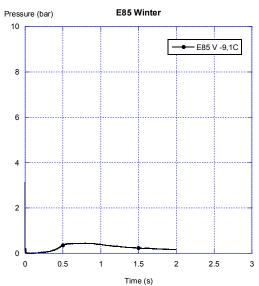


Figure 13 Pressure curve for the tests with E85W at -9,1 °C. The tests conducted at +0,5 °C and -3,8 °C gave no ignition.

4.3.2 Lead-free petrol, summer quality

As shown in Table 9, a total of six test series have been conducted with petrol, LF95S.

The tests conducted with LF95S were conducted over the temperature range from approximately +2°C to -25°C and within this range ignition was obtained for temperatures below approximately -22°C. As shown in Figure 14, the tests at -22,2°C and -23,8°C exhibit a very slow combustion development which implies that this is very close to the upper explosion point (UEP). No tests have been conducted for petrol to determine the size of the combustion range and the lower explosion point. The tests do therefore not give an indication of the maximum explosive pressure or the maximum rate of pressure increase for petrol.

Table 9 Collation of the tests with LF95S. If not otherwise stated, the pressure and pressure increase rate are averaged for a single ignition test.

Test	Date	Fuel	$T_{\mathbf{f}}$	T_{g}	P _{fp}	\mathbf{t}_{fp}	\mathbf{v}_{fp}	n _{ex} /n _{tot}	Note
nr			(°C)	(°C)	(bar)	(ms)	(bar/s)		
6	070119	Petrol vapour	+2,4	+2,1				0/3	
8	070122	Petrol vapour	-7,5	-8,0				0/3	
10	070123	Petrol vapour	-15,0	-15,5				0/3	
16	070129	Petrol vapour	-18,1	-19,2				0/3	
14	070125	Petrol vapour	-22,2	-23,5	3,5	1085	3,4	3/3	
12	070124	Petrol vapour	-23,8	-25,2	3,4	1090	3,1	4/4	1)

$T_f = Temperature fuel (°C)$	t _{fp} = Time to first pressure peak (ms)
$T_g = Temperature gas (^{\circ}C)$	v _{fp} =Average pressure increase rate until the first
P_{fp} = Pressure at first peak (bar)	peak (bar/s)
(over pressure)	n_{ex}/n_{tot} = Number of detected ignitions relative to the
	number of ignition tests

¹⁾ The cited pressure and pressure increase times are an average of ignition tests 1-3. Ignition test 4 (retest with a new sample of fuel vapours) gave a maximum pressure of 4,4 bar at 770 ms.

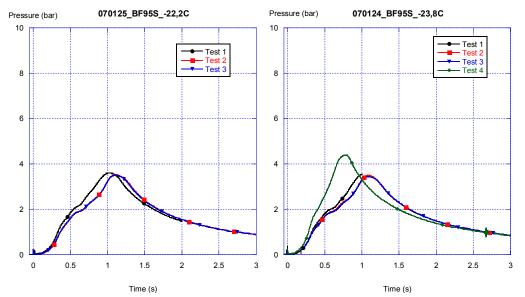


Figure 14 Pressure curves from the tests with LF95S (BF95S in diagramme). Test 4 at -23,8 °C is a re-test with a new test sample which gave a somewhat faster reaction at higher pressure.

4.3.3 Test gases propane and ethylene

As shown in Table 10 a total of four test series have been conducted with test gases, two series with $(4,6\pm0,3)$ % propane in air and two series with $(8\pm0,5)$ % ethylene in air. One series with each type of test gas was conducted at the start of the project, partly to test the explosion chamber and accompanying instrumentation, and one test series when most of the test program was completed (see Figure 15).

If the results from the different tests are compared one can determine that the repeatability between the three bomb tests in each test series is very good concerning the time to the first pressure peak, $t_{\rm fp}$, while there is a tendency for the first pressure peak to increase, $P_{\rm fp}$, somewhat between each test. This may be due to the successive heating of the bomb due to three combustion tests run in sequence. The pressure is somewhat different between both test series, while the time until the first pressure peak is almost identical for both test series.

As shown in the results, the gas mixture containing ethylene exhibits a significantly faster combustion and a somewhat higher explosive pressure. The time $(t_{\rm fp})$ until the first pressure peak was on average approximately 35 ms for ethylene while it was approximately 70 ms for propane. This clearly shows the difference between these two test gases and corresponds to the classification in explosion group IIA and IIB.

Table 10 Collation of the results from the bomb test with test gases where the results are presented as the average of three separate tests. The presentation of pressure and pressure increase rate are averaged from single ignition tests.

Test	Date	Fuel	P _{fp}	$t_{\rm fp}$	$v_{ m fp}$	n_{ex}/n_{tot}
nr			(bar)	(ms)	(bar/s)	
1	061221	IIA propane	8,4	73	115	3/3
18	070215	IIA propane	7,8	68	115	3/3
2	061221	IIB ethylene	9,2	36	256	3/3
19	070215	IIB ethylene	8,0	35	229	3/3

$T_f = Temp$	erature fuel (°C)	t _{fp} = Time to first pressure peak (ms)
$T_g = Temp$	erature gas (°C)	v _{fp} =Average pressure increase rate
$P_{fp} = Press$	ure at first peak (bar)	until the first peak (bar/s)
(over	pressure)	n_{ex}/n_{tot} = Number of detected ignitions
		relative to the number of
		ignition tests

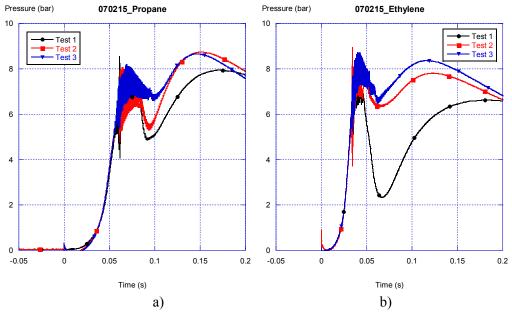


Figure 15 Pressure curves from bomb tests with a) propane and b) ethene (test #18-19).

4.3.4 Comparison between experimental data from different fuels

The results of the tests with E85S are compiled in Figure 16, using a "representative" pressure curve from each temperature level. These clearly show the impact of the gas composition depending on the temperature. The results from the tests at the two highest temperatures where ignition was obtained, ± 1.5 °C and ± 0.2 °C, are not shown as the pressure and the rate of pressure increase were so low that the pressure curve almost coincides with the x-axis during the given time period (see Figure 11). This shows that the combustion at the upper explosion point (UEP) is very slow. A maximum is reached at approximately ± 0.0 °C for both the pressure at the first peak (± 0.0) and the time until the first peak, (± 0.0). At the lower explosion point (LEP) the combustion rate decreases but the boundary to the inflammable mixture is much sharper than at the higher temperature boundary.

The pressure curves from the two tests with LF95S are shown in the same way in Figure 16. These tests represent the upper explosion point (UEP). As shown for E85S, the combustion is very slow under these conditions. As these tests were not conducted at lower temperatures there is no information available concerning the lower explosion point (LEP) of this petrol or at which temperature this petrol mixture shows its maximum combustion rate.

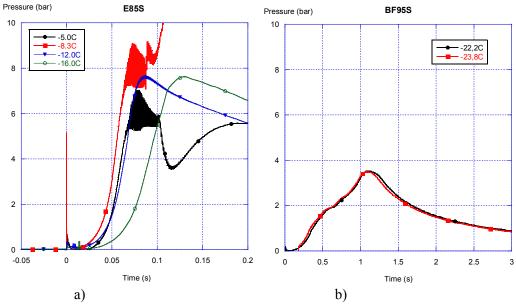


Figure 16 Pressure curves from four of the E85S tests and the two tests with LF95S. (Note the different scales on the x-axes).

A summary of all tests is given in Figure 17 where the pressure at the first peak (P_{fp}) is given as a function of the fuel temperature. The time until the first pressure peak (t_{fp}) is also given in this figure for each temperature level. The figure clearly shows that the temperature range for a flammable mixture for the different fuels. Concerning the temperature boundaries for the flammable range, the number of tests was too limited to be able to define this fully. In order to do this it would be necessary to conduct further tests with a smaller temperature interval.

In general however, the results show a flammable range from approximately -18 °C (LEP) up to approximately +2 °C to +5 °C (UEP) for E85S. The upper explosion point (UEP) for E85W was determined to be approximately -8 °C to -9 °C while that for LF95S was determined to be just under -20 °C. The tests do not, however, give any information concerning the lower explosion limit (LEP) for E85W or LF95S.

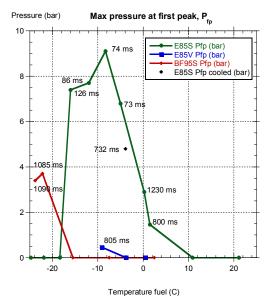


Figure 17 Summary of the results from all ignition tests with E85 and petrol, LF95S, where the pressure (P_{fp}) and the pressure increase time (t_{fp}) are presented.

One important aspect of the tests has been to "classify" the combustion characteristics of E85 as this provides the basis for which protection model should be applied to each application, e.g. requirement and type of flame arresters.

The pressure curve for the test conducted at -8,3 °C with E85S is shown in Figure 18 together with representative pressure curves from the latter test series (070215) conducted with ethylene and propane. As shown in the figure, the results from the gas mixture with $(4,6\pm0,3)$ % propane coincided relatively well with those from the test conducted using fuel vapours with E85S, while the results from the tests with ethylene show a significantly faster pressure development. The measured pressures are essentially comparable. If one compares the maximum pressure rate of rise from Table 8 - Table 10, these correspond to 123 bar/s for E85S, 115 bar/s for propane and approximately 230-255 bar/s for ethylene.

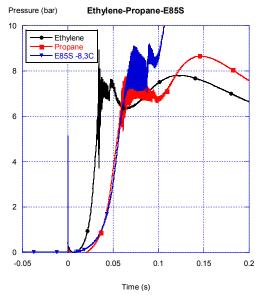


Figure 18 Pressure curves from testing of E85S at -8,3°C compared to the pressure curves obtained from thetest gas mixtures, propane and ethylene respectively.

Work Package 3: Consequences of ignition of a flammable gas mixture in a fuel tank

The aim of Work Package 3 was to determine the consequences of a possible ignition of fuel vapours in a fuel tank designed for cars. "Worst-case" conditions were assumed, i.e., no consideration has been taken to the probability of the occurance of these scenarios.

In order to achieve these "worst case" conditions in the tests, the empty tanks were filled with a test gas mixture of propane and air $((4,6\pm0,3))$ % propane in air) which represents the pressure increase conditions in an optimal mixture of E85-vapour and air according to the tests in Work Package 2, chapter 4.3.4. In other words, the tanks did not contain E85-fuel or some other fluid. The gas mixture was ignited and the course of ignition was recorded using pressure measurements and video film.

The ignition experiments were conducted in SP's explosions laboratory.

5.1 Test objects and experimental set-up

The ignition tests were conducted using fuel tanks for cars from four different car manufacturers, according to Table 11. Three of the tanks were made from plastic and the fourth was made from steel. Two of the tanks were new and two were used.

Table 11 Details of the fuel tanks that were used in the ignition tests in WP3.

I able II	Details of the fact tanks that were used in the ignition tests in 1110.						
	Material	Volume*) (l)	Material refuelling pipe	Age of the Tank	Allowed fuel use		
Tank A	Steel	55	Plastic	Used, for year -97	Petrol		
Tank B	Plastic	60	Steel	Used, for year -04	Petrol		
Tank C	Plastic	55	Steel	New, for year -07	Petrol or E85		
Tank D	Plastic	68	Steel	New for year -07	Petrol or E85, (ORVR)		

^{*)} Nominal volume according to the manufacturer

In the tests, all tanks were equipped with original tank fittings, with connections for the fuel pipe, sensor cable, etc. The used tanks were in good condition without visual damage. The steel tank did not have any rust, with the exception of some superficial rust around the seams in the tank.

No consideration has been taken in the tests to the function of the internal or external system for vapour recovery, which for example has significance for the presence of E85-vapour at the opening of the refuelling pipe. In the case of tank D with an Onboard Refuelling Vapour Recovery system (ORVR), the parts for the vapour recovery system were installed on the tank according to specifications during the tests.

Further, no consideration has been taken of whether the tanks were constructed to avoid the risk for electrostatic charge or discharge, which probably has significance for the ignition of vapours from an electrostatic spark.

5.2 Experimental procedure

5.2.1 Filling with the gaseous mixture

In order to mimic the flammability characteristics of an optimally explosive mixture of fuel vapour from E85, a test gas mixture of propane and air was used. The fuel tank and the refuelling pipe were flushed with the test gas mixture until a homogeneous mixture with the correct concentration was established in the same manner as in the bomb tests (see chapter 4.2.2). To establish an efficient distribution of the test gas mixture to the different parts of the tank, a system of tubes was used inside the tank to distribute the gas.

When flushing was completed, the inlet and outlet for the test gas mixture were closed. The tests with ignition inside the tank were conducted with the tank lid closed. In the tests with ignition at the refuelling pipe, the tank lid was open, see Table 12.

5.2.2 Ignition of the gaseous mixture

A spark plug connected to a conventional inductive electronic ignition system for cars was used as the ignition source. The same ignition system was used in the bomb tests conducted in WP2 (see chapter 4.1.3).

In the ignition tests in the refuelling pipe, the spark plug was mounted immediately outside the pipe opening. The spark gap was positioned approximately 10 mm from the pipe's exterior and 20 mm above the opening. In order to maintain the concentration of the fuel vapours in the tank, the refuelling pipe was covered with a plastic bag, see Figure 19.

In the tests with ignition inside the tank, the spark plug was placed approximately in the middle of the tanks upper side, close to the tank fittings, see Figure 20.

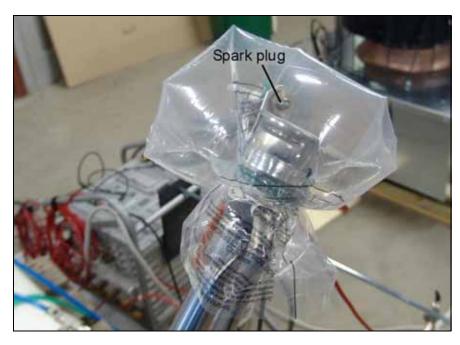


Figure 19 Test set up in the tests where ignition was conducted at the refuelling pipe. The spark plug was mounted immediately outside the pipe opening which was covered by a plastic bag to retain the concentration of the fuel vapours.

5.2.3 Pressure measurement and documentation

The pressure upon ignition was recorded using two piezo-resistant pressure gauges, one placed inside the tank and one in the refuelling pipe, see Figure 20. The gauges were mounted in a hole in the tank or the refuelling pipe's wall.

The gauge in the refuelling pipe was placed approximately in the middle of the pipe. A low pass filter with 3 dB at 5 kHz ± 10 %, according to Chapter 15.1.2 in IEC 60079-1 [22], was used to filter the pressure signal.

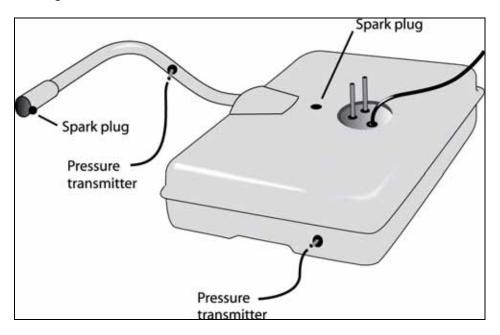


Figure 20 Sketch of the tank used in the ignition tests. In the tests where the ignition occurred inside the tank, the spark plug was placed close to the tank fittings on the top of the tank.

In order to document the course of ignition, the tanks were filmed using a video camera in each test. In some cases two or three video cameras were used to give different film angles. This documentation was conducted using standard, digital video cameras with a picture speed of 25 pictures/second.

5.2.4 Experimental program

In total eight tests were conducted according to the conditions summarised in Table 12. In the tests the tanks were places on a soft base comprised of two 8 cm thick polyethylene mattresses, except in the case of test 8 with tank D, when the tank was mounted in a chassis for the car model in question.

Table 12 Summary of test conditions in the ignition tests.

Tank Test nr		Ignition site	Tank mounted	Comments
Steel tank A	1	Refuelling pipe	On soft base	Without tank lid
Plastic tank B 2 Refue		Refuelling pipe	On soft base	Without tank lid
Plastic tank C 3 Inside tank		Inside tank	On soft base	With tank lid
	4	Refuelling pipe	On soft base	Without tank lid
Plastic tank D	5	Inside tank	On soft base	With tank lid
	6	Refuelling pipe	On soft base	Without tank lid
	7	Refuelling pipe, with fuel nozzle	On soft base	Repeat of test 6 with fuel nozzle in refuelling pipe
	8 Inside tank		Mounted on chassis	With tank lid

5.3 Results of ignition tests in fuel tanks

A summary of the results is provided below while the detailed results for each tank is provided in chapter 5.3.1 - 5.3.4.

Ignition of the test gas mixture in the fuel tanks gave rise to a pressure in the tanks of the order of 2-8 bar, according to Table 13 below. Ignition at the refuelling pipe (tank C) gave a higher pressure in the tank (7,5 bar) compared to ignition inside the tank (4,9 bar). Relatively high pressures were recorded in the refuelling pipe, of the order of 5-37 bar, however without any visible damage or deformation of the pipe.

All plastic tanks cracked due to the pressure in those cases where the test gas mixture was ignited. In such cases, a flame could be seen through the openings that were formed. The cracks were 40-90 cm long. The steel tank did not crack but its fitting were thrown away and a short duration flame came through the fitting opening. The fitting was mounted in a hole in the upper side of the tank which also contained the pressure level sensor and the fuel pipes.

In the test with the tank mounted in a real car chassis for the particular car model in question, one could observe that the ignition in the tank deformed the underbody above the tank by approximately 10-15 cm. The mounting fittings for the tank in the underbody were also deformed.

In the case of plastic tank D, the check valve between the refuelling pipe and the tank, stopped the spread of a flame from the tank to the refuelling pipe and vice versa.

Table 13	Summary	of test	results from	the ignition	tests performed	in fuel tanks
I able 13	Summary	oi iest	I coulto II om	the ignition	tests belief med	mi luci tanks.

Tank	Test nr	Ignition position	Pressure in	Pressure in
			tank	refuelling pipe
			(bar)	(bar)
Steel tank A	1	Refuelling pipe	2,3	34,5
Plastic tank B	2	Refuelling pipe	4,7	4,8
Plastic tank C	3	Inside tank	4,9	20,3
	4	Refuelling pipe	7,5	36,3
Plastic tank D	5	Inside tank	2,2	<0,1
	6	Refuelling pipe	< 0,1	7,1
	7	Refuelling pipe with	< 0,1	7,1
		fuel nozzle		
	8	Inside tank	2,3	<0,1

5.3.1 Observations from Test 1 – Metal tank A

The fuel vapours were ignited at the refuelling pipe. The maximum pressure recorded in the refuelling pipe was 34,5 bar while 2,3 bar were recorded inside the fuel tank, see Figure 21. When ignition occurred, the tank expanded and obtained a rounder shape. The tank fitting was thrown away, accompanied by a bang and a short-duration flame (<1 s) from the fitting opening. The approximate flame length was 2-5 m, a large part of the flame was, however, outside of the camera angle. After ignition, the tank retained its deformation (rounder shape) and the tank fitting was missing. No visible cracks could be seen in the tank or the refuelling pipe.

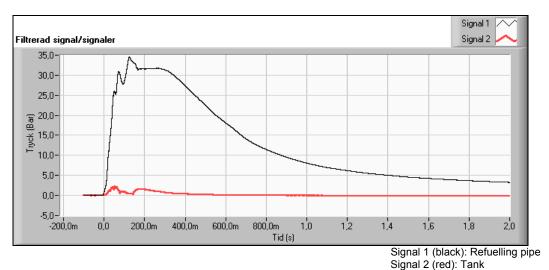


Figure 21 Recorded pressure in steel tank A, in the refuelling pipe and in the tank. Ignition in the refuelling pipe.

5.3.2 Observations from 2 – Plastic tank B

The fuel vapours were ignited at the refuelling pipe. The maximum pressure recorded in the refuelling pipe was 4,8 bar while 4,7 bar were recorded inside the fuel tank, see Figure 22. When ignition occurred, the tank expanded and cracked along the seam on one side of the tank. A short-duration flame (<1 s) was emitted from the crack. The approximate flame length was 2-3 m, a large part of the flame was, however, outside of the camera angle. The crack was approximately 90 cm long. The tank fitting became loose (and fell into the tank) and plastic parts were thrown way from the tank. A short-duration flame (<1 s, length <1 m) was also

emitted from the hole left by the tank fitting. No visible damage could be seen on the refuelling pipe. In an indentation in both the upper and lower sides of the tank, parts of the plastic had come loose and left a hole, approximately 5x4 cm and 3x6 cm in size respectively.

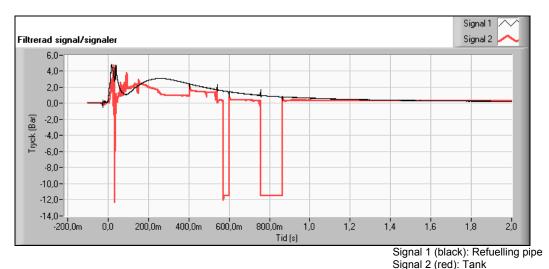


Figure 22 Recorded pressure in plastic tank B, in the refuelling pipe and in the tank. Ignition in the refuelling pipe. (Major disturbances on the tank pressure measurements.)

5.3.3 Observations from tests 3 and 4 – Plastic tank C

The fuel vapours were ignited inside the tank in test 3. The maximum recorded pressure inside the tank was 4,9 bar while that in the refuelling pipe was 20,3 bar, see Figure 23. When ignition occurred, the tank expanded and cracked on the upper side, with a bang and a short-duration flame (<1 s) emitted from the crack. The approximate flame length was 2-4 m. The crack was 43 cm long. No visible damage was seen on the refuelling pipe. The outer (black) part of the tank lid came loose

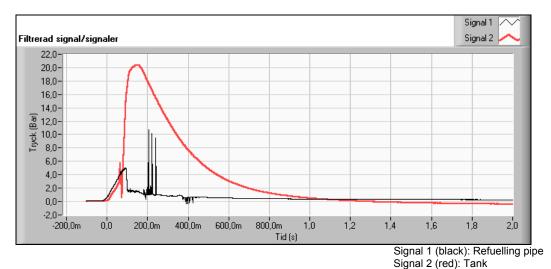


Figure 23 Recorded pressure in plastic tank C – test 3, in the refuelling pipe and in the tank. Ignition inside the fuel tank.

The fuel vapours were ignited in the refuelling pipe in test 4. The maximum recorded pressure in the refuelling pipe was 36,3 bar while that inside the fuel tank was 7,5 bar, see Figure 24. When ignition occurred, the tank expanded and cracked on the upper side, with a bang and a short-duration flame (<1 s) emitted from the crack. The approximate flame length was 2-4 m. The crack was 44 cm long. No visible damage was noted at the refuelling pipe.

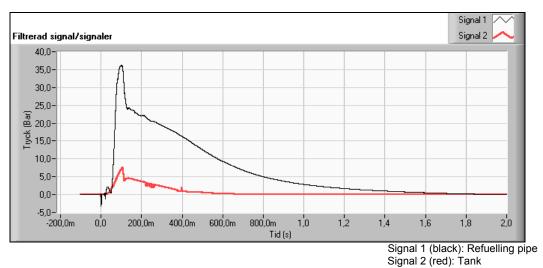


Figure 24 Recorded pressure in plastic tank C – test 4, in the refuelling pipe and in the tank. Ignition in the refuelling pipe.

Note: In tank C close to the inlet of the tank, in the lower part of the refuelling pipe, there is a fitting in plastic that works as a check valve, which prevents fuel from flowing in the wrong direction. The fuel that flows down the refuelling pipe presses the plastic membrane down so that it opens while fuel from the other direction holds the membrane against a frame so that the fuel cannot flow in that direction.

5.3.4 Observations from tests 5 to 8 – Plastic tank D

The fuel vapours were ignited inside the fuel tank in test 5. The maximum pressure recorded inside the tank was 2,2 bar while no increase in pressure was noted in the refuelling pipe, see Figure 25. When ignition occurred the tank expanded and cracked, partly in a seam close to the connection between the refuelling pipe and the tank, with a bang and a short-duration flame (<1 s) emitted from the crack. The approximately flame length was 1 m. The crack was 35 cm long. No ignition was noted in the refuelling pipe (<0,1 bar).



Figure 25 Recorded pressure in plastic tank D – test 5, in the refuelling pipe and in the tank. Ignition inside the fuel tank.

The fuel vapour was ignited in the refuelling pipe in test 6. The maximum recorded pressure in the refuelling pipe was 7,1 bar while no pressure increase (<0,1 bar) was noted in the fuel tank,

see Figure 26. When ignition occurred, a bang and short-duration flame (<1 s, length <0,5 m) were emitted from the refuelling pipe. The pressure recording indicated that no ignition was obtained inside the tank and therefore no damage was noted to the tank.

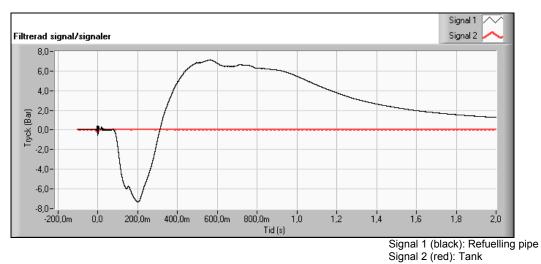


Figure 26 Recorded pressure in plastic tank D – test 6, in the refuelling pipe and in the tank. Ignition in the refuelling pipe.

The fuel vapour was ignited in the refuelling pipe in test 7, which in this case had a fuel nozzle in the opening. The aim was to determine if the fuel nozzle made any difference relative to the results seen in test 6. The maximum pressure recorded in refuelling pipe was 7,1 bar while no pressure increase was recorded (<0,1 bar) inside the fuel tank, see Figure 27. When ignition occurred, a bang and a short-duration flame (<1 s, <0,5 m) were emitted from the opening of the refuelling pipe. No visible damage could be discerned on the refuelling pipe. The pressure recording indicated that no ignition was found inside the tank and therefore no damage could be seen to the tank.

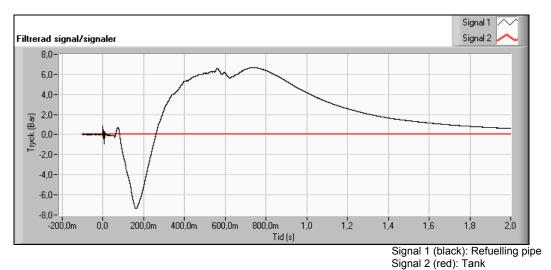


Figure 27 Recorded pressure in the plastic tank D – test 7, in the refuelling pipe and in the tank. Ignition in the refuelling pipe with a fuel nozzle in its opening.

The fuel tank was mounted below the underbody to the specific car model in test 8, to mimic a real installation. The fuel vapour was ignited inside the fuel tank to obtain "worst-case" conditions.

The maximum pressure recorded inside the tank was 2,3 bar while no pressure increase (<0,1 bar) was seen in the refuelling pipe, see Figure 28. When ignition occurred, the tank expanded and cracked, in part along a seam close to the connection to the refuelling pipe, emitting a bang and a short-duration flame (<1 s). The approximate length of the flame was 1 m. The crack was approximately 45 cm long. The opening for the tank lid was damaged and the lid fell off. The underbody was deformed by approximated 10-15 cm above the tank. The mounting fittings for the tank on the underbody were also deformed.

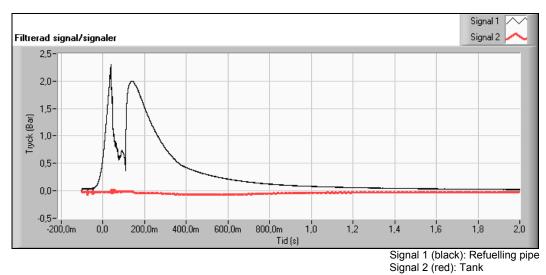


Figure 28 Recorded pressure in plastic tank D – test 8, in the refuelling pipe and in the tank. In this test the tank is mounted as per usual under the chassis of the specific car model. Ignition inside the fuel tank.

Note: In the inlet to tank D, where the refuelling pipe is connected to the actual tank, there is a fitting in plastic that works as a check valve, which prevents fuel from flowing in the wrong direction. A spring presses a movable plastic lid against the opening. The fuel that flows down the refuelling pipe presses the lid down so that it opens while fuel from the other direction is unable to pass. This check valve, in combination with the rest of the construction, is probably the reason why spread of the flame from the refuelling pipe to the tank (and vice versa) is prevented.

Work Package 4: Fire development in a pool fire under a fuel tank containing E85

The aim of WP 4 was to investigate whether there is any difference between fire development in case of a spill fire beneath a fuel tank filled with E85 compared to that with petrol. At SP Fire Technology, standard fuel tank tests are conducted according to UN regulations, ECE regulation nr 34, Annex 5, paragraph 5 [25], EEC directive 70/221 [26] [27] and TRIAS [28]. These tests are part of the technical evaluation required for Type Approval of a vehicle. Fire tests according to these regulations are in principal identical, i.e. the fuel tank is filled to 50% of its capacity with fuel, exposed to a specific fire for 2 minutes, after which the fire exposure is terminated. The remaining fire in or around the tank is extinguished, after which the tank is inspected for leakage. The ECE Regulation requires that no leakage is to be found after the fire exposure, it is however allowed to have a hole in the tank above the fuel surface. These tests are specifically for plastic tanks and no similar test requirement is present for steel tanks.

In those cases where plastic tanks are unable to meet the requirements in the regulations, it is often due to the fact that the material is too thin in particularly exposed parts, e.g. on a corner. In some cases, a hole may be formed above the fuel surface where the tank wall does not have any cooling from the fuel and in certain cases this can result in leakage before the stipulated time period without leakage has been passed. If the support arrangement of the tank is not properly designed relative to the geometry of the tank, the fire exposure can even lead to a total collapse of the tank during the test. When leakage occurs during these tests, the tests are terminated as quickly as possible and the damage is inspected and the reason for the damage analysed.

Based on our experience from these tests, there has never been a recording of an "inner explosion" in a tank that has been tested which could, e.g. due to a melted hole in the tank. This indicates that fuel vapours inside a tank filled with petrol is too fuel rich under normal conditions, i.e., the fuel-air ratio lies above the upper explosion limit (UEP).

The results from WP2 show that E85 fuel produces flammable vapour in a closed tank at higher temperatures than petrol. In conjunction with an external fire at low surrounding temperature, this could mean that vapours inside the tank could ignite, e.g. if a hole were to be formed in the plastic. The tests in WP3 investigated that the consequences of the ignition of fuel vapours in an empty tank while those tests in WP4 focus on the consequences of an external ignition source close to a tank containing fuel. One of the most important issues is whether the presence of fuel in the tank can dramatically aggravate the consequences of ignition inside the tank compared to those observed in WP3, for example due to the presence of splashing fuel.

6.1 Test objects and experimental set-up

Three of the types of fuel tanks used in WP3, tank A, C and D, were also used in these tests. In order to produce a simple experimental set up and comparable conditions, the tanks were mounted freely in an open test rig. Original tank straps were used for each tank so that the installation would mimic real conditions as far as possible, see Figure 29.

A pool fire was used as the ignition source (tray size 0,5 x 0,5,m, height 0,15 m). The tray was placed on the floor immediately under the tank. The tray was filled with 7,5 l (30 mm) water and 17,5 l (70 mm) heptane. The distance between the fuel surface in the pool and the under side of the tank was approximately 230 mm which corresponds to the approximate free distance under the tank mounted in a car. It should be noted that the test conditions are somewhat different to those defined in ECE regulation nr 34, Annex 5, paragraph 5 [25] where the tank is usually tested in a chassis that is as complete as possible (as this has been seen to effect the results). Further, the size of the pool fire is smaller than specified in the ECE regulation.

In order to achieve "worst case" conditions the tanks were filled with only 15 litres E85S in the tests which corresponds to a degree of filling of approximately 22-27%. This amount of fuel was deemed sufficient to create the necessary conditions for splashing fuel while simultaneously promoting a relatively large gas volume inside the tank which could exacerbate the effect of an ignition.

Based on the results from WP2, the tanks and fuel were pre-conditioned to approximately - 20 °C to increase the probability that the tanks would contain flammable fuel vapours when the tank was exposed to a fire for a minute or two. To further ensure worst case conditions, the tank was mainly exposed to the fire on the side of the tank that was free from ancillary connections. This mode of exposure was chosen to obtain a quick heating of the tank wall and to potentially melt a hole in the plastic tank, while at the same time minimising heating of the fuel inside the tank.

The temperature inside the tank was measured with two thermocouples to control the conditions inside the tank. One was located in the fuel, approximately 10 mm above the bottom of the tank while the other was placed above the fuel surface in the fuel vapour. The thermocouples were shielded, type K thermocouples with a diameter of 1 mm.

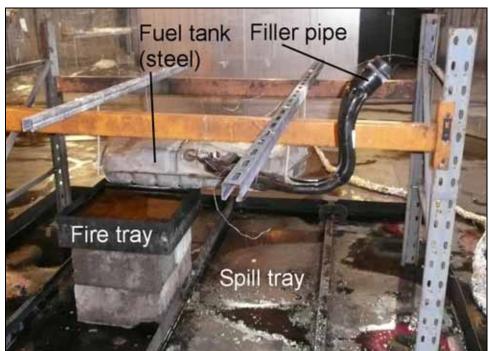


Figure 29 The test set up for the fire exposure tests in WP4. One side of the tank was exposed to the majority of the fire to maximise heating of the tank walls while heating of the fuel was minimised.

6.2 Experimental procedure

The tanks and the fuel were pre-conditioned separately in a freezing chamber for approximately 24 hours prior to the tests. Before pre-conditioning, the tanks were prepared for the tests as far as possible, including mounting the refuelling pipe, the tank straps, thermocouples, etc, to minimise the time needed to mount them into the rig just before the experiments.

When all preparations had been completed for each test, the tanks was taken out of the freezer and mounted in the rig. The thermocouples were connected and 15 l E85S were filled in the

tank. At the same time the fuel was added to the fire tray. Temperature measurement was started as soon as the thermocouples had been connected to obtain as much information as possible of the heating of the tank and fuel prior to the fire exposure.

When the filling was completed the heptane pool fire was ignited and time of ignition recorded. The tank was exposed to the fire and the course of the tests was documented visually as well as by a video camera.

The exposure to the pool fire was not stopped at 2 min (as prescribed in the ECE regulations) but continued significantly longer. The aim was that the fire exposure would give rise to a hole in the wall of the tank or at some connection on the tank, so that the flames could ignite the fuel vapours inside the tank. When this criterion had been reached the test was terminated and the fires in the pool and the tank were manually extinguished.

6.3 Results of the fire exposure

In total, three fire exposure tests were conducted. A summary of the results is given below while detailed results for each type of tank are given in sections 6.3.1- 6.3.3.

As seen in Figure 30, there is a significant difference between the plastic tanks and the steel tank immediately after the start of the fire exposure. Most importantly, one can note the significantly faster temperature increase of the temperature of the fuel vapour in the steel tank (test 3) compared to the plastic tanks. Immediately before 2 minutes, however, a hole in the walls of both of the plastic tanks caused an immediate temperature increase. Visually this could be confirmed as the ignition of the fuel vapours inside the tanks which caused the emission of a short-duration but violent flame from the side of the tank through the hole that had been produced. The ignition was somewhat more violent for tank C which resulted in a splash of fuel several meters from the tank. As seen in section 6.3.3 and Figure 33, especially the fuel vapour temperature continued to increase rapidly in the steel tank and after approximately 4 minutes exposure a more rapid increase was noted in the fuel temperature. No ignition was seen inside the steel tank, most probably due to the fact that the temperature increased so rapidly that the fuel vapours formed a fuel rich mixture which was outside of the flammability range.

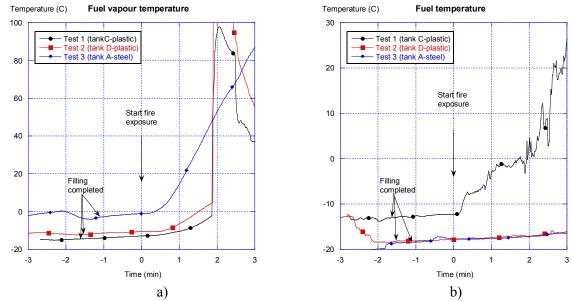


Figure 30 Figure a) shows the recorded temperature of the fuel vapour while b) shows the temperature of the fuel during the final phase of the refuelling until several minutes after the ignition of the pool fire. Tank A = steel, tank C and D = plastic. (Note the different temperature scales on the y-axes.)

In the case of the fuel temperature during the first minutes after fire exposure, one can note a more rapid increase of this temperature in test 1 (plastic tank C) than in the other two tests. One explanation may be the smaller volume of fuel used in this test, about 10 l, possibly in combination with the fact that the thermocouple was not entirely covered by the fuel or that it had come into contact with the bottom of the tank.

As shown in Figure 30, the fuel temperature was slightly different between the three experiments before the start of the fire exposure. At the end of the refuelling, the fuel it was approx. -18 °C in tests 2 and 3 while it was approximately -13 °C in test 1. The reason for the slightly higher temperature in test 1 was determined to be a problem with the freezer (rectified before tests 2 and 3).

The temperature of the fuel vapour was, however, approximately -14 °C in test 1, -12,5 °C in test 2 and -3 °C in test 3. The reason for the higher temperature in test 3 was probably the fact that the steel tank heats up more rapidly during mounting in the rig. This is seen in the rapid temperature increase 2-3 minutes before the start of the fire exposure. During filling of the tank, from approximately 2-1 minutes prior to ignition of the pool fire, a significant temperature decrease was noted which was followed by a temperature increase.

6.3.1 Test 1 – Fire exposure of tank type C (plastic)

The mounting of the tank was started at approximately -5:30 min:s before the start of the fire exposure in Test 1. The refuelling was conducted during the period from approximately -3:10 min:s to -1:40 min:s. As the pressure relief tube was blocked inadvertently, a positive pressure was obtained in the tank during filling and it was not possible to add more than 10 l fuel. At 1:52 min:s after the start of the fire exposure a violent ignition was obtained accompanied by a short-duration flame (<1 s) of several meters length out the side of the tank. As the appearance of the flame is in temporal agreement with the instantaneous temperature increase inside the tank (see Figure 31) this indicates that a hole was formed in the wall of the tank which lead to ignition of the fuel vapours inside the tank. The ignition resulted in a small spill of fuel on the floor, up to several meters from the tank, which gave rise to a spill fire with a flame height of

approximately 0,2-0,4 m. The spill fire had burnt out after approximately 20 seconds after which the fire on the floor self extinguished. The fire in the pool and the tank was extinguished manually approximately 2:30 min:s after ignition.

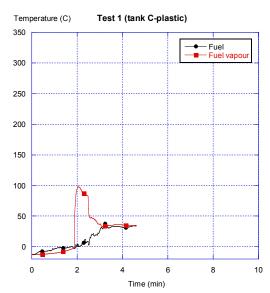


Figure 31 The fuel and vapour temperature during fire exposure in test 1 with tank C (plastic). The x-axis gives the time from start of fire exposure.

6.3.2 Test 2 - Fire exposure of tank type D (plastic)

The mounting of the tank was started at approximately -7:20 min:s before the start of the fire exposure in Test 2. The refuelling was conducted during the period from approximately -2:15 min:s to -1:35 min:s. At 1:53 min:s after the start of the fire exposure ignition was obtained accompanied by a short-duration flame (2-3 s) of several meters length out the side of the tank. As the appearance of the flame is in temporal agreement with the instantaneous temperature increase inside the tank (see Figure 32) this indicates that a hole was formed in the wall of the tank which lead to ignition of the fuel vapours inside the tank. No spill of fuel from the tank was noted but after some few seconds the tank began to leak and fuel ran into the pool fire. The fire in the tray and the tank was extinguished manually approximately 2:20 min:s after ignition.

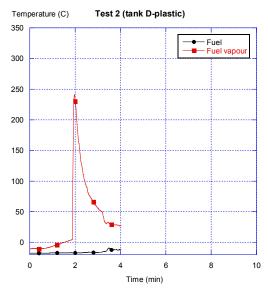


Figure 32 The fuel and vapour temperature during fire exposure in test 2 with tank D (plastic). The x-axis gives the time from start of fire exposure.

6.3.3 Test 3 - Fire exposure of tank type A (metal)

The mounting of the tank was started at approximately -6:00 min:s before the start of the fire exposure in Test 3. The refuelling was conducted during the period from approximately -2:15 min:s to -1:05 min:s. At 4:55 min:s after the start of the fire exposure the fuel began to flow out through the pressure relief pipe connected to the refuelling pipe. The fuel ignited after 5:03 min:s, which resulted in a 1-1,5 m² pool fire on the floor under the tank which lead to an increase in the fire exposure (see Figure 33). At 5:15 min:s the pool fire had increased to approximately 2-3 m² which resulted in the entire tank being exposed to flames. At approximately 5:50 min:s, the spill fire had decreased again to approximately 1 m². This implies that the tank was still not leaking and that the fuel had been pressed out by the positive pressure in the tank. At approximately 6:00 min:s a jet flame, approximately 1,5-2 m in length was seen rising upwards from the top of the tank for approximately 10-12 s, after which it could no longer be distinguished from the other flames around the tank. At approximately 6:45 min:s, the fuel spill on the floor had been almost entirely depleted which resulted in a decrease in the fire intensity again. Two intensive flames could, however, be seen from the top of the tank. The fire was extinguished manually after approximately 13:50 min:s.

Both the visual observations and the measurements indicate that there was no ignition of the gases inside the tank as the fuel vapour most probably was fuel rich due to the long period of heating in the beginning of the test and the high fuel temperature.

After the test it was possible to determine that the jet flame had emitted from a small hole in a connection to the tank which had formed when a rubber seal had melted, which allowed the emission of fuel vapours. Similarly, the two intensive flames that were noted later in the test were obtained from holes on the top of the tank allowing the emission of fuel vapour.

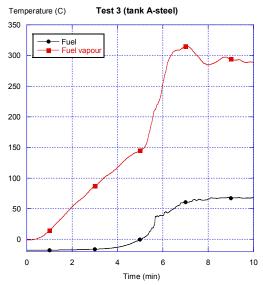


Figure 33 The fuel and vapour temperature during fire exposure in test 3 with tank A (steel). The x-axis gives the time from start of fire exposure

Work Package 5: Fuel concentrations and composition around the filling opening when refuelling

The aim of WP5 was to investigate the concentration and composition of the fuel vapours which can be pressed out of the refuelling pipe in conjunction with refuelling, both with and without a vapour recovery system (stage 2) activated. The tests aimed to provide an indication of how the gas mixture differs from that obtained under equilibrium conditions (WP1) and how the risk zone around the refuelling opening can be characterised. Finally, the intention was that the results would provide important information concerning the need/risk/environmental benefits of a vapour recovery system for E85.

The tests were divided up into two phases. In the first phase an IR camera was used which reacts to hydrocarbons and could, therefore, give a visual picture of the vapour emissions around the refuelling opening during refuelling.

This information was then used as the basis for planning of phase 2 where gas samples were taken in different positions around the refuelling opening during refuelling. These samples were then analysed to determined their concentration and composition.

7.1 Initial tests using the GasFindIR-camera

An IR camera, GasFindIR, was borrowed from FLIR Systems AB to obtain a coarse picture of the gas emissions around the refuelling opening.

GasFindIR is a newly developed IR camera which makes it possible to find gas leaks of volatile organic compounds (VOC) in a simple manner, see Figure 34 [29].





a) IR camera GasFindIR from FLIR Systems AB which was used to obtain a coarse picture of the gas emissions around the refuelling opening during tanking. b) An example of the type of picture that the camera shows where the dark grey area to the left of the refuelling opening indicates the presence of fuel vapour.

The camera works in real time with 25 pictures per second and can be connected to a video recorder for documentation. The gas leak is seen as grey-black "smoke" on the screen.

The camera was used both to film the refuelling process for a number of car models at petrol stations, and to film the refuelling process with a "test tank" that was used at the fluid measurements laboratory at SP in conjunction with a number of different tests.

Using the recordings of the refuelling process, a general picture of the distribution of the emissions in conjunction with such an activity could be established. This information was used for detailed planning of the gas analysis conducted in phase 2.

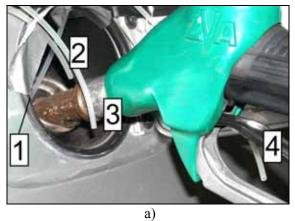
7.2 Gas analysis around the filling opening

Based on the information obtained from the IR films, four points were selected for sampling of the fuel vapour during the refuelling process. These positions were:

- Position 1 approximately 20 mm from the refuelling pipe opening (immediately outside of the "inner" connection for the fuel nozzle)
- Position 2 approximately 20 mm inside the car body, immediately above the fuel nozzle spout
- Position 3 level with the car body, immediately under the fuel nozzle spout
- Position 4 immediately under the handle of the fuel nozzle.

The positions are also shown in Figure 35 a) where it is possible to see the ends of the sampling tubes with the exception of position 1 where the sampling tube is not fully visible.

After numerous pre-tests using different sampling methodologies, a technique was chosen using a vacuum pump to extract the air/fuel vapours into glass vials through septum seals in their lids. In each vial, two small openings were made, one connected to the vacuum pump via a small tube and the other connected to a small tube leading to the sampling site, see Figure 35 b). The vials each had a volume of 2 ml and the sampling flow was controlled to 100 ml/min per vial. The gas sampling to the vials was started 5 s after the refuelling was started and continued for 30 seconds. This gave a theoretical gas exchange of 25 times, i.e., the sample that was subsequently tested corresponds to late in the sampling period. According to the IR films in phase 1 it is, however, probably that the concentrations are relatively stable during the refuelling process. Directly after the vacuum pump was turned off the sampling tube was removed to secure the environment inside the vials. The gas phase in the vials was analysed using gas chromatography in the same manner as in WP1.



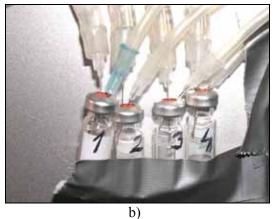


Figure 35 The photos show a) sampling points during the refuelling process (position 1 is not fully visible), b) the vials that were used for storing the gas samples and during the post-sampling analysis.

Refuelling tests were conducted in this manner on three occasions using two different car models (tank C and Tank D according to Chapter 5). One of the car models (tank C) was tested both with and without a vapour recovery system activated.

The other car model (tank D) was equipped with an ORVR -system (Onboard Refuelling Vapour Recovery system). The vapours from the tank are guided through an active coal canister during refuelling which captures the hydrocarbons contained in the out flowing air. This model was tested only with the gas recovery system connected.

The fuel dispensing and gas recovery system (stage 2) that were used were laboratory test equipment but had the same function as a standard system. The fuel dispensing pump has a flow of 40 l/min and a fuel nozzle of type Elaflex ZVA 200 GRV3. Gas volume recovery degree (recovered gas volume relative to the delivered fuel volume), was 102 % when the gas recovery system was activated which can be judged to be representative for typical vapour recovery systems.

The refuelling was conducted indoors in a cold store room, i.e., protected from wind. The temperature of the E85 fuel (E85S) used was between 8 °C and 9 °C which is probably a fairly normal temperature for fuel in an underground tank. Immediately before refuelling, the cars were driven on a road for approximately 10 minutes to pre-condition the conditions inside the fuel tank to be as close as possible to those during normal refuelling at a petrol station.

7.3 Results from the refuelling test

A total of seven video sequences were taken of refuelling processes for five different car/tank types using the GasFindIR camera. Based on this information, and after various method development tests, three sets of samples were taken of fuel vapours around the refuelling pipe during refuelling.

7.3.1 Observations based on the GasFindIR-films

The film sequences from the different refuelling tests show similar conditions for all tests. Almost immediately after refuelling was started, a cloud of vapours comprised of hydrocarbons could be seen around the refuelling opening. The position of the cloud and its distribution varied somewhat during the refuelling, probably due to air movement. One test, conducted with the gas recovery system activated showed that less gas was emitted. Figure 36 shows a selection of photos from 6 s of video sequence taken with the vapour recovery system not activated.

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Figure 36 Examples of picture sequences from the GasFindIR camera during refuelling without the vapour recovery system activated. Emission of the fuel vapours can be seen as grey-black "smoke" on the pictures (selected photos from a 6 second video sequence).

7.3.2 Results of the gas analysis when refuelling

The results from the tests and the subsequent analysis are summarised in Table 14 to Table 16. Pertinent details concerning the test procedure is summaries prior to each table. One can note that there is a marked difference between the gas concentrations outside the refuelling pipe depending on whether the vapour recovery system is activated or not. When the samples from tank D (with ORVR) were analysed, the fuel vapour concentration taken in the refuelling pipe

(pos. 1) was below the minimum detection level, thus the samples in the other vials were not analysed.

<u>Summary of sampling procedure – Tank C</u>

The refuelling was conducted 2007-04-25, without the gas recovery system activated. The remaining fuel volume in the tank was 16 l and the surrounding temperature was approximately 20 °C. The sampling was started approximately 5 seconds after refuelling was begun and continued for approximately 30 seconds. The refuelling was stopped automatically after 59 seconds and the refuelled volume was approximately 39 l.

In this case, two gas samples were taken in sequence in the refuelling pipe (pos. 1) to study repeatability. Gas Sample 1 was taken during approximately 30 seconds while gas sample 2 was taken during the remainder of the refuelling time. The total fuel vapour concentration measured in these samples was 10,2 % and 12,9 %, respectively. The value for Position 1 in Table 14 is the average of these two samples.

Table 14 Summary of the analysis results (%-vol) from the four sampling positions for tank C without the vapour recovery system activated.

	Position					
Species/group	1 Inside refuelling	2 Inside car body	3 Level with the car	4 Beside the fuel nozzle		
	pipe*)	a c a y	body	handle		
Sum C3 (alkanes and alkenes)	0.04	0.02	0.00	0.00		
Sum C4 (alkanes and alkenes)	2.33	1.09	0.15	0.05		
Sum C5 (alkanes and alkenes)	4.23	2.02	0.28	0.10		
Sum C6 (alkanes and alkenes)	1.35	0.71	0.09	0.04		
Sum C7 (alkanes and alkenes)	0.15	0.06	0.01	0.00		
Sum C8 (alkanes and alkenes)	0.07	0.03	0.00	0.00		
Sum aliphatic hydrocarbons (C3 – C8)	8.17	3.93	0.53	0.20		
Sum aromatic hydrocarbons	0.08	0.02	0.00	0.00		
(C6 + C7 + C8)						
MTBE	0.25	0.19	0.03	0.01		
Ethanol	3.19	1.47	0.15	0.04		
Total sum organic species (%-vol)	11.7	5.6	0.7	0.3		

^{*)} Average of two gas samples taken in sequence during the refuelling process.

Summary of sampling procedure – Tank C

The refuelling was conducted 2007-05-10, with the vapour recovery system activated. The remaining fuel volume in the tank was 5 l and the surrounding temperature was approximately 11 °C. The sampling was started approximately 5 seconds after the refuelling was begun and continued for approximately 30 seconds. The refuelling was stopped automatically after 75 seconds and the refuelled volume was approximately 50 l.

Table 15 Summary of analysis results (%-vol) from the four sampling positions for tank C with

the vapour recovery system activated.

	Position						
Species/group	1	2	3	4			
	Inside refuelling pipe*)	Inside car body	Level with the car body	Beside the fuel nozzle handle			
Sum C3 (alkanes and alkenes)	0.05	0.01	0	0			
Sum C4 (alkanes and alkenes)	2.13	0.25	0.06	0.01			
Sum C5 (alkanes and alkenes)	4.01	0.49	0.12	0.01			
Sum C6 (alkanes and alkenes)	1.27	0.16	0.04	0			
Sum C7 (alkanes and alkenes)	0.12	0.02	0	0			
Sum C8 (alkanes and alkenes)	0.04	0.01	0	0			
Sum aliphatic hydrocarbons (C3 – C8)	7.60	0.94	0.22	0.02			
Sum aromatic hydrocarbons	0.07	0.01	0	0			
(C6 + C7 + C8)							
MTBE	0.66	0.06	0.01	0			
Ethanol	2.22	0.32	0.05	0			
Total sum organic species (%-vol)	10.5	1.3	0.3	0.02			

<u>Summary of sampling procedure – Tank D</u>

The refuelling was conducted on 2007-05-10, without a vapour recovery system activated. The remaining fuel in the tank was approximately 10 l and the surrounding temperature was approximately 14 °C. The sampling began approximately 8 seconds after refuelling was begun and continued for approximately 35 seconds. The refuelling was stopped automatically after 87 seconds and the refuelled volume was approximately 58 l.

Table 16 Summary of the analysis results (%-vol) from the four sampling positions for tank D (ORVR-system) without the vapour recovery system activated.

Species/group	Position			
	Inside refuelling pipe*)	2 Inside car body	3 Level with the car body	4 Beside the fuel nozzle handle
Sum C3 (alkanes and alkenes)	0	_		-
Sum C4 (alkanes and alkenes)	0	_	_	_
Sum C5 (alkanes and alkenes)	0	-	_	-
Sum C6 (alkanes and alkenes)	0	-	_	-
Sum C7 (alkanes and alkenes)	0	-	_	-
Sum C8 (alkanes and alkenes)	0	-	-	-
Sum aliphatic hydrocarbons (C3 – C8)	0	-	-	-
Sum aromatic hydrocarbons	0	-	-	-
(C6 + C7 + C8)				
MTBE	0	-	-	-
Ethanol	0	-	-	-
Total sum organic species (%-vol)	<0,02	-*)	-*)	-*)

^{*)} Due to the fact that the fuel vapour concentrations inside the refuelling pipe (pos. 1) were below the minimum detection level, the gas samples in the other vials were not analysed.

8 Summary of results and discussion

The overall goal of this project has been to answer several important questions concerning the fire and explosion characteristics of E85 and how this potentially impacts on the risk associated with the use of E85 compared to petrol.

Due to the broad nature of this overall goal, the project has been relatively comprehensive, being divided into several Work Packages (WP) which have each aimed to answer a more limited question. WP 1 and 2 have been aimed towards more fundamental issues concerning E85, while WP 3 to 5 were more applied in nature, aimed towards the risks associated with use, primarily in cars.

The project has provided valuable information which has lead to an increased understanding of the differences between E85 and petrol. There is, however, still a great deal of information needed, e.g., concerning the different qualities of fuel. If such a study were to be conducted one could use the same methodology as that developed in this project.

In the case of WP 3-5, a great deal of valuable information has been obtained but these results should be seen indicative. The tests have been conducted on 2-4 different types of fuel tanks/car models, and considering the number of models and construction solutions that exist, any extrapolation of the results should be made with great care.

The results and experience that has been gained in each WP are discussed below. Even the limitations in the various tests that have been conducted are presented. A summary of the conclusions is presented in Chapter 9 and those areas which have been selected as being most important for future research are presented in Chapter 10.

8.1 Work Package 1 – Fuel composition

The aim of WP1 was to determine the concentration and composition of the fuel vapour that is obtained in a closed vessel at a variety of equilibrium temperatures. E85S was tested at six different temperatures within the temperature range -25 $^{\circ}$ C to + 20 $^{\circ}$ C. Petrol was tested at four different temperatures within the temperature range -25 $^{\circ}$ C to 0 $^{\circ}$ C. The other E85 qualities were only tested at 0 $^{\circ}$ C. The analyses showed that:

- there can be a significant difference between the composition of the liquid phased and that of the fuel vapours that are formed in a closed vessel, e.g. a fuel tank, containing E85.
- despite the fact that the petrol content of E85 is only approximately 15 %, the fuel vapours are dominated by petrol fractions due to the fact that petrol has a higher partial pressure than ethanol.
- the fact that the vapour pressure is important for the composition of the fuel vapours means that the composition of the fuel vapours differs significantly between winter and summer qualities of E85. The proportion of petrol fractions in the vapours from winter quality is greater than that from summer quality of E85.

The tests were conducted under controlled conditions and despite this fact one can see certain differences between the results, e.g. depending on the pre-conditioning time. It is therefore important to be aware of the fact that these differences may be more significant in real life. The analyses in this project were based on small test volumes where one can assume a relatively even concentration. In real application, e.g. fuel tanks or large underground tanks, it is likely

that gradients in concentration would be found. This implies that one would find different concentrations at different positions in the fuel tank or underground tank. Fuel tanks which are in motion or where refuelling is underway, probably afford a certain amount of mixing which could lead to even greater variations.

Other factors which could not be investigated fully within this project include: the effect of all potential fuel qualities (i.e., combinations of ethanol and fuel) which can occur in practice, partly when delivered and partly when in a vehicle is in traffic as many vehicles can use both petrol and ethanol; the effect of a greater number of temperature levels; the effect on the degree of filling as only 25% degree of filling was investigated, i.e., the test vessel was filled with fuel up to 25% of its total volume.

8.2 Work Package 2 – Flammability characteristics

The aim of WP2 was to determine at which temperature range the E85 vapours were flammable, i.e. the upper and lower explosion limits. The aim was also to investigate how the E85 vapours can be represented by a test gas mixture. In total 26 test series were conducted with an average of three ignition tests in every series. The bomb tests showed that:

- the fuel vapours from E85S are flammable within a temperature range from approximately -18 °C (LEP) up to approximately +2 °C to +5 °C (UEP). A certain amount of uncertainty is present concerning the exact temperatures, partly due to the limited number of tests and partly due to the variation in the fuel quality which can affect these temperatures.
- The optimal combustion conditions for E85S, i.e., those that cause the fastest pressure increase and the highest explosion pressure, occurred at approximately -8 °C.
- The upper explosion point (UEP) for E85W was found to be approximately -8 °C to -9 °C. In the case of the petrol tested, LF95S, the corresponding temperature was determined to be approximately -20 °C. Determination of the lower flammability point (LEP) and the temperature for the optimal combustion conditions has not been a part of this project for these two fuels.
- According to the analyses in WP1, the flammability point for E85S correspond to a total
 fuel concentration of approximately 3 % at LEP and approximately 9 % at UEP. The
 fuel concentration at UEP for E85W and LF95S can be estimated to be approximately
 7% while details concerning the LEP are missing. The composition of the fuel mixture
 and the vapour pressure of its various components appears to be very important which is
 why it is better from a practical point of view to refer to the flammability points, UEP
 and LEP (°C), respectively.
- The tests with the test gas mixture (propane/air and ethylene/air respectively) exhibit significant differences, mainly concerning the rate of pressure increase while the time to the first pressure peak was approximately 70 ms for propane while that for ethylene was approximately 35 ms. The pressure increase rate for E85 vapour was 73 ms at the lowest which shows that they have characteristics similar to the propane mixture ((4,6±0,3) % propane in air) which is categorized as explosion group IIA. The maximum recorded explosion pressures were essentially the same.

The tests in the bomb rig worked very well and each test gave both information concerning the ignitability of the fuel and its combustion characteristics. Pre-conditioning in a closed vessel has also ensured that the composition is representative for each specific temperature. A simplification of the methodology would be to evacuate the fuel vapour directly from the

conditioning vessel to the bomb, as was done in a limited number of tests. Even the degree of filling of the tank or vessel can be crucial, in particular if this is less than 20 %, as the UEP-level in particular can be moved to a high temperature [3, 6]. The tests in this WP were conducted with a 25% degree of filling.

8.3 Work Package 3 – Ignition tests in fuel tanks

The aim of WP3 has been to investigate the consequences of ignition of a flammable gas mixture, both inside the fuel tank and at the refuelling opening. In total eight tests were conducted with four different tank types for different car models, three plastic tanks and one steel tank. The tests showed that:

- All plastic tanks cracked due to the pressure shock when the test gas mixture inside the tank was ignited. In conjunction with this ignition a short-duration flame (<1 s) was emitted through the crack that was formed. The cracks were approximately 40-90 cm long. The steel tank did not crack but its tank fitting was thrown away and a short-duration flame came through the hole left by the tank fitting. The flame length in these particular tests varied between <0,5 m and 2-5 m.
- Ignition of the test gas mixture inside the fuel tank gas rise to a positive pressure inside the tanks of the order of 2-8 bar. The refuelling pipe registered a relatively high pressure, of the order of 5-37 bar, although there was no visible damage or deformation of the pipe.
- All, except one test, were conducted with the fuel tanks lying freely in a soft base. One
 test was conducted with the tank mounted in a real chassis. The ignition in this case
 caused a positive pressure in the fuel tank which caused deformation of the underbody
 by approximately 10-15 cm. The support fittings for the tank in the underbody were
 also deformed.

It should be noted that the tests aimed to simulate possible conditions (worst case) without taking the probability of ignition into account. The primary aim was rather to study the consequences of an ignition in an optimal fuel/air mixture. The results show that the shape of both the tank and the refuelling pipe has an impact on the consequences. If, for example, a check valve is present in the refuelling pipe, this can (depending on its design) assist in restricting an ignition at the opening of the refuelling pipe from spreading to the tank. Only one test has been conducted with the tank mounted in a real chassis. Therefore, information concerning the impact of mounting of the tank in a real vehicle is very limited as is the effect of having fuel in the tank. Extrapolation of the results from this WP should be done with great care.

8.4 Work Package 4 – Fire exposure of fuel tanks

The aim of WP4 was to study potential differences in the fire development in a spill fire under a fuel tank containing E85 compared to that containing petrol. In total three fire tests were conducted using three different types of fuel tanks for different models of cars. The tests show that:

Plastic tanks and steel tanks perform differently when exposed to a fire. The plastic
material is a good insulator and the fuel vapours inside the tank do not react as rapidly
to the temperature change due to the fire exposure as do those inside the steel tank. The
plastic does, however, melt more readily under the influence of an external, large fire

exposure which can lead to the opening of a hole in the tank wall within a few minutes (just under 2 minutes in these tests).

- In both tests conducted with plastic tanks, the fuel vapours inside the tank ignited in conjunction with a breach in the plastic. A short-lived flame (<1-3 s), several meters in length, resulted. In one of the tests, this breach also resulted in a fuel spill which gave rise to a short-lived spill fire. Prior to the fire exposure, the fuel and the tank were both pre-conditioned to approximately -20 °C.
- The temperature of the fuel vapours inside the steel tank increased relatively rapidly. Therefore a pressure increase was seen inside the tank which resulted in a flow of the fuel out through a pressure relief valve, causing a spill fire. Further, a jet flame was seen in conjunction with the melting of a rubber seal to a connection which allowed fuel vapours to be released. No ignition of the fuel vapour inside the tank was seen in this test.
- The results from the tests are closely coupled to the test conditions and the different types of tanks used. Even if there was no ignition of the fuel vapour inside the steel tank in these tests, this is no guarantee that this could not happen under unfavourable conditions.

These spill fire tests were also focussed on worst case conditions without consideration of the probability that these conditions could arise. In order to achieve these conditions the tests were run with both the tanks and the fuel at low temperatures while the fire impact was chosen to minimise potential heating of the fuel in the tanks. The probability that these conditions could be reproduced in a real life situation is difficult to determine but it is clear that the number of potential fire scenarios that could occur in real life is great. Considering the fact that only three tests were conducted, all with E85 as the fuel in the tanks, it is clear that one cannot extrapolate too far from these results. One thing that can be noted from these tests is that the E85 vapours were ignited in both tests with plastic tanks. It is our assessment, based on long experience of fire testing of plastic tanks according ECE regulation 34, that this would probably not occur if the tests were conducted in the same way with petrol.

The effect of the ignition that was seen was not dramatic but it is unclear which fuel mixture was in the tanks when ignition occurred. The effect of the position of the tank in a test rig compared to a real installation in a car is also difficult to evaluate. In the case of the steel tank, the effects are also strongly dependent on how the different fixtures and attachments are connected to the tank, which makes it difficult to generalise the results of a single test.

Based on the results of the previous WPs it is, however, possible to determine that the risk for more drastic consequences requires relatively extreme conditions including extreme cold in combination with a limited/well directed fire impact. Under such conditions, even petrol could represent a risk. In general, the ignition of fuel vapour in a fuel tank, independent of the fuel, corresponds to a certain risk for, e.g., fire rescue services personnel close to a car but the consequences probably do not affect the overall risk picture associated with a car fire.

8.5 Work Package 5 – Fuel concentrations when refuelling

The aim of WP 5 was to determine the fuel concentrations and composition present around the refuelling pipe in a vehicle in conjunction with refuelling. In total three full tests were conducted with two main types of tanks. The tests showed that:

- In the case of tank C (which probably corresponds to "conventional" tanks), one can verify that the fuel vapour concentration inside the refuelling pipe was approximately 10-12% which is probably above the flammability limit. The fuel vapour concentration outside the refuelling pipe was, however, within flammability limits (approximately 5-6%) when the gas recovery system was not activated. When the gas recovery system was activated, very low concentrations of fuel vapours were measured at all points outside the refuelling pipe. These concentrations were probably below flammable limits.
- The test with tank D, with the ORVR-system, showed that the fuel vapour concentration inside the refuelling pipe was below the minimum detection level for the analysis instruments. Based on this fact, one can draw the conclusion that the risk for ignition is significantly reduced provided the system is working correctly.
- It is of interest to note that the fuel vapours emitted in conjunction with refuelling agree well with the analysis data from WP1. This means that the fuel vapours contain mainly petrol fractions despite the high concentration of ethanol in the liquid phase.

The number of tests and types of tanks tested was very limited in this test series considering the large number of car models on the market. As all possible fuel combinations could potentially be present in the fuel tanks during refuelling, the gas concentrations and composition could vary significantly. Further, the effect of temperature, wind and the presence of a vapour recovery system, etc, will also have a direct effect on the extent of the "cloud" of fuel vapour produced when refuelling. It is, however, clear that a flammable mixture could be present around the refuelling opening, in particular in the absence of a vapour recovery system. This is a strong indication that one should, as far as possible, eliminate the risk for static electricity. This is true both in terms of the design of the vehicle and the design of the refuelling station.

8.6 Comparison with other experimental investigations

Some comparison of the results, primarily from WP1 and 2, can be made with results and conclusions from the other experimental investigations presented in Chapter 2. It is important to remember that both the experimental methodology and the fuel quality differ, but one can draw the following general conclusions:

- The SAE-report [3] shows that the flammability limits for the E85 included in that study lie between approximately -35 °C (LEP) and +3 °C (UEP). When the degree of filling is below approximately 20%, the upper explosion point is moved up and at, e.g., 10% degree of filling it is estimated to be approximately 10 °C and at 1 % the UEP is about 20 °C. Even the lower explosion point is moved upwards somewhat but not as significant. The results from this report compare favourably with the results from the SAE study. The UEP is in very good agreement while the LEP in the SAE-report is somewhat lower.
- PTB [6] cites an UEP of approximately 3,5 °C for E85, summer quality at 20% degree of filling. The UEP for E85, winter quality is cited as -6 °C for a 10% degree of filling. As shown in Table 1 in Chapter 2.1, the UEP increased with a decreasing degree of filling and is cited as +18 °C and +17 °C, respectively, for for the two E85 qualities at 1% degree of filling. Compared to the results from the project, the UEP is equivalent for E85S while that for E85W is somewhat higher. No determination of LEP has been made by PTB.
- The tests of MESG that have been conducted show that E85 vapours from petrol/ethanol mixtures with <97%-vol of ethanol in the liquid phase can be classified as IIA, while those with a higher content of ethanol should be classified as IIB1 [7].

This agrees well with this project which showed the best agreement between fuel vapours from E85 and test gas mixtures of propan/air, which are classified as explosion group IIA.

• The ignition tests of E85-vapours conducted for SPI in an underground tank also show a relatively good agreement with this project [12]. The tests with a fuel temperature of approximately 11 °C and a degree of filling of approximately 20%, confirmed that fuel vapour could not be ignited, even after dilution with air. At a temperature of approximately 4 °C and a 1% degree of filling, ignition could be obtained, but first after dilution with air. Considering the differences in test scale these results are seen to correlate well with in the results from this project. In comparison to the UEP seen at 1% degree of filling in both the SAE-report and the PTB investigation, the underground tank tests indicate a somewhat lower UEP. This translates to a certain margin of safety in the large scale application compared to smaller scale results.

9 Conclusions

The most important conclusions of this project are summarised below.

In the case of the specific data for E85 and petrol given in points 1-3 below, it should be noted that this data is valid for the fuel qualities (batches) included in this study and has not been verified for other fuel qualities. Further, the degree of filling in these tests was 25%. A lower degree of filling could result in movement of the UEP to higher temperatures. This means that a risk for ignition could arise at higher surrounding or fuel temperatures that those given here.

It is also important to note that the results from the applied tests are closely connected to the specific test objects and the test methodology that has been chosen. The number of tests is also very limited and care should be taken when extrapolating the conclusions in points 8-10 below to other conditions. These conclusions are not necessarily representative for all car models and fuel tanks available on the market, nor can they be seen to be representative of all possible ignition or fire scenarios.

- 1) The fuel vapour in a closed vessel containing E85, are composed mainly of petrol fractions, i.e. of the order of 70-90%. The concentration varies depending on the fuel quality (e.g., E85S or E85W) and the temperature.
- 2) The high proportion of petrol fractions in the fuel vapour implies that the flammability limits are significantly different relative to those for pure ethanol.
- 3) The lower explosion point (LEP) for E85 of summer quality (E85S) was found to be approximately -18°C while the upper explosion point (UEP) was approximately +2°C to +5°C.
- 4) The upper explosion point (UEP) for E85 of winter quality (E85W) was found to be approximately -8 °C to -9 °C
- 5) The upper explosion point (UEP) for lead free, 95-octane petrol of summer quality (LF95S) was found to be approximately -20 °C
- 6) E85 belongs to explosion group IIA, in the same way as petrol.
- 7) Fuel vapours from E85 are flammable at higher temperatures than petrol which translates to a somewhat increased risk compared to petrol. The change from summer to winter qualities of E85 for the cold part of the year compensates for this increased risk to a certain degree, but does not negate the increased risk entirely.
- 8) Ignition of the fuel vapours in the refuelling pipe or inside the fuel tank can, under worst case conditions, lead to a pressure increase inside the tank which can cause deformation or rupture of the tank. Short-lived flames should be expected from the refuelling pipe opening or cracks in the tank in this case. It is, however, possible to prevent spread of the flame into the tank, depending on the tank design.
- 9) A spill fire under a fuel tank containing E85 can, under unfavourable temperature conditions and fire impingement, lead to an ignition inside the tank, resulting in short-lived flames and potential spills of burning fuel. The same can be said for petrol. This can translate into a risk for e.g. rescue personnel in the immediate vicinity of a vehicle but it probably does not affect the overall risk associated with a car fire.
- 10) Flammable fuel vapours were found immediately outside the refuelling opening when a gas recovery system was not activated. This risk is probably significantly less with vehicles with a working ORVR-system.

10 Future work

- It would be possible to obtain a more complete and detailed picture of the flammability limits of E85 and petrol, and the effect of different fuel qualities or variations, if the need arises. To do this further tests would be needed.
- The tests in WP1 and 2 have been conducted on a relatively small scale and only with a 25% degree of filling. The pre-conditioning tests and gas analyses should be conducted on a larger scale, partly to investigate direct scaling effects and partly to study to which degree one can find large variations in concentration in larger fuel tanks or underground tanks. Further, the effect of the degree of filling should be investigated on a larger scale.
- The investigations that have been conducted within this project have provided a great deal of information concerning the composition and ignition characteristics of fuel vapours which arise in a closed vessel containing E85. The results show that these characteristics can be strongly influenced even by components which are present in relatively small proportions (e.g. 15% petrol relative to 85% ethanol). In an effort to make a move to renewable fuels, other types of fuels are being developed together with E85, e.g. for diesel powered vehicles. The same evaluation procedure should be used to evaluate the ignition and fire characteristics of these fuels as well, in order to be able to take correct risk reduction measures.
- Before a vapour recovery system is activated on all E85-dispensers, the classification
 and function of potential flame protection systems should be verified to ensure that they
 provide an acceptable level of protection against ignition of fuel in the proximity of the
 fuel nozzle.
- The consequences of the ignition of fuel vapours inside the tank or at the opening of the refuelling pipe were investigated in WP3, without taking account of the probability or presence of an ignition source. The dominant ignition source is probably static electricity. In an investigation conducted by UK IP and others [20] shows that even if the number of fires reported in conjunction with refuelling is relatively few, there are a number of external variables that can have a significant impact on this frequency. The design of the fuel tank system is of course important, but even the design of the vehicle in general, the type of interior material, the properties of the tires, and the surface at the petrol station are all important parameters. The probability of the presence and effect of different types of ignition sources should be investigated more systematically together with the potential impact of different fuel qualities, in order to reduce the risks further. Further, there are probably no (or few) reports of ignition sources inside petrol tanks due to the fact that petrol vapours inside the tank are normally too fuel rich to ignite. As seen in this report, however, the probability of the presence of a flammable mixture inside a tank containing E85 is higher. Thus, the probability that there could be ignition sources inside the fuel tank is of greater interest in fuel tanks for E85. In this case the most probable ignition sources would include sparks or hot surfaces on electronic circuits or components inside the tank. Failures which could occur in such circuits should be considered.

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Appendix 1 – Fuel Specifications

Below is a summary of the specifications for the fuels used in this project.

11.1.1 E85S (Summer quality)

The fuel was delivered by SEKAB Biofuels & Chemicals and they have provided the following information for the batch of fuel used in the project.

- Recepie: 85,2 vol% ethanol, 12,3 vol% petrol, 2,1 vol% MTBE, 0,4 vol% isobuthanol and 1 ppm red dye.
- Petrol specification: Vapour pressure 61,8 kPa.
- Ethanol specification: Water content 0,1 weight%, evaporation residue 0,25 mg/l, higher alcoholes 2 g/l, methanol 0,8 vol%.
- Result of fuel analysis: pH 7,0, initial boiling point 58 °C, density 0,783 kg/litre. Calculated vapour pressure 36 kPa.

11.1.2 E85W (Winter quality)

The fuel was delivered from SEKAB Biofuels & Chemicals and they have provided the following information for the batch of fuel used in the project.

- Recepie: 78 vol% ethanol, 2,1 vol% MTBE, 0,4 vol% isobuthanol and remaining part petrol (19,5%)
- Petrol specification: Vapour pressure, approx. 88 kPa.
- Result of fuel analysis: Initial boiling point 51,6 °C, density 0,7777 kg/litre, water content 0,26 weight%, conductivity 0,48 µS/cm. Calculated vapour pressure, approx. 50 kPa.

11.1.3 Lead-free petrol, 95-octane (summer quality)

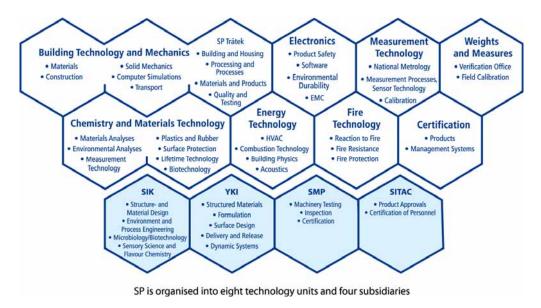
The petrol was delivered by Norsk Hydro Olje AB and was manufactured at Preem refinery in Lysekil, Sweden. Below is an abstract of the analysis results from Preem when loading the batch of fuel on a ship for transport to the Hydro fuel depot.

- Reference/designation: Ship ref: 34373, ship M/T Oktavius, designation: M95 E5-bas Sommar ua
- Aromatic content 34,7 %V/V, benzene content 0,7 %V/V, density at 15°C 743,9 kg/m³, octane, RON 95,3, Oxyg: MTBE content <0,2%V/V, vapour pressure (DVPE) 61,3 kPa, water content 70 mg/kg.

According to information obtained, 5% of ethanol was added at Hydro before delivery.

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