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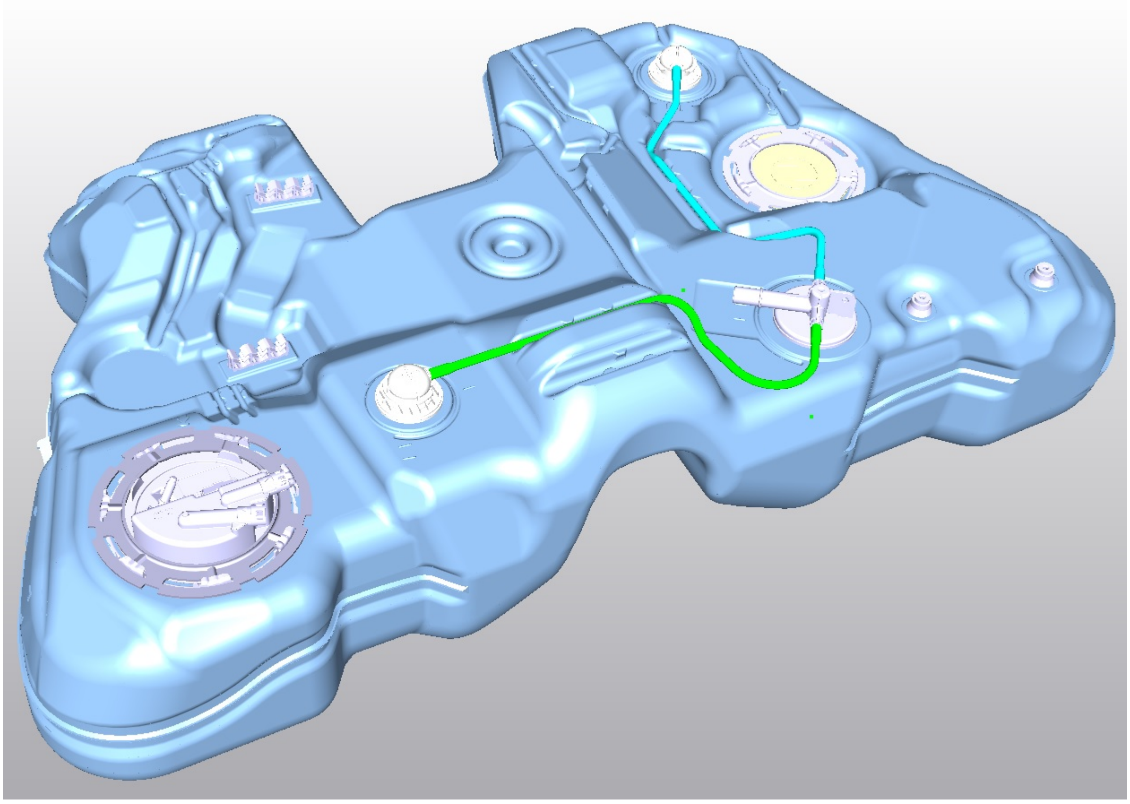

Fuel degradation in vented PHEV fuel tanks

A study that investigates how the gasoline Reid Vapor Pressure (RVP) is affected by temperature variations

Master's thesis within Master Programme Sustainable Energy Systems

SOFIA FRÄNDBERG

Department of Chemistry and Chemical Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2016

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Abstract

During the past few decades scientists and politicians have agreed that human activities contribute to the rising temperatures on earth that are causing troubles to our planet. In Europe, cars are responsible for 12 percent of the CO_2 emissions and to be able to lower the emission from this sector Plug-in Hybrid Electrical Vehicles (PHEV) have been developed. These cars can utilize the power from both an internal combustion engine and an electrical motor, lowering the emissions to the atmosphere. With new technologies new problems arise and if a PHEV is utilizing only the electrical motor during an extended time period the fuel will be stored on-board the vehicle and degrade.

This study was based on practical experiments where gasoline was exposed to CARB temperature cycles and temperature steps to investigate how the degradation process was proceeding. The main focus was to study how the Reid vapor pressure (RVP) was affected by on-board storage. Two gasoline blends with very different properties were used, LEVIII and BogeyI. When increasing the temperature of the gasoline the vapor pressure was increased causing hydrocarbons to evaporate. At the same time the gas phase in the fuel tank was expanding according to the ideal gas law. As a result of these two effects, hydrocarbons were expelled from the fuel tank. The hydrocarbons were collected in an activated carbon canister that was continuously weighted in which way the evaporation process could be studied. Also, a lot of experiments were performed to map how different parameters such as exposed gasoline surface area and gasoline volume were affecting the evaporation process.

The results show that a larger surface area between the gasoline surface and the gaseous surrounding results in a faster evaporation process. A larger area-to-volume ratio between the fuel tank walls and gasoline also results in a faster evaporation process due to a better heat transport. A smaller liquid volume results in a larger gaseous volume in the fuel tank and is also resulting in a greater amount of expelled hydrocarbons. The ideal gas law was used to calculate the theoretical amount that should evaporate, but for some systems the gas law was not valid since the endothermic evaporation process was proceeding too fast, which lowered the gas phase temperature.

If a low volatile gasoline blend is stored on-board a vehicle for three months it might cause problem with engine start. If a high volatile gasoline blend is fueled during winter and is still left in the fuel tank during summer, large amounts will evaporate. The activated carbon canister will not be able to adsorb these huge amounts that will instead evaporate out in the atmosphere which is not desirable.

Keywords: Volvo Cars, vapor pressure, gasoline, RVP, fuel degradation, evaporation, CARB, EVAP system, canister adsorption.

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Sofia Frändberg, Gothenburg, May 2016

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1 Introduction

During the past few decades there has been an ongoing discussion about the earth's climate. Scientists and politicians are agreed that human activities contribute to the rising temperatures on earth that cause problems like melting of glaciers [1]. The increased amount of greenhouse gases in the atmosphere can also cause unforeseen events such as an increased quantity of natural disasters as well as the force of these events. To tackle these problems the amount of greenhouse gas emissions from industrialized countries must be reduced by up to 60-80 percent compared to the levels year 1990 [2].

In 2013, 23 percent of the global carbon dioxide (CO_2) emissions came from the transport sector, making it the second largest contributing sector after electricity and heating [3]. In Europe, cars are responsible for about 12 percent of the CO_2 emissions [4]. A lot of people are depending on the usage of their cars and thus, new technologies must be developed that allows people to continue to use their cars without the greenhouse gas emissions.

1.1 Background

To reduce the greenhouse gas emissions new methods and engines are developed by the car industry. One of the most promising solutions on a short term is the Plug-in Hybrid Electrical Vehicle (PHEV). These cars have both an internal combustion engine (ICE) and an electrical motor, which lowers the emissions compared to a conventional vehicle. These reductions of emissions are necessary since the target is to reduce the CO_2 emissions from the transport sector to 30% below 2005 levels by 2050 [5]. Despite the fact that PHEV's are already out on the market, there are still some issues to solve to be able to develop the technique further.

1.1.1 Plug-in Hybrid Electrical Vehicle

In comparison with a conventional vehicle (CV), a plug-in hybrid electrical vehicle has two engines. One regular ICE that works in the same way as in a CV and one electrical motor [6]. The power supplied to the electrical motor is stored in a battery that can be charged from the electric grid and by brake energy recuperation. The electrical motor allows the PHEV to utilize more renewable energy, generated from resources such as solar, wind and water, which in turn lower the greenhouse gas emissions. A schematic of the principle for a PHEV is shown in Figure 1.1.

Volvo cars' approach to the PHEV is to combine the positive effects of reduced emissions with a better performance of the vehicle [7]. Volvo call their PHEV technology for a twin engine system since it may utilise the power from both engines at the same time. Up to 50 km/h only the electrical motor is used which means no

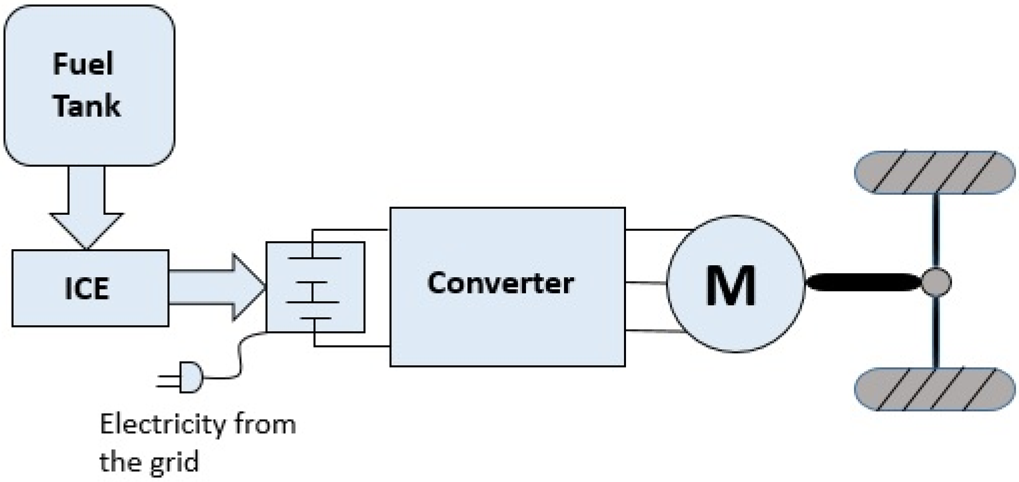


Figure 1.1: Schematic picture of a PHEV powertrain, where M is the electrical motor and ICE the internal combustion engine.

emissions and a rear wheel drive. At higher velocities the electrical engine run the rear wheels and the internal combustion engine run the front wheels, which gives the car a four wheel drive with a high performance.

1.1.2 Why PHEV?

Today there are over one billion vehicles on earth and this number is expected to reach two billion as the developing countries improve their standards [8]. Historically, cars have been using fossil fuels to run an internal combustion engine, which results in huge emissions of greenhouse gases such as CO_2. To be able to increase the number of vehicles up to two billion something has to be done to lower the emissions from this sector.

Some companies, such as Toyota and Hyundai, are doing research on the possibility to use hydrogen powered fuel cells on-board the vehicle to produce electricity, that in turn will run an electrical motor [9]. Many other companies, such as Volvo cars are going for the PHEV, which can utilize both a liquid fuel, such as gasoline or diesel, and electricity. One thing is certain, electricity is the future for the car industry. Research is also being done to develop electrical vehicles (EV) that are only utilizing an electrical motor. There are still a lot of problems with this technique though [6]. The batteries needed for the EV's are very expensive, takes a long time to charge and the driving distance is shorter than for a CV. The PHEV on the other hand might be cheaper than the EV, depending on the battery size, and the driving distance for a PHEV is in the same range as for a CV, making it easy for customers to adopt the car into their daily lives [5]. The battery in the PHEV takes a few hours to recharge, but the presence of the internal combustion engine increase the flexibility to when to recharge the battery. Therefor the PHEV is a good transition technology that will buy the researchers and the climate some time while the battery technology is further developed. A big step in the battery technology was recently taken by Tesla who launched their model S utilizing only an electrical motor [10]. The battery takes up to 9 hours to fully charge and has a driving distance of 500 km.

1.1.3 Criteria for the electricity production

If the new electric vehicles such as EV, PHEV and HEV (hybrid electrical vehicle) should be beneficial for the environment it is important to take into consideration what raw materials that are used to produce the electricity. If the electricity is produced from renewable resources such as wind, solar and hydro power or from biofuels, the reduction of greenhouse gas emissions would be significant. If the electricity is produced from fossil fuels such as coal or oil, there are no improvements made, since this only moves the emissions from one place to another. There are however two advantages by removing the emissions from individual cars to a larger unit. The first one is that the emissions are removed from the city centre where a lot of people live and the second advantage is the possibility to use carbon capture and storage (CCS) [1]. By using CCS electricity can be produced by fossil fuels, a technology that is well known, while not contributing further to the global warming since the formed CO_2 can be stored e.g. in porous ground or on the sea floor. With today's energy mix there are no or very small advantages of using electricity over combustible fuels since coal is the fuel that is placed on the margin [1]. This means that if one more unit of electricity should be produced, that will be done by coal since that is the most profitable option.

A suggestion for the future is to integrate electrical vehicles (EV, PEV, PHEV) into a smart grid, where the car batteries would act as an energy storage [6]. If there is a surplus of renewable energy production this energy can be stored in car batteries and then be put back into the grid when there is a deficit of renewable energy. This would lower the need for fossil fuels in the electricity production. The integration of car batteries into the grid would also remove peak production of electricity, which is often produced from fossil fuels, further contributing to the reduction of greenhouse gas emissions [1].

1.1.4 Possible issues with the PHEV technology

Since the PHEV is utilizing electricity from a battery to gain some power the consumption of gasoline will decrease. As a result, gasoline might be stored on-board the vehicle over an extended period of time. By on-board storage, the composition of the gasoline might change since volatile components will evaporate. A change in gasoline composition might influence crucial parameters such as engine start, which is not desirable. Also, the quality of the gasoline is different between summer and winter to compensate for the difference in outside temperature. For example, the fuel at the gas-station contains more volatiles during winter since the outside temperature is lower than during summer. Then another problem arises, what if the costumer fuels the vehicle during summer and still have fuel of summer quality left in the tank during winter, can this compromise engine start?

Since the PHEV technology is new to the market, no studies have been done so far to investigate if on-board storage can compromise crucial parameters such as engine start. One of the most important parameters to study is the vapor pressure, that is, the pressure of the vapor in equilibrium with its liquid. As volatile components boil off, this pressure will decrease, which might cause problems to the vehicle performance [11].

1.2 Objectives

The purpose of this thesis is to examine how the gasoline Reid vapor pressure is affected by extended on-board storage in a PHEV. The aim is to investigate how the change in vapor pressure affects important features such as engine start. The project also aims at developing a theoretical model that describes the vapor pressure as a function of different parameters such as fuel quality, temperature and fuel tank size and geometry.

1.3 Boundaries

The aim of this project is to investigate fuel systems using gasoline. Systems utilizing other type of fuels, such as diesel, will not be included in this thesis. The experiments will be restricted to only two types of gasoline blends, LEVIII and BogeyI. The main focus will be to investigate how the vapor pressure is affected by temperature cycling and only vented fuel tank systems will be tested.

1.4 Issues to be examined

- Investigate if there is a relation between the vapor pressure and amount of boiled-off hydrocarbons.
- How is the vapor pressure affected by stirring?
- How does the area between the liquid phase and gas phase affect the vapor pressure?
- Is the vapor pressure change affected by the ratio between the gas/liquid volume?
- Does the geometry of the fuel tank influence the evaporation process?
- How is the evaporation process affected on-board a vehicle?
- Construct a model that defines the vapor pressure change as a function of different parameters such as fuel quality, temperature and fuel tank size and geometry.
- Is it possible to start the internal combustion engine during all conditions? If not, under which conditions can problems with engine start occur?
- For how long time can gasoline be stored on-board a vehicle without compromising the performance of the vehicle?

2 Theory

In this section some theory is presented that will be helpful when interpreting the results. The main focus is to describe the fuel system and gasoline fuels.

2.1 The fuel system

Figure 2.1 gives an overview of the main components of the gasoline fuel system. The main task for the fuel system is to provide the engine with fuel which is done from the fuel tank via the fuel pump and feed line. The fuel tank is also connected to a canister, a filter of activated carbon. The task of the canister is to adsorb hydrocarbons that evaporate from the fuel tank during events such as refueling and when the car is parked. The canister in turn is connected to the purge valve via the purge line, which is the way to regenerate the hydrocarbons from the canister. When the internal combustion engine is running a vacuum arises that will withdraw hydrocarbons from the canister to the engine where they will be combusted, avoiding emissions of hydrocarbons to the atmosphere [12].

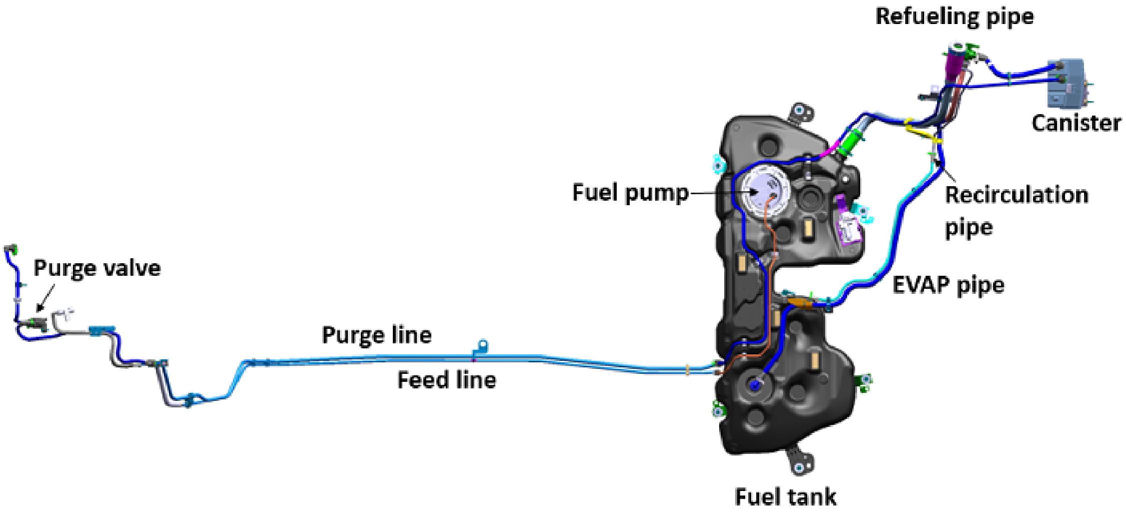


Figure 2.1: An overview of the gasoline fuel system.

The legislation for hydrocarbon emissions differs between different parts of the world. Where the legislation is less strict vented systems are allowed, which means that the fuel tank pressure is always atmospheric. If the temperature in the system increase, volatile components in the gasoline will evaporate, the gas phase will expand, and to avoid a pressure increase the evaporated hydrocarbons are expelled to the canister where they will be stored until engine start. In some parts of the world the legislation for hydrocarbon emissions are much more stringent and a different solution is required. The fuel tank system is then sealed, which means that the pressure will increase in the fuel tank as the temperature increases. Thus ideally, no hydrocarbons are transported to the canister, but are kept within the fuel tank. There are of course an upper allowed pressure limit of the system to prevent it from bursting.

The connection between the fuel tank and refilling pipe is the recirculation pipe which exists for several reasons. One of them is to reduce the flow of hydrocarbons to the canister while refueling. If the gaseous volume in the fuel tank is large while refueling, hydrocarbons will evaporate fast to saturate the gas phase. This will make the gas phase expand and the gases are transported via the recirculation pipe and back in to the fuel tank to avoid an over pressure to build up and to avoid hydrocarbons to leak out in the atmosphere.

Figure 2.2 shows a canister and its three connections. The hydrocarbons expelled from the fuel tank are entering the canister through the inlet marked with a 1. Ideally the hydrocarbons are leaving the canister through the outlet marked with a 2 by purging and are transported to the engine. A third outlet is also added that is open towards the atmosphere to prevent overpressures in the system. If the activated carbon filter is full, hydrocarbons will be vented to the atmosphere through outlet 3.

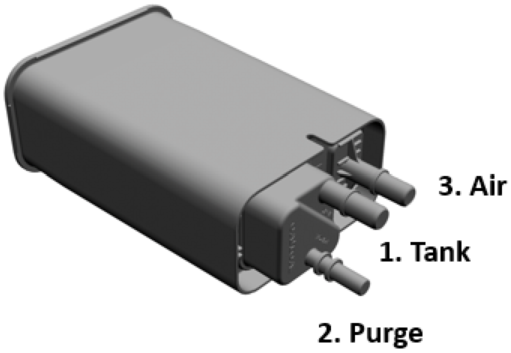
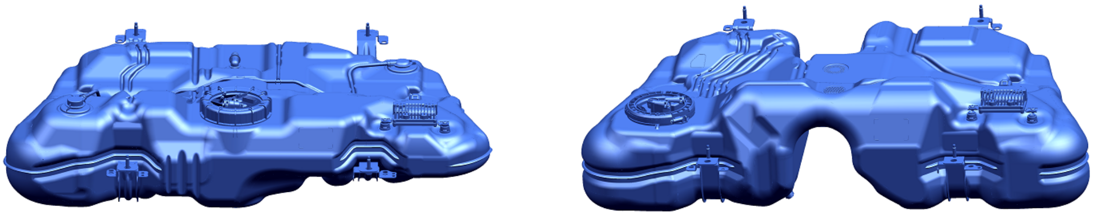


Figure 2.2: The activated carbon canister is used as a protection system and will adsorb hydrocarbons to prevent them from entering the atmosphere.

The protection system with the canister is called EVAP system which is an abbreviation for EVAPorative Control System. The adsorption process that binds the hydrocarbons to the activated carbon surface is an exothermic process, which implies that the process is ongoing even when the engine is switched off [12], [13]. The capacity of the adsorption process is limited and if the activated carbon filter is full, hydrocarbons will pass right through and out in the atmosphere. The surface area needed for the adsorption process is hence an important parameter, and the canister volume must be large enough to prevent hydrocarbon leakage. The activated carbon filter is installed to adsorb hydrocarbons, but is also adsorbing water. In a fuel system, water is supplied through the air used to purge the canister [14]. The water is adsorbed in the carbon filter, taking up space which is not desirable. Fortunately, the adsorption potential of hydrocarbons are greater than for water, resulting in desorption of water to allow hydrocarbons to adsorb instead. There are two types of adsorption processes, physical and chemical [15]. In the physical process the adsorbate accumulates by weak Van der Waals forces making it easy to desorb the adsorbate again. Chemical adsorption involves chemical bounds which are more difficult to break making it more difficult to reverse such process. Hydrocarbons and water adsorb to the activated carbon by the former phenomenon making it easy to purge the canister.

When a car is parked it will be exposed to temperature cycles over the day. The temperature increases during daytime and decreases during night time. While increasing the temperature hydrocarbons will evaporate from the fuel tank to the canister. When the temperature in the system decreases again, hydrocarbons will condensate back into liquid phase inside the fuel tank, causing an underpressure. If the underpressure is large enough it can result in back purge which means that hydrocarbons are desorbed from the canister and drawn back into the fuel tank [15].

There are three types of fuel tank geometries available, saddle shaped, flat and L-shaped. The geometry difference between a flat tank and a saddle tank is displayed in Figure 2.3. The flat fuel tank shown in Figure 2.3a is generally used in Two Wheel Drive (2WD) vehicles and the saddle shaped fuel tank shown in Figure 2.3b is normally used in All Wheel Drive (AWD) vehicles to fit the cardan shaft. The L-shape is somewhere in between these two geometries with only one saddle.



(a) Flat fuel tank

(b) Saddle shaped fuel tank

Figure 2.3: Geometry difference between fuel tanks.

2.2 Properties of liquid fuels

The basic definition of a fuel is a substance that, when heated, undergoes chemical reaction with an oxidiser to generate heat [16]. There are a lot of different properties that are important for liquid fuels, such as auto-ignition temperature, octane number (gasoline), cetane number (diesel), flash point, smoke point and vapor pressure. The parameters important for gasoline will be presented in the Gasoline section below.

The combustion of a liquid fuel happens in two steps, where the fuel is first evaporated and then combusted [16]. The evaporation process is endothermic and enough energy must be supplied for the evaporation to occur [17]. For short chained fuels, such as gasoline, the molecules are tightly bound to each other and are thus difficult to ignite thermally [16]. On the other hand the small molecules easily evaporate, causing a higher vapor pressure. The large concentration of fuel gas makes it very easy to ignite by an external source, such as a high-energy spark. If the fuel is stored over an extended time these volatile components will evaporate causing the vapor pressure to be reduced and thus, might be more difficult to ignite. Diesel fuels are heavier than gasoline and the larger molecules can easily be ignited thermally by compression.

Volvo Cars have performed testing to find a lower vapor pressure limit where it gets difficult to start the internal combustion engine (ICE) with a gasoline fuel. So far a summer fuel of low volatility and a vapor pressure of 42.4 kPa has been tested, where the fuel was successfully ignited at minus 30°C. Since the ICE was successfully started there is so far no defined lower vapor pressure limit where it might be risk of engine start failure.

2.2.1 Gasoline

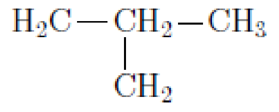
Gasoline is extracted from crude oil and consist of paraffins, olefins, iso-paraffins and aromatics that are all different types of light hydrocarbons, see Figure 2.4 for structural examples [16]. Gasoline must be volatile to be able to evaporate fast enough in the engine, but cannot be too volatile since that would be a risk when handling the fuel. To compensate for different outside temperatures the gasoline composition differs throughout the year. During winter more volatile components are added to the gasoline blend to ensure the evaporation process is fast enough. During summer the most volatile components are not added since that would give rise to an unnecessary leakage of volatile components to the atmosphere. Since hydrocarbons are highly toxic to human health the release of hydrocarbons to the atmosphere must be kept as low as possible [13].

$H_3C-CH=CH-CH_3$

Oleofins: Butene, C_4H_8

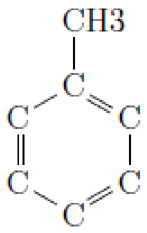
$H_3C-CH_2-CH_2-CH_3$

Paraffins: Butane, C_4H_{10}



$$\begin{array}{c} H_2C-CH_2-CH_3 \\ | \\ CH_2 \end{array}$$

Iso-paraffins: isobutane, C_4H_{10}



Aromatics: Toluene, $C_6H_5CH_3$

Figure 2.4: Four examples of molecules that are included in gasoline.

Some important properties of gasoline are auto-ignition temperature, octane number and vapor pressure. The auto-ignition temperature is the lowest temperature required to cause self-sustained combustion during atmospheric conditions in the absence of a spark [16]. This temperature is 370 °C for gasoline, why a spark is needed to ignite it. The octane number is a very important property of gasoline and describes the tendency of gasoline to experience auto-ignition as the pressure is increased. A lower octane number indicates a higher tendency to experience auto-ignition. If a part of the gasoline volume is combusted by auto-ignition a large pressure wave emerges, causing the engine to vibrate and give rise to a noise called knocking. This is not desirable, so it is crucial to have a high enough octane number to have the correct properties of the gasoline.

The main components in gasoline are paraffins and aromatics, see Figure 2.4 [18]. Paraffins are saturated linear hydrocarbons chains with good ignition performance, but can easily cause knocking. To reduce the tendency of the gasoline to knock, iso-paraffins and aromatics are added to the blend. Iso-paraffins are saturated branched hydrocarbons and aromatics are circular hydrocarbons. These compounds are less volatile than the paraffins. To further increase the knock-resisting properties, components containing oxygen can be added to the blend. Typical compounds are alcohols, such as ethanol, which also contributes to make the fuel more environmentally friendly. However, too much alcohols can damage the materials in the fuel-injection equipment and cause problems such as corrosion, so a fraction of 5-10 percent ethanol is a typical number [18].

2.2.2 Vapor pressure

The pressure of a gas in equilibrium with its liquid is called the vapor pressure of the substance [11]. In a system with two or more components there are three parameters influencing the vapor pressure: temperature, pressure and composition [11]. As the temperature in a liquid increases, the movement of the molecules increases and thus the vapor pressure increases since more molecules have high enough energy to escape the liquid. For a substance to be able to evaporate, the vapor pressure of the substance has to be higher than the surrounding gaseous pressure. This implies that a lower surrounding pressure will cause more molecules to evaporate into gaseous phase. A substance that contains a large fraction of volatile components will cause a high vapor pressure while a substance with a lot of heavy compounds will have a low vapor pressure during ambient conditions.

Since the vapor pressure is dependent of temperature where a higher temperature results in a higher vapor pressure, a lot of different standards have been developed for measuring the vapor pressure. One of them, the Reid Vapor Pressure (RVP) is defined as the absolute vapor pressure exerted at 37.8 °C (100 F) [19]. This standard is frequently used as an indication of the volatility. There are different methods available to measure the RVP. The ASTM D6378 method measure the absolute vapor pressure against a vacuum to receive the true vapor pressure [19]. ASTM D5191 is also frequently used and the resulting vapor pressure is 1 kPa lower then with the D6378 method.

All systems strives to be at equilibrium. A physical equilibrium is defined by the chemical potential as: *at equilibrium, the chemical potential of a substance is the same throughout a sample, regardless of how many phases are present* [17]. At equilibrium, the chemical potential, μ, is equal in all phases and throughout each phase. In a system with many components, the chemical potential for each component in each phase is also the same at equilibrium. If the chemical potential is not equal between two points, a flow will occur from the point with highest potential to the point with lowest potential. This flow will result in a lowering of the Gibbs free energy of the system according to equation 2.1, where dG is the change in Gibbs energy, μ is the chemical potential in point 1 and 2, and dn is the resulting mole flow to equal the chemical potentials. Only when the chemical potentials are equal and the Gibbs energy is equal to zero, the system is in equilibrium.

$$dG = (\mu_2 - \mu_1)dn \tag{2.1}$$

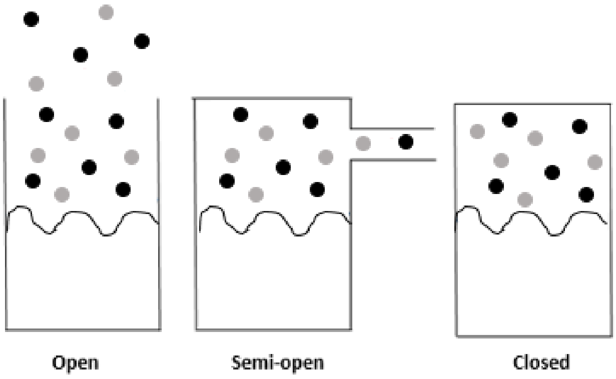


Figure 2.5: Schematic picture of open, semi-open and closed systems.

There are three possible systems available, open, semi-open and closed, and they are all demonstrated by schematic pictures in Figure 2.5. All systems are trying to establish an equilibrium between the liquid and gaseous phase, but the results becomes a bit different. In an open system evaporated molecules will expand freely into the surrounding atmosphere [17]. As the vapor moves out in the atmosphere the concentration gets lower by the liquid surface, causing even more volatile components to evaporate to try to maintain the equilibrium. In a closed system the molecules cannot escape but will be trapped inside the limited volume and as a result an equilibrium will be established between the two phases. The evaporation process will cause the pressure in the container to increase. In a semi-open system liquid molecules will evaporate to saturate the gaseous phase. Since the system is open towards the atmosphere the same amount that is evaporated is expelled to the atmosphere to avoid a pressure increase. Additionally, if the temperature is increased in the system the gaseous phase will expand, causing even more molecules to be expelled from the container. If the vapor pressure of the substance in the container is lower than the atmospheric pressure there is no driving force that will allow the molecules to escape the container once the equilibrium has been established.

When raising the temperature in open and semi-open systems, the liquid will start to boil when the vapor pressure is the same as the external pressure [11]. In a closed system the liquid will not start to boil as the temperate is increasing. Instead both the vapor pressure and vapor density will increase since more molecules are in gaseous phase, and the density of the liquid phase will decrease somewhat because of the increasing movement of the molecules.

2.3 The ideal gas law

The properties of gases at low pressures can be described by the ideal gas law, see equation 2.2, where P is the gas pressure, V the gas volume, n the number of moles, R the gas constant equal to 8.314 $J/molK$ and T the temperature of the gas [17]. At low pressures, all gases more or less obey the ideal gas law, where atmospheric pressure at sea level counts as low pressure. A mixture of ideal gases behaves like a single perfect gas where the total pressure of the mixture is described as the sum of the partial pressure of each component, see equation 2.3.

$$PV = nRT \tag{2.2}$$

$$p_{tot} = p_1 + p_2 + ... + p_n \tag{2.3}$$

By assuming that gasoline vapor obey the ideal gas law the theoretical mass expelled from the fuel tank to the canister during a temperature increase can be calculated as described below. This also includes the assumption that the gasoline is not boiling inside the fuel tank. There are two effects that contribute to the expelled hydrocarbon mass. Firstly, more hydrocarbons will evaporate to saturate the warmer gas phase and secondly, the gas phase will expand according to the gas law.

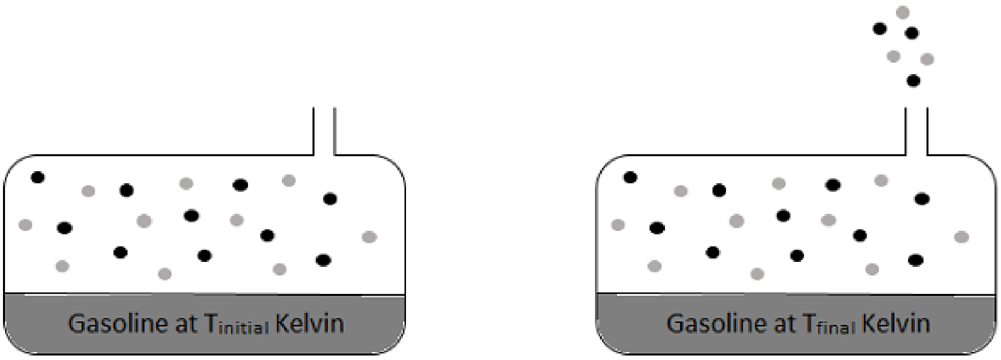
The total pressure inside the fuel tank is always atmospheric since the system is open towards the atmosphere. The pressure exerted by the fuel vapor is the same as the vapor pressure when the system is at equilibrium. The gasoline partial pressure will always be the vapor pressure and the air partial pressure must adjust itself to always have a atmospheric total pressure in the fuel tank. When the temperature is increased from $T_{initial}$ to T_{final} the fuel vapor pressure will increase causing fuel to evaporate. At the same time the gas phase will expand due to the higher molecular motion. To allow the gasoline partial pressure to increase but still not allow the total pressure to increase some air must be expelled from the container. But since the gas phase is a mixture of both air and fuel some fuel molecules will be expelled as well. The amount that will leave the fuel tank is described by the air mole difference, see equation 2.4.

$$\Delta n = n_{air,initial} - n_{air,final} \tag{2.4}$$

Since the expelled gas is a mixture of fuel and air a mean fuel concentration of the gas is calculated according to equation 2.5. The amount of expelled hydrocarbons is then calculated from equation 2.6, where $M_{fuelgas}$ is the average molar mass of fuel vapor which is approximately equal to 69 g/mol [20].

$$c_{HC} = \frac{n_{fuel,initial} + n_{fuel,final}}{n_{air,initial} + n_{air,final}} \; (mol\ HC/mol\ air) \tag{2.5}$$

$$m_{HC} = \Delta n \cdot c_{HC} \cdot M_{fuelgas} \tag{2.6}$$



$$P_{tot} = 101.3\ kPa$$
$$P_{fuel,initial} = P_{Vapor\ pressure\ at\ T_{initial}}$$
$$P_{air,initial} = P_{tot} - P_{fuel,initial}$$
$$R = 8.314\ J/molK$$
$$T_{initial}\ (K)$$
$$n_{fuel,initial} = \frac{P_{fuel,initial} \cdot V}{R \cdot T_{initial}}$$
$$n_{air,initial} = \frac{P_{air,initial} \cdot V}{R \cdot T_{initial}}$$

$$P_{tot} = 101.3\ kPa$$
$$P_{fuel,final} = P_{Vapor\ pressure\ at\ T_{final}}$$
$$P_{air,final} = P_{tot} - P_{fuel,final}$$
$$R = 8.314\ J/molK$$
$$T_{final}\ (K)$$
$$n_{fuel,final} = \frac{P_{fuel,final} \cdot V}{R \cdot T_{final}}$$
$$n_{air,final} = \frac{P_{air,final} \cdot V}{R \cdot T_{final}}$$

Figure 2.6: Effects of a temperature increase in a vented fuel tank.

2.4 Heat transfer

There are two types of heat transfer important to this study, convection and conduction. The former is energy exchange between a surface and an adjacent fluid and the latter is due to molecular interactions [21]. The heat convection is described by equation 2.7 and the heat conduction be equation 2.8, where h is the convective heat transfer coefficient in W/m^2K and k is the thermal conductivity in W/mK. ΔT is the temperature difference, A is the area and q is the resulting heat transfer. The heat conduction is defined in one direction and is thus denoted with a subscript x.

$$q = hA\Delta T \tag{2.7}$$

$$q_x = -kA\frac{dT}{dx} \tag{2.8}$$

The two equations above are often combined to describe the heat transport in real systems [21]. Equation 2.9 and Figure 2.7 describe the heat transfer from one fluid to another via a wall with thickness L. As shown the heat transfer is described as the total temperature difference between the hot and cold side. As a result, a larger temperature difference will result in a greater heat transport. It can also be noted that a larger area will result in a greater heat transfer.

$$q_{tot} = \frac{T_h - T_c}{\frac{1}{h_h \cdot A} + \frac{L}{k \cdot A} + \frac{1}{h_c \cdot A}} \tag{2.9}$$

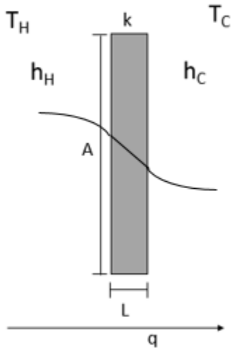


Figure 2.7: Schematic picture of the heat transport from a hot fluid to a cold fluid through a wall of thickness L.

A third type of heat transfer is radiation described by equation 2.10 where A is the area, T is the temperature and σ is the Stefan-Boltzmann constant [21]. Radiation will not be present in the experiments performed during this thesis, but is of importance for fuel tanks on-board vehicles since the asphalt in the roads will radiate heat.

$$q = A\sigma T^4 \tag{2.10}$$

3 Materials

Two gasoline blends were used to perform the experiments during this thesis, LEVIII and BogeyI. Some physical data is presented in table 3.1 for the fuel blends.

Table 3.1: Physical data for LEVIII and BogeyI gasoline blends.

Fuel type	Specified RVP (kPa)	Density (g/litre)
LEVIII	48.6-50.6	749
BogeyI	90-96	734

The volumes of the jerrycan and the fuel tanks used in the study are presented in Table 3.2. There is a certain volume available for liquid gasoline in the containers, but there is also an extra expansion volume adding up to the total volume.

Table 3.2: Volumes of the jerrycan and fuel tanks.

Container	Volume available for liquid (litre)	Expansion volume (litre)	Total volume (litre)
Jerrycan	20	1.5	21.5
2WD fuel tank	71	13.7	84.7
AWD fuel tank	71	13.7	84.7
Vehicle fuel tank	71	3	74

The canisters used in this study are presented in Table 3.3. The SPA canister was used in the experiment where evaporation was caused by gas composition change and the EUCD canisters in all other experiments. Bax1500 is better at adsorbing hydrocarbons fast but can start to desorb again after a few days. The Bax1100 bind the hydrocarbons tighter but not as fast.

Table 3.3: Properties of the canisters.

Canister	Activated carbon volume	Activated carbon type
EUCD	2.1 litres	Bax1500
SPA	1.7 litres + 0.8 litres	Bax1500 + Bax1100 + scrubber

The canister weight data was collected in a program designed in MATLAB. Since the computers used to log the data did not have access to MATLAB the code was rewritten to an exe format. The MATLAB code and exe-file is valid for Sartorius LP5200P scales. To log the temperatures a program named VMD Comtest was used for the experiments with fuel tanks and the vehicle and EasyView for experiments with the jerrycan.

The vapor pressure gauge used to measure the vapor pressure is a MINIVAP VPX-pert. The gauge measure the vapor pressure against a vacuum. Before injecting the sample, the measuring chamber is rinsed three times with the sample fluid. A sample of 1 mL is then injected into the 5 mL measuring chamber, and a piston is withdrawn in three steps to create the vacuum.

4 Methodology

The study was divided into four parts where each part led one step closer to reality. At first an expression was established that describes the vapor pressure as a function of evaporated mass. Secondly a lot of experiments were performed with a stainless steel jerrycan to investigate how different parameters such as exposed gasoline area affect the evaporation process. The experiments in the third part were performed in different geometry fuel tanks to investigate how the evaporation process was affected. As a fourth and final part the fuel degradation was studied on-board a vehicle. The experiments were performed with two different gasoline fuels, LEVIII with an initial vapor pressure of approximately 48 kPa and BogeyI, with an initial vapor pressure of approximately 90 kPa.

4.1 Vapor pressure as a function of evaporated amount of gasoline in an open system

To establish the relation between vapor pressure and evaporated amount of gasoline four tests were performed in an open system, two with LEVIII and two with BogeyI. The difference between the two tests with the same gasoline blend was the sampling method used to tap the gasoline from the storage barrel. With the first method the fuel was tapped using a fuel pistol and with the second method the gasoline was first pumped through a cooling coil to lower the vapor pressure close to zero. This method ensures that almost no hydrocarbons evaporate during the tapping process, and consequently, the vapor pressure was not affected.

Figure 4.1: The vapor pressure gauge to the left performing a vapor pressure test of the gasoline in the glass bottle to the right.

The gasoline was tapped to a glass bottle that was placed on a scale in a fume hood to register the initial weight. The bottle was shaken a few times to ensure a homogeneous blend and the vapor pressure was measured with a vapor pressure gauge, see Figure 4.1. To perform the measurement, the cover was removed from the bottle and replaced with some aluminium foil to avoid hydrocarbon leakage. The test was performed at 37.8 °C (100 F) with the ASTM D6378 method to receive the Reid Vapor Pressure (RVP). Immediately after the vapor pressure measurement the new weight was registered since each measurement requires about 6 grams of gasoline, and this weight loss must be accounted for. In the two cases with cooled gasoline, the bottle was now placed in a warm water bath to increase the temperature of the gasoline up to room temperature. The experiment was then continued in the same way for all four cases. The glass bottle was kept open to allow hydrocarbons to evaporate into the fume hood. Compressed air was bubbled through the gasoline to speed up the evaporation process and to retain a well-mixed blend, see Figure 4.2. When about 10 grams had been evaporated the cover was put back on and the bottle was shaken a few times to make sure the blend was homogeneous, the weight was registered and the vapor pressure was measured in the same way as described above. This procedure continued until the vapor pressure reached about 5 kPa.

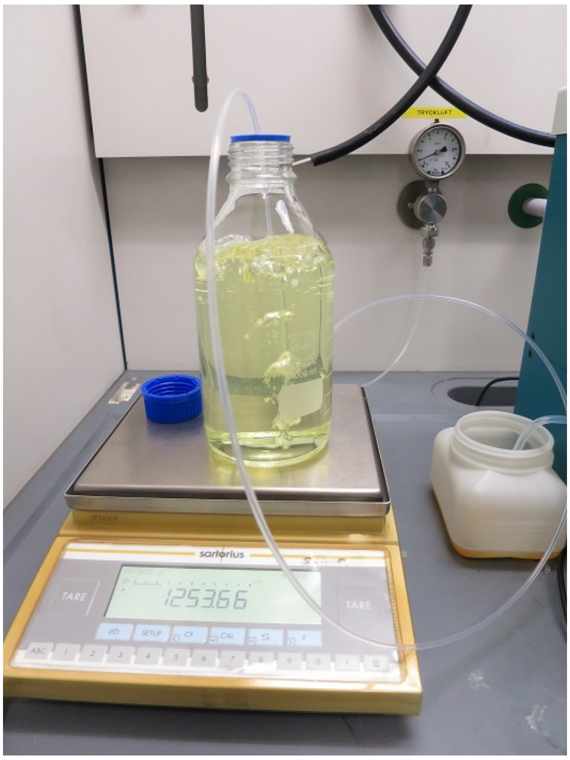


Figure 4.2: Gasoline is boiled off by bubbling compressed air through it.

To ensure that no external factors were affecting the results, the experiment was also performed in two alternative way with LEVIII. Since the vapor pressure gauge used 6 grams of gasoline per measurement, an experiment was performed to investigate if it affects the results. A cold gasoline sample was poured into four different beakers and 0, 1.4, 2.9 and 4.9 mass percent was evaporated from the different beakers.

The vapor pressure was then measured for each beaker. A second experiment was performed to investigate if the process is significantly dependent of temperature. A glass bottle with LEVIII gasoline was placed on a heating plate and the gasoline was allowed to evaporate in to the fume hood at $35 - 45\,°C$ by using compressed air and 5 data points were obtained.

To be able to study the fuel degradation on a molecular level samples were prepared now and then during the evaporation process and analysed in a gas chromatograph (GC) with a Flame Ionization Detector (FID) to receive the composition of the gasoline as it was degraded. The column that was used is 60 meters long with a diameter of 320 micrometres, and has a non-polar stationary phase with a thickness of 3 micrometres. The oven had an initial temperature of 25 °C that was kept for 10 minutes, the temperature was then increased by 10°C/minute until it reached 250°C and then kept there for 10 minutes. Two of the most volatile components in gasoline are butane and pentane. To be able to decide which peaks in the chromatogram that belongs to these two compounds a standard solution was prepared with butane and pentane dissolved in heptane. The standard was also analysed in the GC and put into the same chromatogram as the respective gasoline blend.

4.2 Fuel degradation by temperature variations

The degradation process was studied by exposing gasoline to temperature variations using a Sealed Housing for Evaporative Determination, from here on denoted SHED. The SHED is a chamber where the temperature can be varied under constant pressure since the chamber will compensate for a volume increase/decrease due to the temperature variations. Experiments were performed with a stainless steel jerrycan, individual fuel tanks and a fuel tank on-board a vehicle. The jerrycan/fuel tanks were connected to a canister that was placed on a scale, continuously measuring the weight. When the temperature in the system was increased more hydrocarbons had enough energy to escape the liquid. Also, the increased temperature was causing the gas phase inside the jerrycan to expand according to the ideal gas law. To avoid an overpressure in the system the evaporated hydrocarbons were expelled to the canister where they were adsorbed. Thus by continuously weighing the canister the evaporation process could be studied. A few thermocouples were also added to each array to be able to study the temperatures both in the SHED and at different locations inside the jerrycan/fuel tanks. Both the canister weight and the temperatures were measured once a minute during the whole experiments.

The jerrycan/fuel tanks were exposed to temperature variations as described by schematic pictures in Figure 4.3. To the left a CARB temperature cycle is described and to the right a temperature step. The temperature in the CARB cycle is increased during twelve hours from 18.33 °C to 40.55 °C and then decreasing back to 18.33 °C again to simulate the temperature variations over the day, for further details, see the Appendix B.2. With the temperature step the temperature was increased immediately from 18.33 °C to 40.55 °C. The CARB temperature cycle is frequently used by the car industry since it is some sort of worst realistic case that could occur.

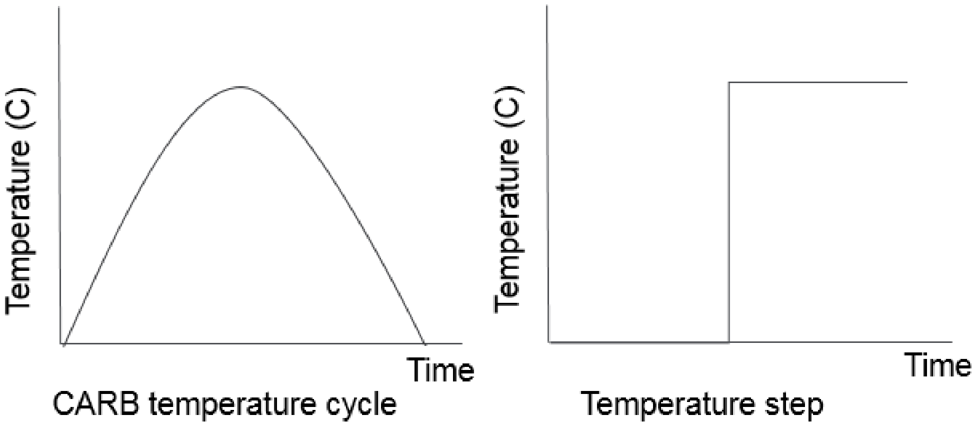


Figure 4.3: Schematic picture of a CARB temperature cycle and a temperature step. The minimum and maximum temperatures are equal to 18.33 °C and 40.55 °C.

4.2.1 Experiments with a stainless steel jerrycan

During experiments with fuel tanks and vehicles there are a lot of parameters that are influencing the results that are difficult to control. The car is shielding the fuel tank and it is difficult to know where the fuel is situated inside a saddle shaped fuel tank. To gain more control of the experiments a stainless steel jerrycan was used to simulate a fuel tank, see Figure 4.4. Stainless steel was chosen to have the possibility to use a magnetic stirrer to simulate the movement of the gasoline in a fuel tank while driving the vehicle. The jerrycan was modified according to Figure 4.4. Two thermocouples were inserted into the jerrycan, one in liquid phase and one in gaseous phase, and an outlet for connecting the gaseous phase of the jerrycan to a canister was added. Since only one thermocouple was used in each phase it is important to remember that the measured temperatures only describe that point and not the entire bulk phase.

The jerrycan was filled with gasoline, placed in a mini-SHED and coupled to a canister placed on a scale in a fume hood via a Teflon hose. Teflon was chosen since the material can withstand the gasoline. To start with, the jerrycan was exposed to a temperature step instead of the CARB temperature cycle. This was done to allow the system to reach equilibrium at both temperatures which should allow a maximum amount of hydrocarbons to evaporate. Before the experiment started the canister and gasoline weights were registered and the vapor pressure was measured. When the experiment was finished the new weights were registered together with the new vapor pressure.

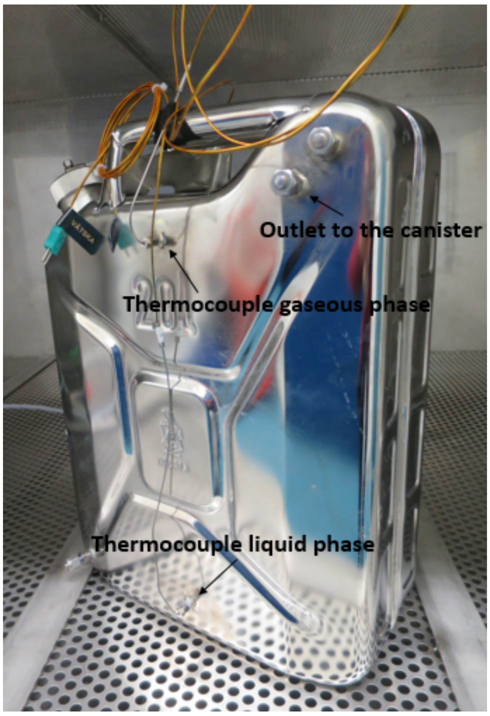


Figure 4.4: The stainless steel jerrycan that was used in the experiments.

The Teflon hose between the jerrycan and the canister was several meters long and the majority of it was placed outside the mini-SHED. To prevent condensation of hydrocarbons in the hose, warm ambient air from the mini-SHED was pumped through the system together with the hydrocarbons. After the first experiment it was evident that ambient air was a bad choice of carrier gas, why it was substituted with compressed air. Also, the thermocouple measuring the mini-SHED air temperature was replaced since it seemed to measure the temperature incorrectly. These changes gave great improvements of the results.

When performing a step the temperature was first set to 18.33 °C and kept there for approximately 6 hours to make sure thermal equilibrium was established. The temperature was then raised to 40.55 °C and kept there for at least 16 hours to again make sure thermal equilibrium was established. The temperature step was used to gain a worst case, since the system was allowed to reach equilibrium. In reality, the temperature is increasing during daytime and decreasing during night time and equilibrium might not be established, why it is more realistic to use a temperature cycle to describe this behaviour. When performing CARB temperature cycles the temperature was first set to 18.33 °C and kept there for 6 hours to have thermal equilibrium in all phases. Then either one or three cycles were performed.

The purpose with the jerrycan experiments was to investigate how different parameters affect the evaporation process. The parameters that were varied were the exposed area between the two phases, the ratio between liquid and gaseous phase inside the jerrycan, temperature steps versus temperature cycles and stirring versus no stirring. The time to reach equilibrium was studied and also how well the temperature of the gasoline follows the surrounding temperature. One experiment was also performed to investigate how two half temperature steps relate to a full step.

By varying the area between the two phases while keeping the liquid volume constant the area-to-volume ratio was also changed as explained by Figure 4.5. The area in area-to-volume ratio is the area of the jerrycan that was exposed to the surrounding, through where the heat transport occur, and not the area between liquid and gaseous phase inside the jerrycan. This ratio was also affected by varying the liquid volume while keeping the surface area constant.

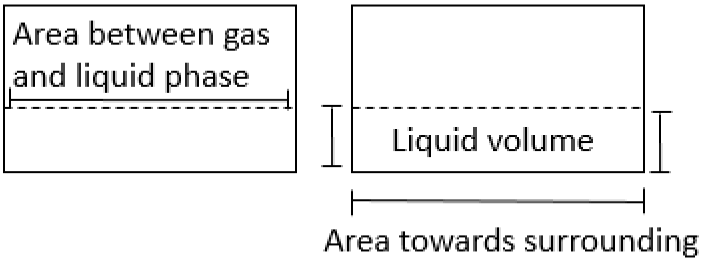


Figure 4.5: Schematic picture of the definitions of area and area-to-volume ratio.

Table 4.1: Performed experiments with the stainless steel jerrycan. A liquid volume of 8 litres corresponds to 40 vol%.

Fuel type	Liquid volume	Stirring	Orientation	Temperature variation
LEVIII	8 litres	No	Standing up	Step
LEVIII	8 litres	No	Standing up	Step
LEVIII	8 litres	No	Lying down	Step
LEVIII	4 litres	No	Lying down	Step
LEVIII	12 litres	No	Lying down	Step
LEVIII	8 litres	No	Standing up	Cycle, 24 h
LEVIII	8 litres	No	Lying down	Cycle, 24 h
LEVIII	8 litres	No	Standing up	Cycle, 72 h
LEVIII	8 litres	No	Lying down	Cycle, 72 h
LEVIII	8 litres	No	Lying down	Half step, first half
LEVIII	8 litres	No	Lying down	Half step, second half
LEVIII	8 litres	Yes	Lying down	Step
BogeyI	8 litres	No	Lying down	Step

All the performed experiments with the stainless steel jerrycan are presented in Table 4.1. A liquid volume of 8 litres corresponds to 40 % of the jerrycan volume and was chosen since EVAP-testing are generally performed with this volume. The fuel was exchanged between each experiment to always have a fresh fuel with high initial vapor pressure. To investigate how the evaporation process was affected over time, a longer experiment was also performed with a regular jerrycan. The jerrycan was filled with 4 litres (20 vol%) of gasoline. An outlet in gaseous phase was added to transport the expelled hydrocarbons to the fume hood where they were vented. The jerrycan was placed in the SHED together with the stainless steel jerrycan and was exposed to the same steps/cycles. Now and then the weight of the gasoline was measured together with the vapor pressure to follow the fuel degradation over time.

The canister performance is lowered as more and more hydrocarbons are adsorbed to the activated carbon surface. To minimize the influence of this parameter the canisters were purged with compressed air with a flow of 2 litres/minute for at least 24 hours before starting an experiment. By doing so both hydrocarbons and water were desorbed from the activated carbon surface. An initial presence of water might result in desorption when more hydrocarbons are transported to the canister. That would result in a weight decrease which would interfere with the results. Normally the purge is caused by pulling the hydrocarbons from the canister but with the method used here the hydrocarbons are pushed through the canister. This method of purging was used throughout all the experiments during this thesis.

4.2.2 Relation between evaporation and the geometry of the fuel tank

To get a step closer to reality, experiments were performed with fuel tanks. To perform the experiments one AWD and one 2WD fuel tank was placed in the SHED and connected to one canister each, see Figure 4.6. Each canister was placed on a scale, which in turn was placed in a pallet to protect the scale from the air flow in the SHED. Since the canister was placed at some distance from the fuel tank an extra prolonged hose had to be added to the array. A few thermocouples were added to each fuel tank. In the 2WD tank they were placed at 15 mm, 35 mm and 65 mm respectively from the bottom of the tank to measure the liquid temperature. One thermocouple was also placed 15 mm from the top of the tank to measure the gaseous temperature inside the tank, see the top image in Figure 4.7. In the AWD fuel tank the thermocouples were placed at 15 mm, 35 mm, 65 mm and 130 mm from the bottom respectively, and one 15 mm from the top, see the bottom image in Figure 4.7. The thermocouples were used to investigate if the temperature was varying throughout the bulk phase. The position of the thermocouples was chosen based on tank tables that describe the liquid height in the fuel tanks as a function of liquid volume. The positions were chosen in a way that allowed experiments with both 20 % and 40 % liquid volume. The performed experiments are presented in Table 4.2.

The different gasoline volumes were decided based on two criteria. The first one was to utilize the geometry difference, so the AWD fuel tank should only have gasoline present in one of the saddles resulting in a small area between liquid and gaseous phase and a small area-to-volume ratio. This could then be compared with a large surface area and area-to-volume ratio that was achieved in the 2WD fuel tank. The second parameter was that there had to be enough gasoline in the fuel tanks to be able to measure the liquid temperature properly. The thermocouples should not be placed too close to the fuel tank walls since the measured temperature might then be influenced by other parameters than just the gasoline temperature. This could mainly be a problem in the 2WD fuel tank since the area is greater there. These two conditions gave an interval of 6-35 litres and to have some margins, 20 vol% and 40 vol% was chosen, that is, 14.2 and 28.4 litres respectively. 40 vol% was also chosen since that is a standard volume when performing EVAP-testing.

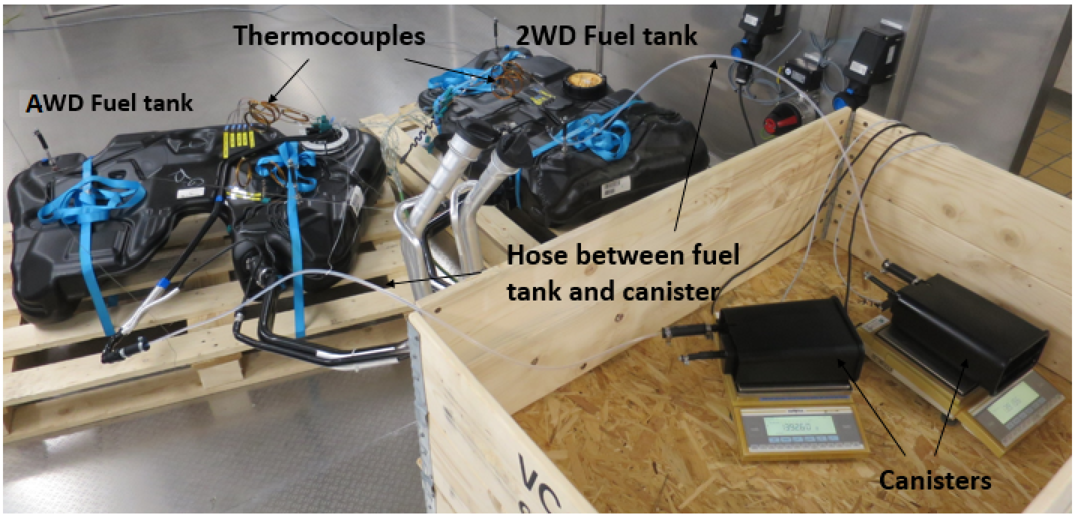


Figure 4.6: The experimental setup used to perform the experiments with fuel tanks.

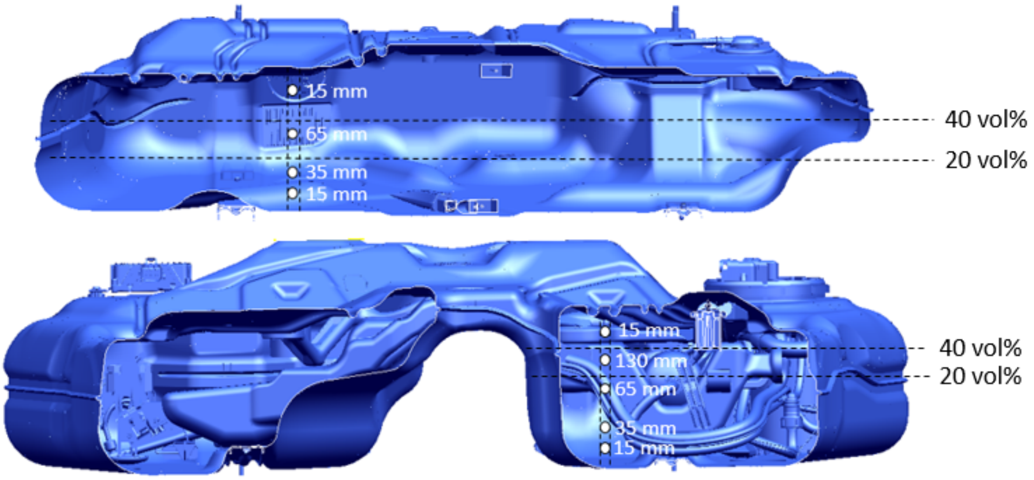


Figure 4.7: A schematic picture of the placement of the thermocouples in the fuel tanks.

To make sure all the gasoline was placed in the same saddle in the AWD fuel tank it was tilted before starting the experiment so that any gasoline in the second saddle was transferred to the correct side. This was extra important when the fuel tank was moved a long way from the refiling station to the SHED. The canister weight and vapor pressure were registered both prior to and after each experiment. In these experiments the weight of the liquid gasoline could not be measured as it could with the jerrycan. Instead it was calculated by multiplying the gasoline volume with its density. This was also done for the jerrycan and the error was only about 0.5 % which is assumed to be acceptable. The gasoline was substituted with fresh fuel before each experiment. The working capacity of the canister is approximately 130 grams of hydrocarbons so in experiments with LEVIII longer than 72 hours, the canister was substituted for a fresh one. With BogeyI the canister had to be exchanged after every cycle.

Table 4.2: Performed experiments with fuel tanks.

Fuel type	Liquid volume	Dimension	Temperature variation
LEVIII	14.2 litres (20 %)	2WD	CARB-cycle, 72 h
LEVIII	14.2 litres (20 %)	AWD	CARB-cycle, 72 h
LEVIII	28.4 litres (40 %)	2WD	CARB-cycle, 120 h
LEVIII	28.4 litres (40 %)	AWD	CARB-cycle, 120 h
BogeyI	28.4 litres (40 %)	2WD	CARB-cycle, 96 h
BogeyI	28.4 litres (40 %)	AWD	CARB-cycle, 96 h

4.2.3 Fuel degradation on-board a vehicle

So far the study has been focusing on understanding the evaporation process and investigating how different parameters influence the fuel degradation. As a final part of the thesis a few experiments were performed with a vehicle to see how the evaporation process was affected by on-board storage. A Volvo XC90 with a saddle shaped fuel tank was used. To be able to continuously measure the canister weight an external canister was used. The hose between the fuel tank and the car canister was disconnected, and an extended hose was added between the fuel tank and the external canister as shown in Figure 4.8. The fuel tank was prepped with two thermocouples, one in liquid phase placed 15 mm from the bottom of the tank and one in gaseous phase placed 15 mm from the top. One thermocouple was also placed in the SHED to measure the surrounding temperature.

The fuel tank was filled with 28.4 litres (40 vol%) of LEVIII gasoline. The gasoline was not changed between the experiments since such a small amount was expelled to the canister each day. When performing the experiments with individual fuel tanks the entire liquid phase was placed in one of the saddles by tilting the fuel tank to gain a better control of the experiments. In these experiments that was not possible and the fuel distribution in the fuel tank was unknown, even though the level sensor in the fuel tank gave an indication that all the gasoline was placed in the same saddle.

Figure 4.8: The car canister is located by the right rear wheel. An extended hose was added to be able to place an external canister on a scale.

The performed experiments are presented in Table 4.3. At first the scale was placed inside the SHED as shown in Figure 4.8 which gave very strange looking results. It seemed like the evaporation process was proceeding several hours after the temperature reached its maximum level. To try to find an explanation to this behavior the flow from the fuel tank was directed to a Flame Ionization Detector (FID) instead of the canister to investigate if there was a flow of hydrocarbons when the scale signal proposed so. To make sure the system was not leaking the recirculation pipe, described in the theory chapter, was disconnected. Two experiments were performed in this way. In the first experiment the flow was directed to the FID and in the second the flow was directed to the canister during a two day CARB cycle. The original experiment was also performed again to make sure the results were repeatable. At last one experiment was performed in the same way as with the jerrycan, with the scale and canister located outside the SHED, to investigate if the temperature variations inside the SHED was affecting the setup. Compressed air was pumped through the hose in the same way as described in chapter 4.2.1 to avoid condensation.

Table 4.3: Performed experiments with the vehicle.

Fuel type	Temperature variation	Measuring method	Recirculation pipe
LEVIII	CARB-cycle, 72 h	Scale	open
LEVIII	CARB-cycle, 24 h	FID	open
LEVIII	CARB-cycle, 24 h	FID	closed
LEVIII	CARB-cycle, 48 h	Scale	closed
LEVIII	CARB-cycle, 72 h	Scale	open
LEVIII	CARB-cycle, 72 h	Scale, outside SHED	open

4.3 Fuel degradation by change of gas phase composition

In an attempt to speed up the evaporation process further to study the fuel degradation over time, one experiment was performed where the gas phase composition in the fuel tank was changed. The experimental setup is shown in Figure 4.9.

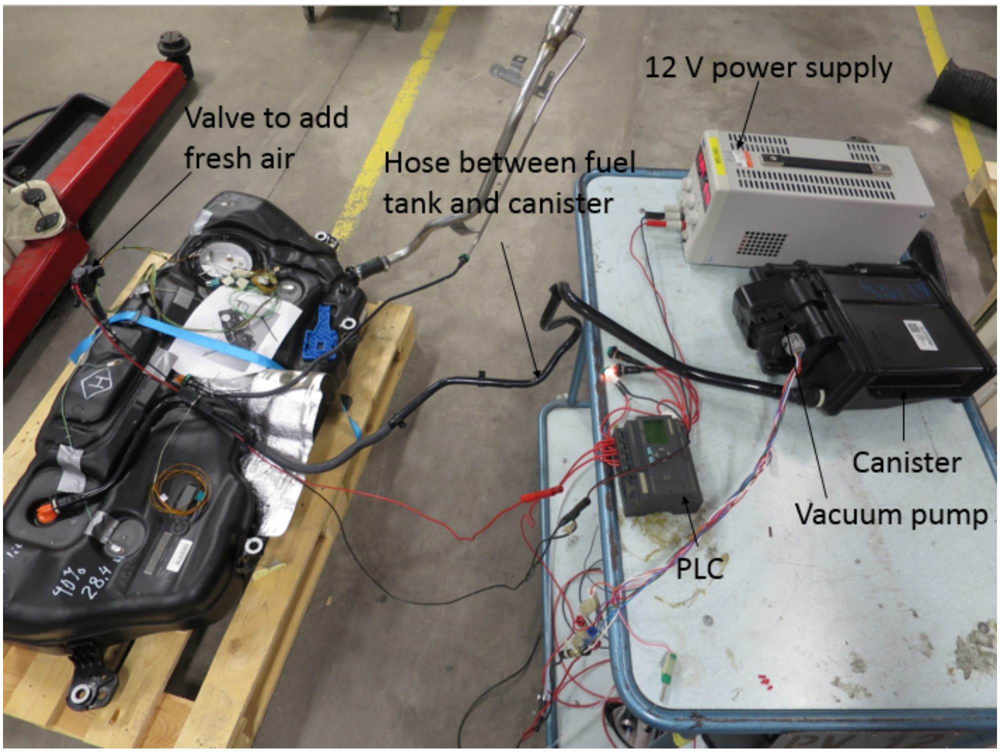


Figure 4.9: The experimental setup used to speed up the evaporation process to study the fuel degradation over an extended time.

A programmable logic controller (PLC) was programmed according to Figure 4.10 to control a vacuum pump and a valve connected to the fuel tank. A canister was also connected to the setup to adsorb the expelled hydrocarbons, but for this experiment the canister weight was not measured continuously. The AWD fuel tank was filled with 14.2 litres (20 vol%) of gasoline in one of the saddles. The setup described by the control-scheme works as follow. When starting the PLC the vacuum pump was turned on for 15 minutes causing an under pressure in the fuel tank. Five seconds before the pump was turned off the valve was opened to allow fresh air to enter the fuel tank. The valve was kept open during one minute before closing again and the system was left switched off for 14 minutes and 5 seconds before starting another cycle. The reason for opening the valve a few seconds before turning of the vacuum pump was to avoid back purge. The fresh air caused evaporation of hydrocarbons to saturate the gaseous phase which in turn was causing the gaseous volume to expand, transporting hydrocarbons to the canister where they were adsorbed. Because of the fast evaporation process the canister had to be replaced twice a day during the first five days and then once every 24 hours. The canister weight was registered both prior to and after it was connected to the setup and in that way the evaporated amount was measured. Each time the canister was substituted for a fresh one a vapor pressure sample was collected to follow the degradation. While one canister was used in the experiment the other was purged with compressed air in the same way as described in chapter 4.2.1.

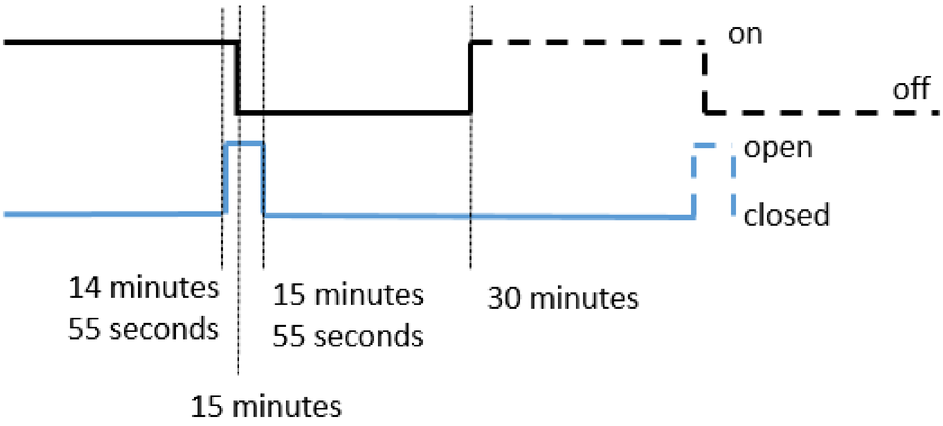


Figure 4.10: The control-scheme used to program the PLC. The upper line represent the vacuum pump and the lower line the valve used to add fresh air to the fuel tank.

4.4 Sensitivity analysis

A lot of parameters were a bit uncertain in the experiments and to gain better understanding for how these parameters influence the results some sensitivity analyses were performed.

The three thermocouples used in the jerrycan experiments were tested to investigate their accuracy. The PT100-sensor in the mini-SHED was used to do this. The three thermocouples were placed close to the sensor and five temperature steps were performed at 20 °C, 25 °C, 30 °C, 35 °C and 40 °C. The temperature was allowed to stabilize at each step for a few hours and then a mean value was calculated from the stabilized values.

When taking the vapor pressure sample it is impossible to know where in the bulk phase the sampling occurs. To investigate if this affected the results a glass bottle filled with gasoline was left open in a fume hood for 18 hours and then two vapor pressure samples was collected, one from the top and one from the bottom of the bottle. Also, three samples were collected after each other from the jerrycan and analysed.

The system with the jerrycan was leaking to some extent in all the experiments. This was noticed since the weight of the gasoline was decreasing more than the canister weight increased. There were two options to where the leakage could occur, through the rubber gasket in the cap to the jerrycan or it did just go straight through the canister without adsorbing. To test the former a gauge that detect hydrocarbons was held close to the cap. To test the second option the hydrocarbon gauge was held by the canister outlet and the out coming flow from the canister was also led via a FID to detect any hydrocarbons escaping the canister.

To decide the accuracy of the results from the vapor pressure gauge, test were performed using n-Pentane with a high purity and well known vapor pressure. The vapor pressure was measured 11 times at 37.8 °C to receive the RVP. According to the manufacturer the measured value should be within the range of $\pm 1.2\,kPa$ of the true value.

5 Results and discussion

The experimental results are presented in this section and are discussed along the way. The results are presented in the same order as described in the methodology chapter.

5.1 Vapor pressure as a function of evaporated amount of gasoline in an open system

The vapor pressure as a function of evaporated mass of gasoline is presented in Figure 5.1 for both BogeyI and LEVIII. The slope of the BogeyI curve is steep and quite constant until about 30 mass% has been evaporated with a minor change in slope at about 16 mass%. Then the slope is leveled out before making a final drop at the end. The slope of the LEVIII curve is steep in the beginning and then flatten out when about 12 mass% has been evaporated. The slope is constant until 36 mass% has been evaporated then the slope drops very fast to again be constant. The change in slope is described by the gasoline composition. Initially there are a lot of volatile components in the gasoline that easily evaporates in to the atmosphere. When the most volatile components with highest vapor pressure has evaporated only the heavier ones remain which are affecting the vapor pressure to a lesser extent, resulting in a reduced slope of the curves. Since BogeyI has a higher initial content of volatile components the vapor pressure was reduced faster than for LEVIII. Note that all gasoline blends will have their own individual evaporation curve. Since BogeyI and LEVIII are very high and low volatile fuels respectively, the curves for most other fuels are expected to lie between the two curves displayed below.

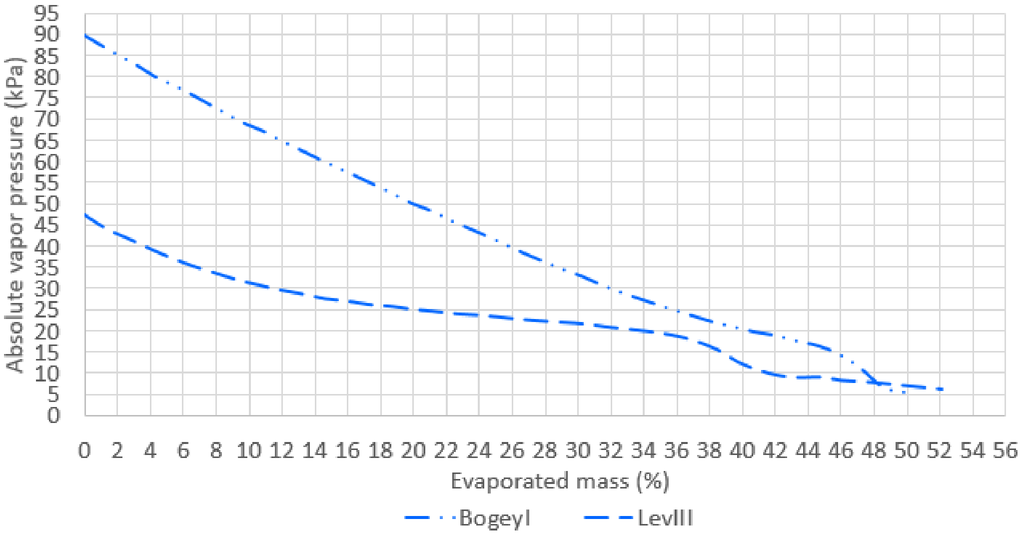


Figure 5.1: The evaporation curve for BogeyI and LEVIII.

Figure 5.2 shows the molecular composition of initial and aged LEVIII fuel obtained by gas chromatography (GC). The blue curves are LEVIII and the red curve in the upper chromatogram is the standard containing butane, pentane and heptane. As shown in the lower chromatogram the most volatile components have evaporated and only the heavier, less volatile components are still present. This indicates that the evaporation process goes from left to right in the chromatogram allowing the most volatile components with highest vapor pressure to evaporate first, confirming the theory of the reducing slope observed in Figure 5.1. A similar graph for BogeyI is included in the Appendix A.1, and shows the same behaviour. Note that the scale of the y-axis differs between the two chromatograms in Figure 5.2 and also between the graphs for BogeyI. This is only due to different sample sizes and does not give absolute values of the content of different components between the samples. The graphs only describe the evaporation process.

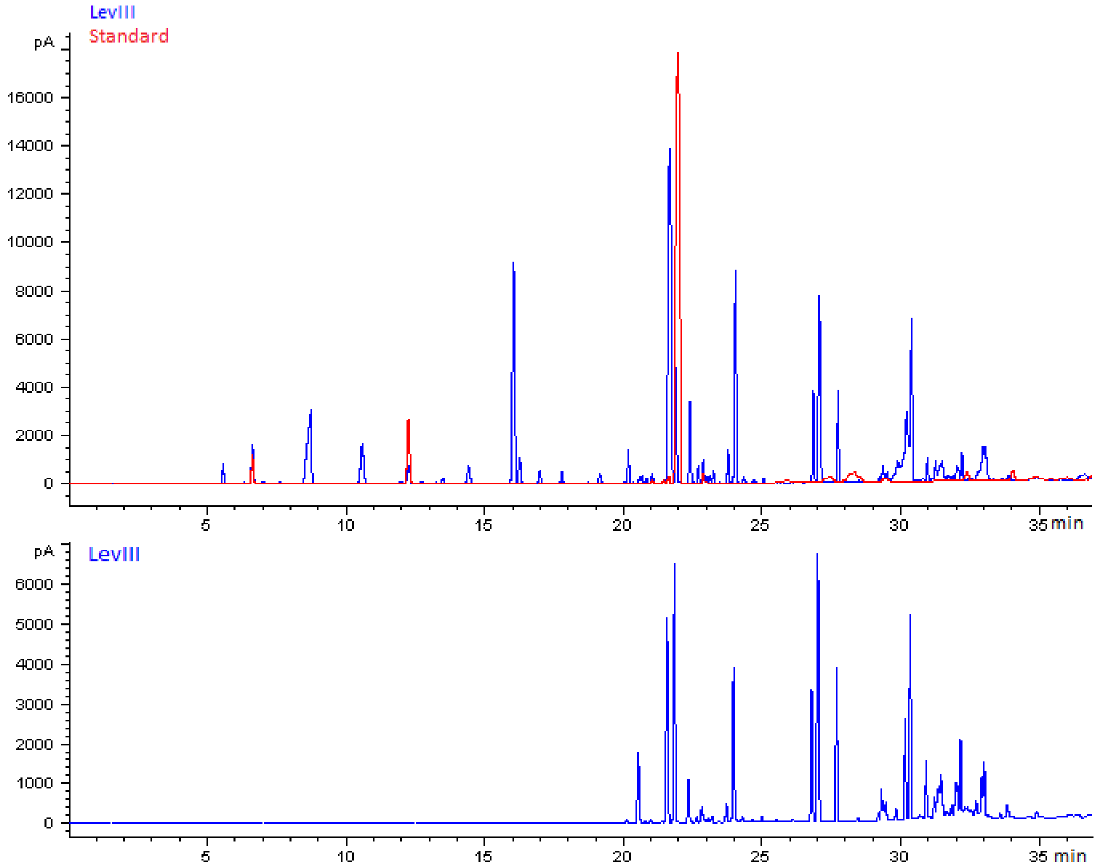


Figure 5.2: LEVIII gasoline composition, initially and after 51 mass% had been evaporated.

Two alternative experiments were performed to investigate if the vapor pressure gauge and the temperature at which the evaporation process occur have a significant impact on the results. Neither of the parameters was affecting the behaviour of the LEVIII curve in Figure 5.1 significantly. The only effect of increasing the temperature was a faster evaporation process. It took less time to evaporate 10 grams at 35 – 45 °C than at room temperature, but the effect on the vapor pressure was approximately the same. The curves in Figure 5.1 are thus valid for all evaporation processes between room temperature and 45°C which covers the CARB temperature cycle.

5.1.1 Importance of sampling method

The sampling of gasoline was performed in two different ways to investigate how the results were affected. The experiment was performed with both LEVIII and BogeyI resulting in four samples. The vapor pressures measured immediately after sampling for the four samples are presented in Figure 5.3 together with the specified values for each fuel. The specified value is given as a range which is included in the graph. As shown, the vapor pressure is lower when using the fuel pistol compared to the cold sample method. The vapor pressure for LEVIII sampled with the fuel pistol is even lower than allowed by the specifications. These results show the importance of sampling method. Since gasoline is very volatile, the initial vapor pressure will vary depending on how the sample is prepared and who is preparing the sample. It is very important to be meticulous when working with gasoline to eliminate as many errors as possible.

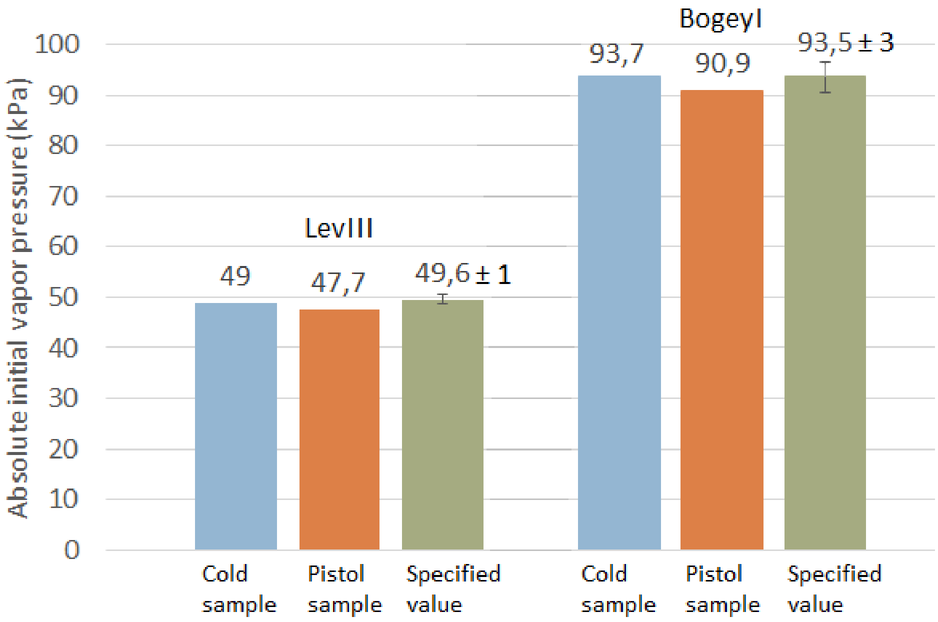


Figure 5.3: Measured vapor pressure with the two different sampling methods and the specified acceptable range.

Fortunately it is possible to compensate for a poorer sampling method by shifting the curve from the fuel pistol sample to the right in Figure 5.1. The error by doing so is a maximum of 1.3 % for BogeyI and 2.4 % for LEVIII. As a result the curve from the cold sampling method can be used for all samples of the same gasoline blend, independent of initial vapor pressure. From the two curves two equations were established that describe the final vapor pressure as a function of evaporated mass and initial vapor pressure. The final vapor pressure is described by equation 5.1 for LEVIII and equation 5.2 for BogeyI, where Δm is the mass percent that have been evaporated. The vapor pressure is given in kPa. The equations are valid until 20 mass% and 40 mass% has evaporated for LEVIII and BogeyI respectively.

$$RVP_{final,LEVIII} = 0.049(\Delta m)^2 - 2.054\Delta m + RVP_{initial,LEVIII} \tag{5.1}$$

$$RVP_{final,BogeyI} = 0.0123(\Delta m)^2 - 2.2481\Delta m + RVP_{initial,BogeyI} \tag{5.2}$$

5.2 Fuel degradation by temperature variations

A vapor pressure curve was constructed for both LEVIII and BogeyI with the vapor pressure gauge and are presented in Figure 5.4. The curves describe the vapor pressure of each gasoline blend as a function of temperature. As shown, a higher temperature results in a higher vapor pressure since more molecules have enough energy to escape the liquid. With a temperature increase from 18.33 °C to 40.55 °C the vapor pressure increase by 31 kPa for LEVIII and 52 kPa for BogeyI. Note that the vapor pressure curve will vary as the gasoline composition changes. These two curves are only valid for fresh fuel. The curves were used in combination with the ideal gas law to calculate the theoretical mass that should evaporate for each experiment as described in Chapter 2.3 and the Appendix B.3.

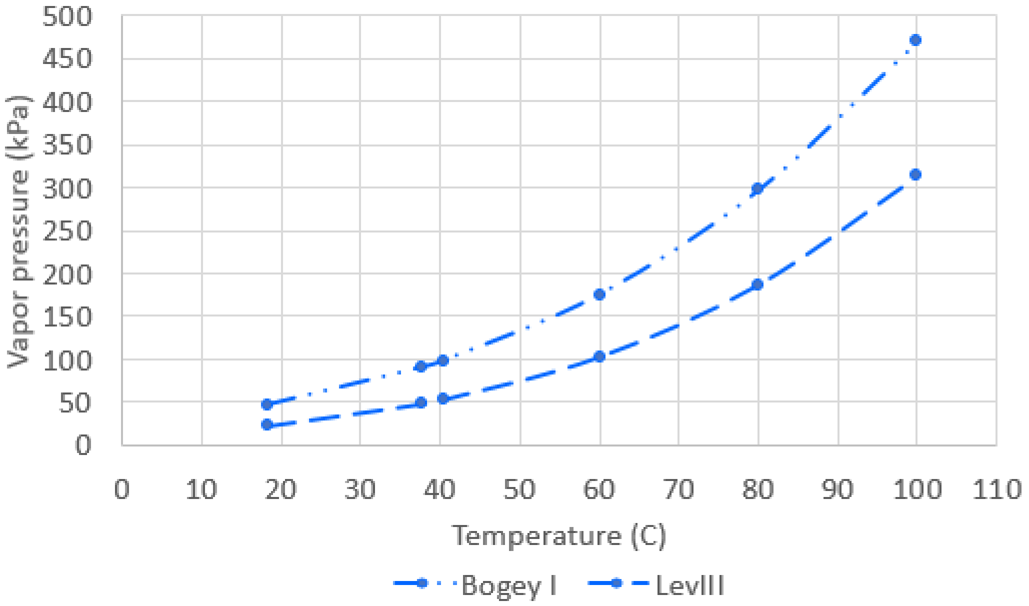


Figure 5.4: Vapor pressure curves describing the vapor pressure as a function of temperature for LEVIII and BogeyI.

The focus in this section will be to describe the evaporation process and temperatures since it was difficult to relate a small amount of expelled hydrocarbons to the vapor pressure, since there were too many errors involved. The vapor pressure will be discussed more in chapter 5.3 where the fuel degradation over time is described.

5.2.1 Experiments with a stainless steel jerrycan

In this section the results from the experiments with the stainless steel jerrycan are presented. Experiments were performed with both CARB temperature cycles and temperature steps.

5.2.1.1 Temperature step with ambient air as carrier gas

The continuously measured temperatures and canister weight during a temperature step with ambient air used as carrier gas is presented in Figure 5.5. As shown, the thermal equilibrium in liquid phase is re-established 6 hours after raising the temperature from 18.33°C to 40.55°C. Since the gasoline partial pressure (same thing as vapor pressure at equilibrium) is below atmospheric pressure there is no driving force that will transport hydrocarbons to the canister once equilibrium has been established. Thus, the canister weight should be constant when thermal equilibrium was reached. Also, the initial temperature of the gasoline was about 21 °C and then lowered to 18.33 °C, meaning that no hydrocarbons should be transported to the canister during these conditions. Still the canister weight was increasing during thermal equilibrium. One hypothesis to describe the weight gain is that water from the ambient air used as carrier gas was adsorbed in the canister. The relative humidity was measured to be about 20 % which corresponds to about 3.5 grams of water per cubic meter of ambient air. With a pump flow of 2 litres per minute this means 3.5 grams of water that can adsorb in the canister per 8 hours, corresponding to 0.44 grams/hour. That is approximately the amount shown in Figure 5.5. It can thus be concluded that ambient air is not a good choice of carrier gas when working with an activated carbon canister. Another strange feature in the graph below is that the SHED air temperature is shown to be a few degrees lower than the gaseous and liquid temperatures, which should not be the case. The thermocouple was therefore substituted with a new one.

Due to the above described hypothesis some adjustments described in the methodology section were performed. One of the adjustments was to change carrier gas, from ambient air to compressed air, and that gave great improvements of the results. The canister weight was now stabilized when thermal equilibrium was reached but it was still difficult to stabilize the scale signal at 18.33 °C. The hoses connected to the canister were relaxing causing fluctuations to the scale signal. Since the initial temperature of the gasoline was about 21 °C and the temperature was lowered immediately to 18.33°C, no evaporation should occur during these conditions and thus, the value of the canister weight was put to zero at 18.33 °C for all the proceeding experiments.

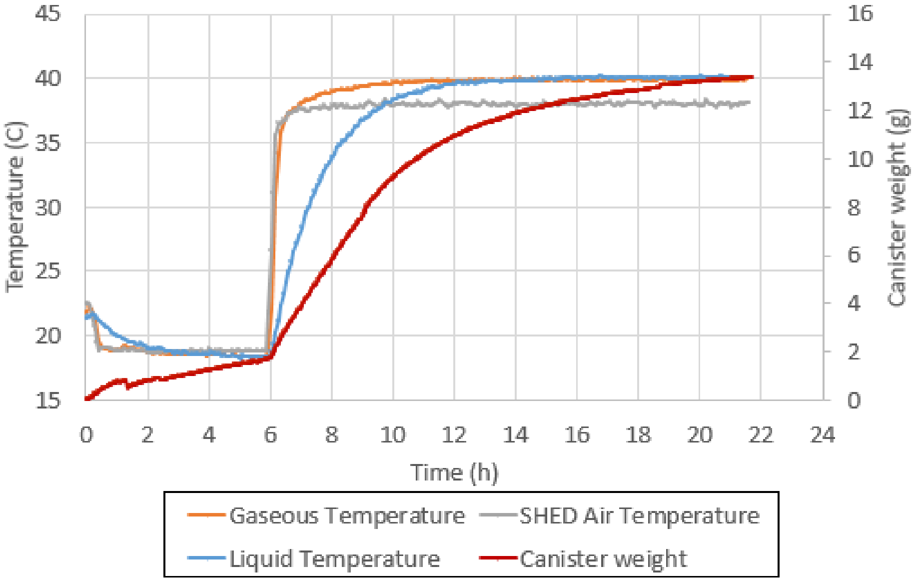


Figure 5.5: Continuously measured temperatures and canister weight with LEVIII fuel and ambient air used as carrier gas. After 6 hours the temperature was raised from 18.33 °C to 40.55 °C.

The relaxation was affecting the scale signal during the whole course of the experiment and the resulting graphs from the raw data should not be used directly to gain absolute values. The graphs still show the trend of the evaporation process but to gain the absolute value of the canister adsorption, the canister itself should be weighted both prior to and after the experiment. In the graphs presented in this thesis the error has been compensated for by multiplying all the data points by the actual measured canister weight divided by the received value from the raw data.

5.2.1.2 How the evaporation process is affected by liquid area

A lot of different parameters were tested according to Table 4.1 in the methodology section. All the performed experiments with a temperature step follow the same trend as shown in Figure 5.5, with the exception of constant canister weight at equilibrium. The first parameter tested was how the area between liquid and gaseous phase affect the evaporation process. The continuously measured canister weights and temperatures from the two experiments are presented in Figure 5.6. As shown in the top graph, the final canister weight gain was close to the same in both cases but the evaporation processes to get there were different. With the jerrycan laying down the evaporation process was proceeding faster as shown by the upper curve. This is due to the larger area-to-volume ratio which generates a faster heat transport together with a larger surface area from where the evaporation occurs. The equilibrium was established 7 hours after the evaporation started with the larger surface area. With a smaller surface area and a smaller area-to-volume ratio the evaporation process was proceeding with a lower speed and required 12 hours to reach equilibrium. Since the available gaseous volume was the same regardless if the jerrycan was standing up or laying down, and the system was allowed to reach equilibrium, the expelled amount should be the same with both setups, which was also the case.

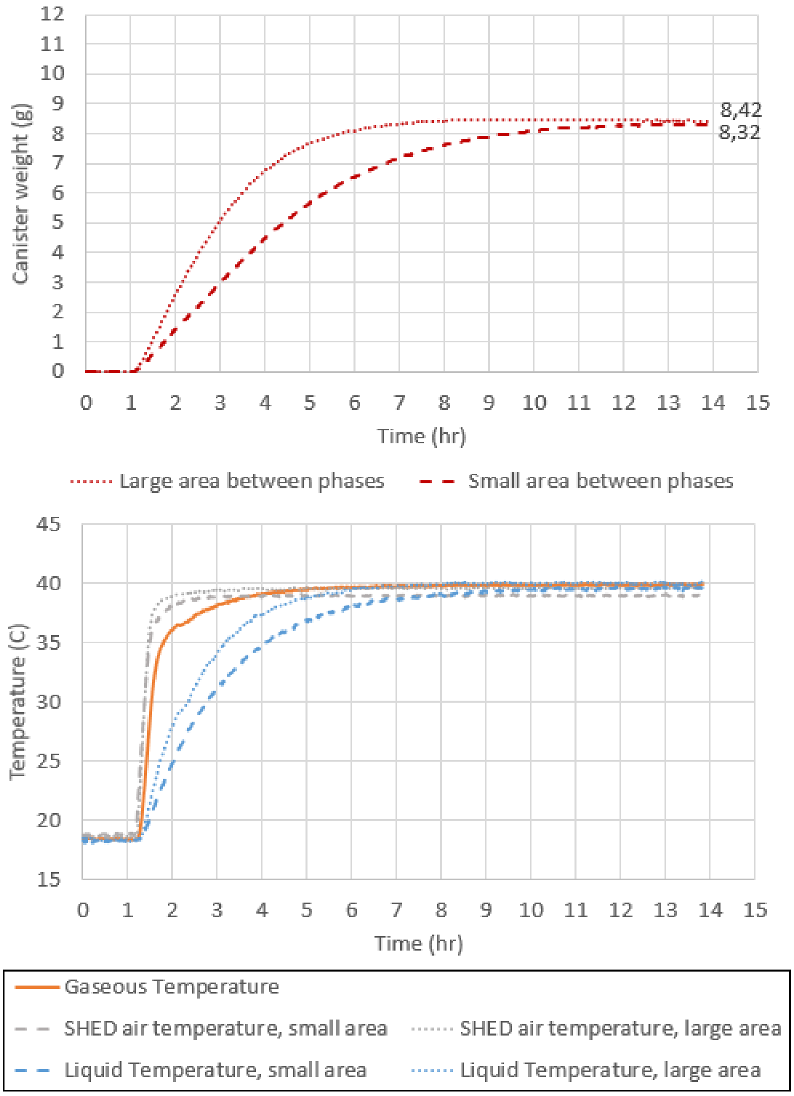


Figure 5.6: Continuously measured canister weights and temperatures from experiments with LEVIII fuel exposed to a temperature step. The jerrycan was placed laying down and standing up to generate a large respectively small area between liquid and gaseous phase.

The bottom graph in Figure 5.6 display the temperatures, where the gas phase temperature is described by the same curve for both experiments. The SHED air temperature is described by two different curves since the temperature was increasing slightly different. This is probably due to the control system in the mini-SHED. That the SHED air temperature behaves slightly different between the experiments is also shown in the Appendix A.2, where it is very evident that the slope of the SHED air temperature is different between the experiments. As shown the temperatures in liquid phase follow the same behaviour as the canister weight curves does. Also, the temperatures in liquid phase are lagging behind the SHED air temperature due to the thermal inertia in the liquid. This is more evident with a smaller area-to-volume ratio.

With a larger area-to-volume ratio the evaporation process proceeds faster and as a result the gaseous temperature was lagging the SHED air temperature more than with a slower evaporation process. This is due to the fact that the evaporation process is endothermic and thus requires energy. With a smaller area between the two phases the evaporation process is slower and the gaseous temperature keeps up better with the SHED air temperature.

5.2.1.3 How the evaporation process is affected by liquid volume

Three experiments were performed to investigate how the evaporation process was affected by the liquid volume inside the jerrycan. The resulting canister weights, SHED air temperatures and liquid temperatures are presented in Figure 5.7. A smaller liquid volume results in a larger gaseous volume inside the jerrycan, causing more hydrocarbons to evaporate to saturate the gaseous phase. Consequently the evaporation process was proceeding faster and a larger amount of gasoline was expelled to the canister with less gasoline in the jerrycan as shown by the top graph. It took 4, 6 and 9 hours respectively to re-establish the equilibrium with 20, 40 and 60 vol%.

As shown in Figure 5.7 the liquid temperature differs between the different experiments. With a larger liquid volume the liquid temperature has more difficulties to keep up with the SHED air temperature. For example, a larger liquid volume result in a smaller area-to-volume ratio and thus a slower heat transport. This behaviour reflects the evaporation process described by the top graph.

The gas phase temperatures were not included in Figure 5.7 since they are better explained by the graphs resulting from the raw data that are included in the Appendix A.2. As shown from Figure A.2, A.3 and A.4 the gaseous temperature keep up very well with the SHED air temperature with a liquid volume of 20 % but not so good with a larger liquid volume. As stated before, since the evaporation process is endothermic, the gaseous phase should lag behind more with a faster evaporation process. This is seen in the two cases with 40 vol% and 60 vol% respectively but with a liquid volume of 20 % the gaseous temperature keeps up with the SHED air temperature even though the evaporation process is fast. It seems like there is a point between 20 vol% and 40 vol% where the heat transport from the surrounding to the gas phase is dominating over the endothermic evaporation process.

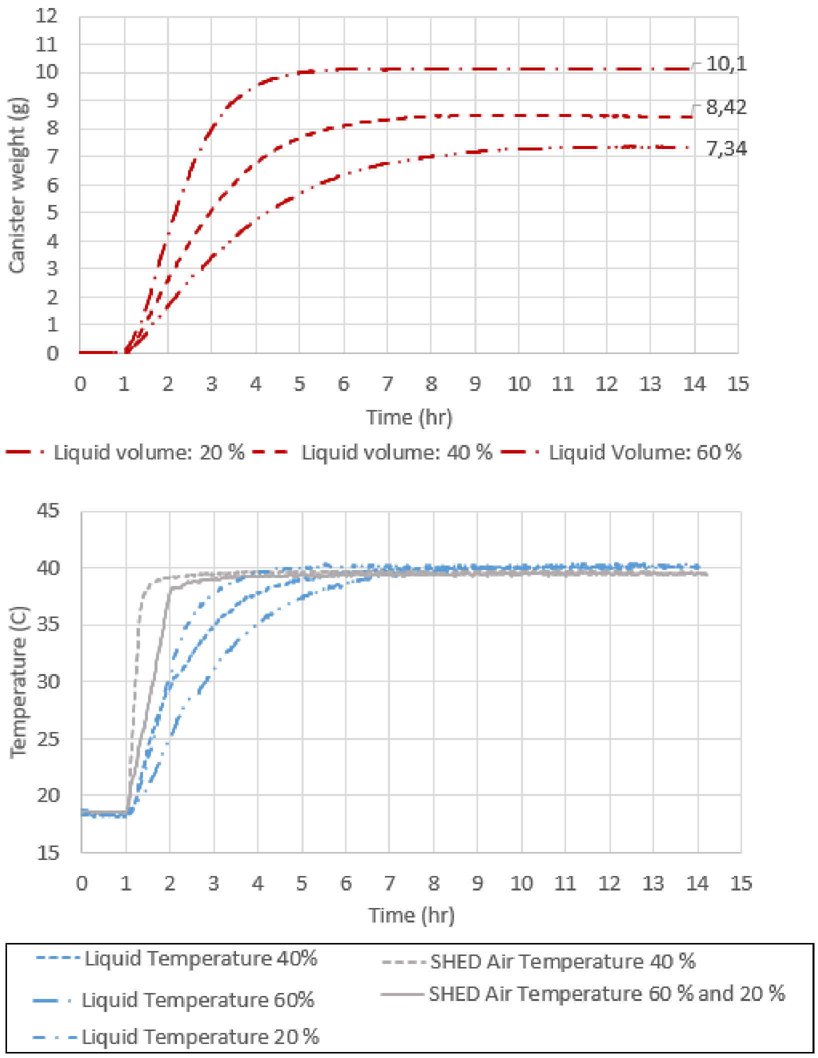


Figure 5.7: Continuously measured canister weights and temperatures from experiments with LEVIII fuel exposed to a temperature step. The liquid volume was equal to 4, 8 and 12 litres of gasoline.

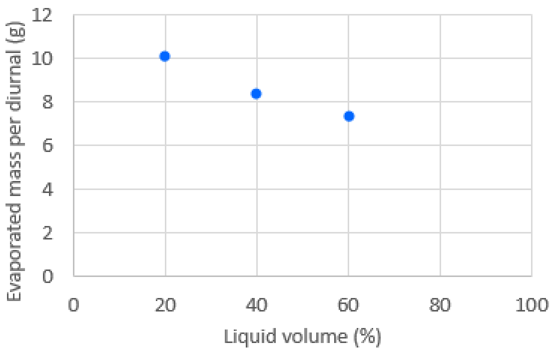


Figure 5.8: Expelled mass as a function of liquid volume with the jerrycan lying down. A smaller liquid volume results in a larger gaseous volume and more hydrocarbons evaporate.

Figure 5.8 describe the mass expelled per day as a function of liquid volume in the jerrycan. The graph gives a perception of how much gasoline that will evaporate from the jerrycan system when filled to different volumes. The graph also displays how a smaller liquid volume results in a larger expelled mass of hydrocarbons.

5.2.1.4 General observations from temperature step experiments

From the five experiments described so far some general observations were made. The slope of the liquid temperature curve was constant until the SHED air temperature reached its maximum, then the slope of the liquid curve was reduced as well. This is explained by the heat transport. While the SHED air temperature was still increasing the absolute temperature difference between the surrounding temperature and the liquid phase was big. Then the thermal inertia in liquid phase was the limiting factor causing the constant slope of the liquid temperature curve. When the SHED air temperature reached its maximum the absolute temperature difference was reduced and became the limiting factor instead.

The slope of the canister weight curve was initially constant and then reduced when the gas phase temperature reached its maximum. The same phenomena is applied here. It is the gaseous temperature inside the jerrycan that decides how much hydrocarbons that will evaporate to saturate the gas phase, and how much the gases in the jerrycan expands. As long as the temperature in gaseous phase was increasing the evaporation process was at its maximum speed limited by the evaporation kinetics. When the gaseous temperature reached its maximum the liquid temperature became the limiting factor and the evaporation speed was reduced. At last the canister weight was stabilized soon after the liquid temperature was stabilized and the entire system was in equilibrium.

5.2.1.5 CARB temperature cycling

Figure 5.9 shows the resulting graphs from the CARB temperature cycling with the jerrycan standing up and laying down causing a small respectively large area between the liquid and gaseous phase inside the jerrycan. The temperatures in gas phase were behaving in the same way in both experiments, so were the SHED air temperatures, and are hence represented by the same curves.

The evaporation processes described by the canister weights in the upper graph are very different compared to the results from the temperature steps. The slope of the curves are more or less constant throughout the whole course, compared to the temperature step where the slope was only constant during the first half and then leveled out. This difference is described by the temperatures. With the CARB cycle the temperature was increased successively over 12 hours instead of instantly as with the temperature step. Note that the evaporation process was following the temperature curves in liquid and gaseous phase regardless of how those curves behaved.

From the time scales in the graphs it can also be noted that the evaporation process stops when the gaseous and liquid temperatures reach their maximum. When the temperature started to decrees in the system, hydrocarbons inside the jerrycan were starting to condensate back into liquid phase which stopped the flow to the canister. This explains why the scale signal is constant after approximately 12 hours. For some reason the evaporation process stops two hours earlier with the larger surface area. This allows the canister weight with the smaller area to catch up with the canister weight with the larger area. Why this is so is hard to say.

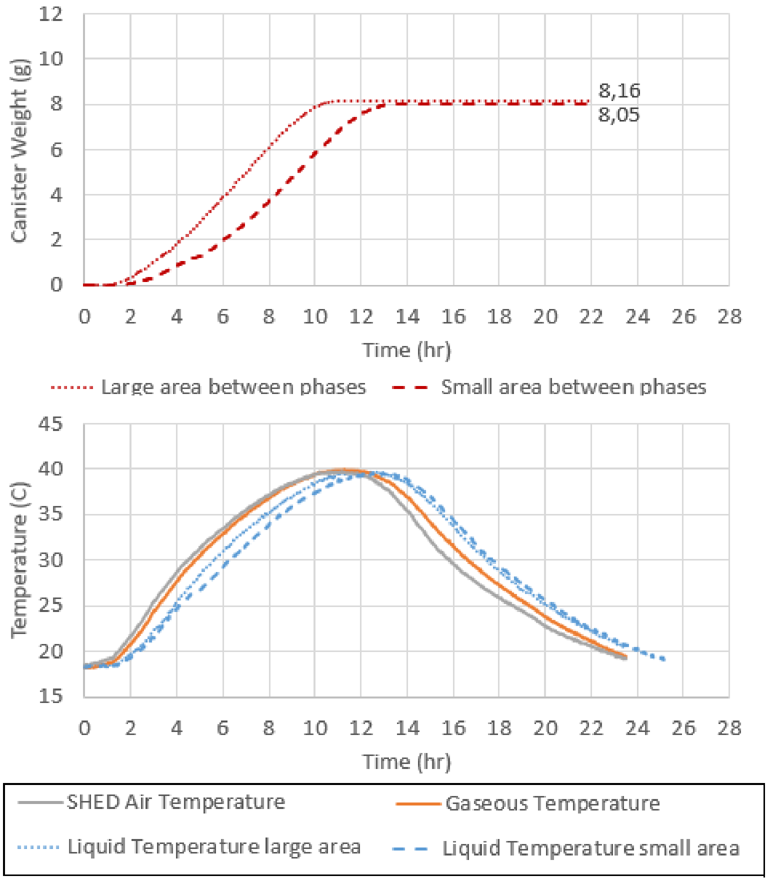


Figure 5.9: Continuously measured canister weights and temperatures from experiments with LEVIII fuel exposed to a CARB temperature cycle.

As shown in the bottom graph in Figure 5.9 the gaseous temperature was following the SHED air temperature very well while increasing the temperature but was lagging behind when the temperature was decreasing. Since the temperature was increased gradually the heat transport could keep up between the air and gas phase. When the temperature was reduced again hydrocarbons were condensed back into liquid phase inside the jerrycan. The condensation process is exothermic, releasing heat to the environment, causing the gaseous temperature to lag behind the SHED air temperature.

With a small area-to-volume ratio the liquid temperature was lagging behind the SHED air temperature somewhat more than with a large ratio, the former curve reaches equilibrium a little bit later than the latter. The two curves follow each other while lowering the temperature. It is reasonable that a smaller area-to-volume ratio is lagging behind more since the heat transport to the liquid is slower. Towards the end of the cycle the liquid temperature with the jerrycan standing up was caught up with the other curve. The equally large temperature differences resulting from this implies that the same amount should evaporate in both experiments and so was also the case seen from the top graph. To get a clearer idea of what was happening during the temperature cycle and to investigate if the evaporation process is similar between several days three consecutive temperature cycles were performed.

Figure 5.10 show the results from three consecutive temperature cycles. Like in the experiments with one temperature cycle, the SHED air temperature and gaseous temperature were following the same course with the jerrycan both standing up and laying down. The liquid temperatures were varying somewhat though, where the temperature with the jerrycan laying down was following the SHED temperature somewhat better and reaches a somewhat higher maximum temperature and lower minimum temperature. The same phenomena is shown here as with one temperature cycle, the gas phase temperature followed the SHED air temperature while increasing the temperature but was falling behind while decreasing the temperature. This is very repetitive throughout all cycles.

More hydrocarbons were evaporating with the jerrycan laying down which should be the case since the liquid temperature was reaching a higher maximum temperature and a lower minimum temperature causing a larger temperature difference. As shown the difference is more than one gram per cycle. According to the ideal gas law, the slightly bigger temperature difference should only result in an extra 0.2 grams with the jerrycan lying down. It seems like the evaporation kinetics with the jerrycan standing up was a limiting factor and the evaporation process could not proceed to its full speed.

As shown, the expelled amount is approximately the same in each step and is equal to 8.77, 8.57 and 8.37 grams with the jerrycan laying down and 7.19, 7.08 and 7.20 grams per cycle with the jerrycan standing up. These numbers are taken from the graph and not from weighing the canister before and after each cycle. This brings an uncertainty to them since the results are affected by the relaxing hoses connected to the canister. It seem like it is fair to say that the same amount is evaporating each day which should be the case since the temperature increase was the same each cycle.

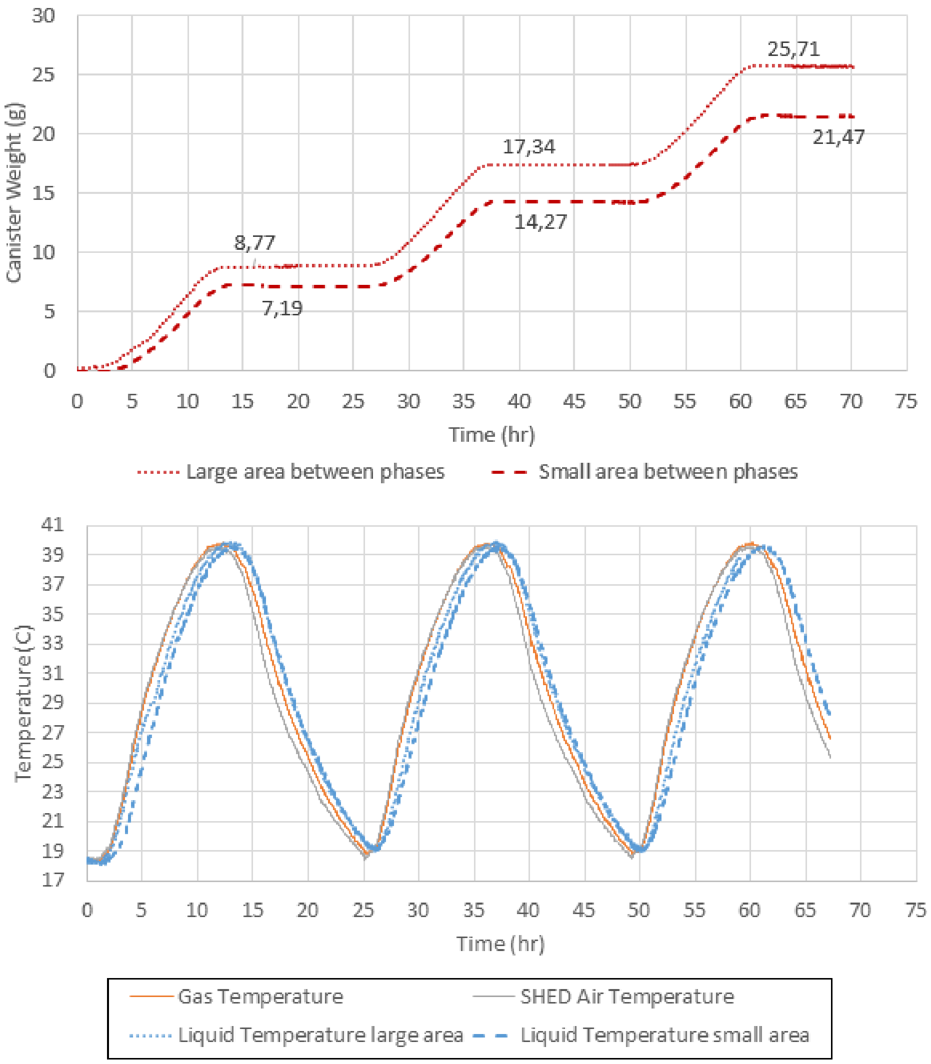


Figure 5.10: Continuously measured canister weights and temperatures from experiments with LEVIII fuel exposed to 3 consecutive CARB temperature cycles.

The expelled amount differs by a few tenths between the temperature step, one CARB cycle and 3 CARB cycles. The results deviate from one another by only a few percent and it is thus reasonable to assume that the system is in equilibrium when performing CARB cycles with the jerrycan filled to 40 vol%. The ideal gas law should then be valid and for most cases the calculated amount lies within 10 % of what was actually observed. The two experiments that deviated from the ideal gas law was the one with stirring, where the temperature was affected by the stirring plate, and the experiment with 60 % liquid volume where 35 % more than expected was expelled. One explanation to the small deviations is that the jerrycan was leaking to some extent in all experiments, which probably affected the evaporation process.

5.2.1.6 Further experiments with the jerrycan

Some further experiments were performed with the jerrycan. The temperature step was divided into two equally big temperature steps to investigate how well it matches the full size step. This also gives an indication of how well the evaporation process follows the ideal gas law. In the first half 3 grams were expelled and during the second half 6.08 grams which sums up to a total of 9.08 grams. That is, 7.8 % more than with the total step, which is an acceptable error. It can be concluded that the ideal gas law is valid for the jerrycan system.

5.2.1.7 The evaporation process for a winter fuel

One experiment was performed with BogeyI gasoline and the results are presented in Figure 5.11. The gasoline was exposed to a temperature step.

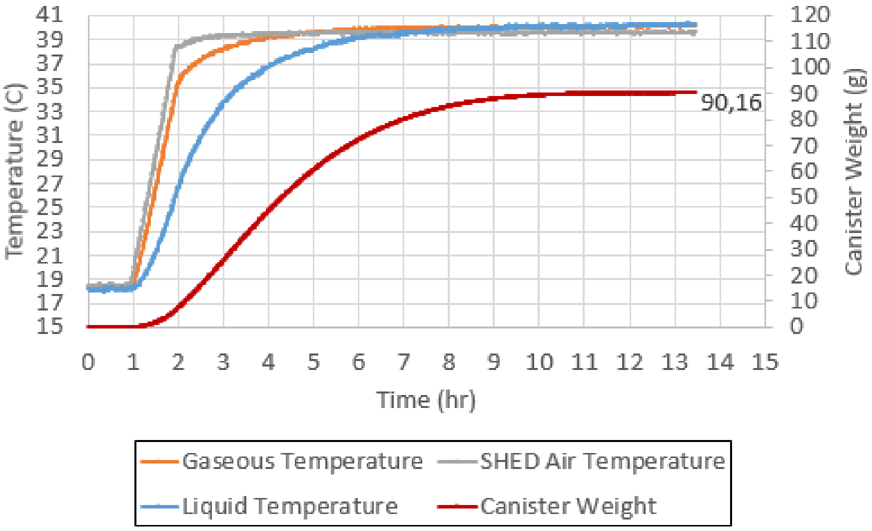


Figure 5.11: Temperatures and canister weight from the experiment using BogeyI gasoline. The large amount of expelled hydrocarbons is due to that the gasoline is boiling inside the fuel tank.

According to the ideal gas law 46 grams should evaporate during a temperature step but in the experiment 90 grams were expelled to the canister. The explanation is that the volatile gasoline blend is boiling inside the jerrycan. At 40.55 °C the vapor pressure of BogeyI is very close to the boiling point according to the vapor pressure curve and because of the high evaporation amount it has probably crossed the line to boiling. As shown, the canister weight curve is stabilizing about 5 hours after the liquid temperature, which was never the case with LEVIII where the weight was stabilized one hour after the liquid temperature. The reason that the canister weight seems to stabilize is simply because the canister was full and could not adsorb any more hydrocarbons. Instead the hydrocarbons were just passed straight through the canister and out in the fume hood. These results imply that still having a winter fuel in the tank while entering summer temperatures is devastating since the large hydrocarbon flow will bleed through the canister and out in the atmosphere.

5.2.1.8 The evaporation process in a dynamic system

All the results presented above have been stationary systems. One experiment was also performed to investigate how the evaporation process was affected by stirring to simulate a vehicle in movement. It turned out to be more difficult than one can think since the magnetic stirrer was getting warm from the motor which was affecting the temperatures inside the jerrycan. To try to eliminate this influence a thin column of air was added between the magnetic stirrer and the jerrycan but the effect could not be entirely eliminated. 9.18 grams were expelled which is 9 % more than without stirring, an acceptable error. It can be concluded that stirring does not affect the evaporation process, at least not significantly.

5.2.2 Relation between evaporation and the geometry of the fuel tank

In this section the results from experiments with standalone fuel tanks are presented. They were exposed to CARB temperature cycles as were filled with either 40 or 20 vol% of gasoline.

5.2.2.1 The evaporation process with a 40 % liquid volume

The resulting graphs from the 2WD and AWD fuel tanks filled with gasoline to 40 vol% are presented in figure 5.12. The top graph shows the evaporation process for the two setups. As seen, the top curve that describes the evaporation process in the 2WD fuel tank is very unstable which is due to the prolonged hose connecting the fuel tank and the canister. The hose was relaxing as the temperature was varying in the SHED which was causing the fluctuations. It was difficult to know in advance if the hoses were placed in a stable positions or not, so it was not possible to adjust the setup to prevent this. Due to the fluctuations the resulting data from the measurements should not be used as a truth but the canister had to be weighted both prior to and after the experiments. The curves presented in this thesis has been compensated in the same way as the jerrycan results, by multiplying each data point with the true canister weight divided by the measured raw data weight.

Disregarding the fluctuations it is shown that more hydrocarbons are evaporating from the 2WD fuel tank than from the AWD fuel tank. According to what has been observed with the jerrycan this should be the case since the area-to-volume ratio is larger for the 2WD fuel tank. This graph displays a phenomenon that did not show in the jerrycan experiments, back purge. After the canister weight had reached its maximum in a temperature cycle, the weight was slightly reduced again. This phenomenon appears because of the underpressure that was built up in the fuel tanks as hydrocarbons were condensed back into liquid phase as the temperature was lowered. The light hydrocarbons that are not attached very strongly to the activated carbon in the canister were desorbing and transported back to the fuel tank. This phenomenon was not shown in the jerrycan experiments because of the continuous flow of compressed air. The back purge effect becomes more evident for each cycle since the canister was then loaded with more hydrocarbons making it easier for them to desorb again. The back purge effect was interfering with weighing the canister prior to and after the experiment since more hydrocarbons had been expelled from the fuel tank than were still present in the canister. To get the whole picture of the evaporation process, the graphs should be interpreted together with the true canister weight.

The two graphs with temperatures display the behaviour in each fuel tank. The top one is the result from the AWD fuel tank where five thermocouples were used in the fuel tank. The temperatures at 15 mm, 35 mm, and 65 mm follow each other very well and are represented by the same curve, and it can thus be concluded that the temperature was equal in the entire bulk phase. The temperature at 130 mm was increasing faster, meaning that the temperature at the liquid surface follow the CARB cycle better than the bulk phase. The gaseous temperature reaches a maximum of 37 °C, which is 3.5 degrees from the maximum temperature in the CARB cycle. In this experiment the SHED air temperature was not measured which was a mistake, but from other experiments performed later on, it seems like the SHED temperature always reaches 40.55 °C and it can be assumed that so was the case even in this experiment.

As already stated the temperature in liquid phase at 130 mm was increasing faster than the bulk phase but when the temperature was decreasing again all four temperatures in liquid phase follow each other. At the point where the gaseous temperature crossed the liquid temperature at 130 mm this temperature started to decrease as well since the surrounding temperature was now lower than the liquid temperature. After the point where the gaseous temperature crossed the bulk phase all the liquid temperatures follow each other as one phase. All four temperatures in liquid phase reach the same minimum temperature and at the same time. The gaseous temperature was reduced much faster and reached a lower level than the liquid temperatures.

The same thing is shown in the bottom graph with the 2WD fuel tank. The temperature at 65 mm was increasing slightly faster than the other two temperatures but were decreasing equally fast. The gas phase temperature was decreasing faster than the liquid temperature. Note from the y-axis that the gas temperature reaches a higher level in the AWD tank than the 2WD. This is contradictory to everything discovered with the jerrycan so far where it has been shown that a larger temperature increase results in a greater amount of expelled hydrocarbons. It is also contradictory since the ideal gas law state that a larger temperature increase should result in a greater expelled mass and so was not the case. The explanation is that since the evaporation process is endothermic and was proceeding faster in the 2WD fuel tank the temperatures were reduced in that fuel tank. This also implies that the ideal gas law cannot be used to describe these systems.

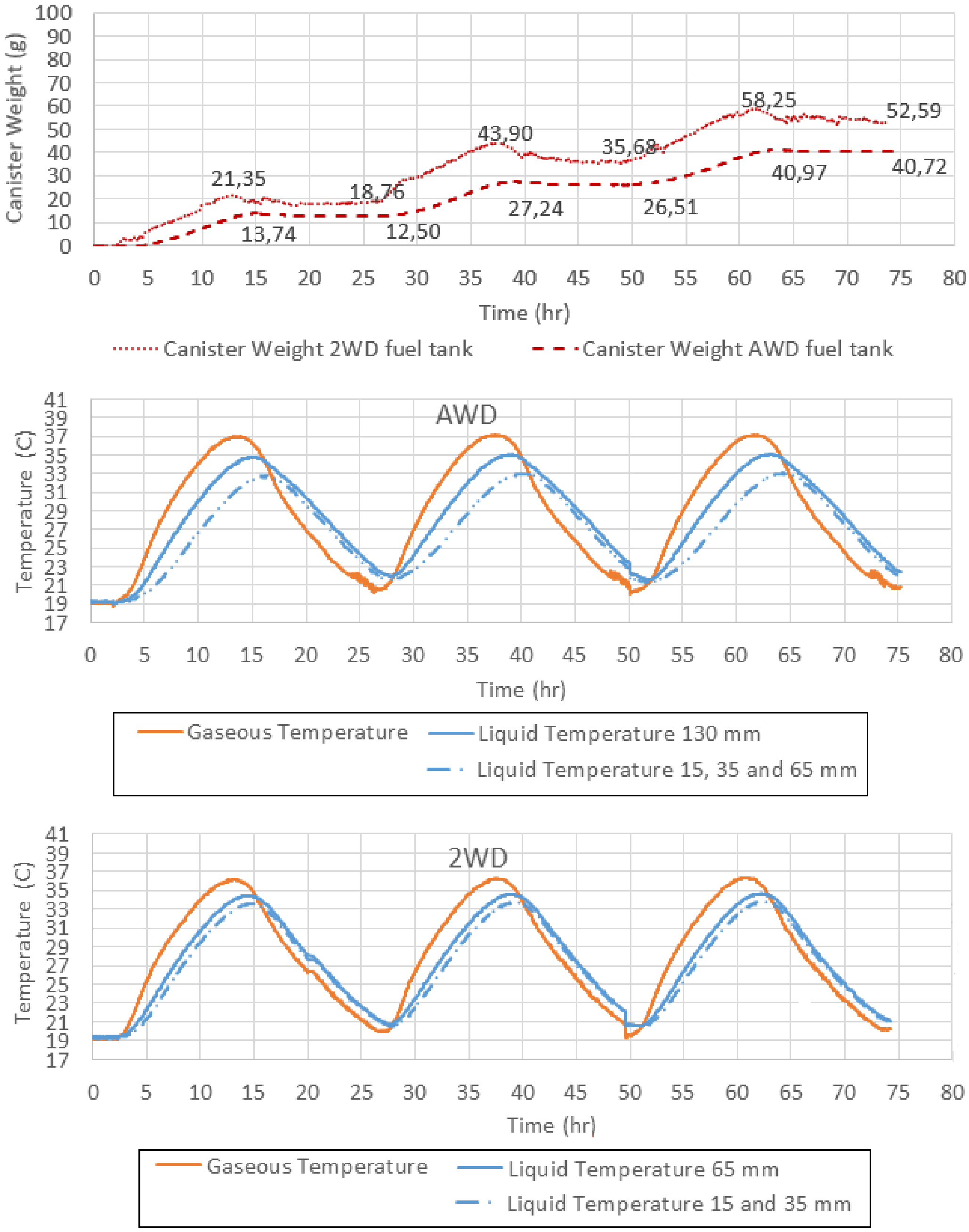


Figure 5.12: Resulting canister weights and temperatures from the experiments with an AWD and 2WD fuel tank filled to 40 vol% with LEVIII gasoline. The strange drop at the end of the second cycle in the bottom curve is due to a canister swap.

5.2.2.2 The evaporation process with a 20 % liquid volume

Figure 5.13 shows the results from an experiment identical to the previous one but with a smaller liquid volume. The experiment was performed in a different SHED which might have influenced the results. It is difficult to know since the SHED air temperature was never measured in this SHED. But based on the results it seems reasonable that the temperatures in the CARB cycle were followed as they should.

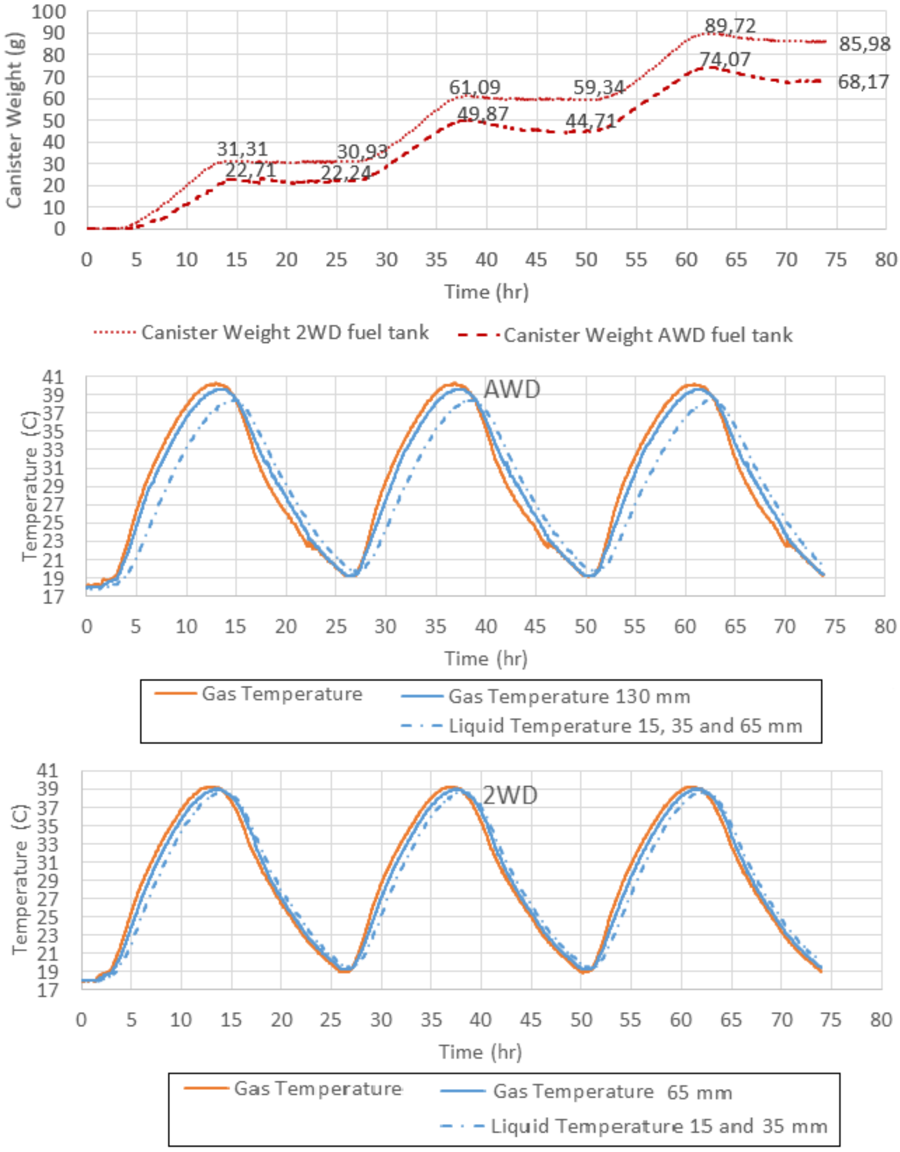


Figure 5.13: Resulting canister weights and temperatures from experiments with an AWD and 2WD fuel tank filled to 20 vol% with LEVIII gasoline.

The same evaporation behaviour was observed here as in the previous experiment. More hydrocarbons evaporate from the 2WD fuel tank than the AWD fuel tank since the area-to-volume ratio and the exposed area between the gaseous and liquid phase is greater. The back purge effect is shown here as well and it is more evident with more hydrocarbons in the canister.

Since the liquid volume was only 20 % in these experiments the thermocouple that was describing the liquid temperatures at the surface in each tank in the previous experiment was now in gaseous phase. The two bottom graphs in Figure 5.12 are now describing the gaseous temperatures 15 mm from the top, the gaseous temperatures at 130 mm and 65 mm for the respective fuel tank and the liquid bulk phase. As shown the temperature measured by the two thermocouples at 130 mm and 65 mm almost keep up with the gaseous temperature measured 15 mm from the top of the tank, but not quite. The temperature is lower closer to the liquid surface since that is where the energy was taken from to sustain the endothermic evaporation process. The liquid temperatures keep up much better with the gaseous temperature than with 40 vol%, even more so in the 2WD fuel tank due to the larger area-to-volume ratio. The temperatures were reaching a higher value in the AWD fuel tank in these experiments too and is described by the same phenomena as with 40 vol%. The temperature at the liquid surface was marginally higher than the bulk phase but one curve is still used to describe the entire liquid phase.

5.2.2.3 Varying liquid volume with constant geometry

When comparing the same fuel tank filled to different volumes it can be seen that all temperatures go higher and lower with 20 vol% compared to 40 vol%. This seems reasonable since the larger area-to-volume ratio should give this result. With a 20 % liquid volume more hydrocarbons are expelled to the canister which should also be true after all the previous experiments.

5.2.2.4 The evaporation process for a winter fuel

One experiment was also performed with BogeyI. According to the resulting graphs 140 grams were evaporating each cycle and since the working capacity is only 130 grams of butane for the canisters it is likely that hydrocarbons were bleeding out of the canister. The gasoline was most likely boiling inside the fuel tank and these results cannot be used to say anything about the evaporation process.

These results are devastating from an environmental point of view since that implies that hydrocarbons will leak out in to the atmosphere in less than one day unless the canister size is drastically increased. Because of these results it is crucial that a winter fuels is not stored in the fuel tank until summer. Since boiling does not occur in closed systems the boiling could be suppressed by pressurize the fuel tank system. It might be so that a sealed fuel tank system is enough to prevent the high volatility gasoline to boil inside the fuel tank. This should be studied further to prevent large hydrocarbon leakage. When the canister was loaded to its maximum limit the back purge effect got even more evident. As much as 35 grams was drawn back into the fuel tank, see Figure A.5 in the Appendix.

5.2.3 Fuel degradation on-board a vehicle

The resulting temperatures and canister weight are presented in Figure 5.14. As shown, the temperatures inside the fuel tank are not following the SHED air temperature at all since the car was shielding the fuel tank. The maximum temperature in gaseous and liquid phase were reached 5 hours after the SHED air temperature. The reason that the temperatures were increasing for another 5 hours is that even though the SHED air temperature was decreasing, it was still higher than the liquid and gaseous temperatures inside the fuel tank. Note that the temperature inside the fuel tank starts to decrease as the SHED air temperature cross those temperatures. The maximum reached temperature was 32.5 °C in gaseous phase and 31 °C in liquid phase. This can be compared with the temperatures in the standalone AWD fuel tank where the temperatures reach 37 °C and 33.5 °C in gaseous and liquid phase respectively (see Figure 5.12). It can also be noted that it takes more than two hours from starting the CARB-cycle before the temperatures inside the fuel tank starts to increase. The slope of the liquid and gaseous phases differs a lot from the SHED air temperature which was not the case with independent fuel tanks.

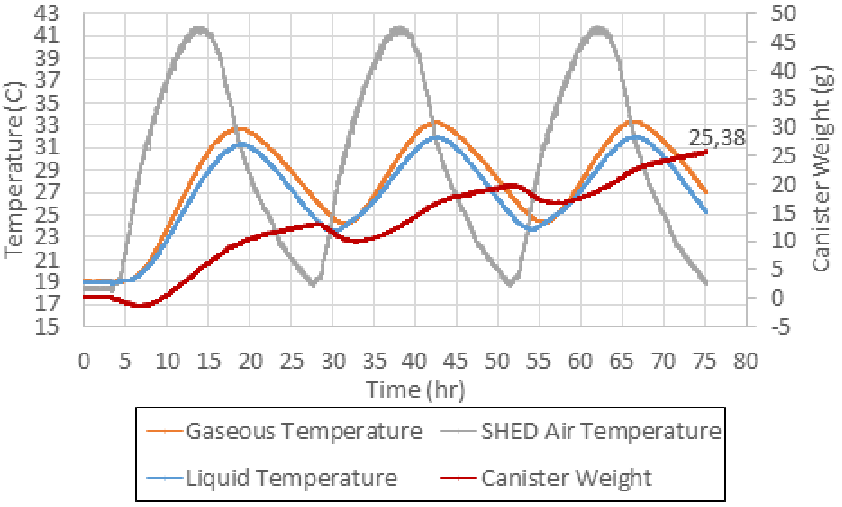


Figure 5.14: Resulting temperatures and canister weight from three consecutive CARB cycles with the fuel tank on-board a vehicle. LEVIII gasoline was used, and the scale and canister were placed inside the SHED.

The behavior of the canister weight is very different from the experiments with both the jerrycan and with standalone fuel tanks. At first, the canister weight was decreasing during a few hours until the liquid and gaseous temperatures start to increase, first then the canister weight started to increase. The slope was then constant until the maximum temperature inside the fuel tank was reached. Unlike the jerrycan and standalone fuel tanks where the canister weight was now constant, the canister weight kept on increasing. The slope is less steep but continues until the SHED air temperature reaches its minimum. Then some sort of back purge effect is shown until the gaseous and liquid temperatures reach their minimum and the behaviour is starting all over again. It seems unreasonable that hydrocarbons continue to evaporate to the canister while the temperature inside the fuel tank was decreasing. To investigate if so was the case the hose from the fuel tank was connected to a flame ionization detector (FID). The result is shown in Figure 5.15. When the temperature in liquid and gaseous phase was increasing the FID registers hydrocarbons and when the temperature was decreasing there was no flow of hydrocarbons. But still the results in Figure 5.14 says otherwise. Since the experiment was performed two times and the results were the same each time it is evident that something in the system was affecting the canister weight.

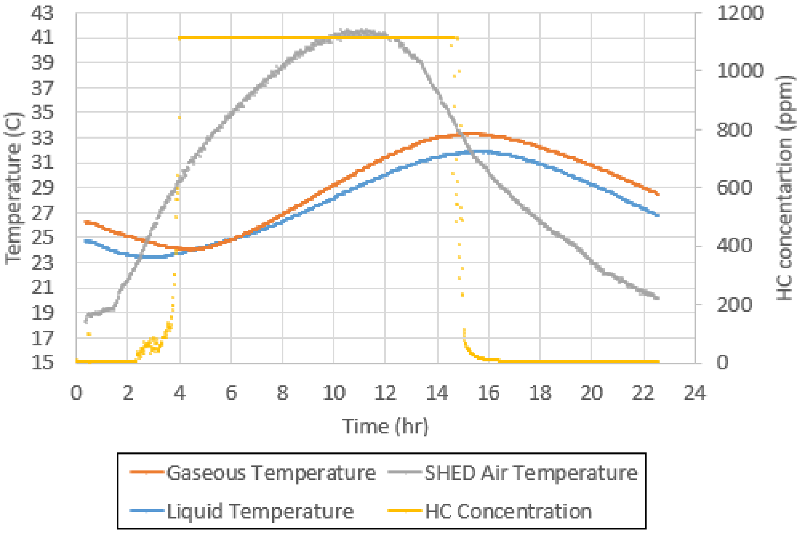


Figure 5.15: Temperatures and FID signal to detect the hydrocarbons evaporating from the fuel tank.

There are only two parameters available that can affect the evaporation process except for temperature, namely composition and pressure. Consequently, it was at first thought that the system might be leaking, causing fresh air to be added to the fuel tank and that this was causing the extra evaporation. Since the fuel tank was filled to 40 vol% the liquid gasoline was up to a level in the fuel tank where it covered the refilling pipe inlet, and the only way air could enter the fuel tank was via the recirculation pipe. Thus, the recirculation pipe was disconnected and two experiments were performed this way. First the flow was led to the canister that was continuously weighted and then the flow was led to the FID. The resulting curves looked exactly the same as Figure 5.14 and 5.15 and it could be concluded that the system was not leaking. Two parameters were then identified that could possibly explain the canister weight curve, either the hoses connected to the canister were relaxing or something was happening inside the canister. To eliminate these parameters the canister was placed outside the SHED and the results are presented in Figure 5.16.

The behaviour of the canister weight is now the same as with the jerrycan and fuel tanks as shown in Figure 5.16. That is, either the hoses or the canister itself were influencing the resulting curve in Figure 5.14. The exact answer to this problem was never solved and it does not affect the evaporation process or the results. The expelled amount of hydrocarbons is the same independent of where the canister is placed.

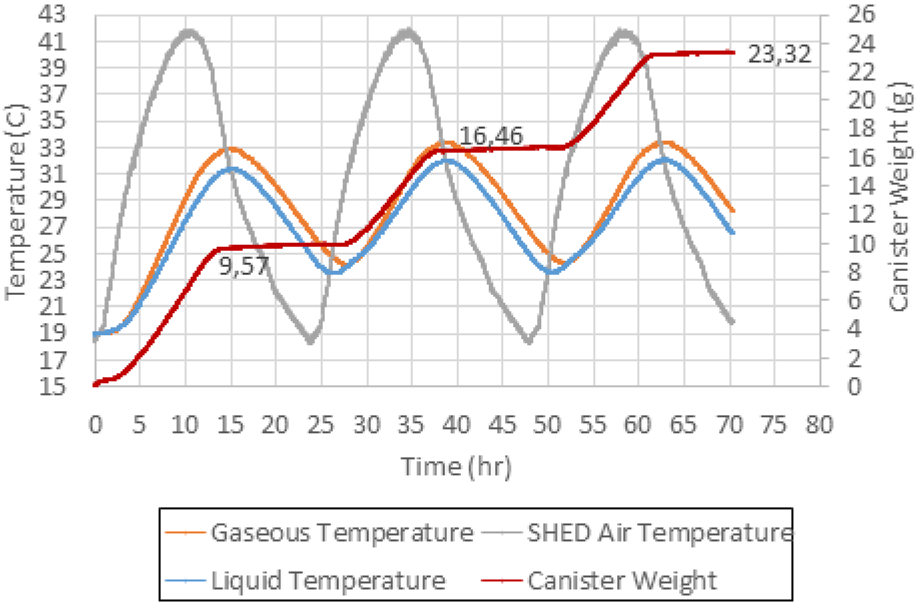


Figure 5.16: Resulting temperatures and canister weight from three consecutive CARB cycles with the fuel tank on-board a vehicle. LEVIII gasoline was used, and the scale and canister were placed outside the SHED.

The temperature increase in liquid and gaseous phase during the first CARB-cycle is a few degrees bigger than the proceeding ones. As a result more hydrocarbons are expelled during the first cycle as shown in Figure 5.14 and Figure 5.16. During these three cycles 25.41 grams and 23.32 grams were expelled respectively which can be said to be almost the same since seven CARB-cycles were performed between these two experiments which have contributed to lowering the vapor pressure and thus the evaporation speed. With the independent AWD fuel tank 40.72 grams were expelled over the first 3 days, that is, 60 and 74.6 percent more which is due to the higher temperatures achieved inside the fuel tank. Since the evaporation speed is much slower on-board the vehicle than with individual fuel tanks, the ideal gas law is valid.

5.3 Fuel degradation over time

All the performed experiments described so far have been performed to investigate how the evaporation process was affected over a short time period. Two experiments were also performed to study the fuel degradation over an extended time. One experiment with a jerrycan that was exposed to temperature cycles and steps, and one with a fuel tank where evaporation was caused by a change in gas phase composition. The results are presented in Figure 5.17 together with all the jerrycan and fuel tank experiments. Here the absolute vapor pressure change is described as a function of expelled mass. The dark blue curve is the same one as shown in Figure 5.1 but described as the vapor pressure difference instead of absolute vapor pressure.

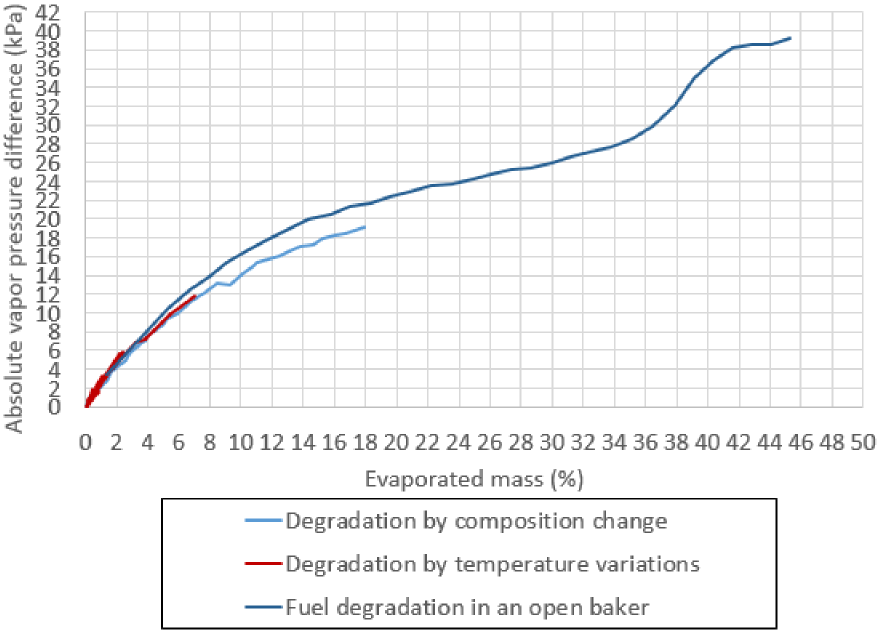


Figure 5.17: Absolute vapor pressure change as a function of evaporated mass for LEVIII.

As shown both the experiment with the jerrycan and the fuel tank are following the dark blue curve to a beginning, until about 7 mass% have evaporated. Then the curve from the vacuum pump experiment starts to diverges somewhat from the open system sample. The jerrycan experiment was not proceeding long enough to say if the same behaviour was applied to that experiment. One of the reasons to the deviation from the dark blue curve is that the initial vapor pressure was 2.5 kPa lower in the vacuum pump and jerrycan experiments than the open system sample. The vapor pressure difference between the fuel tank and the open system is 2 kPa towards the end, why the dark blue curve can be used to describe the entire process. The dark blue curve only includes the mass that was actually evaporated from the open bottle. One curve was also developed that compensated for the mass used by the vapor pressure gauge, but did not describe the evaporation process over time as good. Also, the initial gasoline weight in the fuel tank could not be measured but was calculated by multiplying the fuel density with the liquid volume, resulting in a minor error. Including these errors, the model describes the evaporation process with high accuracy.

As stated in section 2.2, if the vapor pressure gets below 42.4 kPa there might be problems with engine start. With the vacuum pump experiment it took only three days before the vapor pressure was below 40 kPa (which is well below 42.4 kPa), since the evaporation speed was over 6 times as fast as with the CARB temperature cycling with the individual fuel tank and 17.6 times faster than with the vehicle. This evaporation process was very forced and during the first days 150 grams were expelled per day which can be compared with the amount from the vehicle of 8.5 grams. With the jerrycan it took 16 days with combined temperature cycles and steps to reach a level below 40 kPa. Remember that CARB cycles are a very extreme case.

The evaporation speed was reduced as hydrocarbons boiled off as shown by Figure 5.18. This is due to the reduced vapor pressure that will cause a different equilibrium composition in the system. The evaporation speed is also reduced since the most volatile components that require the least energy to evaporate have already been removed from the gasoline.

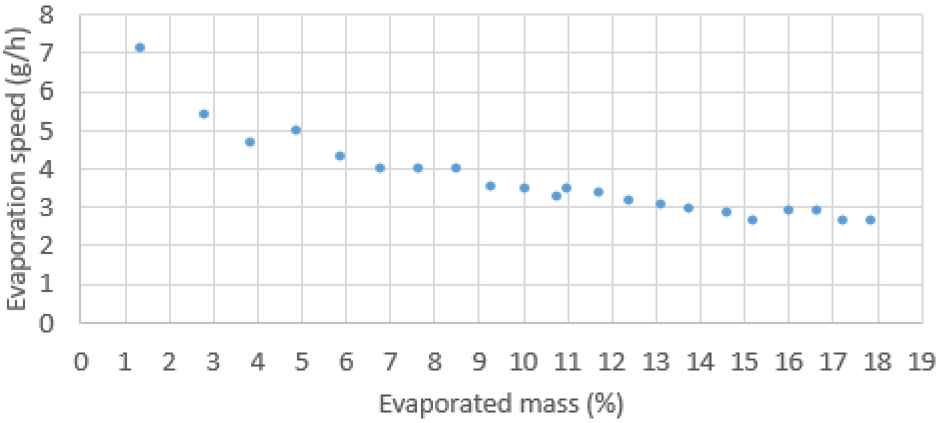


Figure 5.18: Evaporation rate as a function of evaporated mass with the vacuum pump system. As shown the evaporation rate is lowered as hydrocarbons boil off and the vapor pressure is reduced.

With the short experiments it was difficult to relate the expelled amount to the vapor pressure change since the initial vapor pressure varies between each experiment and was thus effected differently. There are also too many errors involved to measure an absolute vapor pressure change due to such a small expelled amount. With the graph in Figure 5.17 it is shown that the system is behaving according to equation 5.1 and it is thus possible to describe the evaporation process over an extended time. The error is less than 1 kPa for the last point in the light blue curve when using equation 5.1. Unfortunately this means that shorter experiment cannot be used to foresee the fuel degradation over time, but longer experiments must be performed.

A rough estimate of how long time gasoline must be stored on-board a vehicle before there might be problems with engine start can be done from the data obtained from the experiments with the car. As already stated, the fuel tank was filled to 40 vol% with LEVIII gasoline and exposed to CARB temperature cycles. 8.5 grams per day were expelled to the canister during these conditions. According to Figure 5.1, 4 mass% must evaporate to be in the risk zone of engine start failure, that is 850 grams, resulting in 100 days on-board storage. This result was obtained by extrapolating the initial evaporation speed over 100 days, but as shown by Figure 5.18 this degradation rate is reduced with time.

5.4 Sensitivity analysis

The result from the PT100 measurement showed that the thermocouple in liquid phase is showing a value that is 0.2 $°C$ too low and the thermocouples in air and gas phase show a value that is 0.1 $°C$ too low. These errors were neglected.

Two experiments were performed to investigate if the vapor pressure was affected by where the sample was taken in the bulk phase. The result was that it did not matter where the sample was collected. The difference between the results was a maximum of 0.2 kPa, which is within the error of the vapor pressure gauge.

By the FID experiment and the hydrocarbon gauge it was concluded that the jerrycan was leaking through the rubber gasket in the cap. There was nothing to do about it but to just keep in mind that this is happening and is a source of error.

A validation test of the vapor pressure gauge was performed and the calculations are presented in the Appendix B.1. The 99.9 % confidence interval on the mean value is 107.8 ± 0.164 kPa. That is, with a confidence interval of 99.9 % the measured value will be within 0.16 kPa from the true value. That is a very good accuracy and way better than what was promised by the manufacturer.

6 Future work

A more extensive study should be performed to investigate how well the different systems really follow the ideal gas law. If the vehicle system follow the gas law, further studies could be done to develop a model that describe the vapor pressure as a function of expelled hydrocarbon mass, and also the time it takes to reach a certain vapor pressure level.

Since the BogeyI gasoline is boiling in the jerrycan and individual fuel tanks systems, studies should be performed to see if so is the case even when the fuel tank is onboard a vehicle. If so is the case it might be beneficial with a sealed system to suppress the boiling.

This thesis has been focusing on vented fuel tanks but studies should also be performed with sealed fuel tanks. Since the system is sealed the pressure inside the fuel tank will increase and decrease as the temperature is varying. There are however a higher and lower allowed pressure limit to prevent the system from bursting, but it is desirable to have as low limits as possible since higher allowed pressures results in more expensive fuel tanks.

7 Conclusion

An expression was developed for both LEVIII and BogeyI to describe how the vapor pressure is reduced as hydrocarbons boil off. This model can only be used to describe the fuel degradation over time. With experiments that are only a few days long there are too many errors involved. It was not possible to construct one model that describes all systems during all conditions.

A larger area between the liquid and gas phase in a fuel tank will generate a larger expelled amount of hydrocarbons. As a result, the fuel tank geometry is an important parameter to take into consideration when studying fuel degradation. A larger area-to-volume ratio will increase the heat transport rate and hence also the evaporation speed. A smaller liquid volume implies a larger gaseous volume in the fuel tank and thus more evaporated and expelled hydrocarbons. The evaporation process is not significantly dependent of stirring.

The jerrycan system and fuel tanks on-board a vehicle can be described by the ideal gas law. Individual fuel tanks cannot be described in this way since the fast endothermic evaporation process is interfering with the gas law. It is consequently not possible to perform experiments with an individual fuel tank to describe the behaviour on-board a vehicle.

If LEVIII gasoline is stored in the fuel tank during 100 days, and is exposed to all the worst case parameters, there might be problems with engine start. If BogeyI gasoline is exposed to CARB temperature cycles it will bleed through huge amounts of hydrocarbons already the first day which is devastating from an environmental point of view.

Since gasoline is very volatile is it very important to be meticulous when working with gasoline to eliminate as many errors as possible. Since the canister is adsorbing water it is also very important to work in a dry environment to make sure it is only the fuel evaporation process that is studied.

The scale and canister should be placed in a constant temperature environment when studying the evaporation process and not inside the SHED. The temperature variations inside the SHED can affect the resulting curves but does not in any way influence the evaporation process.

The evaporation process can not be studied over just a few days to determine the fuel degradation over an extended time. There are to many errors involved and the small expelled amount does not influence the vapor pressure enough to get accurate results. It is thus necessary to study the fuel degradation over an extended time to gain an understanding for the evaporation process.

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A Appendix 1

Here some additional graphs are presented that describe the results further.

A.1 Gas chromatography

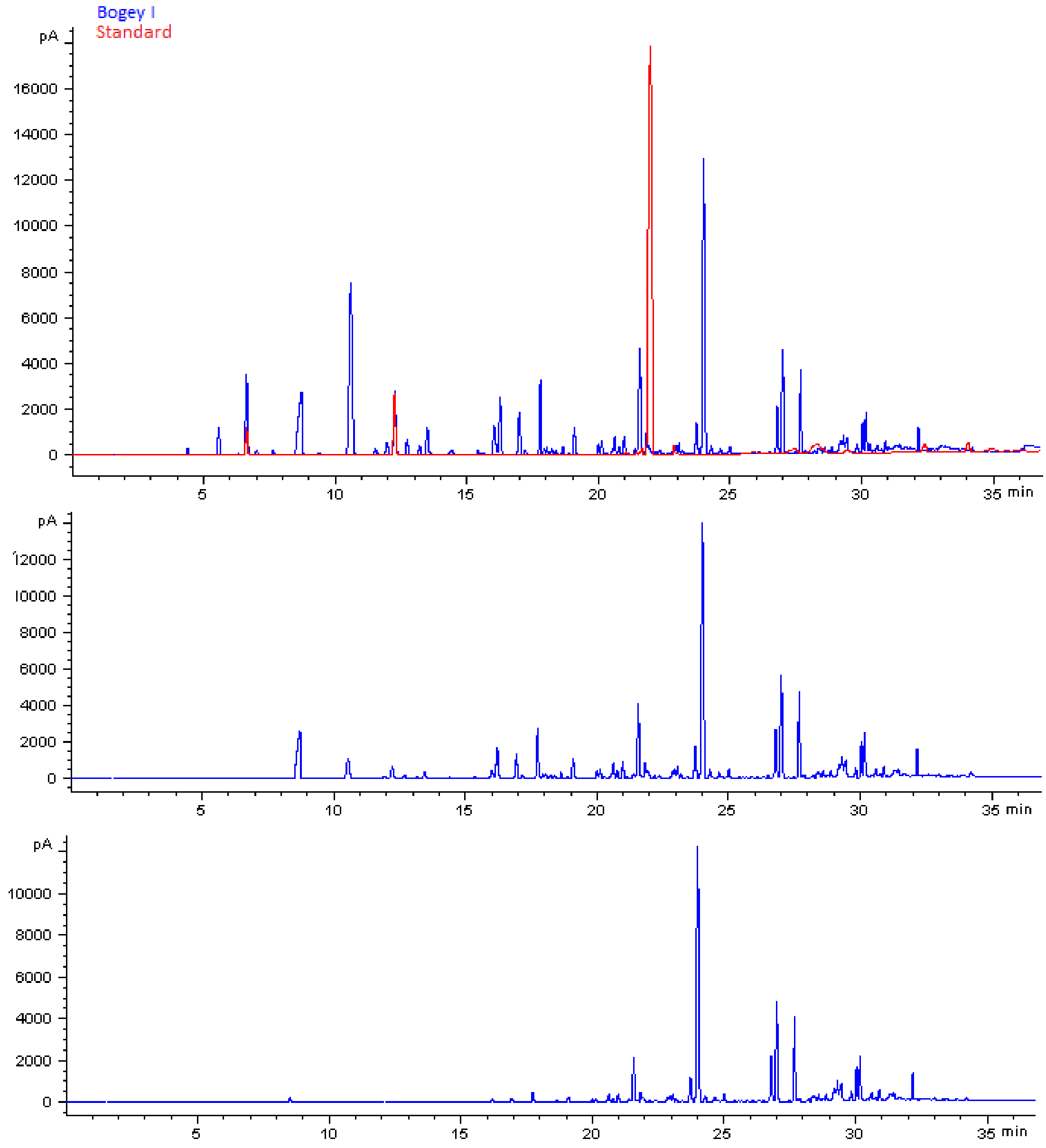


Figure A.1: BogeyI gasoline composition initially and after 16 and 47 mass% had been evaporated.

A.2 Graphs to further describe the evaporation process

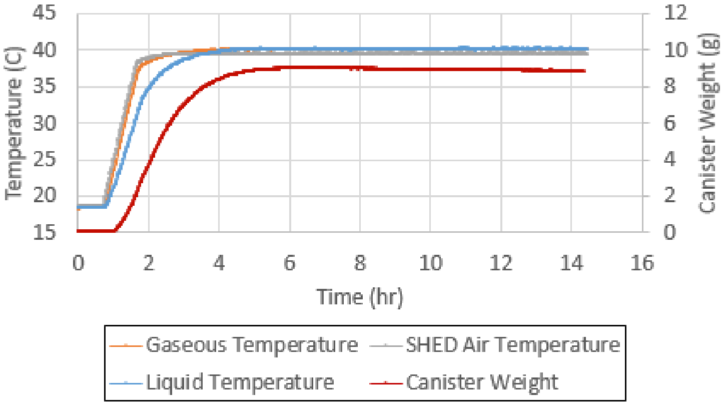


Figure A.2: Temperatures and canister weight with a 20 % liquid volume with the jerrycan lying down using LEVIII fuel.

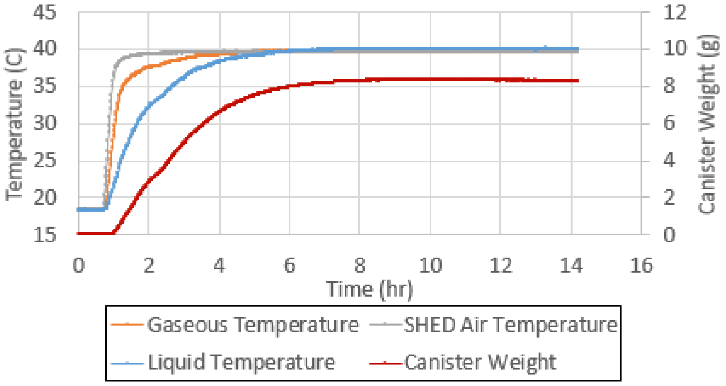


Figure A.3: Temperatures and canister weight with a 40 % liquid volume with the jerrycan lying down using LEVIII fuel.

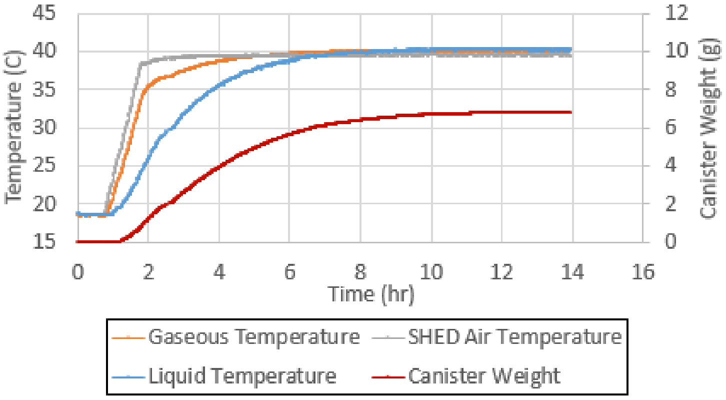


Figure A.4: Temperatures and canister weight with a 60 % liquid volume with the jerrycan lying down using LEVIII fuel.

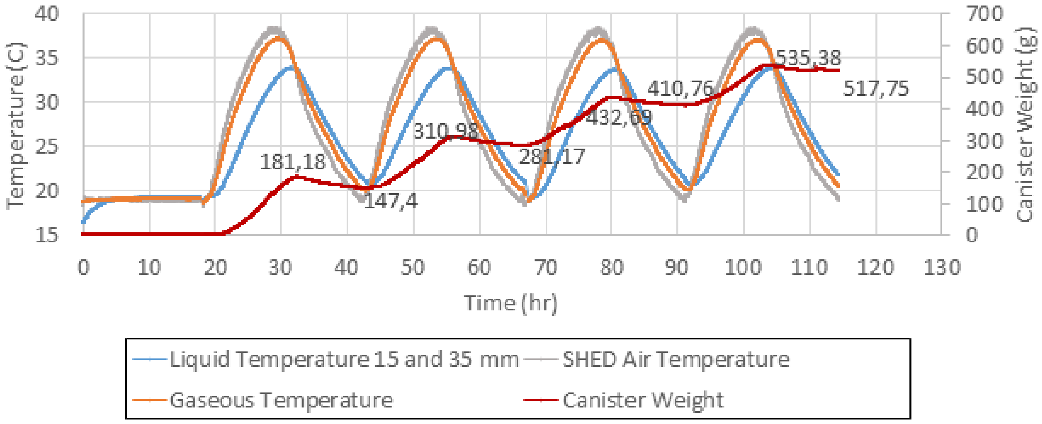


Figure A.5: Temperatures and canister weight with a 40 % liquid volume with the 2WD fuel tank using BogeyI gasoline.

B Appendix 2

Here some additional information is added. The calculations to obtain the confidence interval for the vapor pressure gauge and the CARB temperature cycle.

B.1 Confidence measurements of the vapor pressure gauge

The measured values are presented below. The mean value is 107.83 kPa and the range is 0.3 kPa. The 99.9 % confidence interval on the mean value is 107.8 ± 0.164 kPa, resulting in a maximum deviation from the mean value of 0.2 %. Also, the mean value is very close to the true value of the vapor pressure for n-pentane that is equal to 107.76 kPa.

107.7	107.7	107.8	108.0	108.0	107.9
107.8	107.7	107.7	107.9	107.9	

The confidence interval of the mean value was calculated using equation B.1, where $\bar{X}$ is the mean value, S is the standard deviation, n is the number of measured data points and $t_{\alpha/2}$ is the T-distribution. The T-distribution is equal to 4.587 for a 99.9 % confidence interval for n=11 [22]. The standard deviation, S, is the square root of the variance S^2 that is calculated using equation B.2, where x_i is each measured data point.

$$\bar{X} \pm t_{\alpha/2} S/\sqrt{n} \tag{B.1}$$

$$S^2 = \frac{n \sum x_i^2 - (\sum x_i)}{n(n-1)} \tag{B.2}$$

B.2 The CARB temperature cycle

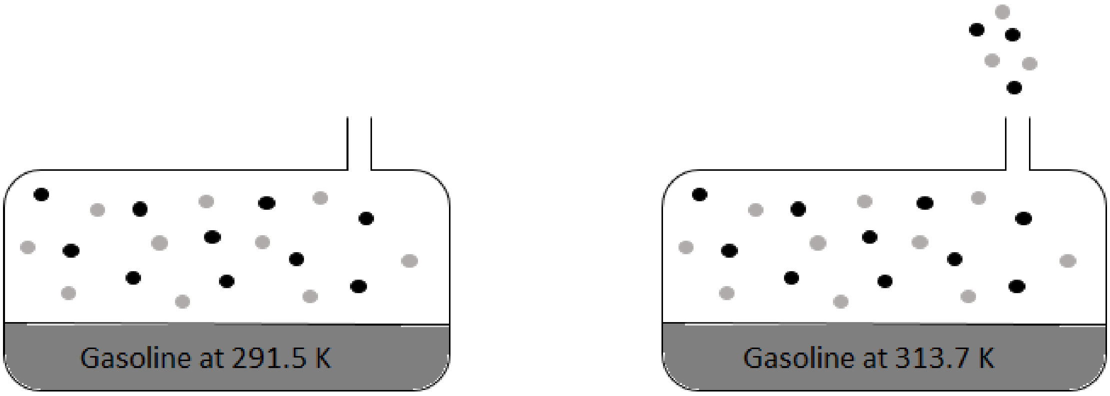
Table B.1 describe the CARB temperature cycle hour by hour. The cycle takes 24 hours to perform with a minimum temperature of 18.33 $^{\circ}C$ and a maximum temperature of 40.55$^{\circ}C$. The CARB temperature cycle is some sort of worst possible case that has occurred in California.

Table B.1: The CARB temperature cycle used in the experiments

Time (hr)	Temperature ($^{\circ}C$)
0	18.33
1	19.22
2	22.55
3	26.83
4	30.05
5	32.55
6	34.77
7	36.72
8	38.44
9	39.66
10	40.5
11	40.55
12	40.11
13	38.39
14	35.16
15	31.55
16	29.11
17	27.11
18	25.44
19	24.05
20	22.22
21	21.11
22	20.11
23	19.16
24	18.33

B.3 Calculation example with the ideal gas law

Here, one example is introduced to show how the ideal gas law was used to calculate the theoretical amount to be expelled from the fuel tank during a temperature increase. This is the example with BogeyI gasoline with a temperature step. This method includes both the fact that hydrocarbons will evaporate and the gas phase will expand as a result of the temperature increase.



$$P_{tot} = 101.3\ kPa$$
$$P_{fuel,initial} = 46{,}8\ kPa$$
$$P_{air,initial} = P_{tot} - P_{fuel,initial} = 54.5\ \text{kPa}$$
$$R = 8.314\ J/molK$$
$$T_{initial} = 291.5\ K$$
$$n_{fuel,initial} = \frac{P_{fuel,initial} \cdot V}{R \cdot T_{initial}}$$
$$n_{air,initial} = \frac{P_{air,initial} \cdot V}{R \cdot T_{initial}}$$
$$V = 13.5 \cdot 10^{-3} m^3$$

$$P_{tot} = 101.3\ kPa$$
$$P_{fuel,final} = 97.6\ kPa$$
$$P_{air,final} = P_{tot} - P_{fuel,final} = 3.7\ \text{kPa}$$
$$R = 8.314\ J/molK$$
$$T_{final} = 313.7\ K$$
$$n_{fuel,final} = \frac{P_{fuel,final} \cdot V}{R \cdot T_{final}}$$
$$n_{air,final} = \frac{P_{air,final} \cdot V}{R \cdot T_{final}}$$
$$V = 13.5 \cdot 10^{-3} m^3$$

Figure B.1: A schematic setup over the initial and final system and all the values.

$$n_{fuel,initial} = \frac{P_{fuel,initial} \cdot V}{R \cdot T_{initial}} = \frac{46.8 \cdot 13.5}{8.314 \cdot 291.5} = 0.26\ mol$$

$$n_{air,initial} = \frac{P_{air,initial} \cdot V}{R \cdot T_{initial}} = \frac{54.5 \cdot 13.5}{8.314 \cdot 291.5} = 0.30\ mol$$

$$n_{fuel,final} = \frac{P_{fuel,final} \cdot V}{R \cdot T_{final}} = \frac{97.6 \cdot 13.5}{8.314 \cdot 313.7} = 0.51\ mol$$

$$n_{air,final} = \frac{P_{air,final} \cdot V}{R \cdot T_{final}} = \frac{3.7 \cdot 13.5}{8.314 \cdot 313.7} = 0.02\,mol$$

$$\Delta n_{air} = n_{air,initial} - n_{air,final} = 0.3 - 0.02 = 0.28\,mol$$

$$c_{HC} = \frac{n_{fuel,initial} + n_{fuel,final}}{n_{air,initial} + n_{air,final}} = \frac{0.26 + 0.51}{0.3 + 0.02} = 2.4\,(mol\ HC/mol\ air)$$

$$m_{HC} = \Delta n_{air} \cdot c_{HC} \cdot M_{fuelgas} = 0.28 \cdot 2.4 \cdot 69 = 46\,grams$$