An analysis of the influence of phosphorus poisoning on the exhaust emission after-treatment systems of light-duty diesel vehicles

at

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by

Maria Isabel Toral del Río
Student Number: 20691378

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Supervisor:
  Dr. Maylis Auphan de Tessan
Co-Supervisor:
  Dr. Ernst Ferg
  Felix Haack
  Pr. Dr. Ing. Holdack-Janssen
Abstract

Climate change has become a discussion topic of exponentially increasing urgency and importance among world leaders of all disciplines. These changes are brought about by the emission of so-called Greenhouse gases from various human activities. The primary cause of CO₂ emissions is the burning of the Earth’s supply of non-renewable natural fossil fuels like coal, oil and natural gas. The world first agreed on the prevention of “dangerous” climatic changes at the Earth Summit in 1992. The Kyoto Protocol of 1997 was the first step toward protection of the atmosphere and prescribes restrictions on emission pollutants. Since then the vehicle gas emissions are being controlled by means of different gas emissions norms, like the European Union Norm in Europe. The automotive manufacturers and suppliers are collectively working on reducing overall vehicle emissions. They are focusing on several different emission limiting possibilities, for example improved engine design, special fuel development and exhaust gas treatment systems.

The exhaust gas treatment process requires continuous controlling and management of the exhaust gas emissions while driving a vehicle. Certain factors such as high emission temperatures have a negative influence on the life span of these systems. Their functionality and durability is also known to be reduced by the presence of chemical poisoning species like sulphur, phosphorus, zinc and calcium. The chemical poisoning species are produced during combustion of fuel and engine oil. They are therefore contained in the exhaust emissions and can poison the catalyst when passing over it.

Phosphorous poisoning is particularly problematic and should be reduced considerably. This study involves the investigation of the phosphorous poisoning process and aims to provide clarity regarding the influences of different fuel and oil compositions on the severity of the process. Engine oil and biodiesel are two major sources of phosphorous poisoning. The phosphorus contained in biodiesel fuel is a natural component and can be minimized during the refining procedure. In contrast to others studies, the biodiesel fuel used during this project was SME (Soya Methyl Ester) with a 20% biodiesel content. This choice of fuel was made because of the increasingly important role that this type of biodiesel is playing in the European
market and the future tendency to increase the percentage of biodiesel in the mixture with standard diesel fuel.

The phosphorus contained in engine oil is a necessary additive to retain the antioxidant and anti-wear properties of the oil. This study examined the poisoning influences from the most commonly used phosphorus containing oil additive, Zinc Dithiophosphates (ZDDP), as well as a Zn-free, phosphorus containing anti-wear oil additive. This formulation provides information about the phosphorus poisoning process as caused by the engine oil in the absence of Zn in the oil additives.

The results show how the phosphorus content in biodiesel fuel affects the functionality of the exhaust gas treatment systems and the importance of reducing the permitted content of phosphorus contained in the fuel. Reducing the phosphorus content in the fuel will conserve the functionality of the exhaust gas treatment systems during their operational life and thereby protect the environment from emission pollutants. It also provides insight into the differences in the poisoning processes when the phosphorus deposited on the catalyst comes from biodiesel fuel and when it comes from the engine oil. Finally the results also illustrate the influence of different phosphorous forms contained in engine oil additives on the catalyst poisoning process. This information could be used for the development of new oil additive formulations.
Acknowledgements

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- The oil additives supplier company Lubrizol, for their advice on compiling the final report.
- All the Volkswagen colleges that were involved in this project.
- Dipl. Ing. Charel Marais for his support and help throughout the duration of this research project.
Declaration:

I hereby declare that this dissertation is my own work. It is being submitted for the degree of Master in Technology (Chemistry) at the Nelson Mandela Metropolitan University.

It has not been submitted before for any degree or examination in any other University.

Signed ______________________, Maria Isabel Toral del Rio
Date   January 2008
This thesis is subject to confidentiality restrictions. Publication is only possible after written authorization by Volkswagen AG. Parts of this work will be submitted for journal publication if explicit written authorization is received from Volkswagen AG.

Various parts of this report were presented to Volkswagen, Lubrizol and Johnson Matthey in progress report meetings throughout the duration of the project. The final results were presented to all project partners in February 2007.
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Introduction

The number of vehicles in the world and their life span has increased quickly in recent years. With the European energy crisis, vehicle manufacturers concentrate their efforts on engine development in order to reduce the specific fuel consumption, improve the output and strongly reduce pollution.

The preservation of air quality through the reduction of atmospheric pollution is of high priority in the automotive industry. Furthermore the European gas emissions norms are continuously reducing the values for vehicle gas emission limits, especially for diesel engines. Diesel engines have been improved to reach high performance levels while the emissions are controlled through engine design and modifications.

There are three main complementary areas where emissions can be controlled. Firstly in engine design, where the Volkswagen Group is at the top of this development with its FSI® and TDI® engines. Secondly in fuel development, where emissions can be reduced by using fuel types with lead-free additives and low sulphur content or new alternative fuels like natural gas. Finally, exhaust gas treatment, where Johnson Matthey is working on the development of systems like Diesel Oxidation Catalysts or or Diesel Particle Filters that can be implemented to reduce emissions.

The exhaust gas-treatment processes requires continuous processing of the exhaust gas with the use of systems like catalytic converters and pollutant traps which are associated with active devices requiring periodic regeneration. A combination of an oxidation catalyst, a particle filter and a reduction system is the adaptation of this technology to the specific treatment of diesel emissions. The exhaust gas-treatment systems are not perfect and certain factors are known to reduce the functionality and durability of the catalyst, for example the emission temperature and the phosphorus content of the emissions from engine oil and biodiesel. These factors need to be studied to provide a better understanding of the source of these problems and what can be done to minimize their negative influence.
In this project the phosphorus poisoning produced in the gas-treatment systems will be studied. The phosphorus content in engine oil is a necessary additive to retain the anti-oxidant and anti-wear properties of the oil. Lubrizol have assisted in this project by providing a range of experimental formulations designed to investigate various lubricant compositional influences on exhaust gas-treatment systems. The phosphorus present in biodiesel fuel is a natural component and can be reduced during the refining procedure.

During the operation of the engine, phosphorus is deposited on the exhaust gas-treatment system, reducing the efficiency of the catalyst.

The aim of the project was to obtain a better understanding of the phosphorus poisoning mechanism that originates from different phosphorus sources and provide possibilities to eliminate or at least reduce its effect on catalyst poisoning.
I. Basic concepts

1 Engine

The design, power and efficiency has changed considerably over the last few decades. The two main types of engines used to power modern automobiles are gasoline and diesel engines. In gasoline engines the ignition of the fuel in the combustion chamber is achieved by means of a spark plug. The combustion of the fuel creates gases of high temperature which expand rapidly generating a downward force on the piston which initiates the movement of the crank shaft.

The diesel engine is another type of internal combustion engine which requires no spark plugs, but instead makes use of compression ignition. Heat is generated when air is compressed in the combustion chamber and when fuel is injected into the chamber, the heat from the compression process ignites the fuel 41. This project involved work with diesel engines only and therefore gasoline engines will not be discussed in further detail.

1.1 Diesel combustion

The diesel engine was invented in 1892 by Rudolf Diesel and since then increased in its popularity, where they are currently being used extensively in light passenger vehicles.

The following paragraph describes the process inside the cylinder during the basic diesel cycle:

a) The piston starts at the top until the intake valve open. The piston moves down to let the engine take in a cylinder-full of air. This is called the intake stroke

b) The compression stroke then follows with both the intake and exhaust valve closed and the piston moving back up to compress the air. When the piston reaches the top of its stroke, the fuel is injected into the chamber.
c) Both valves remain closed as the fuel/air mixture charge in the cylinder ignites and expands, driving the piston down. This is the power stroke.

d) Once the piston reaches the bottom of its stroke, the exhaust valve opens and the exhaust gas leaves the cylinder. This is the exhaust stroke.

![Figure BC.1: Cross section of a diesel engine combustion chamber](image)

A. intake stroke, B. compression stroke, C. power stroke, D. exhaust stroke.

Some diesel engines are equipped with electrical glow plugs to assist with starting the engine under cold conditions. The glow plug assists the ignition process of the fuel by providing an extra heat source to the compression of the air. The power of the engine is controlled by varying the volume of fuel injected into the cylinder. The timing of the combustion process must be precisely controlled to provide low emissions with optimum fuel efficiency.
2 Fuel

There are two main types of diesel fuel that are currently being used, namely petroleum diesel and biodiesel. Petroleum diesel is mainly produced by the refining of crude oil, coal or natural gas, whereas biodiesel is obtained from renewable plant extracts.

Two different types of biodiesel are used in this project. They are raps methyl ester and soya methyl ester. The phosphorus content of these biodiesel fuels causes extensive and complex problems in the exhaust gas-treatment systems and these occurrences will form part of this study.

2.1 Diesel/Biodiesel

**Diesel** The common type of diesel is derived from non-renewable resource that are mainly made up of hydrocarbons derived from the cracking of petroleum.

**Biodiesel**, as an alternative to petroleum-based diesel fuel, is made from renewable resources such as vegetable oils, animal fats, trap grease or cooking oil. To obtain biodiesel, the vegetable oil or animal fat is subjected to a chemical process called transesterification. In this reaction, the vegetable oil or animal fat is reacted in the presence of a catalyst with an alcohol (ethanol or methanol) to give the corresponding alkyl esters of the fatty acid mixture that is found in the parent vegetable oil or animal fat (Figure BC.2).
Figure BC.2: Transesterification reaction

The most common vegetable oils are: rapeseed/canola, soybean, cottonseed, palm, peanut, sunflower, safflower and coconut.

Biodiesel can be mixed with petroleum diesel fuel to form a blend. It is referred to as BXX, where XX represents the volume percentage of biodiesel fuel in the blend.

Methanol is used as the alcohol for producing biodiesel because it is the least expensive alcohol, although other alcohols such as ethanol or iso-propanol may yield a biodiesel fuel with better fuel properties. Often the resulting products are also called fatty acid methyl ester (FAME) instead of biodiesel.

The vegetable oils and animal fats are treated from alkyl esters because the kinematic viscosity of the biodiesel is much closer to that of petrodiesel. The high viscosity of untreated oils and fats usually leads to problems in the diesel engine such as causing deposits on engine parts and thereby impairing engine performance.

The fuel property that best indicates this suitability is the cetane number (tendency of a fuel to auto-ignite at the temperature and pressure present in the cylinder). In addition to the cetane number several other properties are important for determining the suitability of biodiesel as a fuel. Heat of combustion, pour point, cloud point, kinematic viscosity, oxidative stability and lubricity are the most important of these properties.

Some advantages and disadvantages of biodiesel when compared to petrodiesel are:

- Biodiesel is derived from a renewable resource thereby ensuring long term availability and reduces the dependence on the non-renewable petroleum.
• It is biodegradable, thereby reduces the long term impact the environment in terms of spillage.
• Results in a reduction of most unwanted exhaust emissions (with the exception of nitrogen oxides, NO\textsubscript{x}).
• Excellent lubricity. This is an important fact that is steadily gaining importance with the increased use of low-sulphur petrodiesel fuels, which have greatly reduced the lubricity. Adding biodiesel at low levels (1-2\%) restores the lubricity of the fuel.
• Currently biodiesel is more expensive than petrodiesel. However, this might change as production of the biodiesel increases and the cost of crude oil increases.
• Has a lower stability when exposed to air.
• Has worse cold flow properties when compared to petrodiesel\textsuperscript{21}.
• Diesel and biodiesel have different evaporation temperature.

2.2 Characteristics and properties of Diesel and Biodiesel

The classification of diesel and biodiesel is determined by different characteristics and properties that are specified in fuel standard norms that indicate the quality of the fuels. The European norm (EN), the American norm (ASTM) or international norms (ISO) are a few examples of the classifications that are used world-wide.

One of the most important properties is its readiness to auto-ignite at the temperature and pressure present in the cylinder when the fuel is injected. The laboratory test that is used to measure this tendency is the cetane number (CN) test. The Cetane Number is a dimensionless descriptor of the ignition quality of a fuel. It is a prime indicator of the fuel quality. Most of the engines are designed to work within a range of CN, 40-50.

A fuel with lower energy content per litre will cause the engine to produce less peak power. The engine operator will still be able to meet the demand for power but a greater volume of fuel will have to be injected.

Petrol diesel and biodiesel fuels are susceptible to start-up and performance problems when vehicles and fuel systems are subjected to cold temperatures. The tendency of a fuel to solidify or gel at low temperatures can be quantified by the cold
point (CP) and pour point (PP). With addition of additives the CP and PP of the fuel can be modified to inhibit solidification and eliminate agglomeration.

*The Viscosity* affects the atomization of a fuel during injection into the combustion chamber and influences the formation of engine deposits and the loss of power.

The production of a cleaner fuel could lower the *lubricity* of fuel and result in problems with the fuel injection technology.

*The Flashpoint* is the temperature at which the fuel will give off enough vapour to produce a flammable mixture: 52-66°C for diesel fuel. An important advantage of biodiesel is that it has very high flashpoint, <150°C.

The fuel injection systems are usually made of carbon steels which are prone to *corrosion* when in contact with water. The water content of fuels can affect the stability of the fuel and can produce corrosion. Some other compounds such as sulphur in fuel can also be corrosive.

Fuel filters are designed to stop foreign materials from entering into the fuel injection system. *Sediments* can be formed when fuels are exposed to high temperatures and to the oxygen in air. Biodiesel is expected to be more susceptible to oxidative degradation than petrol diesel fuel because of the low oxidative stability of unsaturated compounds found in fuel.

*Oxidative stability* is a characteristic that is only important to consider in the case of biodiesel fuel. Auto-oxidation can occur in presence of water, because of the double bonds in the chains of many fatty acid compounds. To reduce the effect of oxidative damage of the biodiesel, natural or synthetic antioxidants are used. The oxidative stability can be determined using the Rancimat method. Here a biodiesel sample is exposed to a moving air current with a temperature of 50 to 220°C. The lightly volatile halogenated hydrocarbons enter the Rancimat apparatus mixed with air and are absorbed in a measurement solution (distilled water). By analysing the conductivity of this solution it is possible to determine the oxidative stability of the sample. The biodiesel must have a minimum oxidative stability of 6 h as measured by the Rancimat method at 110°C.

### 2.3 Poisoning compounds in Petrodiesel and Biodiesel emissions

Under ideal circumstances the combustion of the fuels in the engine produces only carbon dioxide and water vapour as emissions. Since the combustion is not ideal, the
heterogeneous fuel-air mixture in the cylinder contributes to the formation of soot particles during the fuel combustion process. These particles are formed in high-temperature regions of the combustion chamber in which the air-fuel ratio is fuel-rich and consists mostly of carbon with small amounts of hydrogen and inorganic compounds. An important property to consider when using biodiesel is its ability to reduce the total particle emissions from an engine. 

$NO_X$ emissions are associated with high gas temperatures and lean fuel conditions. The use of biodiesel as fuel increases the $NO_X$ emissions, which is in contrast to most other emission pollutants that decrease with its use. 

$Sulphur$ can only be found in diesel and not in biodiesel. The sulphur that is present in diesel, will be oxidized to sulphur oxide. The sulphur oxides can react with water vapour to form sulphuric acid and other sulphate compounds. The Environmental Protection Agency (EPA) mandated by 2006 that diesel fuel should contain not more than 15 ppm of sulphur. With the reduction of sulphur in petrol diesel, it will also be reduced from the exhaust emissions and allow the introduction of a catalyst exhaust gas-treatment for diesel engines$^{21}$. Previously high sulphur content in the petrol diesel would extensively contaminate the exhaust catalyst. 

$Phosphorus$ is only present in biodiesel. The phosphorus could produce problems on the catalyst exhaust gas-treatment of diesel engines. The phosphorous content in biodiesel is determined by the EN 14214 (European Biodiesel Norm) not be higher than 10ppm. Phosphorus is present in biodiesel as phospholipids. Phospholipids are fat derivatives in which one fatty acid has been replaced by a phosphate group in a long chained hydrocarbon. They are soluble in nonpolar solvents (such as ether and chloroform) and are relatively insoluble in water.

![Phospholipid formulation](image)

**Figure BC.3:** Phospholipid formulation

Phospholipids of various types are present as minor components in most crude oils and are mostly removed during the refining process. They may be recovered in a by-
product, generally called lecithin, which is a mixture of phospholipids and triacylglycerols. Lecithin can also differ in concentration and type from one oil to another: soybean oil, rape oil, cottonseed oil, palm oil, peanut oil, sunflower oil, etc. The main phospholipids in crude lecithin are usually phosphatidylcholines, phosphatidylethanolamines, phosphatidylinositol, and phosphatidic acids. The phosphorus poisoning of the exhaust gas-treatment system is not only produced by the phosphorus content in biodiesel but also by the phosphorus content in the engine oil.

3 Engine oil

Engine oil are used for friction reduction, heat removal, corrosion reduction and the suspension of contaminant in moving engine parts. The majority of engine oils are derived from crude oil, but synthetic oils are also used. Additives are used to give the engine oil different proprieties. The design of a lubricant is a complex balance of the properties in the base oil and the performance enhancing additives.

Friction is reduced by maintaining a film of lubricant between surfaces that are moving with respect to each other, preventing the surfaces from coming into contact and subsequently causing surface damage. Viscosity is one of the most important properties of lubricating oil. It affects the sealing properties of oils and the rate of oil consumption. The satisfactory operation of any given piece of equipment depends on using an oil with the proper viscosity at the expected operating conditions. Kinematic viscosity is normally used to characterize lubricants. The viscosity of any fluid changes with temperature, increases as temperature decreases. ASTM Method D 2270 provides a means to calculate a viscosity index (VI) to enable a comparison between petroleum based oils with respect to viscosity variations with temperature.

Heat removal is another important function of a lubricant. The lubricant acts as a coolant, decreasing the heat generated by either friction or other sources such as combustion. In performing this function, the lubricant must remain relatively unchanged. Changes in thermal and oxidative stability will decrease a lubricant's efficiency.
In addition, the lubricant should remain effective in the presence of outside contaminants. Contaminants are for example water, acidic combustion products, and particle matter. Additives are generally used in minimizing the adverse effects of contaminants and to maintain the lubricant properties.

3.1 Lubricant base

A lubricant usually consists of a base fluid, generally of petroleum origin, combined with additive chemicals that enhance the various desirable properties. Base fluids are essentially obtained from two main sources: the refining of petroleum crude oil and the synthesis of relatively pure compounds with properties that are suitable for lubricants.

Petroleum lubricating oils are made from the higher boiling portion of the crude oil that remains after removal of the lighter fractions. This accounts for much of the possible variation in physical characteristics and performance qualities of base oils that are derived from different crude sources.

The synthetic lubricant oils are prepared by chemical reaction of lower molecular weight materials to produce a fluid of higher molecular weight designed to provide certain predictable properties. The synthetic lubricants have improved thermal and oxidative stability, more desirable viscosity/temperature characteristics, improved low-temperature properties, superior volatility characteristics and preferred frictional properties compared to petroleum-based fluids.

Synthetic materials can be used over a wider temperature range than petroleum base fluids in the same viscosity range. Certain synthetic lubricant base stocks can be blended with petroleum oils to obtain necessary high-temperature volatility and low-temperature viscosity characteristics when the proper petroleum base oils are unavailable.

3.2 Lubricant properties

Some of the most important properties necessary for satisfactory lubricant performance are:
1. Low volatility under operating conditions. Volatility characteristics are essentially inherent in the choice of a base oil for a particular type of service and can not be improved by the use of additive materials.

2. Satisfactory flow characteristics in the temperature range of use. Flow characteristics largely depend on the choice of base oil; however, they can be improved through the use of pour point depressants and viscosity modifiers.

3. Superior stability or ability to maintain desirable characteristics for a reasonable period of use. While these characteristics depend on the base oil to some extent, they are primarily associated with additive materials, which enhance base fluid properties in this area. Lubricant stability is affected by the environment in which it operates. Factors such as temperature, oxidation potential and contamination with water, unburnt fuel fragments, and corrosive acids limit the useful life of a lubricant. This is the area where additives have made a major contribution in improving the performance characteristics and extending the useful life of lubricants.

4. Compatibility with other materials in the system is partially associated with the base oil, but the additive chemistry can have a major influence on such characteristics\(^{38}\).

### 3.3 Lubricant additives

Additives can be classified as materials that impart new properties to or enhance existing properties of the lubricant or fuel into which they are incorporated\(^{38}\). The principal types of engine lubricant additives are described in the following table:
<table>
<thead>
<tr>
<th><strong>Table BC.1: Lubricant Additive Types</strong></th>
<th></th>
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</thead>
<tbody>
<tr>
<td><strong>Detergents</strong> (Metallic Dispersants)</td>
<td>Salicylates</td>
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<td></td>
<td>Sulfonates</td>
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<td></td>
<td>Phenates</td>
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<td></td>
<td>Sulfophenates</td>
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<tr>
<td><strong>Ashless Dispersants</strong></td>
<td>N-substituted long-chain alkenyl succinimides</td>
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<td></td>
<td>High-molecular-weight esters and polyesters</td>
</tr>
<tr>
<td></td>
<td>Amine salts of high-molecular-weight organic acids</td>
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<td></td>
<td>Mannich base derived from high-molecular-weight alkylated phenols</td>
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<tr>
<td></td>
<td>*Copolymers of methacrylic or acrylic acid derivatives containing polar groups such as amines, amides, imines, imides, hydroxyl, ether, etc.</td>
</tr>
<tr>
<td></td>
<td>*Ethylene-propylene copolymers containing polar groups as above</td>
</tr>
<tr>
<td><strong>Oxidation and Bearing Corrosion Inhibitors</strong></td>
<td>Organic phosphites</td>
</tr>
<tr>
<td></td>
<td>Metal dithiocarbamates</td>
</tr>
<tr>
<td></td>
<td>Sulphurized olefins</td>
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<td></td>
<td>Zinc Dithiophosphates</td>
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<tr>
<td><strong>Antioxidants</strong></td>
<td>Phenolic compounds</td>
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<td></td>
<td>Aromatic nitrogen compounds</td>
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<td></td>
<td>Phosphosulphurized terpenes</td>
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<tr>
<td><strong>Viscosity Modifiers</strong></td>
<td>Polymethacrylates</td>
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<td></td>
<td>Ethylene-propylene copolymers</td>
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<td>Styrene-diene copolymers</td>
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<td></td>
<td>Styrene-ester copolymers</td>
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<tr>
<td><strong>Antiwear Additives</strong></td>
<td>Organic phosphites</td>
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<td></td>
<td>Sulphurized olefins</td>
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<td>Zinc dithiophosphates</td>
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<tr>
<td></td>
<td>Alkaline compounds as acid neutralizers</td>
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<tr>
<td><strong>Pour Point Depressants</strong></td>
<td>Wax alkylated naphthalene</td>
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<td>Polymethacrylates</td>
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<td></td>
<td>Crosslinked wax alkylated phenols</td>
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<td>Vinyl acetate/fumaric-acid-ester copolymers</td>
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<td>Vinyl acetate/vinyl-ether copolymers</td>
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<td></td>
<td>Styrene-ester copolymers</td>
</tr>
</tbody>
</table>
3.3.1 **Detergents**

Their function appears to be the dispersing of particle matter rather than cleaning up existing dirt and debris. Materials of this type are generally molecules having a large hydrocarbon "tail" and a polar head group. The tail section serves as a solubilizer in the base fluid, while the polar group is attracted to contaminants in the lubricant. Some representative types of metallic dispersants are: Sulfonates, Salicylates, Phenates and Phenol Sulfide Salts and Thiophosphonates.

3.3.2 **Ashless dispersants**

The use of ashless dispersants is a major development in the additive field. These materials may be categorized into two broad types: high-molecular weight polymeric dispersants used to formulate multigrade oils and lower molecular weight additives for use where viscosity modification is not necessary. These additives are much more effective than the metallic types in controlling sludge and varnish deposits that result from intermittent and low-temperature gasoline engine operation. Compounds useful for this purpose are characterized by a polar group attached to a relatively high molecular weight hydrocarbon chain. The polar group generally contains one or more of the elements nitrogen, oxygen and phosphorus. The more widely used commercial products: N-Substituted Long-Chain Alkenyl Succinimides, High Molecular Weight Esters or Mannich Bases from High Molecular Weight Alkylated Phenols.

These ashless dispersants may serve the dual function of dispersant and viscosity modifier. They have two different structural features: those that are similar to materials employed as viscosity modifiers and those of polar compounds (which convey dispersion).

3.3.3 **Oxidation and Metal Corrosion Inhibitors**

The function of an oxidation inhibitor is to prevent deterioration of the lubricant associated with oxygen attack. These inhibitors either destroy free or interact with peroxides involved in the oxidation mechanism. Among the widely used antioxidants are phenolic types and zinc dithiophosphates. The first are considered to be of the chain-breaking variety, whereas the second are believed to be peroxide destroyers.
The corrosion of metal is generally considered to be due to the reaction of the acid with the oxides of the metal. In engine operation, these acids either originate from products of incomplete fuel combustion that find their way into the lubricant as blow-by gases or are produced from lubricant oxidation. Oxidation inhibitors can significantly reduce this tendency.

Detergents can reduce corrosion by neutralizing the corrosive acids. Other inhibitors such as zinc dithiophosphates and phosphosulphurized olefins not only inhibit oxidation but also form a protective film on the bearing surface, making it resistant to acid attack.

Zinc Dithiophosphates (ZDDP) (Peroxide Destroying) are of great commercial importance in engine lubricants. They not only serve as antioxidants but also provide both antiwear and bearing corrosion protection. The zinc dithiophosphates are made as follows:

![Zinc Dithiophosphate](image)

Figure BC.4: Zinc Dithiophosphate

where R = alkyl or aryl. Both alkyl and aryl derivatives are employed commercially. Alkyl derivatives are generally more effective as antiwear additives. Aryl derivatives have a higher degree of thermal stability. Both the antiwear and thermal stability characteristics of the alkyl compounds can be varied by using different alcohols. The principal alkyls are propyl, butyl, hexyl, octyl, and mixtures of these. It should be noted that the overall performance characteristics of ZDDPs are not related to the decomposition temperature. The ZDDP works by protecting the surface under conditions where elastohydrodynamic lubrication breaks down. The films should inhibit adhesion between the contacting surfaces. ZDDP has the ability to function in different ways with great success.

In engines that are exposed to these additives, the ZDDP has the undesirable tendency to produce zinc- and phosphorous-containing emissions, which are
potentially damaging to both catalyst performance and to the environment\textsuperscript{13}. Most of the phosphorus deposited on the catalyst surface forms phosphates such as zinc phosphate, aluminium phosphate, zinc calcium phosphate and cerium phosphate as non amorphous form. It can however also be deposited as amorphous phosphorus forms, when the circumstances are not optimal to allow a deposit as non amorphous form. The phosphorus is usually first deposited on the front of the catalyst surface and results in a deactivation and reduction of the catalyst activity area that contain Pt, Pd or Rh. The effect of phosphorus contamination in the catalyst increases with increasing vehicle mileage\textsuperscript{24}.

Phosphate Esters, \((\text{RO})_3\text{P}=\text{O}\), (e.g. \(\text{R}=\text{CH}_3\text{C}_6\text{H}_4\)) can be used as ashless phosphorus compound to substitute the ZDDP, but are much less common. They are used in synthetic base fluids for some applications\textsuperscript{34}.

3.3.4 **Antiwear Additives**

Wear is the loss of metal with subsequent change in clearance between surfaces moving relative to each other. If continued, it will result in equipment malfunction. Among the principal factors causing wear are metal-to-metal contact, presence of abrasive particle matter, and attack of corrosive acids. Metal-to-metal contact can be prevented by adding film-forming compounds that protect the surface either by physical absorption or chemical reaction. The zinc dithiophosphates (ZDDP) are widely used for this purpose and are particularly effective in reducing wear in valvetrain mechanisms. Other effective additives used contain phosphorus, sulphur, or combinations of these elements. Abrasive wear can be prevented by effective removal of particle matter by filtration of both the air entering the engine and the lubricant used during engine operation. Corrosive wear is largely the result of acidic blowby products formed during fuel combustion. This type of wear can be controlled by using alkaline additives such as basic phenates and sulfonates.

3.3.5 **Viscosity modifiers**

Viscosity modifiers comprise a class of materials that improves the viscosity/temperature characteristics of the lubricant. This modification of rheological properties results in increased viscosity at all temperatures. The viscosity increase is
more pronounced at high temperatures which significantly improves the viscosity index of the lubricant. Viscosity modifiers are generally oil-soluble organic polymers with molecular weights ranging from about 10,000 to 1 million. The polymer molecule in solution is swollen by the lubricant and the volume of the swollen entity determines the degree to which the polymer increases viscosity. The performance of these polymers also depends on shear stability or resistance to mechanical shear and on their chemical and thermal stability. A performance balance must be established which takes into consideration shear stability and viscosity needs as well as thermal and oxidative stability in actual engine operation.

3.3.6 Pour point depressants
Pour point depressants prevent the freezing of oil at low temperature. This phenomenon is associated with crystallization of the paraffin wax that is present in mineral oil fractions. To provide low pour points, the refiner removes wax components in a process known as dewaxing. Complete dewaxing would reduce the yield of lubricant oil to an uneconomical level. Therefore, the dewaxing process is supplemented by using additives that lower the pour point of the oil. Pour point depressants do not prevent wax from crystallizing in the oil, but are absorbed by the wax crystals and reduce the amount of oil occluded on the crystal. Reducing the crystal volume permits lubricant flow.

4 Emissions in engines
Emissions can be defined as substances that are discharged into the air by various processes, especially by internal combustion processes. In discussions regarding the composition of combustion engine exhaust emissions, the following terms are used repeatedly: carbon dioxide, nitrous oxide, particle matter and hydrocarbons. However, it is rarely mentioned that these substances constitute only a fraction of total exhaust gas emissions. The approximate composition of the exhaust emissions of diesel engines can be seen in the following figures.
The emissions from diesel engines are composed of three phases: solids, liquids and gases. The combined solids and liquids are called particles and are composed of dry carbon, inorganic oxides and liquids. The liquid is a combination of unburnt diesel fuel and lubricating oils. The gases are hydrocarbons, carbon monoxide, nitrogen oxides and sulphur dioxide.

The injection system provides the correct proportion of fuel and air to ensure the complete combustion of fuel. Diesel fuel is injected under pressure into the engine cylinder where it mixes with air and the combustion occurs.

$$C_xH_y + \left( x + \frac{y}{4} \right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$  \hspace{1cm} \text{Ec: BC1}

Under perfect combustion conditions only $N_2$, $CO_2$ and $H_2O$ are produced ($N_2$ comes from the air and passes through the engine without any reaction), but with an incomplete combustion $CO$, Hydrocarbons, soot, $SO_2$ and $NO_X$ are also produced. Those components that are already present in the atmosphere ($O_2$, $N_2$ and $H_2O$) can be categorised as safe. $CO_2$, which is present in the atmosphere as a natural gas, is on the border between safe and harmful due to its categorisation. It is not poisonous, but in higher concentrations it can contribute towards the greenhouse effect. $CO$, $C_xH_y$, $SO_2$, $NO_X$ and particles are categorised as harmful.

The following figure shows a summary of the intake and exhaust components of the combustion cycle which takes place in the diesel engine:
Figure BC.6: Intake and exhaust gas components

Description of diesel exhausts gas components:

- **Oxygen (O₂):** It is a primary component of air and, like nitrogen, is drawn in through the air filter.

- **Nitrogen (N₂):** Nitrogen is an elementary component of air and is transported into the combustion chamber through the air intake. The largest proportion of the nitrogen induced is discharged again in pure form in the exhaust gases. Only a small proportion of the nitrogen combines with oxygen O₂ to form nitrogen oxide NOₓ.

- **Carbon dioxide (CO₂):** It is produced by the combustion of the fuel. It is not dangerous, but CO₂ plays a major role in the greenhouse effect.

- **Water (H₂O):** It is partly induced by the engine (atmospheric humidity) and partly produced by the combustion of the fuel. Water is a harmless exhaust gas component.

- **Carbon monoxide (CO):** It is a result of the lack of oxygen in the fuel combustion and is produced due to the incomplete combustion of diesel fuel. It is difficult to detect without special equipment, and under normal conditions in open air, carbon monoxide will oxidise to carbon dioxide CO₂ within a short period of time.

- **Hydrocarbons (CₓHᵧ):** These are molecules (for example C₆H₆ and C₈H₁₈) that are produced during an incomplete combustion of fuel. They are
considered to be harmful and have different effects on the human body. Some hydrocarbons irritate the sensory organs while others are carcinogenic. Combined with sunshine and NO\textsubscript{X} in open air, hydrocarbons produce Ozone and what is commonly known as smog.

- **Nitrogen Oxides (NO\textsubscript{x}=NO+NO\textsubscript{2}):** are compounds of nitrogen N\textsubscript{2} and oxygen O\textsubscript{2}. It is formed at high temperatures and high pressures from a mixture with high oxygen content during the combustion cycle. It is a precursor of ozone-smog and must be controlled.

- **Particle matter (PM):** are produced by the combustion process of the Diesel engine when there is an oxygen deficiency. It is a complex composition of solid and liquid material. The composition of particle matter will depend on the particular engine. Particle matter are microscopic carbon spheres with a diameter of approximately 0.05 µm. The core is surrounded by hydrocarbons, metal oxides, phosphours and sulphur. It has a significant health impact on humans and is classified as “human carcinogen” or “probable human carcinogen”.
  Particle matter is often fractionated in terms of sulphate, soluble organic fraction (SOF), or volatile organic fraction (VOF), and carbon or soot.

- **Sulphur dioxide (SO\textsubscript{2}):** It is produced by the combustion of diesel containing sulphur. It has a characteristic smell and is a colourless gas. Sulphur dioxide is very harmful for the exhaust catalyst’s efficiency. However the sulphur content in fuels is being reduced in the EU and biodiesel fuel do not contain any sulphur.

The permitted amount of hydrocarbons, carbon monoxide, nitrogen oxides and diesel particle matter emitted into the air is prescribed by exhaust gas norms.
4.1 Exhaust gas Norms

There are different exhaust gas norms, but all of them are attempting to protect the environment from the emissions produced by engines. In Europe the European Union Norm defines the permitted emissions for passenger and commercial vehicles.

The European Union (EU) set various emission limits for passenger cars in 1993. These have been subsequently lowered in 1996, 2000 and again in 2005. For passenger cars and light commercial vehicles the emission standards and fuel composition, including sulphur levels, have been achieved for 2000 and 2005.

The emissions standards are categorised from EU I to EU V. The approval of new vehicle models that are produced in the automobile industry have to comply to these prescribed emission limits.

The EU IV Norm is currently enforced from year 2005 and substitutes the EU III. It dictates a reduction of the allowed exhaust gas limit values as show in the table BC.2.

In 2008 EU V will decrease the emission limits even further, requiring further development in the post-treatment of exhaust gases. These plans to reduce the particle limit value for diesel passenger vehicles even further, requires that in future all diesel passenger vehicles must be fitted with a particle filter\(^{30}\).

In South Africa the exhaust gas norm corresponding to EU I was introduced in 2005\(^ {40} \).

<table>
<thead>
<tr>
<th>Table BC.2: European exhaust gas norm</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_x)H(_y) + NO(_x) (g/Km)</td>
</tr>
<tr>
<td>Euro I, 1993</td>
</tr>
<tr>
<td>Euro II, 1996</td>
</tr>
<tr>
<td>Euro III, 2000</td>
</tr>
<tr>
<td>Euro IV, 2005</td>
</tr>
<tr>
<td>Euro V, 2007</td>
</tr>
</tbody>
</table>
4.2 Reduction of emissions

The development of individual automotive technologies alone is not enough to reduce certain exhaust gas components and fuel consumption. The answer is to look at vehicles as an integral whole and match all the automotive components to one another. Taking this holistic approach to vehicle development as a basis, three main exhaust emission control strategies can be defined:

- Engine design and modifications
- Exhaust gas treatment

4.2.1 Engine design and modifications

There are some different strategies to reduce the emissions through engine design and modifications: aerodynamics, weight saving, engine management system, engine and gearbox optimisation, fuel tank purging, exhaust gas recirculation, downsizing.

4.2.2 Exhaust gas treatments

The diesel engine operates with a surplus of oxygen in the fuel/air mixture. The oxygen content need not be controlled by the lambda probe, and an oxidation catalytic converter undertakes the task of catalytic cleaning by using the high residual oxygen level in the exhaust gas. As a result, the concentrations of hydrocarbons and carbon dioxide are substantially reduced. The particle matter typically emitted by a diesel engine is made up of a range of components which only the hydrocarbons are oxidised in the oxidation catalytic converter. The resulting residues of the particle matter can only be collected by special particle filters\textsuperscript{29}.

5 Exhaust gas exhaust gas-treatment systems

Using exhaust gas-treatment systems, the emissions can be controlled to fulfil the European gas emission norms.

All new passenger vehicles are now fitted with catalysts, which are positioned in the exhaust system, either near to the engine (close-coupled), or further down the
tailpipe (underfloor). Harmful gases are converted to harmless products in a reaction with the precious metal that is contained in the catalyst.

EU IV norms specify that the exhaust gas-treatment systems must have a life span of at least 100 000 km and that all components should maintain their properties for at least the specified mileage.

5.1 Emission control systems

Diesel control emissions are complex and require complicated catalytic treatment, diesel particle filters and new technologies that require accurate controls\textsuperscript{17,39}. There are two groups of diesel exhaust gas-treatment devices: diesel traps and diesel catalysts.

*Diesel traps*, are primarily diesel filters, that control diesel particle matter emissions by physically trapping the particles. The major challenge in the design of diesel filter systems is to regenerate the trap after collecting particle matter in a reliable and cost-effective manner. This is called a Diesel Particle Filter (DPF) and can also incorporate an oxidation catalyst.

*Diesel catalysts*, on the other hand, control emissions by promoting chemical changes in the exhaust gas. The exhaust gases pass through the heterogeneous catalyst and reacts with the catalyst on the contact surface. These systems are most effective in the treatment of gaseous emissions, hydrocarbons and carbon monoxide\textsuperscript{39}.

The following table lists some of the common technologies used to control emissions.
Table BC.3: Different technologies to control emissions

<table>
<thead>
<tr>
<th>Technology</th>
<th>Reaction Type</th>
<th>Reduced Emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel Oxidation Catalyst (DOC)</td>
<td>Oxidation</td>
<td>CO, C_xH_y</td>
</tr>
<tr>
<td>Diesel Particle Filter (DPF)</td>
<td>Retention of PM of diesel exhaust gas in Filter</td>
<td>PM</td>
</tr>
<tr>
<td>Selective Catalytic Reduction (SCR)</td>
<td>Selective catalytic reduction by ammonia/urea</td>
<td>NO_x</td>
</tr>
<tr>
<td>NOx storage catalyst</td>
<td>Oxidation/Reduction</td>
<td>NO_x</td>
</tr>
</tbody>
</table>

Often a combination of the different technologies is employed in order to maximize the emission reductions of PM, C_xH_y, CO and NO_x.

5.1.1 Diesel Oxidation Catalyst

Function

A Diesel Oxidation Catalyst (DOC) is installed after the engine for the control of CO and hydrocarbon emissions. The system is a proven, efficient technology, which converts large fractions of toxic emissions, chemically transforming hydrocarbons and CO to water vapor and carbon dioxide according with the following reaction equations.

\[
CO + \frac{1}{2} O_2 \rightarrow CO_2 \quad \text{Ec: BC 2}
\]

\[
C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2} H_2O \quad \text{Ec: BC 3}
\]

The conversion of CO and C_xH_y in the system requires oxygen and is accelerate by the use of suitable catalyst.

A catalyst is a material that increases the rate of chemical reactions without any changes in the catalyst structure or surface. The reactants are converted to products faster, implying that reactions can take place at lower temperatures. This saves both energy and reactor material. The active catalytic components are often dispersed on high surface area support carries, in order to maximize the number of active sites^{17}.
Assembly

The DOC is composed of a steel mantel, a mat and a ceramic structure (figure BC.7). The *steel mantel* is an extension of the emission system after the engine. The *mat* is a support system between the steel mantel and the ceramic structure. It protects the ceramic from the steel shell expansions at high temperatures, preserves the ceramic temperature and assures the conduction of all the exhaust gases through the ceramic. The *ceramic structure*, in the form of micro channels, is usually made of Cordierit® (2MgO*2Al₂O₃*5SiO₂). The surface area of the ceramic structure is increased by coating it with a secondary surface (washcoat) made of a porous material with oxide particles such as Al₂O₃ (the most commonly used carrier in catalysis), SiO₂, TiO₂ or SiO₂-Al₂O₃ combinations. The carriers are not catalytically active, but they provide stability and enhance the durability of the final catalyst. The catalyst or precious metal is distributed uniformly across the entire surface of the washcoat. The precious metals used are Platinum, Palladium (mostly Platinum) or a combination. The porous carrier support gives the catalyst a high surface area, where the pore size, structural shape of the carrier and the molecular dimensions of the diffusing molecule has an influence on the hydrodynamics of the gas flow. The inner surface, or specific surface, is the total porous surface. With a porous monolith the contact surface where the emissions pass through the monolith is increased and emissions can be oxidized more easily.

DOC systems are not only produced with ceramic substrates, but metal may also be used as the carrier surface for the precious metal required for the catalyst function.

![Figure BC.7: Diesel oxidation catalyst](image)
The DOC is installed after the engine, where the exhaust gas have relatively high
temperatures. The high temperatures aid the precious metals (Pt) in the completion
of the oxidation reaction.

The diesel oxidation catalyst activity can be characterized with the light-off
temperature test. The test is defined as where the 50% light-off temperature is the
temperature at which 50 % of the CO emission pollutants are converted to CO₂.

\[
CO\text{ conversion} = \frac{CO_{Before\,DOC} - CO_{After\,DOC}}{CO_{Before\,DOC}}
\]

The light-off temperature can vary and depends on the emissions components and
on the catalyst aging. Catalyst aging is usually accompanied by catalyst deactivation,
which means that the catalyst will no longer be able to promote chemical changes in
the emissions.

Catalysts can become deactivated by the combustion of oil and diesel counterparts in
high amounts. The unburnt oils and their additives deposit within the catalyst
structure under the cooler operating conditions. Unlike the organic portion of the oil
which is catalytically oxidized, the additives remain are deposited on the catalyst
surface. Zinc, phosphorous, sulphur, and calcium oxide accumulate on or within the
catalyst and contribute to the catalyst deactivation by decreasing the active surface
area pores\textsuperscript{17}.

A new catalyst begins to work with an approximate light-off temperature of 120°C and
could end up as high as 200°C for a used one. Old catalysts require a higher
operation temperature in order to produce the same good hydrocarbon conversion as
a new one.

5.1.2 Diesel Particle Filter

The introduction of Euro IV (2005) and Euro V (2008) requires a continuous decrease
in the allowed level of particles in diesel exhaust gas.

These particles are reduced by a particle filter system. It is necessary to differentiate
between: the diesel particle filter with and without additive.

System with additive: This system is used on vehicles where the particle filter is
installed further away from the engine. Due to the distance the exhaust gas has to
travel from the engine to the particle filter, the required ignition temperature for combustion of the particles can only be reached with the introduction of an additive. (Figure BC.8)

![Figure BC.8: Location of a Diesel Particle Filter with additive](image)

**System without additive:** This system is installed on vehicles where the particle filter is located close to the engine, which results in a reduced distance that the exhaust gas has to travel from the engine to the exhaust gas-treatment system. Although the exhaust gas temperature is still relatively high when it reaches the particle filter, it is not sufficient to burn off all the carbon soot particles. Therefore it is necessary to make modifications to the engine control system in order to inject more fuel per cycle to raise the combustion temperature temporarily. Future diesel vehicles would prefer the use of such systems (Figure BC.9).

![Figure BC.9: Location of a Diesel Particle Filter without additive](image)
5.1.2.1 Diesel Particle Filter with Additive

Similar to the diesel oxidation catalyst, the DPF is composed of 3 elements: a steel mantel, the mat and the ceramic monolith made of AlTi or Silicon Carbide (SiC) with a washcoat of Al₂O₃. The ceramic monolith itself has many macroscopic channels that run parallel and are alternately closed and connected to the next channel. The Silicon carbide is a suitable filtering material with a high mechanical strength, very good resistance to thermal changes, high resistance to wear and good thermal resilience and conductivity.

When exhaust gas enters the filter, particles of carbon are trapped in the input channels, while the gaseous content of the exhaust gas flows through the porous walls of the ceramic filter. (Figure BC.10)

This type of filtration is very efficient with more than 95% filtration of particles. The system produces a pressure drop which increases with the accumulation of particles. This pressure drop may not exceed 100 to 150 mbar in order to maintain engine performance. When the pressure drop becomes too significant, the filter is regenerated to prevent it from becoming blocked and thereby affecting its function. Regeneration is a process that is used for cleaning the DPF by burning off the accumulated particles. During the regeneration phase, the particles of carbon that are stored in the filter are burnt off at a temperature of approx. 500°C. The actual ignition temperature of the particles is about 600-650°C. The DPF is constructed to withstand temperatures of up to 1000°C to ensure that it will not be damaged during the regeneration process. The required exhaust gas temperature for regeneration can only be reached at full throttle with a diesel engine. In order to ensure regeneration of the diesel particle filter under all operating conditions, the ignition temperature of the carbon is lowered by the introduction of an additive and the
exhaust gas temperature is raised by the engine management system. The regeneration occurs every 500-700 kilometres, depending on the way the vehicle is driven and the process lasts about 5-10 minutes. There are no noticeable changes in vehicle performance and the driver is not aware that regeneration is occurring.

The additive is an iron-rich substance which is dissolved in a hydrocarbon mixture. It can be found for example on the vehicle in a separate fuel tank in the spare wheel compartment. The additive is mixed automatically with the fuel in the tank via the fuel return line each time the fuel tank is replenished. This occurs by means of a particle filter additive pump which is actuated by the engine control unit. The amount of fuel replenished is determined by the engine control unit, which draws information from the fuel tank sensor. Each time additive is added to the fuel tank, the concentration of iron molecules in the fuel is 10 ppm (parts per million). This equates to an approximate ratio of 1 litre of additive to 2800 litres of fuel. The additive in the fuel deposits itself on the particle filter together with the carbon soot.

5.1.2.2 Diesel Particle Filter without Additive

The catalytic coated diesel particle filter is located in the exhaust system after the turbocharger, in close proximity of the engine. (Figure BC.11)

The most common filter systems are made up of an oxidisation catalyst and a particle filter that have been combined to form one unit, the catalytic coated diesel particle filter. It joins the functions of the oxidisation catalyst and the diesel particle filter in a single component. Thanks to the design of this particle filter system and the
installation position close to the engine, the particles can be burnt off continuously without the addition of a fuel additive.

The construction of a diesel particle filter without additives is described in figure BC.12.

![Figure BC.12: Building the Diesel Particle Filter without additives](image)

The carbon soot particles from the exhaust gas are filtered by the catalytic coated diesel particle filter and while functioning as an oxidisation catalyst, it also cleans the exhaust gas of hydrocarbons and carbon monoxide which are converted into water and carbon dioxide.

The DPF without additives is composed of 3 elements, like the catalyst and the DPF with additives: a steel mantel, the mat and the ceramic monolith made of AlTi or Silicon Carbide (SiC) with a washcoat and precious metal on the surface. The ceramic monolith is made of many macroscopic channels that run parallel and are alternately closed and connected to the next channel. In this way, inlet and outlet channels are created that are separated by filter walls.

The silicon carbide filter walls are porous and are coated with a mixture of aluminium oxide and ceroxide. This mixture serves as a carrier layer for the catalytic converter. The carrier layer is coated with a precious metal (generally platinum) which acts as the catalyst. (Figure BC.13)
Since the channels are sealed alternately in the direction of flow from the inlet and outlet side, the carbon soot contaminated exhaust gas must flow through the porous silicon carbide filter walls. When this happens, the carbon soot particles are retained in the inlet channels and the gaseous components pass through the walls. The diesel particle filter requires a certain length in order to provide a large storage volume for the carbon soot. In addition, it must be coated enough platinum in order to maintain the desired catalytic properties. The catalytic coating of the diesel particle filter is separated into zones across the length of the filter. In the front zone there is a larger quantity of platinum than the rear zone. The following are advantages of the zone-like coating:

- In normal operating mode of the engine the diesel particle filter heats up quickly in the front area. Due to the higher concentration of platinum in the front zone of the catalyst, the filter has a very fast catalytic effect that results in a very short response time.
- In regeneration mode, the rear area of the diesel particle filter becomes very hot as the carbon soot is burnt off. Due to these high temperatures the platinum breaks down over a period of time. Therefore, the expensive raw material is not used as intensively in the rear zone.
- A further reason for using less platinum in the rear zone is ageing of the diesel particle filter. During operation, more and more deposits are built up in the rear area from combustion, which impair the catalytic effectiveness of the platinum.
The diesel particle filter must be cleaned of the particles of carbon soot regularly to prevent it from becoming blocked and its function thereby being affected. During the *regeneration* phase, the particles that have accumulated in the particle filter are burnt off (oxidised). With regeneration of the catalytic coated particle filter, passive regeneration and active regeneration are separated. Again the driver will not be aware that regeneration is occurring.

*Passive regeneration* is when the carbon soot particles are burnt off continuously without intervention from the engine management system. The particle filter is positioned in close proximity to the engine to assure that exhaust gas temperatures of 350-500 °C are obtained for example during motorway driving. The carbon soot particles are thereby converted into carbon dioxide by a reaction with nitrogen oxide. This gradual process occurs slowly and continuously through the platinum coating, which functions as a catalyst (Figure BC.14).

![Figure BC.14: Passive regeneration of the diesel particle filter](image)

The nitrogen and oxygen present in the exhaust gas are converted to nitrogen dioxide via the platinum coating.

\[
NO_x + O_2 \rightarrow NO_2 + \frac{x}{2}O_2 \quad \text{Ec: BC 5}
\]

The nitrogen dioxide (NO₂) reacts with the carbon (C) of the carbon soot particles. As a result, carbon monoxide (CO) and nitrogen monoxide (NO) are formed.
The carbon monoxide (CO) and nitrogen monoxide (NO) combine with oxygen (O$_2$) and form nitrogen dioxide (NO$_2$) and carbon dioxide (CO$_2$).

$$\text{NO}_2 + \text{C} \rightarrow \text{CO} + \text{NO}$$  \hspace{1cm} \text{Ec: BC 6}

$$\text{CO} + \text{NO} + \text{O}_2 \rightarrow \text{NO}_2 + \text{CO}_2$$  \hspace{1cm} \text{Ec: BC 7}

With *active regeneration*, the carbon soot particles are burn off through a targeted increase in the exhaust gas temperature by the engine management system. In urban traffic with low loads on the engine, the exhaust gas temperatures for passive regeneration of the particle filter are too low. Since the carbon soot particles cannot be broken down, deposits build up in the filter. As soon as a certain level of carbon soot deposits is reached in the filter, active regeneration is initiated by the engine management system. This process lasts for approximately 10 minutes. The carbon soot particles are burnt off to carbon dioxide at high exhaust gas temperatures from approximately 600 °C (Figure BC.15).

*Figure BC.15: Active regeneration of the diesel particle filter*

When this happens, the carbon from the soot particles oxidises with oxygen and forms carbon dioxide.
The future tendency in engine design is towards using the diesel particle filter without additives. The diesel particle filter aging is determined, as for the DOC, with a 50% light-off temperature test.

5.1.3 Selective Catalyst Reduction and Exhaust Gas Recirculation

With the Diesel Oxidation Catalysts (DOC) and Diesel Particle Filters (DPF) the PM, CO and HC emissions are controlled, but the NO\textsubscript{X} emissions are not. In order to reduce the NO\textsubscript{X} emissions, DOC and DPF can be combined with other exhaust gas-treatment technologies, like Selective Catalyst Reduction (SCR) and with a modification to the engine called an Exhaust Gas Recirculation (EGR) system.

SCR systems add a reductant (usually ammonia or urea) to diesel exhaust gas to reduce NO\textsubscript{X} to N\textsubscript{2}. As the name implies, NO\textsubscript{X} is selectively reduced by reacting it with a reagent, usually ammonia (NH\textsubscript{3}) or an ammonia-based reductant such as urea, across an SCR catalyst which reduces the NO and NO\textsubscript{2} to N\textsubscript{2} and water, as shown below.

\[
\begin{align*}
4NO + 4NH_3 + O_2 &\rightarrow 4N_2 + 6H_2O &\text{Ec: BC 9} \\
2NO_2 + 4NH_3 + O_2 &\rightarrow 3N_2 + 6H_2O &\text{Ec: BC 10}
\end{align*}
\]

Where there is a mixture of NO and NO\textsubscript{2} present in the exhaust gas stream, the following, somewhat faster reaction will occur in parallel:

\[
NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O
\]  

Ec: BC 11
Most SCR catalysts use base metal chemistry, employing platinum, vanadium, tungsten, titanium, silica and/or zeolite-based materials depending on the required temperature range of operation. At low temperatures (175-250°C) platinum is used, for medium temperatures (300-450°C) vanadium is used and at higher temperatures (350-600°C) zeolites are used. These can be extruded into a honeycomb structure or coated directly onto a metallic or ceramic honeycomb support. The reduction of NOx is dependent on the volume, reductant concentration, operating temperature and activity of the SCR catalyst. The major factors influencing catalyst selection include process gas temperature and a thorough examination of potential contaminants such as particle and catalyst poisons. The majority of the SCR catalysts in use today are designed to function in the 315-425°C temperature range where conversions in excess of 95% are routinely achieved.

The reagent injection system should be designed to ensure complete mixing of the reagent with the gas as an aid to the conversion process. Ammonia is used as the reductant at a 1:1 mole (or volume) ratio. Some unreacted ammonia will pass or “slip” through the process and this slip ammonia is usually limited by regulation to less than 20ppm and in some cases, less than 5ppm. As a precaution, a slip catalyst may also be used to remove any residual ammonia from the stream prior to venting. An aqueous solution of urea can also be used. This decomposes in the exhaust stream in two stages to form ammonia and carbon dioxide (CO2).

EGR involves recirculating a portion of the engine’s exhaust gas back to the charger inlet or intake manifold in the case of naturally aspirated engines. In many systems, an intercooler lowers the temperature of the recirculated gases. The cooled recirculated gases have a higher heat capacity and contain less oxygen than air, which lowers the combustion temperature in the engine and thereby reducing NOx formation.
5.1.4 NOx storage catalyst

The NOx storage catalyst is also used for the control of NOx emissions in diesel engines. Diesel engines are generally operated under lean conditions, meaning there is an excess of oxygen present in the combustion process. The CO and CxHy that are normally present in exhaust emissions need an excess of oxygen to be oxidized, but NOx needs the stoichiometric oxygen amount to be reduced. The NOx content in the emissions is first accumulated in a NOx storage catalyst and then reduced to nitrogen.

The accumulation of the NOx is achieved by using barium carbonate or barium oxide in addition to the typical precious metal components in the catalyst. These barium components are able to store nitric oxide under lean engine conditions. The nitric oxide is oxidised to NO2 on the precious metal (usually platinum) catalyst and the NO2 then forms barium nitrate in the presence of barium carbonate and oxygen. During the storage process a shell of nitrates is built up on the surface of the barium-particle and to enable further storage, the NO2 has to permeate through this nitrate shell to the core of the particle, thereby decreasing the storage reaction rate.

\[
NO + \frac{1}{2} O_2 \Leftrightarrow NO_2 \quad \text{Ec: BC 12}
\]

\[
BaCO_3 + 2NO_2 + \frac{1}{2} O_2 \Leftrightarrow Ba(NO_3)_2 + CO_2 \quad \text{Ec: BC 13}
\]

![Figure BC.16: NOx storage in a NOx storage catalyst](image)
Due to the limited storage capacity of the catalyst, it has to be regenerated periodically. Regeneration is achieved by allowing the engine to run very rich for a short period of time. Under these conditions there is a lack of oxygen in the exhaust gas and the nitrate reacts with carbonate or carbon monoxide and immediately produces nitrogen.

The regeneration process is much faster than the storage process and therefore the regeneration period can be much shorter than the storage period.

\[
Ba(NO_3)_2 + 3CO \rightleftharpoons BaCO_3 + 2NO + 2CO_2 \quad \text{Ec: BC 14}
\]

\[
NO + CO \rightleftharpoons \frac{1}{2}N_2 + CO_2 \quad \text{Ec: BC 15}
\]

The NO\textsubscript{x} can only be stored under exhaust conditions where the emission temperature is between 250 and 500°C.

The sulphur content in fuel tends to poison the NO\textsubscript{x} storage catalyst. The control of the sulphur content in fuel reduces and/or eliminates this problem. Once sulphur has accumulated on the catalyst, emission temperatures of 650°C are necessary to remove the sulphur poisoning from the system\textsuperscript{35}.

### 5.2 Catalyst deactivation

As indicated before the catalyst components (Pt, Pd) are dispersed as fine particles in order to obtain a high surface area, thereby maximizing the number of active sites (Figure BC.18).
The catalyst deactivation can occur thermally, mechanically and chemically. The three types of deactivation affect both the diesel oxidation catalyst and diesel particle filter.

### 5.2.1 Thermal deactivation

The dispersion of the catalyst on the washcoat surface is affected by the nature of the catalytic species, the carrier and the process gas environment. High emission temperatures affect the catalyst as follows:

*Sintering of the catalytic component* occurs when small “groups” of catalyst material (Pt) are formed on the surface where agglomeration of the fine particles reduces the effective catalyst sites (Figure BC.19).

![Figure BC.18: Catalytic sites dispersed on a high surface area Al₂O₃ carrier bonded to a monolith](image1)

![Figure BC.19: Conceptual diagram of sintering of the catalytic component on a carrier](image2)
This condition can be measured by selective chemisorption techniques in which a thermally aged catalyst adsorbs much less adsorbate than a new one. Certain rare earth oxides such as CeO₂ and La₂O₃ have been effective in reducing sintering rates of Pt in the automobile exhaust catalytic converter\textsuperscript{17}.

\textit{Carrier sintering} is produced with the closing of the pores during aging. In a catalyst with an Al₂O₃ washcoat, the loss of surface area is associated with a gradual loss of the internal pore structure (Figure BC.20).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{carrier_sintering.png}
\caption{Conceptual diagram of carrier sintering\textsuperscript{17}}
\end{figure}

When the sintering occurs, the pore gets progressively smaller, introducing pore diffusion resistance. This phenomenon is determined by a decrease in the activation energy of the reaction. If the pore is completely closed, the reactants could not react with the catalytic species inside. The occurrence of the mechanism is primarily detected by BET surface area measurements and pore size distribution (Hg porosimetry)\textsuperscript{17}.

\textit{Catalyst species-carrier Interactions} occurs when the active catalytic component (Pt) reacts with the carrier. This results in a loss of catalyst surface area, reducing its efficiency.
5.2.2 Chemical poisoning

A common cause of catalyst deactivation results when impurities are adsorbed on the catalyst surface, blocking active catalyst sites. There are two mechanisms by which poisoning occur: selective poisoning and nonselective poisoning.

*Selective poisoning* occurs when a substance reacts directly with an active site (Pt), decreasing its activity or selectivity for a reaction. Some poisons react chemically with the catalytic component. Others merely adsorb onto sites and block that site from further reaction. When the carrier reacts with a constituent in the gas stream to form a new compound, pores are generally blocked, resulting in increased diffusional resistance. This will cause a decrease in the activation energy. Bulk chemical analysis, surface analysis, and loss of chemisorption area are procedures commonly used to characterize this type of deactivation.

*Nonselective poisoning* occurs when particles are deposited on the washcoat or precious metal surface. These mechanisms are nondiscriminating in the poisoning effect and are due to the physical deposit on the outer surface of the catalyst. This mechanism of deactivation is referred to as masking. Bulk and surface chemical analysis is commonly used for detecting the nature of the masking agent. Accompanying masking is a decline in surface area caused by pore blockage\(^\text{17}\) (Figure BC.21).

![Figure BC.21: Conceptual diagram showing masking or fouling of the catalyzed washcoat\(^\text{17}\)](image_url)

Chemical species such as sulphur, phosphorus, zinc and calcium, can poison the catalyst when they pass from the engine oil or fuel to the catalyst surface.
Sulphur is an inhibitor, which strongly competes with the exhaust pollutants for space on the active catalyst surface. The chemistry of sulphur compound inhibition in emission control systems' performance is quite complex. Upon combustion, sulphur is oxidised to sulphur oxides, primarily sulphur dioxide (SO₂) with small amounts of sulphur trioxide (SO₃) which both inhibit the catalytic function of automobile exhaust catalysts. The degree of sulphur inhibition varies according to the sulphur level of the fuel, the catalyst formulation, catalytic function, combustion products from various air/fuel mixtures and exhaust temperature range. This poisoning of the exhaust gas treatment system by sulphur has been reduced by a combination of lowering the levels of this type of impurity in fuel and by developing more robust after treatment system formulations.

The main sources of zinc, calcium and phosphorus poisoning are the lubricant additives in the engine oil. Volatilisation and combustion of engine oil in the cylinder can result in deposition of phosphorus, zinc and calcium compounds on the surface of the catalyst that were carried out of the combustion chamber via the exhaust gas. The phosphorus content in biodiesel is another source of the phosphorus poisoning. The exact phosphorus poisoning process is currently not known and will form part of this study. The after treatment system may be poisoned by build up of matter on the surface of the catalyst preventing access of the exhaust gas to the catalytically active metal sites, or by reaction of the poisons with components of the catalyst formulation producing undesirable products.

Different phosphorus poisoning compounds are found on the aged catalyst/washcoat surface. This depends on the biodiesel and oil phosphorus level, the after treatment system formulation, catalytic function and exhaust temperature range. Some of the phosphorus poisoning compounds identified are: CaZn₂(PO₄)₂, CePO₄, CaCePO₄, Ca₃(PO₄)₂, AlPO₄ or Zn₂P₂O₇ (Glass phase).

5.2.3 Mechanical deactivation

The mechanical deactivation of the catalyst is an irreversible process with the loss of the catalyst washcoat via attrition or erosion. The catalyst breaks down when the emissions have a too high velocity and extreme temperature fluctuations. The washcoated monoliths can also physically break, thereby reducing the active catalyst sites.
Washcoat loss is observed by preparing a cross-section of the honeycomb catalyst and scanning the wall of the channel with an optical or scanning electron microscope. This loss of catalytic material is irreversible\(^\text{17}\).

In this study the influences of phosphorus poisoning on exhaust gas-treatment systems will be examined taking all factors and processes discussed in this chapter into consideration.
II. Experimental methodology

In this chapter the aging and analysis processes for the engines, exhaust gas-treatment systems, fuels and oils that were used will be described.

*Part one:* Study of the phosphorus poisoning produced by different biodiesel fuel types. This type of poisoning was examined with two different tests:

1. Comparison of the effects of different fuel types on the catalyst and on the engine. For this test an SDI engine (it provides the possibility of studying the deactivation of a catalyst at high temperature) was run with the same type of Diesel Oxidation Catalyst, the same oil type and different fuel types: Diesel fuel “DK”, Biodiesel “B20S” (20%vol SME, soya methyl ester, and 80%vol diesel), Biodiesel “B20SR” (10%vol SME, 10%vol RME, raps methyl ester, and 80%vol Diesel) and Biodiesel “B20R” (20%vol RME and 80%vol Diesel).

2. Phosphorus poisoning on the catalyst from different phosphorus concentrations in the same fuel type. Only one fuel type is used and the effects on the catalyst and on the engine are compared for different phosphorus concentrations in the fuel. For this test a TDI engine was run with the same Diesel Oxidation Catalyst type, the same oil type (commercial oil) and the same fuel type (biodiesel B20S) with different phosphorus concentrations. Biodiesel, B20S, was used as base fuel and the concentration of phosphorus in the fuel was varied for each test. Tributylphosphate was then added to the base fuel to produce biodiesel B20S with 25, 50 and 100ppm phosphorus respectively. 800 litres of fuel was prepared with each concentration for the catalyst aging tests.

The biodiesel fuel type SME is becoming very popular in Europe. However there is not much information about its influence on the catalyst and the engine and therefore the work on this project was both important and interesting. Furthermore, the future tendency is to use more SME as Biodiesel and with a higher % volume in diesel. Therefore, it was especially important to examine Biodiesel with a 20% volume of SME.

*Part two:* Study of the phosphorus poisoning produced by engine oil. For this part different oil types are used. The effects of these different oil types on the catalyst and
on the engine are compared. For this test a TDI engine was run with the same Diesel Particle Filter type, the same fuel type (without Phosphorus) and different oil types. The three oil types are as follows: “Oil A” is a commercial 0W-30 Euro III oil meeting VW 50300 and VW50601 standards (Phosphorus concentration of approx. 900ppm), “Oil B”, is an experimental modification of the OS191877 oil that is currently used at Volkswagen. It is formulated with conventional ZDDP anti-wear technology, but has a higher phosphorus concentration (approx. 1600ppm). “Oil C” is formulated with the same phosphorus levels as Oil B (approx. 1800ppm), but makes use of a Zn-free, phosphorus containing anti-wear component. Oils B and C were specially designed for this project by Lubrizol in order to accelerate the phosphorus poisoning process.

1 Study of the phosphorus poisoning produced by fuel

As indicated before the phosphorus poisoning produced by fuel was examined with two different tests. The first test implied the comparison of the effects of different fuel types on the catalyst and on the engine. The second test implied the phosphorus poisoning on the catalyst from different phosphorus concentrations in the same fuel type.

1.1 Aging of Diesel Oxidation Catalyst with different fuels

1.1.1 Instrumentation

The figure EM.1 shows a schematic representation of equipment used for the aging process and required measurements with different types of fuel. The engine (SDI), exhaust gas-treatment system (DOC) and measurement system (Emissions and temperature) that were used during the aging test are represented. The two measurement points for emissions and exhaust gas temperatures are located before and after the exhaust gas-treatment system respectively.
1.1.1.1 Engine

An SDI engine was used for the aging of the Diesel Oxidation Catalyst. This engine produces a high exhaust gas temperature, which provides the possibility of studying the deactivation of a catalyst at high temperature.

For each test the oil filter, fuel filter, air filter and the injection system were replaced and after each test the injection system were examined to determine if the different fuel types have different influences on them.

The technical data of the SDI engine is described in the following table.
### Table EM.1: Technical data of the SDI engine

<table>
<thead>
<tr>
<th>Characteristic of the SDI Engine</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Power (KW)</td>
<td>55</td>
</tr>
<tr>
<td>Max. Torque (Nm) @ RPM (1/min)</td>
<td>140 @ 4200</td>
</tr>
<tr>
<td>Capacity (cm³)</td>
<td>1968</td>
</tr>
<tr>
<td>Compression ratio</td>
<td>19</td>
</tr>
<tr>
<td>Cylinder</td>
<td>4</td>
</tr>
<tr>
<td>Fuel</td>
<td>D15 diesel sulphur &lt;10</td>
</tr>
<tr>
<td>Exhaust gas-treatment</td>
<td>EGR and DOC</td>
</tr>
<tr>
<td>Injection system</td>
<td>PDE</td>
</tr>
<tr>
<td>Exhaust gas Norms</td>
<td>Euro IV</td>
</tr>
</tbody>
</table>

1.1.1.2 Exhaust gas-treatment system

The Diesel Oxidation Catalyst (DOC) that was used as the exhaust gas-treatment system was supplied by Johnson Matthey Catalysts in England. For this project four DOCs were used and different catalyst parameters were determined before the aging test. The light-off temperature was determined before, during and after the aging process and after each test different analysis were done on each DOC (See 1.1.2.3 of the experimental methodology).

It is important to remember that the light-off temperature is defined as the temperature at which 50 % of the emission pollutants are transformed. CO and CₓHᵧ, especially CO, are the principal emissions used to characterize the activity of the catalyst. The CO and CₓHᵧ emission concentrations were measured according to the FTIR-Spectroscopy (Fourier-Transformation Infrared Spectroscopy). The measurement of the CₓHᵧ emission concentration is not as reliable as the CO measurement. The CO and CₓHᵧ concentration before the catalyst must remain approximately constant during each catalyst test in order to have a realistic activity comparison of each DOC.

The following table shows the technical data of the DOCs used.
Table EM.2: Technical data of the DOC

<table>
<thead>
<tr>
<th>Characteristics of the DOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size (mm)</td>
</tr>
<tr>
<td>Formulation</td>
</tr>
<tr>
<td>Substrate Type</td>
</tr>
<tr>
<td>Manufactured On</td>
</tr>
<tr>
<td>Cust. Order No</td>
</tr>
<tr>
<td>CSD Order No</td>
</tr>
<tr>
<td>Cust Batch</td>
</tr>
</tbody>
</table>

1.1.1.3 Fuel type

The different fuels that were used consisted of one commercial diesel fuel and two types of Biodiesel that all have low Sulfur contents. The Biodiesel types that were used are RME (Raps Methyl Ester) and SME (Soya Methyl Ester). RME Biodiesel is used more commonly in Europe than SME. It was important to compare the Biodiesel types, because the future tendency is toward using more SME Biodiesel.

The actual Biodiesel proportion in Diesel is approx. 5% volume, but the tests were done with a 20% volume Biodiesel, which it is the future tendency.

The characteristics of the Diesel and Biodiesel that were used are shown in table EM.3.

Table EM.3: Technical data of Diesel and Biodiesel

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>DK</th>
<th>B100S</th>
<th>B100R</th>
<th>B20S</th>
<th>B20SR</th>
<th>B20R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, 15 °C</td>
<td>g/ml</td>
<td>0,812</td>
<td>0,867</td>
<td>0,855</td>
<td>0,827</td>
<td>0,832</td>
<td>0,831</td>
</tr>
<tr>
<td>Kinematic viscosity, 40 °C</td>
<td>mm²/s</td>
<td>2,505</td>
<td>3,956</td>
<td>3,956</td>
<td>2,6805</td>
<td>2,665</td>
<td>3,956</td>
</tr>
<tr>
<td>Oxidation Stability</td>
<td>h</td>
<td>-</td>
<td>4,175</td>
<td>2,975</td>
<td>11,17</td>
<td>11,08</td>
<td>9,88</td>
</tr>
<tr>
<td>Acid number</td>
<td>mg KOH/g</td>
<td>0,018</td>
<td>0,584</td>
<td>--</td>
<td>0,128</td>
<td>0,094</td>
<td>0,071</td>
</tr>
<tr>
<td>Calcium</td>
<td>mg/kg</td>
<td>0,5</td>
<td>nn</td>
<td>&lt;0,1</td>
<td>0,1</td>
<td>&lt;0,1</td>
<td>&lt;0,1</td>
</tr>
<tr>
<td>Iron</td>
<td>mg/kg</td>
<td>nn</td>
<td>nn</td>
<td>nn</td>
<td>nn</td>
<td>nn</td>
<td>nn</td>
</tr>
<tr>
<td>Sodium</td>
<td>mg/kg</td>
<td>nn</td>
<td>nn</td>
<td>nn</td>
<td>nn</td>
<td>nn</td>
<td>nn</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>mg/kg</td>
<td>nn</td>
<td>nn</td>
<td>nn</td>
<td>nn</td>
<td>nn</td>
<td>nn</td>
</tr>
<tr>
<td>Sulfur</td>
<td>mg/kg</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Silicium</td>
<td>mg/kg</td>
<td>0,8</td>
<td>&lt;0,1</td>
<td>nn</td>
<td>0,7</td>
<td>0,5</td>
<td>0,5</td>
</tr>
<tr>
<td>Zinc</td>
<td>mg/kg</td>
<td>0,2</td>
<td>&lt;0,1</td>
<td>&lt;0,1</td>
<td>0,1</td>
<td>nn</td>
<td>&lt;0,1</td>
</tr>
</tbody>
</table>

nn: Not detectable
1.1.1.4 Oil type

The commercial 0W-30 Euro III oil meeting VW 50300 and VW50601 was used as oil during the aging process. This commercial oil was used because of the engine specifications (Table EM.4).

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Oil characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density by 15 °C</td>
<td>g/ml</td>
<td>0,853</td>
</tr>
<tr>
<td>Kinematical viscosity, 40 °C</td>
<td>mm²/s</td>
<td>53,55</td>
</tr>
<tr>
<td>TBN</td>
<td>mg KOH/g</td>
<td>9,7</td>
</tr>
<tr>
<td>Ca-Content</td>
<td>ppm</td>
<td>3000</td>
</tr>
<tr>
<td>P-Content</td>
<td>ppm</td>
<td>900</td>
</tr>
<tr>
<td>Zn-Content</td>
<td>ppm</td>
<td>100</td>
</tr>
<tr>
<td>S-Content</td>
<td>ppm</td>
<td>4310</td>
</tr>
<tr>
<td>Mg-Content</td>
<td>ppm</td>
<td>200</td>
</tr>
</tbody>
</table>

1.1.2 Methodology

1.1.2.1 Selecting the engine operating points for the aging program and light-off temperature test

An engine characteristic map was produced by performing a series of tests with the engine using different engine speeds and loads while measuring the emission composition and temperatures. From the resulting map it is then possible to determine a series of significant engine operating points to ensure an aging process and light-off temperature test that will provide aging of the catalyst with emissions and temperatures that represent real driving conditions. The engine characteristic map and the chosen operating points can be seen in Attachment EM.1 to EM.3.

The engine operating points that were chosen from the characteristic map to define the aging process are shown in table EM.5:
The engine operating points for the light-off temperature were chosen to have almost constant emission values, especially in the case of CO. [Attachment EM.4 to EM.6]. It was done in order to obtain relatively constant emissions values to compare the catalyst realistically. This ensured that the procedure for the catalyst aging test was always the same for all fuel tests.

The chosen operating points for the light-off temperature test is shown in table EM.6.

| Table EM.6: Engine operating points used to determine Light-off temperature |
|-----------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| RPM (1/min) | Load (Nw) | Time (s) | CO (ppm) | HC (ppm) | Temperature (°C) |
| 1. 1500 0 1500 484 81 81 |
| 2. 1500 5 1500 485 94 98 |
| 3. 1500 10 1500 444 89 108 |
| 4. 1500 15 1500 441 90 110 |
| 5. 1500 20 1500 429 90 132 |
| 6. 1500 25 1500 412 88 144 |
| 7. 1500 30 1500 392 92 155 |
| 8. 1500 35 1500 361 91 167 |
| 9. 1500 40 1500 355 90 182 |
| 10. 1500 45 1500 328 91 197 |
| 11. 1500 50 1500 308 91 211 |
| 12. 1500 55 1500 283 89 227 |
| 13. 1500 60 1500 251 95 243 |
The aging of the catalyst over time can be seen with the light-off temperature tests and the influence of different fuels on the performance of each catalyst can also be compared with this test. At the end of the aging process, each catalyst was analysed.

1.1.2.2 Aging process

After selecting the operation points for the aging process and the light-off temperature test the same procedure was followed for all fuel types:

1. Before the start of each test, an oil change is performed and the air filter, oil filter, fuel filter and injection system are replaced on the engine.
2. A full load test is performed at the start of the aging program.
3. Installation of a new DOC system after the engine, before each aging fuel test.
4. The first light-off temperature test is performed by running the engine for around 5 hours according to the light-off temperature operation points.
5. The engine is cycled through 12 x 8 cycles of the aging program operating points, which amounts to an aging time of the DOC of 42 hours (approx. half of the total aging time).
6. The second light-off temperature test is performed (around 5 hours again).
7. This is followed by another 12 x 8 cycles of the aging operating points. (around 42 hours of aging again). The aging process of the catalyst is then complete (total aging time of approx. 84 hours).
8. A final light-off temperature test is run (around 5 hours again).
9. The DOC system is removed from the engine.
10. Another full load test is performed at the end of the aging program after which the results are compared to those of the full load test before the aging.
11. The oil is drained from the engine, noting the exact amount of oil that was used during the aging process. A sample of the oil is taken before and after each aging step and analysed in a laboratory.
12. The injection system is removed from the engine before commencing the next fuel type test.

After the final aging process was completed, a light-off temperature test was done for each tested DOC. The reason for this is to obtain a realistic comparison between all the aged DOCs, since the engine properties change during the aging process. The
engine changes during the run period, so with the final light-off temperature test of every aged DOC at the same time, the results can be compared. This is summarized in figure EM.2.

![Aging process of every DOC](image)

**Figure EM.2**: Aging process diagram: SDI Engine and DOC

1.1.2.3 Analysis- and measurement systems

**Engine test stand**

On the engine test stand the exhaust emissions components were measured with different measurement systems while running the engine.

SESAM (System for Emission Sampling and Measurement) equipment was used for the measurement of the gas emissions components. The SESAM equipment uses the FTIR-Spectroscopy (Fourier-Transformation Infrared Spectroscopy) principle with a dynamic measurement of the gas emissions components. The system can measure 25 infrared active gas emissions components per second. One SESAM unit was used between the engine and the catalyst and other was used after the catalyst. The amount of soot in the exhaust emissions was determined with a Smoke Meter. A portion of undiluted emissions goes through a filter cartridge and the soot is trapped in the filter. A light shines onto the filter and the reflected light is measured with a Photocell. When the soot content of the emissions increases, the filter colour
becomes darker resulting in the absorption of light. The reflected light is an indication of the soot collected on the filter\textsuperscript{3}.

*After treatment systems*

The DOCs were analysed by at Johnson Matthey Catalysts Laboratories in England because of their extensive experience and instrumentation. The DOCs were submitted to post mortem analysis to investigate the thermal history of the catalyst, the catalyst poisoning (particularly for phosphorus) and the location and morphology of the phosphorus deposition. The following experimental techniques were used:

- Physical examination of the catalyst for any external physical damage.
- Analysis of the washcoat composition using X-ray Fluorescence (XRF).
- Investigation of the crystal structure of the washcoat and identification of the crystalline phosphorus phase using the X-ray diffraction (XRD).
- Determination of the washcoat specific surface area (SSA) using the nitrogen physisorption 5-point BET method.
- Determination of the Phosphorus location throughout washcoat and the morphology of the washcoat using the scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis and with Wavelength Dispersive X-ray analysis, (WDX).

The analyses of fuels, oils and injection systems were all done locally in the laboratories of the Volkswagen AG in Wolfsburg.

*Fuel analyses*

A sample of each fuel was taken and different parameters were analysed according to the following European Norms (Table EM.7):
**Table EM.7: European Norms used for the Diesel fuel analyses**

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Norm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density by 15 °C</td>
<td>Kg/l</td>
<td>EN ISO 12185</td>
</tr>
<tr>
<td>Kinematic viscosity, 40 °C</td>
<td>mm²/s</td>
<td>DIN EN ISO 3104</td>
</tr>
<tr>
<td>Acid number</td>
<td>mg KOH/g</td>
<td>ASTM D 974</td>
</tr>
<tr>
<td>Entire pollution</td>
<td>ppm</td>
<td>DIN EN 12662</td>
</tr>
<tr>
<td>ICP</td>
<td>ppm</td>
<td>In-house Method</td>
</tr>
</tbody>
</table>

**Oil analyses**

A sample of fresh oil before the test and old engine oil after every run was taken and different parameters were analysed corresponding to the European Norms (Table EM.8):

**Table EM.8: European Norms used for the oil analyses**

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Norm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematic viscosity, 40 °C</td>
<td>mm²/s</td>
<td>DIN 51562</td>
</tr>
<tr>
<td>TBN</td>
<td>mg KOH/g</td>
<td>DIN 3771</td>
</tr>
<tr>
<td>Fuel content</td>
<td>%</td>
<td>In-house Method</td>
</tr>
<tr>
<td>ICP</td>
<td>ppm</td>
<td>DIN 51391     DIN 51396</td>
</tr>
</tbody>
</table>

**Injection systems**

Before and after the aging tests, the flow rate of each injection system was measured using specially formulated oil at a pressure of 100 bar and temperature of 40 °C, following the standard injection system procedure from Robert Bosch⁴⁰. A surface analysis of every injection system was done using the scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis in order to determine the deposited elements on the surface. Photos of every injection system were taken and documented.
1.2 Aging of a Diesel Oxidation Catalyst with a single fuel with different phosphorus concentrations

The fuel test with different phosphorus concentrations was done in order to determine how the phosphorus from the Biodiesel affects the catalyst. For this test a TDI engine was driven with the same Diesel Oxidation Catalyst type, the same oil type (commercial oil) and the same Biodiesel type with different Phosphorus concentrations. The future tendency in Europe is to use biodiesel of the type B20S (20%vol SME and 80%vol diesel) more extensively and therefore B20S was the fuel chosen to be used in this project.

The Tributylphosphate has similar proprieties to the phosphate contained in Biodiesel and is completely soluble in Biodiesel over a range of concentrations. The phosphate addition was done to accelerate the phosphorus aging on the catalyst.

It is possible to simulate different driving distances of the engine by using fuel with different phosphorus concentrations because running the engine with a fuel with a high phosphorus concentration will cause the simulated driving distance to increase in comparison to a fuel with a lower phosphorus concentration. It is possible to calculate the required phosphorus content in the fuel by assuming minimum desired driving distances that are to be simulated. The required phosphorus content in the fuel was calculated at 25, 50 and 100 ppm (rounded-off values) for assumed minimum desired driving distances of approximately 25.000, 50.000 and 100.000.

The following table shows the calculated phosphorus content in fuel and the actual simulated kilometres that are expected result from running the engine with 800 litres of fuel with the respective phosphorus content.
Table EM.9: Phosphorus in fuel and kilometres simulated

<table>
<thead>
<tr>
<th>P content in fuel (ppm)</th>
<th>Fuel (l)</th>
<th>Km simulation P content in fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>800</td>
<td>28.600</td>
</tr>
<tr>
<td>50</td>
<td>800</td>
<td>67.200</td>
</tr>
<tr>
<td>100</td>
<td>800</td>
<td>143.000</td>
</tr>
</tbody>
</table>

Following the actual exhaust gas norm in Europe, EU IV, the exhaust gas-treatment systems must function correctly for a driving distance of 100,000 km.

1.2.1 Instrumentation

The figure EM.4 shows a schematic representation of equipment used for the aging process with doped fuels. The engine (TDI), after treatment system (DOC) and measurement system (Emissions and temperature) than were used during the aging test are represented. The measurement points for emissions and exhaust gas temperatures are the same as used in the previous test.
1.2.1.1 Engine

A TDI engine was used for the aging of the catalysts during the tests with Biodiesel with different phosphorus concentrations. A Diesel Oxidation Catalyst (DOC) exhaust gas-treatment system was used because of its relatively small size. In a small catalyst, the poisoning process happens relatively quickly and an acceleration of this process is easier to produce than with a big catalyst.

For each test the oil, oil filter, fuel filter, air filter and the injection system was changed and the oil was analysed after each test. The engine was run with a total of 800 litres of doped B20S fuel for the aging process of each catalyst. The injection system was changed and examined after every 400 litres to determine if different phosphorus concentrations in the fuel would have different influences on them.

The technical data of the TDI engine is described in table EM.10.

<table>
<thead>
<tr>
<th>Characteristic of the TDI Engine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power (KW)</td>
</tr>
<tr>
<td>Max. Torque (Nm) @ RPM (1/min)</td>
</tr>
<tr>
<td>Capacity (cm³)</td>
</tr>
<tr>
<td>Compression ratio</td>
</tr>
<tr>
<td>Cylinder</td>
</tr>
<tr>
<td>Fuel</td>
</tr>
<tr>
<td>Exhaust gas-treatment</td>
</tr>
<tr>
<td>Injection system</td>
</tr>
<tr>
<td>Exhaust gas Norms</td>
</tr>
</tbody>
</table>

1.2.1.2 Exhaust gas-treatment system

For this test a different type of Diesel Oxidation Catalyst (DOC) was supplied by the catalyst supplier Johnson Matthey Catalysts in England.

In total, four DOCs were aged during this project. A fresh DOC (without aging) was used to compare the light-off temperature of a catalyst that was not aged to the light-
off temperature of the catalysts that were aged with B20S with different phosphorus concentrations. The light-off temperature was determined after the aging process and after each test different analyses were done on each DOC. As described in section 1.2.2.3 of the experimental methodology.

During the catalyst aging the emissions of the tests run with pure B20S and with B20S (25ppm P) were not measured because of technical problems with the SESAM unit.

The technical data of the DOCs that were used are described in the following table.

<table>
<thead>
<tr>
<th>Characteristic of the DOC</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size (mm)</td>
<td>144,3 x 118,4 x 76,2</td>
</tr>
<tr>
<td>Formulation</td>
<td>90 g/ft³ /1Pt:0Pd:0Rh</td>
</tr>
<tr>
<td>Formulation: Rear</td>
<td>40 g/ft³ /1Pt:0Pd:0Rh</td>
</tr>
<tr>
<td>Substrate Type</td>
<td>CGW350</td>
</tr>
<tr>
<td>Manufactured On</td>
<td>26. Sep 05</td>
</tr>
<tr>
<td>Cust. Order No</td>
<td>FOC</td>
</tr>
<tr>
<td>CSD Order No</td>
<td>SAM13809/1</td>
</tr>
<tr>
<td>Cust Batch</td>
<td>SN2207</td>
</tr>
</tbody>
</table>

1.2.1.3 Fuel type

The different fuel options consist of the same Biodiesel type with different phosphorus concentrations. The Biodiesel type that was used was SME (Soya Methyl Ester), a Diesel type with a 20% Biodiesel volume (B20S). This decision was made because of the increasingly important role that SME is playing in the European market.

The technical data of the Biodiesel is shown in table EM.12.
Table EM.12: Technical data of B20S with and without phosphorus as additive

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>B20S 2. supplier</th>
<th>B20S-25ppmP</th>
<th>B20S-50ppmP</th>
<th>B20S-100ppmP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematic viscosity, 40 °C</td>
<td>mm²/s</td>
<td>2,970</td>
<td>2,771</td>
<td>2,967</td>
<td>2,984</td>
</tr>
<tr>
<td>Entire pollution</td>
<td>ppm</td>
<td>8,45</td>
<td>6,92</td>
<td>7,86</td>
<td>6,80</td>
</tr>
<tr>
<td>Oxidation stability</td>
<td>h</td>
<td>18,94</td>
<td>--</td>
<td>42,50</td>
<td>44,19</td>
</tr>
<tr>
<td>Acid number</td>
<td>mg KOH/g</td>
<td>0,058</td>
<td>0,006</td>
<td>0,010</td>
<td>0,007</td>
</tr>
<tr>
<td>FAME Content</td>
<td></td>
<td>18,6</td>
<td>9</td>
<td>7,1</td>
<td>7</td>
</tr>
<tr>
<td>Calcium</td>
<td>mg/kg</td>
<td>&lt;0,1</td>
<td>0,1</td>
<td>&lt;0,1</td>
<td>&lt;0,1</td>
</tr>
<tr>
<td>Magnesium</td>
<td>mg/kg</td>
<td>&lt;0,1</td>
<td>nn</td>
<td>&lt;0,1</td>
<td>&lt;0,1</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>mg/kg</td>
<td>0</td>
<td>0,4</td>
<td>24</td>
<td>54</td>
</tr>
<tr>
<td>Sulfur</td>
<td>mg/kg</td>
<td>nn</td>
<td>nn</td>
<td>nn</td>
<td>nn</td>
</tr>
<tr>
<td>Silicon</td>
<td>mg/kg</td>
<td>0,6</td>
<td>0,6</td>
<td>0,6</td>
<td>0,5</td>
</tr>
<tr>
<td>Zinc</td>
<td>mg/kg</td>
<td>0,1</td>
<td>nn</td>
<td>0,1</td>
<td>0,1</td>
</tr>
</tbody>
</table>

nn: Not detectable   --: Not measured

1.2.1.4 Oil type

The oil type is the same Castrol PBG Long life II as used in the fuel tests and is prescribed by the engine specifications (Table EM.13).

Table EM.13: Technical data of the Oil, Castrol PBG long life II

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Oil characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density by 15 °C</td>
<td>g/ml</td>
<td>0,853</td>
</tr>
<tr>
<td>Kinematical viscosity, 40 °C</td>
<td>mm²/s</td>
<td>53,55</td>
</tr>
<tr>
<td>TBN</td>
<td>mg KOH/g</td>
<td>9,7</td>
</tr>
<tr>
<td>Ca-Content</td>
<td>ppm</td>
<td>3000</td>
</tr>
<tr>
<td>P-Content</td>
<td>ppm</td>
<td>900</td>
</tr>
<tr>
<td>Zn-Content</td>
<td>ppm</td>
<td>100</td>
</tr>
<tr>
<td>S-Content</td>
<td>ppm</td>
<td>4310</td>
</tr>
<tr>
<td>Mg-Content</td>
<td>ppm</td>
<td>200</td>
</tr>
</tbody>
</table>
1.2.2 Methodology

1.2.2.1 Selecting the engine operating points for the aging program and light-off temperature test

The same procedure was followed as for the first fuel test to determine the aging process and the light-off temperature points, see 1.1.2.1 of this part. The engine was run with diesel and biodiesel (B20S) fuel and the emissions and temperatures were measured. The aging operating points were chosen from experience to represent a realistic aging of the catalyst. [Attachment EM.7 to EM.12]. Since temperatures higher than 460 °C were not possible because of engine test bench limitations, the engine was run with lower temperature emissions to get a phosphorus aging of the DOC (Table EM.14).

<table>
<thead>
<tr>
<th>Table EM.14: Aging engine operating points for DOC aging with B20S</th>
</tr>
</thead>
<tbody>
<tr>
<td>RPM (1/min)</td>
</tr>
<tr>
<td>1.</td>
</tr>
<tr>
<td>2.</td>
</tr>
<tr>
<td>3.</td>
</tr>
<tr>
<td>4.</td>
</tr>
<tr>
<td>5.</td>
</tr>
<tr>
<td>6.</td>
</tr>
<tr>
<td>7.</td>
</tr>
<tr>
<td>8.</td>
</tr>
<tr>
<td>9.</td>
</tr>
<tr>
<td>10.</td>
</tr>
<tr>
<td>11.</td>
</tr>
</tbody>
</table>

The engine operating points for the light-off temperature were chosen to provide the most information possible. The engine was run with different operating points with the exhaust gas temperature ranging from 0 to 200 °C. This is different to the previously performed light-off temperature tests, since the engine is not only run at one engine speed with different load points, but at different engine speeds and different load points. This produces very detailed information about the catalyst activity.
The methodology of the catalyst aging test was the same for all B20S tests (with and without phosphorus additive).

1.2.2.2 Aging process

After determining the aging operating points and defining the light-off temperature test, the following aging process was followed:

1. Oil change and installation of new oil filter, fuel filter and injection system.
2. Installation of the DOC system.
3. Aging of the DOC by running the engine with 400 litres of Biodiesel (B20S). The aging points were run approx. 15 times, amounting to a total aging time of the DOC of approx. 75 hours.
4. Change of the injection system.
5. Second part of the aging process of the same DOC, running the engine with a further 400 litres of Biodiesel.
6. Removal of the DOC system.
7. Drain the engine of the oil. It is important to note the exact amount of oil that was used during the aging. A sample of the oil before and after each aging was taken and analysed in a laboratory.
8. The injection systems, which were used during the last 400 litres, were removed from the engine.

At the end of the aging process a light-off temperature test of each DOC, including a fresh DOC, was performed. The light-off temperature test was done using standard diesel fuel for all DOCs to enable a realistic comparison between them. During this final light-off temperature test, the engine was run with different operating points from 0 to 200 °C emission temperature for each DOC for a period of approx. 45 hours per DOC.

The following figure summarizes the aging process.
1.2.2.3 Analysis system

The analyses were similar to that of the fuel test. During the aging test it was not always possible to use the SESAM equipment before and after the catalyst because of technical problems. These problems resulted in a situation where a SESAM unit could only be installed between the engine and the catalyst and not after the catalyst. In the case of the light-off temperature test, the SESAM equipment could be used to measure the emissions before and after the DOC for every engine operating point. The DOCs were also analysed by Johnson Matthey Catalysts laboratories. The same analyses were done for the diesel fuel and biodiesel fuel, but the oxidation stability of the biodiesel fuel was measured additionally. As indicated in the basic concepts, the oxidation stability was measured using the Rancimat method (Table EM.15)\textsuperscript{21}.
### Table EM.15: European Norms used for the diesel and biodiesel fuel analyses

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Norm Diesel</th>
<th>Norm Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density by 15 °C</td>
<td>Kg/l</td>
<td>EN ISO 12185</td>
<td>EN ISO 12185</td>
</tr>
<tr>
<td>Kinematic viscosity, 40 °C</td>
<td>mm²/s</td>
<td>DIN EN ISO 3104</td>
<td>DIN EN ISO 3104</td>
</tr>
<tr>
<td>Oxidation stability</td>
<td>h</td>
<td>--</td>
<td>DIN EN 14214</td>
</tr>
<tr>
<td>Acid number</td>
<td>mg KOH/g</td>
<td>ASTM D 974</td>
<td>ASTM D 974</td>
</tr>
<tr>
<td>Entire pollution</td>
<td>ppm</td>
<td>DIN EN 12662</td>
<td>DIN EN 12662</td>
</tr>
<tr>
<td>ICP</td>
<td>ppm</td>
<td>Home Method</td>
<td>Home Method</td>
</tr>
</tbody>
</table>

---

### 2 Study of the phosphorus poisons produced from oil

The oil tests were done to determine how the phosphorus from the oil affects the catalyst. For this test different oil types were used and the effects of each oil were compared. The phosphorous poisoning process was accelerated by increasing the content of phosphorous in the oil and a modification of the piston rings. The tests for the different oil types were conducted in much the same way and on the same test bench as the tests with the different fuel types. A different engine was used and therefore it was necessary to define a new aging program that suits the particular type of engine.

#### 2.1 Instrumentation

The following figure shows a schematic representation of the test assembly used for the aging test. The engine (TDI), exhaust gas-treatment system (DPF) and measurement systems are represented. Measurement points for exhaust emission composition, gas temperatures and pressures are located before and after the DPF. For this test the pressure drop ($\Delta P$) across the DPF as well as 5 different surface temperatures ($T_{1-5}$) were also measured.
2.1.1 Engine

A Diesel Particle Filter (DPF) exhaust gas-treatment system was used for the oil tests because of the oil supplier specifications and this exhaust gas-treatment system dictates the use of a TDI engine (Table EM.16). For each test the oil was changed and the oil filter, fuel filter, air filter, injection system, camshaft and bucket tappets were replaced. After each test the injection system, the camshaft and bucket tappets were examined to determine if different oil types have different influences on them and if the oils are performing their function correctly.

Table EM.16: Technical data of the TDI engine

<table>
<thead>
<tr>
<th>Characteristic of the TDI Engine</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power (KW)</td>
<td>103</td>
</tr>
<tr>
<td>Max. Torque @ RPM (1/min)</td>
<td>330 @ 4000</td>
</tr>
<tr>
<td>Capacity (ccm)</td>
<td>1968</td>
</tr>
<tr>
<td>Compression ratio</td>
<td>18,5</td>
</tr>
<tr>
<td>Stroke (mm)</td>
<td>95,5</td>
</tr>
<tr>
<td>Cylinder</td>
<td>4</td>
</tr>
<tr>
<td>Fuel</td>
<td>D15 Diesel Sulfur &lt;10</td>
</tr>
<tr>
<td>Exhaust gas-treatment</td>
<td>EGR and DPF</td>
</tr>
<tr>
<td>Injection system</td>
<td>PDE</td>
</tr>
<tr>
<td>Exhaust gas Norms</td>
<td>Euro IV</td>
</tr>
</tbody>
</table>
The engine was modified in order to accelerate the phosphorus poisoning on the catalyst. The acceleration was obtained with a change of the piston rings and thereby increasing the oil consumption of the engine.

2.1.2 Exhaust gas-treatment system

A Diesel Particle Filter supplied by Johnson Matthey Catalysts was used as exhaust gas-treatment systems according to the specification of the oil supplier.

For this project three DPFs were used. The identification of parameters before testing, light-off temperature during and analysis of the DPFs after testing are similar to the procedures for the testing of the DOCs with different fuels (Table EM.17).

<table>
<thead>
<tr>
<th>Characteristic of the DPF</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Size (mm)</strong></td>
</tr>
<tr>
<td>198 x 102 x 174</td>
</tr>
<tr>
<td><strong>Formulation</strong></td>
</tr>
<tr>
<td>Front 64 mm @ 125g/ft3 (4Pt:0Pd:0Rh:1:0)</td>
</tr>
<tr>
<td>Middle 55.25mm @ 50g/ft3 (1Pt:0Pd:0Rh)</td>
</tr>
<tr>
<td>Rear 55.25mm @ 10g/ft3 (1Pt:0Pd:0Rh)</td>
</tr>
</tbody>
</table>

2.1.3 Fuel type

The same type of fuel was used for the entire oil test and is of a very high quality with a very small content of other substances that can interfere in an investigation, for example sulphur (Table EM.18).
### Table EM.18: Technical data of Diesel

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>DK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density by 15 °C</td>
<td>Kg/l</td>
<td>0,812</td>
</tr>
<tr>
<td>Kinematic viscosity, 40 °C</td>
<td>mm²/s</td>
<td>2,505</td>
</tr>
<tr>
<td>Acid number</td>
<td>mg KOH/g</td>
<td>0,018</td>
</tr>
<tr>
<td>Sulfur</td>
<td>mg/kg</td>
<td>nn</td>
</tr>
<tr>
<td>Calcium</td>
<td>mg/kg</td>
<td>0,5</td>
</tr>
<tr>
<td>Zinc</td>
<td>mg/kg</td>
<td>0,2</td>
</tr>
<tr>
<td>Siliceous</td>
<td>mg/kg</td>
<td>0,8</td>
</tr>
<tr>
<td>Magnesium</td>
<td>mg/kg</td>
<td>0</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>mg/kg</td>
<td>nn</td>
</tr>
</tbody>
</table>

nn: Not detectable

2.1.4 **Oil type**

Three different oil types were used. The first, “Oil A”, is used as a reference and is a commercial 0W-30 Euro III oil meeting VW 50300 and VW50601 standards and has a phosphorus concentration of approximately 900ppm. “Oil B”, is an experimental modification of the OS191877 oil that is currently used at Volkswagen, but has a higher phosphorus concentration (approx. 1600ppm). “Oil C” has similar phosphorus levels as Oil B (approx. 1800ppm), but makes use of a Zn-free, phosphorus containing anti-wear component as opposed to the ZDDP anti-wear components contained in Oil A and Oil B (Table EM.19).
Table EM.19: Technical data of the Oils

<table>
<thead>
<tr>
<th>Units</th>
<th>“Oil A” Commercial 0W-30 Euro III oil meeting VW 50300 and VW 50601</th>
<th>“Oil B” baseline OS191877 with high ZDDP as anti-wear</th>
<th>“Oil C” baseline OS191877 with high Zn-free as anti-wear</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematical viscosity, 40 °C mm²/s</td>
<td>53,55</td>
<td>73,82</td>
<td>61,96</td>
</tr>
<tr>
<td>TBN mg KOH/g</td>
<td>9,7</td>
<td>5,7</td>
<td>5,4</td>
</tr>
<tr>
<td>Ash content g/l</td>
<td>1,30</td>
<td>0,90</td>
<td>0,65</td>
</tr>
<tr>
<td>NOACK</td>
<td></td>
<td>7,4</td>
<td>8,2</td>
</tr>
<tr>
<td>Ca-Content ppm</td>
<td>3000</td>
<td>1200</td>
<td>1200</td>
</tr>
<tr>
<td>Zn-Content ppm</td>
<td>100</td>
<td>1800</td>
<td>nn</td>
</tr>
<tr>
<td>S-Content ppm</td>
<td>4310</td>
<td>4300</td>
<td>539</td>
</tr>
<tr>
<td>Mg-Content ppm</td>
<td>200</td>
<td>&lt;10</td>
<td>3</td>
</tr>
</tbody>
</table>

2.2 Methodology

2.2.1 Selecting the engine operating points for the aging program, the light-off temperature test and the characteristic test

The aging process and the light-off temperature were determined for a different engine type. The engine was run with standard diesel fuel and the emissions and temperatures were measured. The aging operating points were chosen to provide a big load on the DPF in order to accelerate the catalyst aging. The aging temperatures were not higher than 250°C, because at higher temperatures a passive regeneration of the DPF would occur.

The operating points that were chosen are described in table EM.20:
The bigger load on the DPF necessitates an “active regeneration” of the DPF. This is done to burn off the particles that have accumulated on the DPF. It is possible to “force” the DPF to regenerate by running the engine at a specific operating point and making a modification in the engine operation. This eliminates the need to wait for the pressure drop across the diesel particle filter to reach the predetermined limit at which the engine control system will usually initiate the regeneration process. It is also possible to control the regeneration of a DPF by initializing the process after a predetermined running time, as was the case in this project. Under the DPF active regeneration engine conditions, the engine produces a modification to the fuel injection mechanism resulting in higher emission temperatures than under normal operation conditions. At such a high temperature the particles that accumulate on the DPF are burned off and the DPF is cleaned.

The chosen active regeneration point was at an engine speed of 2000rpm and a load of 70Nm (Table EM.21).

### Table EM.20: DPF load operating points

<table>
<thead>
<tr>
<th></th>
<th>RPM (1/min)</th>
<th>Load (Nm)</th>
<th>Time (s)</th>
<th>CO (ppm)</th>
<th>HC (ppm)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>830</td>
<td>0</td>
<td>110</td>
<td>222</td>
<td>102</td>
<td>175</td>
</tr>
<tr>
<td>2.</td>
<td>1500</td>
<td>25</td>
<td>180</td>
<td>710</td>
<td>161</td>
<td>185</td>
</tr>
<tr>
<td>3.</td>
<td>3000</td>
<td>25</td>
<td>220</td>
<td>338</td>
<td>113</td>
<td>245</td>
</tr>
<tr>
<td>4.</td>
<td>1200</td>
<td>35</td>
<td>180</td>
<td>679</td>
<td>182</td>
<td>209</td>
</tr>
<tr>
<td>5.</td>
<td>2700</td>
<td>20</td>
<td>220</td>
<td>312</td>
<td>112</td>
<td>216</td>
</tr>
<tr>
<td>6.</td>
<td>1500</td>
<td>25</td>
<td>170</td>
<td>698</td>
<td>164</td>
<td>194</td>
</tr>
</tbody>
</table>

Through experimental testing it was determined that the most suitable engine cycles for this study are nine hours of running under the load operating conditions (see table EM.20) followed by 10 minutes of running under the active regeneration conditions (table EM.21). The time was chosen to prevent the particle content on the DPF from rising above 5 g/l and to facilitate a complete cleaning of the DPF during the regeneration time.
In order to simulate fifty aging hours, the experiment would required six cycles of nine hours of running under load operating conditions and ten minutes of regeneration. Similarly the hundred hours and hundred and fifty hour simulation will require twelve and eighteen cycles of the nine hour load with ten minutes regeneration respectively. It is necessary to change the oil after each fifty, hundred or hundred and fifty aging hours, because the fuel content in the oil is increased during the active regeneration process and would have a negative influence on the characteristic properties of the oil and on the engine performance.

The total aging time of the DPFs was roughly 300 hours, consisting of four repetitions of the fifty aging hours and one cycle of a hundred aging hours. For a total aging time of 450 hours, an extra hundred and fifty hour aging test was done only once.

The engine operating points for the light-off temperature were experimentally determined to have almost constant emission values (especially for CO). The following table shows the operating points that were chosen for the light-off temperature.

<table>
<thead>
<tr>
<th>RPM (1/min)</th>
<th>Load (Nm)</th>
<th>Time (s)</th>
<th>CO (ppm)</th>
<th>HC (ppm)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2500</td>
<td>0</td>
<td>1500</td>
<td>144</td>
<td>71</td>
<td>128</td>
</tr>
<tr>
<td>2500</td>
<td>5</td>
<td>1500</td>
<td>142</td>
<td>72</td>
<td>138</td>
</tr>
<tr>
<td>2500</td>
<td>10</td>
<td>1500</td>
<td>146</td>
<td>74</td>
<td>147</td>
</tr>
<tr>
<td>2500</td>
<td>15</td>
<td>1500</td>
<td>149</td>
<td>77</td>
<td>159</td>
</tr>
<tr>
<td>2500</td>
<td>20</td>
<td>1500</td>
<td>153</td>
<td>78</td>
<td>169</td>
</tr>
<tr>
<td>2500</td>
<td>25</td>
<td>1500</td>
<td>159</td>
<td>81</td>
<td>178</td>
</tr>
<tr>
<td>2500</td>
<td>30</td>
<td>1500</td>
<td>160</td>
<td>84</td>
<td>189</td>
</tr>
<tr>
<td>2500</td>
<td>35</td>
<td>1500</td>
<td>157</td>
<td>84</td>
<td>199</td>
</tr>
<tr>
<td>2500</td>
<td>40</td>
<td>1500</td>
<td>164</td>
<td>89</td>
<td>222</td>
</tr>
<tr>
<td>2500</td>
<td>45</td>
<td>1500</td>
<td>157</td>
<td>90</td>
<td>235</td>
</tr>
<tr>
<td>2500</td>
<td>50</td>
<td>1500</td>
<td>155</td>
<td>54</td>
<td>246</td>
</tr>
<tr>
<td>2500</td>
<td>55</td>
<td>1500</td>
<td>155</td>
<td>61</td>
<td>261</td>
</tr>
<tr>
<td>2500</td>
<td>60</td>
<td>1500</td>
<td>151</td>
<td>66</td>
<td>275</td>
</tr>
</tbody>
</table>

The characterization of the DPF involves measuring the amount of particles that were collected on the DPF during five hours of running under the load operating conditions. It was observed that the weight of the DPFs increased during the test.
period and which indicates that an accumulation of ash occurs on the DPFs over time.

The aging of the catalyst over time can be seen with the light-off temperature tests and with the DPF characteristic test (Table EM.22).

### 2.2.2 Aging process

After the selection of the load operation points, the light-off temperature, the regeneration points and the DPF characteristic test duration, the aging process was as follows for the different oil types investigated:

1. The contact surfaces of the camshaft and bucket tappets are measured before aging.
2. A new air filter, oil filter, fuel filter, camshaft, bucket tappets and injection system are installed on the engine.
3. The DPF is installed.
4. Oil change is performed and the exact amount is measured. Between tests the engine is cleaned with a short run of the engine with the new oil.
5. Full load test at the start of the aging program.
6. First three light-off temperature tests, each test requiring five hours.
7. Characterization of the DPF.
8. Aging of the DPF. Nine hours of running with load operating points following by ten minutes of active regeneration. This operation is repeated with fifty, hundred or hundred fifty hours cycles respectively.
9. Change of the engine oil. After 50, 100 or 150 hours of aging the oil was drained from the engine and the exact amount of oil was documented. A sample of the oil before and after each aging was taken and analysed in the laboratory. With the oil analysis the fuel content in the oil can be determined and the oil consumption during the aging process was calculated. The engine is cleaned with fresh oil of the same type.
10. After the DPF aging, the final three light-off temperature tests are performed.
11. A final characterization test of the DPF is also performed.
12. Remove the DPF from the engine. After the aging the DPFs were examined in the laboratory.
13. Full load test at the end of the aging program and the results were compared with that of the full load test before the aging.
14. The injection system, the camshaft and bucket tappets are removed from the engine and examined in the laboratory. The flow rate of the injection system is determined before and after each aging test in order to compare which oil produces a bigger effect on them. The results are documented and the contact surfaces of the camshaft and bucket tappets are measured to compare the influences of the various oils on the engine.

The aging process is summarized in figure EM.7.
2.2.3 Analysis system

The analyses were similar to that used for the first and second tests, see section 1.1.2.3. In this case one SESAM unit was used between the engine and catalyst and another after the catalyst. The DPFs were again analysed by Johnson Matthey Catalysts laboratories.
III. Results and discussions

1 Study of the phosphorus poisons produced from fuel

1.1 Aging of Diesel Oxidation Catalyst with different fuels

The following table shows the test name and fuel used during the first test.

<table>
<thead>
<tr>
<th>Test Name</th>
<th>Fuel type</th>
<th>RME (%)</th>
<th>SME (%)</th>
<th>Diesel (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DK</td>
<td></td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>B20-S</td>
<td></td>
<td>0</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>B20-RS</td>
<td></td>
<td>10</td>
<td>10</td>
<td>80</td>
</tr>
<tr>
<td>B20-R</td>
<td></td>
<td>20</td>
<td>0</td>
<td>80</td>
</tr>
</tbody>
</table>

In this section of the study the influences of different fuel types on the engine and on the catalyst system was observed. Note, that the same DOC system and same engine oil type were used with different fuel mixtures.

1.1.1 Engine analyses results

1.1.1.1 Injection system inspection

The injection system flow rate was measured, followed by a visual inspection and dispersive element analyses of the injection system surface after every test. The biodiesel that was used did not contain anti-coking agents and the effect of the fuel on the injection system coking could then be observed.

The nominal injection system flow rate has a value of 350 cm$^3$/s with a tolerance of 7 cm$^3$/s. The engine can not run efficiently when the flow rate decreases by more than 6% of the initial value.

The initial flow rate was not obtained after each test, which means that the injection systems were coked during testing and this resulted in an engine power deficit.
The following figure shows the injection system flow rate and photos of the injectors after running the engine with the different fuel types.

The figure shows that the highest loss of flow rate is produced after running the engine with B20S, around 16% of the initial flow rate was lost. The flow rate was reduced by about 13% with B20SR and about 10% with B20R respectively. The smallest flow rate reduction of about 5% was produced when the engine was run with normal diesel.

Photos of the injection systems show that the ones aged with the different biodiesel B20 has a high incrustation of substance on the surface (attachment R.1 to R.4).

A dispersive energy element analysis (EDX) of the injection system surface and crust showed that it contained the deposited elements of C, Si, Ca, Zn, S, P, Al, Mg, Fe and Cu. C in the form of soot or coke is a result of an incomplete combustion of the fuel and oil. Si in the form of SiO₂ is deposited from the fuel while Ca can come from both the fuel and the oil. Zn, Al and Mg come from the oil, whereas Fe and Cu are produced due to engine wear. P and S come from fuel and/or oil.

There were no significant differences between the deposits on the injection systems from diesel, biodiesel and/or different types of biodiesel. See attachment R.5 to R.8.
1.1.1.2 Fuel analyses and fuel consumption results

A fuel sample was analysed in the Volkswagen AG laboratories before each test. The density, kinematic viscosity, oxidation stability, acid number and elemental components analysis is shown in the table EM.3.

Small differences in fuel consumption were observed over time, which can be attributed to the aging of the engine. The changes due to engine aging were observed with an extra control test. At the end of all tests the engine was run again with standard diesel fuel and higher fuel consumption (around 4.2% more) than for the first test was observed (Table R.2).

<table>
<thead>
<tr>
<th>Name</th>
<th>Aging Time (h)</th>
<th>Fuel consumption (l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DK</td>
<td>86</td>
<td>496</td>
</tr>
<tr>
<td>B20-S</td>
<td>84</td>
<td>517</td>
</tr>
<tr>
<td>B20-RS</td>
<td>84</td>
<td>526</td>
</tr>
<tr>
<td>B20-R</td>
<td>84</td>
<td>533</td>
</tr>
</tbody>
</table>

1.1.1.3 Oil Analyses and oil consumption results

The fresh oil and the oil after each test was analysed in the Volkswagen AG laboratories. The following table shows the results of the aged oil analyses.

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Fresh oil</th>
<th>After B20-S</th>
<th>After B20-SR</th>
<th>After B20-R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematic viscosity, 40 °C</td>
<td>mm²/s</td>
<td>53,55</td>
<td>46,59</td>
<td>50,19</td>
<td>49,89</td>
</tr>
<tr>
<td>TBN</td>
<td>mg KOH/g</td>
<td>9,7</td>
<td>10,1</td>
<td>10,2</td>
<td>10,1</td>
</tr>
<tr>
<td>DK Content</td>
<td>%</td>
<td>--</td>
<td>4,89</td>
<td>3,13</td>
<td>3,71</td>
</tr>
<tr>
<td>BD Content</td>
<td>%</td>
<td>--</td>
<td>2,23</td>
<td>2,04</td>
<td>2,34</td>
</tr>
</tbody>
</table>

The kinematic viscosity of each oil after testing was smaller than the viscosity of fresh oil and proportional to the content of fuel in the tested oil. There are differences in content of diesel and biodiesel in the oil after testing with different fuels. No oil samples were taken for the test run with standard diesel. It is
common to find higher biodiesel content in the oil than standard diesel content, because biodiesel has a higher flash temperature. It means that not all the biodiesel that is injected into the cylinders burn, resulting in some mixing into the oil. From experience it is known that with long engine run time the biodiesel content in oil is usually higher than the diesel content. The results of the fuel found in the oil after 86 hours of engine run time are shown in figure R.2. They show higher amounts of diesel in the oil than biodiesel. This is due to the fact that the tests were not run for long enough to produce a higher content of biodiesel in the oil because there is only 20% biodiesel content in the fuel that was used.

![Figure R.2: Content of Diesel and Biodiesel in oil after testing with different fuel types](image)

The oil consumption during each test were similar at about 2,5 g/h. A possible error in measurement could have resulted in inaccurate oil consumption measurement of the B20S test. The following table shows the consumption and aging time results.

<table>
<thead>
<tr>
<th>Name</th>
<th>Aging time (h)</th>
<th>Oil Consumption (g)</th>
<th>Oil consumption (g/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DK</td>
<td>86</td>
<td>200.50 g</td>
<td>2.33</td>
</tr>
<tr>
<td>B20-S</td>
<td>84</td>
<td>84.30 g</td>
<td>1.00</td>
</tr>
<tr>
<td>B20-RS</td>
<td>84</td>
<td>216.23 g</td>
<td>2.57</td>
</tr>
<tr>
<td>B20-R</td>
<td>84</td>
<td>247.52 g</td>
<td>2.95</td>
</tr>
</tbody>
</table>
1.1.2 Emissions results

The emissions produced during the aging of the catalysts are described in the following figure.

![Graph showing emissions results](image)

**Figure R.3**: Midpoint emissions during catalyst aging with different fuel types

The average *hydrocarbon* (C\textsubscript{x}H\textsubscript{y}) emissions during the different fuel aging tests remained relatively constant at 100 ppm. However, the *carbon monoxide* (CO) emissions showed a progressive increase during the run of the engine with the different fuels. The B20R fuel showed three times higher CO emissions in comparison to the DK fuel.

The *nitrogen oxides* (NO\textsubscript{x}) midpoint showed a progressively lower NO\textsubscript{x} emission concentration during the run of the engine with the different fuels. The lowest NO\textsubscript{x} value was for the fuel B20R and the highest value resulted from the test run with DK.

The differences in the soot produced during each test showed that the highest soot value was produced when running the engine with B20R fuel. This is similar to the CO emissions indicating that the formation of soot and CO are related.

In the light of the emission results of NO\textsubscript{x} and soot, the suspicion arises that the exhaust gas recirculation (EGR) valve was not fully functional during the complete test period with the different fuel types, especially in the case of the B20SR and B20R fuel tests. Incorrect operation of this valve could explain the high emissions variations that were produced during the tests. The suspicion could not be confirmed.
until the end of testing and therefore no steps could be taken during testing to rectify the problem. The average temperature during the different fuel aging test was 400 °C. The maximum temperature of the emissions in the catalyst was similar for every catalyst run with different fuel types (Table R.5).

Table R.5: Maximum temperature during aging of the DOC with different fuel types

<table>
<thead>
<tr>
<th>Name</th>
<th>Max. Temp °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>DK</td>
<td>642.4</td>
</tr>
<tr>
<td>B20S</td>
<td>631.2</td>
</tr>
<tr>
<td>B20SR</td>
<td>614.6</td>
</tr>
<tr>
<td>B20R</td>
<td>633.2</td>
</tr>
</tbody>
</table>

1.1.3 Catalyst analyses results

1.1.3.1 Engine Tests

As described in the experimental methodology section, a light-off temperature test was performed before, during and after aging time of the catalysts. These tests were done in order to have an indication regarding the activity of the catalyst during the aging time. [Attachment R.9 to R.16]. CₙHₙ and especially CO, are the principal emissions used to characterize the activity of the catalyst. The measurement of the CₓHᵧ emission concentration is not as exact as the CO measurement. The CO and CₓHᵧ concentration before the catalyst must remain reasonably constant during each catalyst test in order to have a realistic activity comparison of the DOCs.

The following figures show the CO and CₓHᵧ light-off temperature test results of every DOC. First a light-off temperature test is performed on the new and unused catalyst (fresh) before the testing commences (red diagram of the figure R.4 and R.5). After 84 hours of aging, another light-off temperature test is performed with the same fuel that is used for the aging process (blue diagram). The final light-off temperature test was performed with standard diesel fuel after all catalysts have been aged for 84 hours (Yellow diagram). This was done in order to obtain the most constant engine conditions and emissions possible for each final light-off temperature test in order to allow for a realistic comparison of the catalyst test results.
The results showed that the CO concentration through the catalysts during the last light-off temperature test was the same with the same fuel type for every catalyst test. [Attachment: R.17].

Figure R.5 shows similar C\textsubscript{x}H\textsubscript{y} light-off temperature values for the various catalysts run with different fuels. It can be seen from the figure that there is an average difference of approximately 10°C between the light-off temperatures of the catalysts when they are fresh and after the appropriate aging time. Light-off temperature differences of around 100°C give a decisive indication of impaired catalyst activity and therefore the 10°C difference is not very significant in comparison.
Figure R.5: C_{x}H_{y} Light-off temperature of the aged catalyst for different fuel types

The HC concentration through the catalysts during the last light-off temperature test with the same fuel type was almost the same for every catalyst test. [Attachment: R.18]

With the result of both emissions light-off temperature tests it is shown that there are no significant differences in catalyst activity between DOCs aged with different fuel types during a period of 84 hours. It also shows that only a temperature aging was produced in every catalyst after 84 hours of aging.

The aged DOCs were also chemically analysed in order to provide more clarity and to obtain more detailed information about the catalyst aging.

1.1.3.2 Analyses results

Every aged DOC was submitted for post mortem analysis to investigate the thermal history of the catalyst, the catalyst poisoning (particularly by phosphorus) and the location of phosphorus deposition.
a) Physical examination

The general physical conditions of the DOC were good, however they all showed some damaging on both faces of the ceramic support (see attachment [R.19 to R.22]). As expected the inlet face of each part was covered with a dark sooty deposit and a dark discolouration that is extended down into the internal surface of the catalyst. No blocked cells, erosion or loosening of the washcoat was observed. The inlet and outlet face of one of the catalysts can be seen in figures R.6 and R.7.

![Figure R.6: Inlet face of one catalyst](image1)

![Figure R.7: Outlet face of one catalyst](image2)

b) Washcoat composition

The washcoat compositions of the aged DOCs were analysed using X-ray fluorescence (XRF) in order to determinate the platinum, phosphorus, zinc, calcium and sulphur content.

**Platinum**

The XRF analysis of aged catalysts often understates the precious metal content as the aged sample is analysed against a fresh reference sample. The catalysts used have a nominal Pt content of 50 g/ft³. The aged catalysts were analysed in order to determinate if the Pt content after aging had changed. Table R.6 shows the Pt loading on the aged catalyst for the different fuel types, indicating that no significant changes in Pt contain was observed and that all the catalyst maintained a value close to the nominal value.
Table R.6: Average Pt loading on the aged catalyst (g/ft³) for different fuel types

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Average Pt loading (g/ft³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DK</td>
<td>46.5</td>
</tr>
<tr>
<td>B20S</td>
<td>49.6</td>
</tr>
<tr>
<td>B20SR</td>
<td>47.4</td>
</tr>
<tr>
<td>B20R</td>
<td>48.7</td>
</tr>
<tr>
<td>Nominal</td>
<td>50.0</td>
</tr>
</tbody>
</table>

Phosphorus

The phosphorus concentrations as measured by XRF on the catalyst for different fuel types are shown in figure R.8.

The highest phosphorus concentration was found in the front of the catalyst of every DOC. Phosphorus was found in the middle and in the rear of the catalyst only when it was aged with standard diesel fuel.

The catalyst aged with DK had the highest phosphorus poisoning average value with 0.036%, the catalyst aged with B20S had 0.014% and the other two aged catalysts had an average value of 0.018% phosphorus poisoning. The concentrations of the phosphorus poisoning compounds deposited on the catalyst were generally very small, which made the phosphorus poisoning difference between tests insignificant. These differences could be explained by the different performance of the engine for each test as the engine ages.
These catalyst results are in accordance with the fuel analyses, where no phosphorus in any fuel was found. (See table EM.3 of the experimental methodology). But surprisingly, the catalyst run with standard diesel fuel had the highest phosphorus concentration. The phosphorus found on the catalyst come from the engine oil.

*Phosphorus, zinc, calcium and sulphur*

The average values of phosphorus, zinc, calcium and sulphur measured on the catalyst show the highest poisoning element concentrations on the catalyst aged with standard diesel fuel. The sulphur concentration on the catalyst was higher for the catalyst run with B20S (0.041%) than with standard diesel fuel (0.033%). The fuel analyses (Table EM.3) did not show sulphur in the fuel when it was analysed with ICP, but sulphur was found on the catalyst when analyzed by XRF. The figure R.9 shows the average values of the catalyst elements on the different aged catalyst for different fuel types.

![Figure R.9: Average value of the catalyst poisoning elements on the different aged catalysts for different fuel types](image)

There is currently no explanation for the subtle differences in poisoning levels between the tests. It is known that not only the fuel components produce poisoning on the catalyst, but the engine oil components play an important role too. The oil consumption and the poisoning on the catalyst during each test was approximately the same, so it is believed that the poisoning compounds found on the catalyst come primarily from oil.
c) **Washcoat specific area**

The total BET specific surface area of the aged catalyst for different fuel types are shown in figure R.10:

![Figure R.10: Total BET specific surface area of the aged catalyst for different fuel types](image)

The results for all the aged catalysts show essentially the same specific surface area. This makes it clear that running the catalyst with different fuels for 84 hours of aging does not influence the catalyst surface area.

d) **Identification of the crystalline phosphorus phase**

The crystal structure of washcoat for every aged catalyst was examined using XRD. A pure zeolite crystal structure washcoat was found intact and no evidence was found of crystal phase degradation of the washcoat.

The phosphorus concentrations in all aged catalysts were too low for identification by XRD. Furthermore the phosphorus crystal forms are typically found when the emission temperatures are higher than 700 °C and for these tests the engine was run with temperatures under 650°C. Therefore crystal forms on the catalyst were not formed.
e) Phosphorus location and morphology

The washcoat morphology of every aged catalyst was examined using SEM with EDX. The analyses were done of washcoat cross-sections and similar washcoat thickness were found in all four systems and compared. A sample of the cross section where the EDX element measurements were done can be seen in figure R.11.

![EDX Elemental line scan performed through washcoat cross section](image)

**Figure R.11:** EDX Elemental measurements through washcoat cross section

Local inhomogeneity in aluminium (Al) and silicon (Si) contents was found in this catalyst. The elemental line scan across the washcoat width displayed variable but complementary Al and Si levels (figure R.12).

![EDX elemental measurements through washcoat cross section for Al and Si](image)

**Figure R.12:** EDX elemental measurements through washcoat cross section for Al and Si
The following figures show the EDX and WDX measures for phosphorus.

**Figure R.13:** EDX and WDX measures through washcoat cross section for P.

The phosphorus location in the catalyst investigated with EDX shows a high concentration of phosphorus on the upper surface of the washcoat (attachment R.23 to R.26). The WDX shows phosphorus located at the surface of the washcoat layer along with calcium and zinc deposits. Note that there is no direct relation between the colour intensity of the WDX analyses results and the poisoning concentration on the catalyst. The poisoning concentration is uniform across the surface area of the catalyst but during analysis different sections of the surface were analysed more intensely for the respective poisoning compounds. Therefore the intensity of each colour in the figures is not homogenously spread across the surface.

The phosphorus compounds could not be identified because of their amorphous forms and low concentration. No sulphur was found on the catalyst surface.

**Figure R.14:** WDX measurements through washcoat cross section for P, Ca and Zn for DK.
The poisoning compounds elements were found on the catalyst surface at the front of each unit. It is a typical sign of the oil poisoning process where the oil compounds stay at the surface of the catalyst because of their large molecular mass. The phosphorus was located at the surface of the washcoat layer along with calcium and zinc deposits, but the phosphorus was located in a layer on the surface of the washcoat and had not formed a glazed type finish.
1.2 Aging of a Diesel Oxidation Catalyst with a single fuel with different phosphorus concentrations

For the second test the effects of different phosphorus concentration in fuel on the engine, emissions and catalyst were examined. For this test the same type of Diesel Oxidation Catalyst, same oil and same base biodiesel fuel type (B20S) were used. The different phosphorus content in fuel was obtained by means of additives and is summered in Table R.7.

<table>
<thead>
<tr>
<th>Test Name</th>
<th>Fuel type</th>
<th>SME (%)</th>
<th>Diesel (%)</th>
<th>Phosphorus concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B20S</td>
<td></td>
<td>20</td>
<td>80</td>
<td>0</td>
</tr>
<tr>
<td>B20S-25ppmP</td>
<td></td>
<td>20</td>
<td>80</td>
<td>25</td>
</tr>
<tr>
<td>B20S-50ppmP</td>
<td></td>
<td>20</td>
<td>80</td>
<td>50</td>
</tr>
<tr>
<td>B20S-100ppmP</td>
<td></td>
<td>20</td>
<td>80</td>
<td>100</td>
</tr>
</tbody>
</table>

1.2.1 Engine analyses results

1.2.1.1 Injection system inspection

The injection system flow rate was measured after every test bellowed by a dispersive element analysis of the surface. The flow rate was measured after every 400 litres of fuel in order to determine the influence of varying phosphorus content in fuel. It is very important to note that the biodiesel (B20S) that was used contained additives to prevent coking. For the inspection of the aged injection systems the same methodology was used as for the aging test with different fuels types. The nominal injection system flow rate of this injection system type has a value of 475 cm$^3$/s with a tolerance of 9,5 cm$^3$/s. The engine can not run efficiently when the flow rate decreases by more than 6% of the nominal value. The initial flow rate (475±9,5 cm$^3$/s) was not obtained after each test, which means that the injection systems were coked during testing and this resulted in an engine power deficit. Only a small decrease in the flow rate was produced, so the fuel injected into the engine during the entire test was reduced in a small percentage with respect to the initial value.
Figure R.18 shows the injection system flow rate and a photo of the injectors after running with doped B20S.

Note: for every DOC the injection systems were changed in the middle of the aging time for new ones, therefore there are two injection system analyses for each biodiesel test run.

The figure shows the same flow rate deficit for each test. The loss of flow rate after testing was not higher that 6% and therefore the flow rate reduction in this test was insignificant after 400 litres fuel. The phosphorus content in the fuel had no influence on the coking of the injection systems.

In the photos of the injection systems the same incrustation of substance on the surface can be seen as shown in figure R.18 and in attachment R.27 to R.34.

A dispersive EDX of each injection system surface was also done and showed to contain the following elements: C, Si, Ca, Zn, S, P, Mg, Fe and Cu. C and Si could come from the fuel; Zn, Al and Mg from the oil; Fe and Cu due to engine wear and Ca, P and S from fuel and/or oil. No correlation was found between the phosphorus concentration in fuel and the phosphorus deposited on the injection system surface.

There are no notable differences between the deposits on the injection systems from biodiesel with different phosphorus concentrations. See attachment R.35 to R.42.
1.2.1.2 Fuel analyses and fuel consumption results

The fuel analyses can be seen in Table EM.12. The B20S consumption was fixed for every fuel test to be 800 litres. The fuel consumption and aging time is shown in Table R.8. The slight decrease in aging time that is seen for the test with fuel containing 100 ppm P is attributed to a measurement error in the instruments.

<table>
<thead>
<tr>
<th>Name</th>
<th>Aging Time (h)</th>
<th>Fuel consumption (l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B20S</td>
<td>145</td>
<td>800</td>
</tr>
<tr>
<td>B20S-25ppmP</td>
<td>147</td>
<td>800</td>
</tr>
<tr>
<td>B20S-50ppmP</td>
<td>144</td>
<td>800</td>
</tr>
<tr>
<td>B20S-100ppmP</td>
<td>132</td>
<td>800</td>
</tr>
</tbody>
</table>

1.2.1.3 Oil Analyses results and consumption

The fresh oil and the oil after each test was analysed and the results are shown in table R.9.

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Fresh oil</th>
<th>After B20S</th>
<th>After B20S-25ppmP</th>
<th>After B20S-50ppmP</th>
<th>After B20S-100ppmP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematic viscosity, 40 °C</td>
<td>mm²/s</td>
<td>53,55</td>
<td>29,86</td>
<td>49,64</td>
<td>48,85</td>
<td>51,28</td>
</tr>
<tr>
<td>TBN</td>
<td>mg KOH/g</td>
<td>9,7</td>
<td>7,4</td>
<td>9,7</td>
<td>9,2</td>
<td>11,2</td>
</tr>
<tr>
<td>DK Content</td>
<td>%</td>
<td>0</td>
<td>4,45</td>
<td>1,88</td>
<td>2,60</td>
<td>1,23</td>
</tr>
<tr>
<td>BD Content</td>
<td>%</td>
<td>0</td>
<td>18,21</td>
<td>4,15</td>
<td>3,22</td>
<td>2,65</td>
</tr>
<tr>
<td>Calcium</td>
<td>mg/kg</td>
<td>3000</td>
<td>2400</td>
<td>3000</td>
<td>3100</td>
<td>3000</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>mg/kg</td>
<td>900</td>
<td>690</td>
<td>1000</td>
<td>1200</td>
<td>1300</td>
</tr>
<tr>
<td>Zinc</td>
<td>mg/kg</td>
<td>100</td>
<td>820</td>
<td>1000</td>
<td>1000</td>
<td>950</td>
</tr>
<tr>
<td>Sulphur</td>
<td>mg/kg</td>
<td>4310</td>
<td>3280</td>
<td>4150</td>
<td>4240</td>
<td>4110</td>
</tr>
<tr>
<td>Magnesium</td>
<td>mg/kg</td>
<td>200</td>
<td>115</td>
<td>200</td>
<td>200</td>
<td>140</td>
</tr>
<tr>
<td>Iron</td>
<td>mg/kg</td>
<td>0</td>
<td>33</td>
<td>nn</td>
<td>nn</td>
<td>21</td>
</tr>
<tr>
<td>Copper</td>
<td>mg/kg</td>
<td>0</td>
<td>5</td>
<td>nn</td>
<td>nn</td>
<td>4</td>
</tr>
<tr>
<td>Chromium</td>
<td>mg/kg</td>
<td>0</td>
<td>1</td>
<td>nn</td>
<td>nn</td>
<td>1</td>
</tr>
</tbody>
</table>

nn: Not detectable
The same type of oil was used during the entire test time. As for the first test, an oil change was performed before commencing each test.

The *kinematic viscosity* of all oils after testing was smaller than the viscosity of fresh oil. The fuel content in the oil has an important influence in the viscosity and the test run with B20S had the lowest kinematic viscosity because of the possible high fuel content.

Some differences were found in the *fuel content* in the oil after testing. The test run with B20S without phosphorus content had the highest biodiesel content of about 18%. It is very probable that some biodiesel came into the engine oil when the injection systems were changed. It is important to keep in mind that for this test the injection systems were changed during the tests and not only at the end of each test. During the change of the injection systems a high proportion of diesel and/or biodiesel could go into the oil and this could explain the high fuel content in the oil. The other three aged oils had approximately the same fuel content after the aging period. The fuel content was between 2.65% and 4.15% for the biodiesel and between 1.23% and 2.60% for the diesel content in the oil. The biodiesel content in the oil was higher than the diesel content (Figure R.19).

\[
\begin{array}{|c|c|c|c|}
\hline
 & \text{After B20S} & \text{After B20S+25ppmP} & \text{After B20S+50ppmP} & \text{After B20S+100ppmP} \\
\hline
\text{Biodiesel} & 18.21 & 4.15 & 3.22 & 2.65 \\
\text{Diesel} & 4.45 & 1.68 & 2.66 & 1.23 \\
\hline
\end{array}
\]

*Figure R.19: Content of Diesel and Biodiesel in oil after test with doped B20S*

An *elemental analysis* of the fresh oil and of the aged oils was done after each test period and showed that their concentrations of the oil after aging were similar in the case of calcium, zinc, sulphur and magnesium. However differences in the oil phosphorus composition were found. The analyses of the aged oil show an increase of the phosphorus content in oil when it was run with the different doped fuels. The oil
run with B20S had 690ppm phosphorus. The phosphorus content in the oil increased to 1000ppm when the oil was run with B20S+25ppmP and increased further to 1200 and 1300ppm phosphorus after running with B20S+50ppm and 100ppm phosphorus respectively. The high phosphorus concentration in the oil comes from the biodiesel content in the engine oil.

The oil consumption after each test was very different from one test to another. The oil consumptions and aging time can be seen in table R.10.

<table>
<thead>
<tr>
<th>Name</th>
<th>Aging Time (h)</th>
<th>Oil consumption (g)</th>
<th>Oil consumption (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B20S</td>
<td>145</td>
<td>7256</td>
<td>50,0</td>
</tr>
<tr>
<td>B20S+25ppmP</td>
<td>147</td>
<td>1295</td>
<td>8,8</td>
</tr>
<tr>
<td>B20S+50ppmP</td>
<td>144</td>
<td>1050</td>
<td>7,3</td>
</tr>
<tr>
<td>B20S+100ppmP</td>
<td>132</td>
<td>682</td>
<td>5,2</td>
</tr>
</tbody>
</table>

1.2.2 Emissions results

The midpoint emissions during catalyst aging with doped B20S are shown in the following figure.

It is also important to remember that the emissions measurement was not possible for all the tests because of technical equipment problems. During the tests that were run with B20S and with B20S+25ppmP emissions could not be measured because of
serious damage to the measuring equipment. The emissions that were measured for the two remaining tests (B20S+50ppmP and B20S+100ppmP) were similar. The soot was measured for all tests using the smoke meter described in the experimental methodology chapter and the midpoint remained relatively constant at $130 \times 10^{-2}$.

The average temperature during the different fuel tests was measured and it was always at about 310 °C. The maximum temperature of the emissions after the engine was almost the same at 440°C.

The following table shows the maximum temperatures that occurred during aging of the DOC with B20S and doped B20S.

<table>
<thead>
<tr>
<th>Name</th>
<th>Max. Temp °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>B20S</td>
<td>432.61</td>
</tr>
<tr>
<td>B20S+25ppmP</td>
<td>442.01</td>
</tr>
<tr>
<td>B20S+50ppmP</td>
<td>435.93</td>
</tr>
<tr>
<td>B20S+100ppmP</td>
<td>460.17</td>
</tr>
</tbody>
</table>

1.2.3 Catalyst analyses results

1.2.3.1 Engine Tests

As described in the experimental methodology section, all catalysts were first aged and then a light-off temperature test was performed on each aged DOC and on a fresh one using the same fuel type (standard diesel fuel). During this test the engine was run with the different operating points with exhaust gas temperatures of up to 200 °C.

The activity of the catalyst was examined with the transformation of the emissions pollutants, which are represented in characteristic diagrams. The emission pollutant transformation was calculated using the equation BC.4, described in the basic concepts chapter.

A $\text{CO}_{\text{conversion}}$ of 1.0 means that the entire CO produced by the engine is completely transformed in the catalyst and this happens with a high activity of the catalyst. If the catalyst is aged, its activity decreases and the $\text{CO}_{\text{conversion}}$ value will decrease to near zero.

The catalyst activity of the DOCs can be seen in figure R.21.
Figure R.21: Catalyst CO conversion of every DOC after 800 litres fuel

Note: The fresh catalyst was run twice for the light-off temperature test.

The Figures clearly show a decline in the catalyst activities when the catalysts were aged with B20S and with doped B20S. The fresh catalyst shows the highest CO conversion of approximately 1.0 for almost every operating point (dark blue). The
A progressive decline of the catalyst CO conversion was produced when the engine was run with the different fuels with high phosphorus content. It was observed that the concentration of phosphorus in the fuel has an important influence on the catalyst activity.

To provide an indication of the light-off temperature of the catalysts, the CO conversion for every aged DOC was observed at a specific engine speed and load (1000 RPM and Load from 5 to 30Nm). The light-off temperature was recorded when the CO conversion was at 30%, 50% and 80% of the CO produced by the engine. Normally only the 50% of the CO conversion is recorded, but in order to have more information about the catalyst activity, the 30% and 80% of the CO conversion were observed too.

The following figure shows the light-off temperature of the DOCs that were used.
The figure shows an increase in the light-off temperature with the increase of the phosphorus content in the fuel, which means that a decrease of the catalyst activity occurred with an increase in the phosphorus concentration in B20S (See Attachment R.45).

Note that the CO emissions values were constant during the light-off temperature test (Attachment R.44) and that the emissions temperature during aging was constant too, thus enabling a direct comparison of the light-off temperature between the fuels (see Attachment R.43).

The light-off temperature results show that the CO conversion in the catalyst is influenced by the phosphorus poisoning of the catalyst, when the catalyst was run with 800 Litres of B20S with different phosphorus content.

1.2.3.2 Analyses results

The same procedure was used as for the aging of the catalyst with different fuels. The thermal history of the catalyst, the catalyst poisoning (particularly from phosphorus) and the location of phosphorus deposition of every DOC were investigated.
a) Physical examination

Photos of the DOC after aging were taken (attachment R.46 to R.50) showing that they were still in good physical condition. No plugged cells, erosion or loosening of the washcoat could be observed.

The inlet face of each part (including the fresh unit) was covered with a dark sooty deposit and a dark discolouration extends down the internal surface of the catalyst. A progressive darkening of the washcoat was observed with the added phosphorus content in fuel (Figure R.23).

![Figure R.23: Internal surface of the catalysts after aging](image)

Note: the fresh catalyst was run twice with standard diesel fuel to measure the light-off temperature.

b) Washcoat composition

XRF of the DOC were done in order to determinate the distribution of certain compounds across the washcoat.
**Phosphorus**

The phosphorus content distribution on the catalysts is shown in figure R.24:

![Figure R.24: Phosphorus content on the catalyst after running with doped B20S](image)

The highest phosphorus concentration was found in the front section of the DOCs and decreased slightly towards the middle and rear sections. There is a correlation between the phosphorus content in fuel and the phosphorus content found on the catalyst. The fuel with the highest phosphorus concentration produced the highest phosphorus poisoning on the catalyst. The linear correlation between the phosphorus content in fuel and the phosphorus poisoning on the catalyst can be seen in the figure R.25.

![Figure R.25: Correlation between phosphorus in fuel and phosphorus on the catalyst](image)
The fresh catalyst was only run with standard diesel during two light-off temperature tests, but also showed traces of phosphorus. This most probably comes from the phosphorus content in the engine oil.

The kilometres simulation with phosphorus additives was calculated with the maximum permitted content of 10 ppm P in biodiesel fuel according with the EN 14214 specifications and an average engine fuel consumption of 7 litres per 100Km. The results are show in the Table R.12.

**Table R.12**: Phosphorus in fuel and catalyst after run with doped B20S

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>DOC (g)</th>
<th>Average P in DOC (wt%)</th>
<th>P found in DOC (g)</th>
<th>P content in fuel (ppm)</th>
<th>P in 800l Fuel (g)</th>
<th>Km simulation P content in fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>552,8</td>
<td>0,06</td>
<td>0,32</td>
<td>0</td>
<td>0,00</td>
<td>0</td>
</tr>
<tr>
<td>B20S</td>
<td>569,2</td>
<td>0,11</td>
<td>0,62</td>
<td>0</td>
<td>0,00</td>
<td>0</td>
</tr>
<tr>
<td>B20S +25ppmP</td>
<td>571,8</td>
<td>4,82</td>
<td>27,58</td>
<td>24</td>
<td>16,70</td>
<td>27400</td>
</tr>
<tr>
<td>B20S +50ppmP</td>
<td>555,5</td>
<td>7,57</td>
<td>42,04</td>
<td>54</td>
<td>37,58</td>
<td>61700</td>
</tr>
<tr>
<td>B20S +100ppmP</td>
<td>552,8</td>
<td>14,17</td>
<td>78,31</td>
<td>105</td>
<td>73,08</td>
<td>120000</td>
</tr>
</tbody>
</table>

**Zinc, calcium and sulphur**

The XRF analysis was also measured after compounds on the catalyst such zinc, calcium or sulphur.

The average value of zinc, calcium and sulphur content on the catalysts aged with doped B20S (measured with XRF equipment) shows the highest sulphur and calcium content on the fresh catalyst. It is important to note that two lights-off temperature curves were measured with the fresh catalyst, so the poisoning compounds on the fresh catalyst come from the standard diesel fuel or from the oil. The lowest sulphur content on the catalyst was found in the DOC aged with B20S and 100 ppm phosphorus. A decrease of the sulphur content on the catalyst with the increase of the phosphorus content in the fuel was found. This shows that the phosphorus and sulphur are competitive, which means that with high phosphorus poisoning the sulphur poisoning is decreased or does not form at all.

The results, including the phosphorus concentration on the catalyst, are shown in table R.13.
Table R.13: Average Zn, S, P and Ca on the catalyst

<table>
<thead>
<tr>
<th>Fuel type</th>
<th>Zn</th>
<th>S</th>
<th>P</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>0</td>
<td>0.312</td>
<td>0.058</td>
<td>0.023</td>
</tr>
<tr>
<td>B20S</td>
<td>0.009</td>
<td>0.164</td>
<td>0.108</td>
<td>0.005</td>
</tr>
<tr>
<td>B20S+25ppmP</td>
<td>0.005</td>
<td>0.057</td>
<td>4.824</td>
<td>0.005</td>
</tr>
<tr>
<td>B20S+50ppmP</td>
<td>0.005</td>
<td>0.107</td>
<td>7.567</td>
<td>0.005</td>
</tr>
<tr>
<td>B20S+100ppmP</td>
<td>0.009</td>
<td>0.025</td>
<td>14.166</td>
<td>0.005</td>
</tr>
</tbody>
</table>

c) Washcoat specific area

The washcoat specific surface area (SSA) of every aged catalyst was analysed using the BET method after each test with differently doped biodiesel. The results are shown in figure R.26.

![Figure R.26: Total BET specific surface area of the catalyst after being total with doped B20S fuel](image)

The content of phosphorus in the fuel significantly lowered the SSA after running the exhaust catalyst with 800 litres of B20S through the engine.

A linear correlation between the phosphorus content in fuel and the decrease of the SSA of the catalyst is shown in the figure R27.
Figure R.27: Specific surface area of the catalyst after aging and ppm phosphorus content in fuel

The results showed that by running the engine with a fuel that simulate the permitted content of 10ppm of phosphorus in fuel which equates to approximately 30000 Km (800 litres B20S with 25ppm phosphorus), the SSA of the catalyst would be highly reduced.

d) Identification of the crystalline phosphorus phase

The crystal structure of the washcoat of every aged catalyst was examined using XRD and showed that the zeolite crystal structure phase was still in tact with no crystal phase degradation visible. There was a high content of phosphorus on the washcoat, but the phosphorus compounds could not be identified by XRD. This could be due to either the low levels of detection of the instrument or the amorphous structure of the phosphorus phase on the washcoat. Furthermore the catalyst aging temperature during testing may not have been high enough to form defined phosphorus phase on the catalyst. The phosphorus crystalline phase is favoured by high emission temperatures and rich gas conditions.

e) Phosphorus location and morphology

The washcoat morphology of every aged catalyst was examined using SEM with Wavelength Dispersive X-ray analysis (WDX).
The measurements were done through a cross section of the washcoat and big differences in phosphorus concentrations were found between the catalysts aged with different phosphorus content in fuel.

The WDX investigation of the fresh catalyst shows a location of phosphorus concentration with calcium deposits on the upper surface of the washcoat layer. No zinc was detected (Figure R.28).

![Figure R.28: P, Ca and Zn map for fresh DOC](image)

On the catalyst aged with B20S without phosphorus addition, some phosphorus was located on the upper surface of the washcoat layer along with calcium and zinc deposits. This is the typical oil components poisoning on the catalyst surface (Figure R.29).

![Figure R.29: P, Ca and Zn map for DOC aged with B20S](image)

For the catalyst aged with B20S and 25ppm phosphorus, a significant amount of phosphorus penetrated through the washcoat layer while calcium and zinc deposits remained on the washcoat surface (Figure R.30).
The WDX analysis for the catalyst aged with B20S and 50ppm P shows a heavy phosphorus poisoning penetrated through the washcoat layer with the calcium and zinc deposits remaining on the washcoat surface (Figure R.31).

A very heavy phosphorus poisoning penetrated through the washcoat layer for the catalyst aged with B20S and 100ppmP and again the calcium and zinc deposits remained on the washcoat surface (Figure R.32).
The varying phosphorus content in fuel results in a different poisoning of the catalyst than that caused by the phosphorus contained in the engine oil. The phosphorus from the oil burns or vaporizes in the engine, but the resulting particles are bulky and large molecular mass and therefore deposit on the catalyst surface. The phosphorus in fuel burns and passes directly through the catalyst. Because of the small size, it can enter the washcoat pores and deposits are formed not only on the washcoat surface but also inside the washcoat pores. This produces significant and irreversible deactivation of the catalyst function by significantly reduction of the SSA. This implies that the phosphorus content in biodiesel should be kept as low as possible, since it contributes to the deactivation of the exhaust catalyst for diesel systems. This implies that the phosphorus content in biodiesel should be reduced, because of the huge problem that it causes on the catalyst.

1.3 Fuel results conclusion

The tests results for the comparison of the effects of different fuel types on the catalyst and on the engine show that the catalyst was not significantly influenced by the fuel type (DK, B20S, B20SR and B20R) after 84 hours of engine testing, but an influence on the injection system was found after that aging time. The decrease in the flow rate was produced when the engine was run with B20S, followed by B20SR, and then B20R. The smallest decrease in the flow rate was produced by DK fuel. This means the highest coking of the injection system was produced with B20S, which could be particulate associate to the additives to prevent
coking that were not added. The addition of additives could be used to reduce the deficit of the flow rate.

The fuel consumption and the emissions produced during aging indicated changes in the engine during the tests. The emissions show problems with the exhaust gas recirculation (EGR) valve, especially for the tests run with B20SR and B20R. At the end of all tests, the engine was run with standard diesel fuel again and higher fuel consumption than for the first test was observed.

The light-off temperature tests show no significant differences in the aged catalysts when they were aged for 84 hours with different fuel types. Analyses of the catalysts were also done in order to determine if the catalysts were only temperature aged or if other factors contribute to the aging effect.

The catalyst analyses showed similar SSA for the aged catalyst. The same element poison was also produced and was found on the front of each catalyst. Running the engine for 84 hours of aging produced the same elemental deposit on each catalyst surfaces. The typical oil poisoning process was observed here where the oil compounds remained on the surface of the catalyst because of their larger molecular size. The presence of phosphorous on the catalyst surface after aging would come from the oil, because the fuel used for this test contained no phosphorous. The phosphorous was located within the surface layer of the washcoat and had not penetrated significantly into the porous structure of the catalyst. It also did not form the typical glazed finish on the surface.

Only temperature aging was produced on the catalyst after 84 hours of aging with different fuel types.

The test results from the comparison of phosphorus poisoning on the catalyst and the influences on the engine from different phosphorus content in fuel show that the catalysts were affected and the injection systems were not affected after running the engine with 800 litres B20S or phosphorus doped B20S. The biodiesel fuels were supplied as mixtures with additives to prevent coking.

The light-off temperature tests show a progressive decline of the catalyst CO conversion produced when the engine was run with the different fuels with high phosphorus content, which means a decrease of the catalyst activity with the increase of phosphorus concentration in B20S.
Analyses of the catalysts showed that the catalysts’s specific surface area decreased significantly with increased in phosphorus in the fuel.

Phosphorus, calcium and zinc were located on upper surface of the washcoat layer when the catalyst was aged with B20S without phosphorus additive, indicating a typical oil deposit process. Phosphorus penetrated through the washcoat layer and calcium and zinc remained on the washcoat surface when the catalysts were aged with B20S containing a phosphorus additive. The higher the concentration of phosphorus additive in the fuel, the heavier the penetration of phosphorus through the washcoat layer becomes.

2 Aging of Diesel Particle Filter with different types of oil

The poisoning produced by the phosphorus content in oil was investigated by using the same Diesel Particle Filter type and the same fuel type as for the first two tests. Different oils were used with different phosphorus compositions in order to examine the various effects that these may have on different components. The following table shows the test name, fuel and oil used.

<table>
<thead>
<tr>
<th>Test Name</th>
<th>Oil type</th>
<th>Fuel type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil A</td>
<td>Standard oil 1</td>
<td>DK</td>
</tr>
<tr>
<td>Oil B</td>
<td>Standard oil 2 with higher ZDDP concentration</td>
<td>DK</td>
</tr>
<tr>
<td>Oil C</td>
<td>Special oil 2 with higher P concentration but without ZDDP</td>
<td>DK</td>
</tr>
</tbody>
</table>

2.1 Engine component analyses results

The effects on the engine, emissions and exhaust gas-treatment system were examined for different phosphorus concentrations and forms that are found in the engine oil.
2.1.1 Injection system inspection

After running the engine with the different engine oil types the injection systems were examined in order to determine if different phosphorus concentrations and forms in the oil have an influence on them. The injection system flow rate was measured after every test. Photos were taken and an EDX analysis of the injection system surface was done.

For the evaluation of the aged injection systems the same procedure was followed as for the fuel tests.

The nominal injection system flow rate has a value of 425 cm$^3$/s with a tolerance of 9 cm$^3$/s. The engine would not run efficiently when the flow rate is less than 6% of the initial value.

The nominal flow rate was not obtained, which means that the injection system was coked during the test resulting in lower engine power. The lower flow rates measured was different for the different oil tests. The biggest flow rate decrease was measured on the injection system of the test run with Oil A (Figure R.33). The flow rate reduction was about 12% with respect to the nominal flow rate value. The flow rate deficits for the oil B and oil C tests were 4,5% and 5,2% of the nominal value respectively. These results imply that the injection systems that ran with oil B and C were still in acceptable condition after the tests, however the systems with oil A was unacceptable. This would imply that the injection system would have to be replaced.

![Figure R.33: Result of the injection system flow rate and photos after runs with different oil types](image-url)
Photos of the injection system were taken (see attachment R.51 to R.53). The results showed that the injection system aged with Oil A had a high incrustation of deposits on the surface.

The analysis (EDX) of each injection system surface showed that the elements contained on the injection systems surface were Ca, C, O, Si, Zn, S, P, Mg and Cu. C and Si would typically come from the fuel; Zn, Al and Mg from the oil; Fe and Cu due to engine wear and Ca, P and S from fuel and/or oil. There are no significant differences between the elemental compositions of the deposits on the injection systems from one oil type to another (Attachment R.54 to R.56).

2.1.2 Fuel analyses result and consumption

A fuel probe was analysed in the Volkswagen AG laboratories before testing and the results can be seen in the experimental methodology, table EM.18.

The same standard diesel fuel was used during the entire oil test. The high quality of the standard diesel used at the research and development centre of Volkswagen AG permits “clean investigations” (investigations without interference of influencing substances, for example sulphur or phosphorus) and therefore provides a good platform for the study of the influence of oil components.

The second test, run with oil B, had the biggest total fuel consumption in litres. This was expected because of the longer run time with this oil. The aging time and fuel consumption was similar for the oil A and oil C tests.

The fuels consumption and aging time is described in the following table.

<table>
<thead>
<tr>
<th>Name</th>
<th>Aging Time (h)</th>
<th>Fuel consumption (l)</th>
<th>Fuel consumption (l/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil A</td>
<td>338</td>
<td>1312</td>
<td>3.88</td>
</tr>
<tr>
<td>Oil B</td>
<td>523</td>
<td>1883</td>
<td>3.60</td>
</tr>
<tr>
<td>Oil C</td>
<td>336</td>
<td>1390</td>
<td>4.14</td>
</tr>
</tbody>
</table>
2.1.3 Oil Analyses results and consumption

The fresh oils and the tested oils were analysed in the Volkswagen AG laboratories. The fresh oil details are described in section 2.1.4 of the experimental methodology. The following tables show the results from some of the analyses.

![Table R.16: Oil analysis result for oil A test](image)

![Table R.17: Oil analysis result for oil B test](image)
Table R.18: Oil analysis result for oil C test

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Oil C Fresh</th>
<th>Oil C After 50h Aging</th>
<th>Oil C After 100h Aging</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematic viscosity, 40 °C</td>
<td>mm²/s</td>
<td>61,96</td>
<td>56,47</td>
<td>47,56</td>
</tr>
<tr>
<td>TBN</td>
<td>mg KOH/g</td>
<td>5,40</td>
<td>4,70</td>
<td>4,20</td>
</tr>
<tr>
<td>DK Content</td>
<td>%</td>
<td>-</td>
<td>7,25</td>
<td>11,47</td>
</tr>
<tr>
<td>Ash content</td>
<td>g/l</td>
<td>0,65</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Calcium</td>
<td>ppm</td>
<td>1200</td>
<td>1200</td>
<td>1200</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>ppm</td>
<td>1800</td>
<td>1500</td>
<td>1400</td>
</tr>
<tr>
<td>Zinc</td>
<td>ppm</td>
<td>nn</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Sulphur</td>
<td>ppm</td>
<td>539</td>
<td>534</td>
<td>506</td>
</tr>
<tr>
<td>Magnesium</td>
<td>ppm</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

The results showed that the *kinematic viscosity* of all the oils decreased after each test compared to the fresh oil. The decreased in kinematic viscosity can be partly attributed to the leaking of diesel fuel into the oil and the breakdown of the large oil molecules during the testing. The increase in the fuel content of the oil with test time is shown in figure R34.

The *oil components content* found in used oil is not exactly the same than the oil components content for fresh oil. The highest phosphorus content decrease in oil was identified during the oil C test. The phosphorus content was reduced from 1800ppm in the fresh oil to 1400ppm after 100 hours of aging. The phosphorus decrease in oil A was less than 100ppm and in oil B exactly 100ppm after 100 hours aging. The highest zinc and sulphur decrease occurred when the engine was run with oil B. Note that the oil C had no zinc and that the sulphur content in oil C is lower than in the other two oils.

There are different *contents of fuel* in the oils after testing from one test to another. As indicated in the experimental methodology the engine oil was changed after 50, 100 or 150 hours of running because of the high fuel content in the oil and the negative influence this has on the lubrication properties of the oil. Running an engine with such a high content of fuel in the oil risks permanent damage to the engine, because of the severe increase in friction. The fuel content in oil after 50 and 100 hours of running is shown in the following figure. No data for fuel content after 150 hours is displayed because only one oil type was run for this long without changing the engine oil.
The results showed that the test run with Oil A has the lowest fuel content in the oil. When compared to the test runs with the other two oils, oil C had a significant amount of fuel content after the 100 hour test run. This was almost twice the amount as determined for oil A, which cannot be currently explained. It was proven that the fuel content in oil is strongly influenced by the time period for which the engine is run as well as by the type of engine oil that is used.

The oil consumption after Oil B and Oil C test was approximately the same but the oil consumption of the Oil A test was around three times higher. The big oil consumption differences for Oil A could be attributed to the engine run-in time. Oil A was the first oil to be tested and the engine that used during the testing was new. It is known from experience that the initial oil consumption for a new engine is higher than after the specified “running-in“ time because the oil is consumed during initial lubricating stages of the test run.

The following table shows the total consumption and aging time results.

<table>
<thead>
<tr>
<th>Name</th>
<th>Aging Time (h)</th>
<th>Oil Consumption (g)</th>
<th>Oil Consumption (g/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil A</td>
<td>338</td>
<td>3610</td>
<td>10.68</td>
</tr>
<tr>
<td>Oil B</td>
<td>523</td>
<td>1045</td>
<td>2.00</td>
</tr>
<tr>
<td>Oil C</td>
<td>336</td>
<td>1353</td>
<td>4.03</td>
</tr>
</tbody>
</table>
No difference was found in the oil consumption between aging times of 50 hours and 100 hours for the same oil type. The oil consumption after 50 and 100 hours of aging for each oil test can be seen in figure R.35.

![Figure R.35: Result of the oil consumption after 50 and 100h with different oil types](image)

The test run with Oil A has the highest oil consumption after 50 and 100 aging hours and has the lowest fuel content. This high oil consumption was attributed to the fact that the engine was new at the start of the test.

### 2.2 Emissions results

The average emissions produced after the combustion of the fuel in the engine during the aging and regeneration of the catalysts are described in the following figure.
The average values of the hydrocarbon (HC) during the different oil aging tests ranged between 100ppm and 150ppm.

The carbon monoxide (CO) averages were relatively similar for oil A and oil B (between 416 and 444ppm), however the engine that used the oil C showed an increase in the CO concentration of up to 671ppm.

The average nitrogen oxide (NOX) values were 160ppm for the test run with oil A and B, and slightly lower for the test run with oil C (109ppm).

A progressive increase of the soot content of the exhaust gas was noted during the run of the engine with the different oil types. The values ranged from $26 \times 10^{-5}$ with oil A to $120 \times 10^{-5}$ with oil C.

The average temperature after the engine (Temp before DPF) during the different oil aging tests was 200 °C. The midpoint temperature of the emissions before, after and in the catalyst was similar for every catalyst run with different oil types (see Attachment R.57).

The maximum temperatures during aging and regeneration of the DPF before and after the catalyst are shown in table R.20.
Table R.20: Maximum temperature during aging and regeneration of the DPF for different oil types

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Oil A, Max. Temp</th>
<th>Oil B, Max. Temp</th>
<th>Oil C, Max. Temp</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aging of DPF</td>
<td>Regeneration of DPF</td>
<td>Aging of DPF</td>
</tr>
<tr>
<td>Before DPF</td>
<td>250</td>
<td>700</td>
<td>220</td>
</tr>
<tr>
<td>After DPF</td>
<td>220</td>
<td>600</td>
<td>190</td>
</tr>
</tbody>
</table>

The same emissions, except CO, and temperature conditions were produced during each oil test.

2.3 Catalyst analyses results

2.3.1 Characterization of the Diesel Particle Filter

The characterization of the DPF involves measuring the particles that were collected on the DPF during five hours of running under the load operating points (see attachment R.58 to R.60). It was observed that the weight of the DPFs increased during the test period leading to the conclusion that an accumulation of ash occurs on the DPFs over time.

The weight of the DPF for every oil test with time is shown in figure R.37 to R.39.

![Figure R.37: Weight of the DPF for oil A test](image-url)
Similar oil consumption values were produced during the tests with oil B and C, but a very high ash accumulation occurred on the DPF with oil C. The ash content in oil is lower for the oil C than for the oil B. If the ash content in oil and the oil consumption are considered, it is expected that the DPF aged with oil C should have the lowest ash content on the DPF, but this was not the case. The test run with oil A had the highest oil consumption and the highest ash content in oil. So it was expected to find the highest ash content on the DPF, but it was not the case either.

The different ash content on the DPF was explained with a different behaviour of the oil C in the engine: different combustion process, different consumption process, etc. In order to explain these occurrences, the aged catalysts were analysed and light-off temperature tests were done.
2.3.2 Engine Tests

Three light-off temperature tests were performed every 50, 100 or 150 catalyst aging hours and three light-off temperature tests were performed at the end of the aging process. These tests were conducted to provide an indication about the activity of the catalyst during the aging time. [Attachment R.61 to R.63].

It is important to remember that the light-off temperature is defined as the temperature at which 50 % of the emission pollutants are transformed and that it depends on the emissions components and on the catalyst aging. The catalyst loses its activity because of aging and it is shown as an increase in the light-off temperature.

The following figures show the CO light-off temperature of every DPF during aging time for every oil test.

![Figure R.40: Light-off temperature 50% CO for oil A test during aging time](image-url)
The figures show that the biggest increase in light-off temperature corresponds with oil C, which has the highest ash content in the DPF (found during characterization of the DPF). The oil B test had the smallest increase in light-off temperature and had the lowest ash content in the DPF.

The running of the catalyst with different oil types during approximately 350 hours produced different catalyst aging. The test run with oil C produced the biggest influence on the catalyst activity. The different increases in the light-off temperature could be explained with a different behaviour of the oil C in the engine.
2.3.3 Catalyst analyses results

Every aged DPF was analysed to investigate the thermal history of the catalyst, the catalyst poisoning (particularly by phosphorus) and the location of phosphorus deposition.

a) Physical examination
The overall physical condition of the aged DPF catalyst ceramic were still in good conditions, but the DPF aged with oil A showed some damage to the edges. Photos were taken of the DPF after aging (see attachment R.64 to R.66) and no plugged cells, missing plugs or face damage was observed.

b) Washcoat composition
The washcoat compositions of the DPFs were analysed using X-ray fluorescence (XRF). The XRF analysis of aged catalysts often understates the precious metal content as the aged sample is compared to the specifications provided by the supplier for a fresh reference sample. Other compounds like phosphorus, zinc, calcium or sulphur were also measured.

Precious metal
The catalysts used were a three zoned Platinum (Pt)/Palladium (Pd) washcoat system with a nominal content of 125 g/ft$^3$ (4:1:0) at the front 64 mm (2.5"), 50 g/ft$^3$ (1:0:0) in the middle 55,25 mm (2.175") and 10 g/ft$^3$ (1:0:0) at the rear 55,25 mm (2.175"). The aged catalysts were analysed and for all catalysts the Pt and Pd content was close to the nominal value. The following table shows the Pt and Pd loading on the aged catalyst for different oil test at the front, middle and rear zones.
Table R.21: Average Pt and Pd loading on the aged catalyst (g/ft³) for different oil test

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt-loading (g/ft³)</th>
<th>Pd-loading (g/ft³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Front</td>
<td>Middle</td>
</tr>
<tr>
<td>Oil A</td>
<td>90,0</td>
<td>50,3</td>
</tr>
<tr>
<td>Oil B</td>
<td>90,7</td>
<td>48,4</td>
</tr>
<tr>
<td>Oil C</td>
<td>91,3</td>
<td>47,7</td>
</tr>
<tr>
<td>Nominal</td>
<td>100,0</td>
<td>50,0</td>
</tr>
</tbody>
</table>

The measurement of the Pt and Pd content on the aged catalysts was done in order to assess the catalyst after the aging time.

**Phosphorus**

The phosphorus concentrations on the catalyst after 338 hours aging for oil A, 523 hours aging for oil B and 336 hours aging for oil C are shown in figure R.43.

![Figure R.43: Phosphorus concentration on the catalyst for different oil types test](image)

The results showed that the phosphorus content was found in the front, middle and rear section of every aged catalyst. The catalyst aged with oil C had the highest phosphorus content deposit on the catalyst, which was almost three times as high as the catalysts tested with the other two oils.

The high phosphorus content on the catalyst for the oil C test shows again a different behaviour of this oil in the engine as show in the characterization test and in the light-off temperature test, which produces different phosphorus poisoning on the catalyst.
Phosphorus, calcium, zinc and sulphur

Calcium, zinc and sulfur were also found as compounds on the aged catalysts run with different oils. There is a relation between the element content in the oil and the poisoning compounds found on the catalyst but much more phosphorus was found on the catalyst for the test run with oil C, this is explain with the different behaviour of this oil in the engine. The figure R.44 shows the average value of the poisoning compounds on the different aged catalyst with different oil types.

![Figure R.44: Average value of the catalyst poisoning compounds on the different aged catalyst for different oil types](image)

If the front, middle and rear of the aged catalysts are examined, it is found that the highest poisoning element contents are at the front of the catalyst for all poisoning compounds in the case of oil A. The poisoning compounds on the catalyst aged with oil B are found at the front with the exception of sulphur, which is found in equal measure at the front, middle and rear of the catalyst. For the catalyst aged with oil C, zinc (in a very small amount) and calcium poisoning were found at the rear of the catalyst. Sulphur was deposited on all the catalysts and phosphorus was deposited in the middle and on the front of the catalyst (see attachment R.67 to R.69).
c) Washcoat specific surface area

As for the fuel test the washcoat specific surface area (SSA) of every aged catalyst was analysed. The loss of specific surface area is a sign of catalyst aging. The Figure R.45 shows the average SSA of the aged catalyst.

The results show the same specific surface areas (SSA) for the catalysts aged with oil A and oil B, but the specific surface area of the catalyst aged with oil C was drastically reduced. The specific surface area of a fresh catalyst was not measured and therefore the influence from the oils on the SSA of the catalyst can not be determined exactly, but a significant difference in SSA is clearly seen in the tests with oil C.

The phosphorus presence in oil C had produced the lowest SSA in the aged catalyst. The results show that running the catalyst with the oil C during 336 hours the specific surface area of the catalyst will be highly reduced and its function will be significant impaired.

d) Location and morphology of the precious metals and poisoning compounds

An example of the section that was analysed by WDX mapping can be seen in figure R.46.
The distribution of the precious metals on the catalyst was examined for every aged catalyst and the same Pt and Pd dispersion was determined (see figure R.47, R.49 and R.51). The phosphorus, calcium and zinc distribution on the aged catalysts with different oil types are shown in figure R.48, R.50 and R.52. The location of the poisoning compounds on the catalysts investigated with WDX shows similar element poisoning distribution for oil A and oil B (almost exclusively on the surface), but a different distribution for the catalyst aged with oil C (penetrated into the washcoat).

For the catalyst aged with oil A the poisoning compounds were located in a single layer along the outer edges of the substrate. It is the typical oil poisoning process, the oil compounds stay on the surface of the catalyst because of their large molecular mass and their affinity to the catalyst.
The poison element distribution for the catalyst aged with oil B was very similar to that of the catalyst aged with oil A. In both cases the poisoning compounds were located in a single layer along the outer edges of the substrate. High levels of catalyst poisons were detected and concentrated toward the filter inlet. The catalyst aged with oil B has higher levels of phosphorus poisoning compared to the catalyst aged with oil A.

On the catalyst aged with oil C low levels of calcium, zinc and sulfur were detected, but much greater phosphorus poisoning throughout the length of the unit were found. Heavy phosphorus poisoning deposits on the catalyst surface, so the phosphorous can penetrate through the porous structure of the filter walls. The phosphorus content in the oil C causes a different poisoning on the catalyst than the phosphorus content in oil A and oil B.
The different behaviour of the oils on the catalyst could be explained because of the different phosphorus forms in the oils. As indicated before, the oil A and oil B contain commercial phosphorus forms (ZDDP) with different phosphorus concentration, but the oil C has a different phosphorus form (experimental Zn-free phosphate anti-wear component). The phosphorus form in oil C has different characteristics which causes different behaviour when it is used in the engine (different volatility and combustion). See table EM.19 from the experimental methodology section for the detailed characteristics. The table R.67 to R.69 of the oil analyses results and consumption show the different composition compounds in oil after testing. As indicated before, the highest phosphorus content decrease occurs with oil C, so the phosphorus from oil C deposits on the catalyst surface first. At this time there are no other poisoning deposits on the catalyst surface yet, so the phosphorus can penetrate through the washcoat and produce a significant and irreversible deactivation of the catalyst function.

2.4 Oil results conclusions

The test results show that the catalyst and the injection systems were influenced in different ways by the varied phosphorus content and different phosphorus forms in the oil.

The injection systems were unaffected after running the engine for approximately 520 hours with oil B and 340 hours with oil C. Of the three oils, only oil A caused coking which occurred after around 340 hours of testing with oil A. It is to be assumed that the coking was caused solely by the oil, since these tests were run with standard diesel fuel and as shown at the beginning of this chapter (see figure R.1) standard diesel fuel produces minimal coking. The engine’s oil consumption and the different oil quality, ash content and phosphorus content in the oil affected the injection system in a different way for oil A than for the others oils.

The characterization of the catalysts shows that the empty weight increased during the test period and this leads to the conclusion that an accumulation of ash occurs on the catalysts over time. The highest ash deposits on the catalysts were produced during the test run with oil C and the lowest with oil B. The oil C had the lowest ash content (oil A: 1.3, oil B: 0.9 and oil C: 0.65) and the test run with this oil had the same oil consumption as the test run with oil B. The different ash depositions on the
catalysts can be explained by the different behaviour of the oil additives in the engine.

The biggest light-off temperature increase was produced on the catalyst aged with oil C and the smallest on the catalyst aged with oil B. The different increases in the light-off temperature can be explained with the different behaviour of the oil C in the engine.

Running the catalyst with different oil types for approximately 350 or 530 hours produced different catalyst aging. The test run with oil C produces the biggest influence on the catalyst activity.

The specific surface area was highly reduced after aging the catalyst with oil C. Similar element poisoning and distribution was produced on the catalysts aged with oil A and B, but the catalyst aged with oil C had a higher phosphorus poisoning and a different distribution on the catalyst. The poisoning compounds were located in a single layer along the outer edges of the substrate, but high levels of poisoning were detected and concentrated toward the filter inlet. The catalyst aged with oil B has higher levels of phosphorus poisoning compared to the catalyst aged with oil A. It is the typical oil poisoning process where the oil compounds stay on the surface of the catalyst because of their molecular mass. A completely different phosphorus poisoning was observed on the catalyst aged with oil C. Low levels of calcium, zinc and sulphur were detected, but much greater phosphorus poisoning throughout the length of the unit were found. Heavy phosphorus poisoning had penetrated down into the porous structure of the filter walls. The phosphorus content in oil C causes a different poison on the catalyst than the phosphorus content in oil A and oil B.

The different behaviour of the oils in the engine and catalyst could be explained by the different oil additives used in oil. The oil C additives have different characteristics, which produce high volatility and different combustion of the compounds. The oil used during aging was analysed after the tests and the results show different levels of decrease in phosphorus content for each oil.
The highest phosphorus content decrement was produced after running the engine with oil C. The phosphorus moves through the engine system preferentially to other components in the oil. So it is expected that the phosphorus from oil C accumulates on the catalyst very quickly. There are no other elements on the catalyst surface at that time and the phosphorus can penetrate through the washcoat and produce a major, irreversible deactivation of the catalyst function.

Figure R.53: Phosphorus content in oil after different run time for oil A, B and C
IV. Conclusion

The exhaust gas-treatment systems are poisoned by phosphorus during their operational life because of the engine oil and when they are run with fuel containing phosphorus, for example biodiesel. The main source of phosphorus poisoning is the engine oil, but the phosphorus poisoning caused by the use of biodiesel is becoming more important since the use of this type of fuel is becoming increasingly popular. The engine oil needs phosphorus for retaining anti-oxidant and anti-wear properties. The phosphorus is present in biodiesel as a natural component and is usually eliminated during the refining procedure. The study of the phosphorus poisoning was structured in two parts according to the phosphorus source.

Part one: The phosphorus poisons produced from biodiesel fuel. This type of poisoning was examined with two different tests:

1. Comparison of the effects of different fuel types on the catalyst and on the engine. After 84 hours of aging, it was found that the fuel type (DK, B20S, B20SR and B20R) had no influence on the catalyst but flow rate of the engine’s injection system was affected. The biggest decrease in injection system flow rate was produced when the engine was run with B20S and the smallest decrease with DK. The biodiesel was not supplied as mixtures. The mixtures were made at the Volkswagen Centre and additives to prevent coking were not used. The addition of additives could result in a lower deficit of the flow rate. The same element poison was produced on every catalyst.

2. Comparison of phosphorus poisoning on the catalyst and influence on the engine from different phosphorus concentrations in fuel. Biodiesel B20S was used as fuel and it was doped by adding tributylphosphate. The phosphorus was added in order to accelerate the poisoning process and the different concentrations in fuel were used to simulate different distances of driving.
The injection systems were neither affected by running the engine with B20S nor by varying the phosphorus concentration of the doped B20S. The biodiesel fuel was supplied as mixtures and additives to prevent coking were used. It was observed that varying the concentration of phosphorus in fuel has an important influence on the catalyst activity. A correlation between the phosphorus content in fuel and the phosphorus content on the catalyst was found. The most severe poisoning was always produced on the front of the catalyst. Phosphorus, calcium and zinc were located on the upper surface of the washcoat layer when the catalyst was aged with B20S without phosphorus additive. Phosphorus poisoning penetrated through the washcoat layer while calcium and zinc remained on the washcoat surface when the catalysts were aged with doped B20S. This produces major and an irreversible deactivation of the catalyst function. If a catalyst is run with biodiesel with phosphorus content of 10ppm, progressive catalyst deactivation occurs over time and after approximately 30,000Km the catalyst function will be significantly impaired. The phosphorus content in biodiesel should be reduced, because of the major problems that it causes with catalysts.

**Part two:** Study of the phosphorus poisoning produced by different phosphorus concentrations and different phosphorus forms in engine oil on the catalyst and on the engine. Three different oils were used: “Oil A”, is used as a reference and is a commercial 0W-30 Euro III oil meeting VW 50300 and VW50601 standards and has a phosphorus concentration of approximately 900ppm; “Oil B”, is an experimental modification of the OS191877 oil that is currently used at Volkswagen, but has a higher phosphorus concentration (approx. 1600ppm) and “Oil C” has similar phosphorus levels as Oil B (approx. 1800ppm), but makes use of a Zn-free. The injection systems were not affected during tests with oil B and oil C, but they were coking after approximately 340 hours with oil A. The different oil quality, ash content, oil consumption and phosphorus content in the oil affected the injection system. Different oil types produce different catalyst aging and the test run with oil C produced the biggest influence on the catalyst activity. The highest increased in the light-off temperature in the catalyst was produced after the run with oil C. The highest ash deposits were produced when the catalyst was run with oil C.
The catalyst aged with oil C had the highest concentration of phosphorus deposit. The different increases in the light-off temperatures, the different ash depositions on the catalysts and the high phosphorus concentrations on the catalyst could be explained with the different behaviour of the oil C in the engine. The poisoning compounds deposited on the catalysts aged with oil A and oil B were located in a single layer along the outer edges of the substrate. It is the typical oil poisoning process. The catalyst aged with oil B has higher levels of phosphorus poisoning compared to the catalyst aged with oil A.

A completely different phosphorus poisoning was observed on the catalyst aged with oil C. The phosphorus had penetrated down into the porous structure of the filter walls.

The different impacts of the various oils on catalyst can be explained by the different phosphorus form in the oils. The oil C has an experimental Zn-free phosphate anti-wear component as additive, which produces a different volatility and combustion when it is used in the engine. The phosphorus from oil C reaches the catalyst surface first and penetrates through the washcoat, which results in major and irreversible deactivation of the catalyst function.

The type of phosphorus source and the overall formulation shape is more critical to minimising catalyst exposure to phosphorus and subsequent deactivation, than the overall phosphorus content.

Oil additives must be developed in future taking into account these effects in order to maximise durability of catalyst function.

A different phosphorus poisoning is produced by the phosphorus from fuel and the phosphorus from oil. The phosphorus from the commercial oil can burn or vaporize during combustion in the engine, but it is heavy and deposits on the catalyst surface. The phosphorus in fuel burns easily and can enter the washcoat pores to form deposits inside it because of the small size.

This project has brought a better understanding of the phosphorus poisoning process in exhaust after treatment systems. It shows the different phosphorus poisoning levels produced from fuel and oil, as well as the different poisoning processes that occur due to different phosphorus forms in oil. This information can now be used to minimize phosphorus poisoning.
V. Perspective

This project ensured an increased understanding and improved knowledge of the phosphorus poisoning process in exhaust after treatment systems. Different phosphorus poisoning effects from phosphorus content in fuel and phosphorus content in oil were examined.

The phosphorus present in fuel burns in the engine and penetrates through the catalyst washcoat. But the phosphorus present in oil can burn and evaporate producing two different depositions on the catalyst, once on the catalyst surface and another through the catalyst, depending on the phosphorus components present in the oil.

The experiences and results obtained from this project can be used to minimize the catalyst phosphorus poisoning from the two different sources.

The phosphorus poisoning produced from phosphorus content in fuel can be reduced or eliminated with the restriction of the phosphorus content in biodiesel. Currently a content of 10ppm of phosphorus in biodiesel is permitted, but this value must be reduced or completely eliminated if the catalyst activity during the functional life of the catalyst is to be ensured.

The phosphorus poisoning produced by phosphorus content in oil should also be reduced. The oil tests conducted in this study show the important influence of the phosphorus form and properties of the oil additives, especially volatility. Oil containing additives with high volatility (as oil C, Zn-free phosphate anti-wear components) produced the highest level of phosphorus poisoning on the catalyst and oil containing additives with low volatility (as found in oil A and B, with ZDDP) produced the lowest levels phosphorus poisoning on the catalyst.

The type of phosphorus source and the overall formulation shape is more critical to minimizing catalyst exposure to phosphorus and subsequent deactivation than the overall phosphorus content.

A possible new oil formulation could contain additives with lower volatility than the commercial oil in order to produce lower phosphorus poisoning with minimum deposition on the catalyst surface and minimum phosphorus penetration through the washcoat. Another possibility against the phosphorus poisoning from engine oil on the catalyst is the reduction or elimination of phosphorus in oil, but this will have
negative effects on the engine parts. Extensive development and testing is still required in order to produce oil additives with no negative influences on either the catalyst or on the engine.
Bibliography


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Oxidationskatalysatoren mit organischen Phosphor- und Siliziumverbindungen. Dr. Ing. Technischen Universität München, Germany.


Abbreviations

ASTM American Society of Testing and Materials
B20S Mixture of 20% biodiesel SME and 80% standard diesel
B20SR Mixture of 10% biodiesel SME, 10% biodiesel RME and 80% standard diesel
B20R Mixture of 20% biodiesel RME and 80% standard diesel
CN Cetane Number
CP Could Point
DIN Deutsches Institut für Normung
DK1 Standard Diesel
DOC Diesel Oxidation Catalyst
DPF Diesel Particle Filter
EDX Energy Dispersive X-ray
EGR Exhaust Gas Recirculation
EN European norm
EPA Environmental Protection Agency
EU European Union
FAME Fatty Acid Methyl Ether
FSI Fuel Stratified Injection
FTIR-Spectroscopy Fourier-Transformation Infrared Spectroscopy
ICP Inductively Coupled Plasma
P Pressure
PDE Pump-nozzle unit
PM Particle Matter
PP Pour Point
RME Raps Methyl Ether
RPM Revolutions Per Minute
SCR Selective Catalyst Reduction
SDI Saugdiesel mit Direkteinspritzung (Direct injection diesel)
SEM Scanning Electron Microscopy
SESAM System for Emission Sampling and Measurement
SME Soya Methyl Ether
SSA  Specific Surface Area
T    Temperature
TBN  Total Base Number
TDI  Turbo Diesel Injection
WDX  Wavelength Dispersive X-ray
XRF  X-ray Fluorescence
XRD  X-ray Diffraction
ZDDP Zinc Dithiophosphates
Attachment

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1 Attachment experimental methodology

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2 Attachment result Test aging catalyst with different fuels

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3 Attachment result Test aging catalyst with different content of phosphorus in fuel

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4 Attachment result Test aging catalyst with different oils

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![Midpoint Temperature Chart]

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![Load of DPF Chart]
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![Graph showing load of DPF during time for oil B test.](attachment:R.59)

Attachment R.60: Midpoint emission temperature before, after and in DPF.

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![Graph showing light-off temperature for oil A.](attachment:R.61)
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Attachment R.66: Photo of the DPF aged with oil C after aging.

Attachment R.67: Poisoning elements on the catalyst aged with oil A in wt %.

<table>
<thead>
<tr>
<th>Oil A</th>
<th>Front</th>
<th>Middle</th>
<th>Rear</th>
<th>Average</th>
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<tr>
<td>Zinc</td>
<td>0.396</td>
<td>0.037</td>
<td>0.032</td>
<td>0.155</td>
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<tr>
<td>Sulfur</td>
<td>1.189</td>
<td>0.230</td>
<td>0.213</td>
<td>0.544</td>
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<tr>
<td>Phosphorus</td>
<td>0.929</td>
<td>0.173</td>
<td>0.173</td>
<td>0.425</td>
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<tr>
<td>Calcium</td>
<td>0.995</td>
<td>0.077</td>
<td>0.050</td>
<td>0.374</td>
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</table>

Attachment R.68: Poisoning elements on the catalyst aged with oil B in wt %.

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<th>Oil B</th>
<th>Front</th>
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<th>Rear</th>
<th>Average</th>
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<td>Zinc</td>
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<tr>
<td>Sulfur</td>
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<tr>
<td>Phosphorus</td>
<td>1.058</td>
<td>0.378</td>
<td>0.529</td>
<td>0.655</td>
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<tr>
<td>Calcium</td>
<td>0.261</td>
<td>0.018</td>
<td>0.054</td>
<td>0.111</td>
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</table>
Attachment R.69: Poisoning elements on the catalyst aged with oil C in wt %.

<table>
<thead>
<tr>
<th>Oil C</th>
<th>Front</th>
<th>Middle</th>
<th>Rear</th>
<th>Average</th>
</tr>
</thead>
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<tr>
<td>Zinc</td>
<td>0.000</td>
<td>0.000</td>
<td>0.014</td>
<td>0.005</td>
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<tr>
<td>Sulfur</td>
<td>0.033</td>
<td>0.016</td>
<td>0.033</td>
<td>0.027</td>
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<tr>
<td>Phosphorus</td>
<td>3.143</td>
<td>3.262</td>
<td>2.506</td>
<td>2.970</td>
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<tr>
<td>Calcium</td>
<td>0.000</td>
<td>0.000</td>
<td>0.153</td>
<td>0.051</td>
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</tbody>
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