

Fuels and Lubricants of the Future

SYNTHETIC FUELS Commercialization of Low Carbon Methanol

BIOFUELS

Potentials of Biofuels for Passenger Car and Non-road Applications **LUBRICANTS** Base Oil Aging with Contemporary Biofuels

/// GUEST COMMENTARY Wolfgang Maus [WM Engineering & Consulting]

/// INTERVIEW Jens Hadler [APL]

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Rethinking Fuels

Dear Reader,

We owe the level of individual mobility that we know and appreciate today not least to internal combustion engines and fuels, most of which come from fossil resources. But, among other things, the combustion of these fossil fuels generates CO_2 emissions that negatively affect our air quality.

A balanced carbon cycle is essential for the survival of human beings and animals. The combustion of fossil resources disturbs the balance of this cycle. We can re-establish this balance if we implement the results of the UN Climate Conference in Paris. One of the levers for achieving this is CO_2 -neutral traffic. Electric mobility will enable us to achieve zero emissions locally. However, electric mobility is not an all-embracing solution. Worldwide financing, long-distance mobility and heavy goods transportation are not guaranteed.

This gap can be filled by CO₂-neutral fuels with their high energy density. Synthetic fuels are particularly suitable. If they can be produced on a large industrial scale, they can replace fossil-based sources of energy. They could even be used in existing vehicles. Investment for product development and an energy supply system for vehicles are available worldwide and can continue to be used. What is more, synthetic fuels can be specifically designed. As a result, they have the additional potential of soot-free combustion. That would be a breakthrough in air quality. Initial tests are promising.

But we are only at the beginning. Further investment is necessary, not only in research but also in the production of these new fuels. Specifically designed synthetic fuels give us the opportunity not only to start with some millions of new vehicles, but also with more than one billion existing vehicles – with a liberating effect for the industry. New fuels and electric mobility can lead us to sustainable, CO₂-neutral and zeroemission mobility. Only both paths together will take us to our target.

In this special issue, we have put together important information on the fuels and lubricants of the future and examine them from many different aspects. We hope that we can give you new impulses and that you enjoy reading our reports.

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FEBRUARY 2016 Fuels and Lubricants of the Future

New fuels and electric mobility can lead us to sustainable, CO_2 -neutral and zero-emission mobility. Synthetic fuels are particularly suitable. If they can be produced on a large industrial scale, they can replace fossil-based sources of energy.

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There are many initiatives worldwide for using methanol as a fuel and taking advantage of its numerous benefits compared to conventional fuels. Mitsubishi Hitachi Power Systems Europe and Carbon Recycling International shows how the low-CO₂ productionof methanol can already be implemented on a large industrial scale today.

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Because of the regeneration of the diesel particulate filter, unburned fuel from the piston wall leaks into the engine oil and leads to oligomerization. For a better understanding of the autoxidation reaction in the engine oil, simulations of the aging process in the laboratorywere carried out at the Technology Transfer Center Automotive of Coburg University.

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"There is no alternative to the chemically bound storage of energy"

If CO₂ is to be significantly reduced and local emissions are to be minimised there is no alternative to electric mobility, especially in mega cities. However, in the overall context of mobility, the internal combustion engine also has further development potential, especially in combination with alternative fuels and oils. In an interview with MTZextra, Prof. Dr.-Ing. Jens Hadler, Managing Director of APL Group, presents his view of the main focus of future developments and the direction these developments may take.

Prof. Dr.-Ing. Jens Hadler was born in 1966 in Ludwigslust and studied Mechanical Engineering at the Otto-von-Guericke University in Magdeburg. After graduating, he worked as a research assistant at the Institute for Machine Elements and Design, where he completed his doctorate in the field of tribology in 1994. In 1996, he began his industrial career and has since held various management positions at Volkswagen AG. In 2007,

he became head of engine development at Volkswagen. In 2011, he joined APL Group as Managing Director. Hadler is also actively involved in the university environment and has several teaching appointments at academic institutions. He is a an active member of various committees, including the FVV (Forschungsvereinigung Verbrennungskraftmaschinen), where he is a board member.

MTZextra Battery-powered electric vehicles are in the centre of public attention at the moment. However, their CO₂ balance is not always positive with regard to "well-to-wheel" emissions. Wouldn't it be better to optimise conventional powertrains first and then to advance electrification based on that? HADLER _ One should certainly do one while not forgetting the other. Seen from a purely abstract perspective, it is much more efficient to use electricity directly in an electric path, although when it comes to the subject of electrification. we will still have to consider the question of energy storage. We will ultimately find that we need support from chemical energy storage, because it will not be economically feasible to use batteries alone. Therefore, I believe that we need, on the one hand, conventional powertrains with all their challenges, especially with regard to emissions, and on the other hand clear and clean electrification, especially in mega cities. I think that this awareness will increase on a broad base. What is also important in this context is that chemically bound energy storage is the only possibility to achieve CO₂ sinks or closed carbon cycles - especially when mobility is integrated with stationary energy generation for industry and private households.

Greenhouse gas emissions in the transport sector can be reduced by substituting fossil sources of energy by CO_2 -neutral fuels. Does it then make sense to focus on the electric motor or is it not more productive to use renewable electricity for the production of Power to Gas (PtG) and Power to Liquid (PtL) in order to achieve a significant reduction in CO_2 emissions in the entire fleet more quickly?

With regard to efficiency, the electric motor is certainly the best solution in the conversion chain from the battery to the wheel, and it will be required wherever zero emissions need to be achieved locally. On the other hand, in the overall context of mobility and the energy economy, PtL and PtG will play an evident role in the change to a CO₂-neutral use of resources for reasons of storage alone, especially when it is a question of heavygoods and long-distance transport. There are scenarios in which CO₂ can be extracted from the air. That is, of course, very expensive, but one might consider this option and say that the CO₂ required for PtL and PtG can be extracted directly

from the waste air of very energy-intensive industries. Therefore, there must be a very serious discussion about the role of PtL and PtG that takes the overall energy situation into account, just as there should be a similar discussion concerning electric mobility. The use of excess electricity production for storage purposes is just one example. This is

"Politicians has become somewhat quieter on the issue of biofuels after the 'food or fuel' discussion"

going in the direction of coexistence. Therefore, there is no alternative to the chemically bound storage of energy.

Biomass to Liquid (BtL) fuels are being viewed critically, as the reductions in greenhouse gas emissions are marginal and the fuel quality can significantly deteriorate. In this context, what is your opinion of synthetic fuels with an oxygen content, or oxygenates, as future fuels?

Oxygenates are certainly one of many possibilities. When you look back over recent years, we can see that we are actually only at the beginning of the discussion concerning designed fuels. A lot of research and development work is still required before these become a realistic option. According to current knowledge, oxygenates are certainly a possible and correct direction. From an abstract perspective, the preferred fuel of the future would contain less carbon, a lot of hydrogen and more oxygen than today. Oxygenates are one variant that might fit into this category, but a lot of development work is still required with regard to density and other properties, such as distillation and evaporation behaviour. But we are making good progress when we consider OME4 and OME5, in other words the so-called next-generation oxygenates. However, in my view, it is still too early to make any final assessments.

In the excellence cluster "Tailor-Made Fuels from Biomass (TMFB)" at RWTH Aachen University, 2-Methylfuran and 2-Butanone were identified as alternative fuels for use in highly supercharged spark-ignition engines and showed superior properties compared to conventional ROZ95 fuel and ethanol in thermodynamic tests. Are we about to see a breakthrough in designer fuels?

This is an absolutely reasonable and necessary field of research. As I already mentioned, we are at a very early phase of the development of designed fuels, and both of these certainly have a future, as in some cases they burn with extremely low soot in a blend. It is a fact – and this applies to the whole discussion that is being held at the moment on the subject of ethanol, methanol, natural



"We need the electrified internal combustion engine with all its still-unresolved challenges, but we also need clear and clean electric mobility, particularly in mega cities," Hadler says

gas TMFB fuels, oxygenates and others that the key question is not the technology itself but rather the question of how important customer acceptance can be achieved and ultimately how an economically viable business model can be represented in view of the huge investments required. That is perhaps also the main difference to electrification, where the equally necessary investment for a social and political perception of electric mobility is lower by comparison. With regard to the overall energy turnaround, investment in the electricity industry will, however, account for the major proportion of effort compared to PTG/ PTL investment.

The three-year project under the leadership of Ford, in which dimethyl ether (DME) and oxymethylene ether (OME1) are being tested, also goes in this direction. What all these projects have in common is that they aim to produce fuels with less carbon, more hydrogen and more oxygen than is common today. The latest developments show that the search corridor is the right one. But a lot of research and development work is still necessary to answer the question of which of the many possible chemical compounds will win the race in the end. That applies in particular to the issue of reverse compatibility. That is a very decisive issue in view of approximately 1.1 billion existing vehicles worldwide, because it offers a large lever to sustainably reduce emissions immediately.

In the EU, we can expect a further increase in the proportion of biogenic fuels being added to conventional fuels. However, the adaptation of ECU functions to standard-compliant fuel can result in changes in operating conditions when the engines run on pure biofuels. What in your view is necessary in order to exploit the potentials? It remains to be seen whether the biogenic proportions really increase significantly. Even today, the requirement to add 7.5 $\,\%$ to diesel fuels and the 10 $\,\%$ EU requirement for fuels generally are not being fully met. After the intensive "food or fuel" discussions a few years ago, politicians have become a little quieter concerning the issue of biofuels. There is no doubt that waste-to-X processes will be favoured by some stakeholders, but in the context of the energy turnaround they will not be mainstream.



0W20 is currently being introduced in Europe, while 0W16 and 0W12 are under development – Hadler considers a further reduction in friction by oils of around 3 to 5 % to be possible

Can one of the keys to a sustainable reduction of CO_2 emissions be found in the rapid global commercialisation of methanol as a fuel?

Methanol is basically within the above-mentioned search corridor as far as the C-H-O relationship is concerned. A critical aspect is its toxicity, for example compared to ethanol or oxygenates. The investment challenges for methanol are not as great as for other fuels. It is very difficult to predict how this topic will develop in China. One advantage of methanol, and also for ethanol, is that knock resistance and compression can

"We are only at the beginning of the discussion on designed fuels"

be significantly increased compared to the use of conventional ROZ95 fuel. As a result, a reduction of 3 to 5 % CO_2 can be achieved relatively easily in markets that still have a lot of large naturally aspirated engines, such as in China and the USA.

Conventional powertrains still have significant efficiency potentials. Of particular relevance are measures to optimise the drivetrain and transmission. What role is played by the use of low-viscosity oils to reduce friction losses, and what are the main challenges? Development has made a significant leap in the past two to three years. The

introduction of 0W20 is also taking place in Europe and has already been completed at some manufacturers. Japanese manufacturers have been using it for a long time in naturally aspirated in-line engines. Now, of course, there is a further move towards 0W16 and 0W12, where the issue of low-viscosity and the challenges for the engine and the drivetrain must be compensated for by packages of additives or by interaction between the oil, the surface and the manufacturing process. Potentially, I consider a further reduction of friction by oils of around 3 to 5 % to be possible, which can then result in CO₂ reductions of 1 to 2 % depending on the efficiency chain. However, we must proceed systematically, which means that the oil industry, OEMs and Tier 1 must work together on optimisation. Even if we succeed in further minimising oil consumption, we will not manage to reduce it to zero in the foreseeable future. This means that we must succeed in ensuring that the minimal quantities of oil involved in combustion have a minimum influence on the emissions behaviour of the engine. We can only do this in a very intensive cooperation with all those involved.

Professor Hadler, thank you very much for this interview.

High-tech and know-how.



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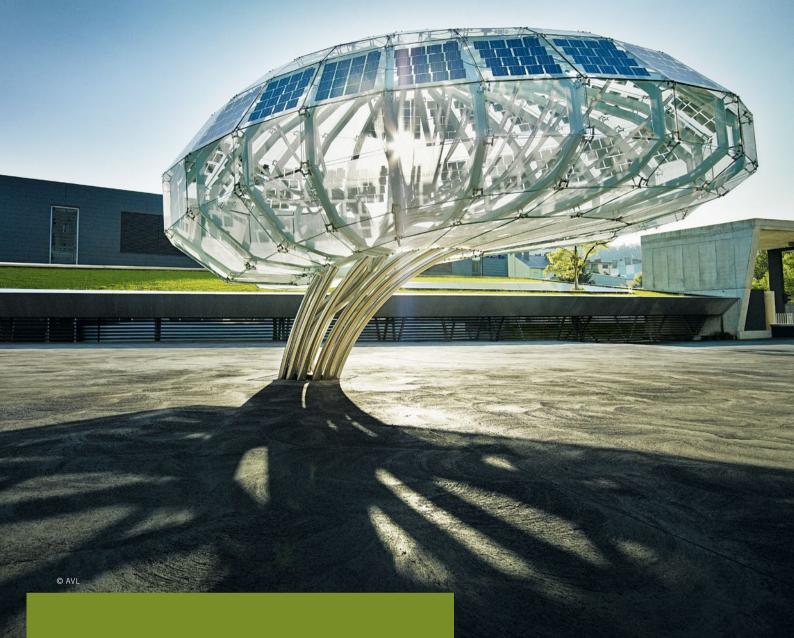
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Testing of Modern Lubricants and Additivated Fuels

Due to current and future legislation, the fuel economy has become the most important topic for the oil industry. AVL presents two innovative technologies to meet the needs of the mentioned industries: Frisc and Dricon.

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GREEN FUELS TO REDUCE VEHICLES EMISSIONS

The transport sector is a major source of air pollution and CO_2 emissions. These emissions are set to increase sharply as the global vehicle fleet is projected to grow dramatically by 2050 mostly in the developing countries. Developed countries have introduced cleaner and more efficient technologies, including green fuels, to sharply reduce vehicles emissions.

FUEL ADDITIVES

Technical innovation in the fuel additives business is a continuous process, which is often driven by legislation. Many additive suppliers are focusing their efforts in the last years to increase the vehicle fuel economy and, therefore, minimizing in this way the emission of CO₂ and of regulated exhaust pollutants. Engine and/or vehicle testing is often needed and furthermore a huge amount of laboratory tests are necessary to produce the required data. The engine developers and car-makers (OEMs), who are manufacturing constantly cleaner and more efficient motors, recognize the importance of the fuel and lube oil additives as part of this evolution to improve the performance and reduce the air pollution [1].

AVL TOOLS

In the last years the oil competence centre was founded at AVL in order to coordinate and centralize all topics related to fuel economy, friction reduction and alternative fuels. Engine and vehicle tests with new additives are costly and can take several days till months to satisfy all needed requirements. AVL developed and patented useful tools to consistently help the oil industry and additive suppliers to check the benefits of their products, saving in this way time and money. One of these tools is Frisc, which is a instrument to reliably and precisely measure the friction force in the engine cylinder. Such measurements give a correlation between friction and fuel economy.

The second tool presented is Dricon, which permits to drive vehicles on chassis dynos automatically, eliminating in this way the human factor, which itself can reduce (up to eliminate) the benefits of the additives on the fuel economy in test phase.

The following example shows the influence of the friction on the fuel economy: In a car of 1350 kg in a NEDC 10 % reduction of friction generates an improvement between 1.5 and 2.5 % of fuel economy, **FIGURE 1**.

FRICTION MEASUREMENT WITH FRISC

The basis for friction measurements under motored and fired conditions in an engine at AVL is a single cylinder engine called Frisc as short term for Friction single cylinder engine. The base part of that engine is operated over the last 10 to 15 years and known to be quite robust

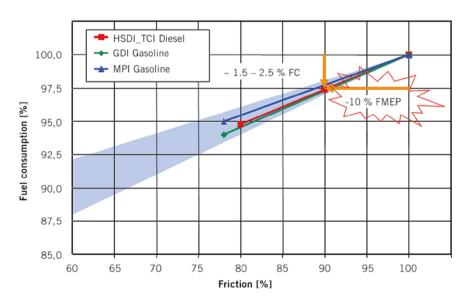
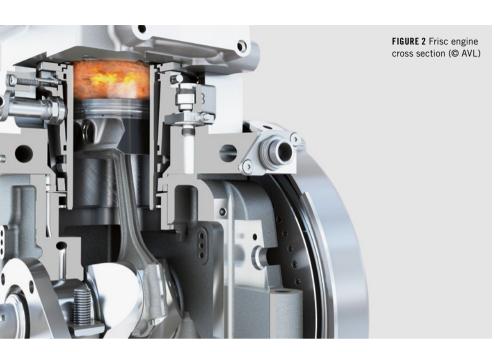


FIGURE 1 The improvement of the fuel economy due to reduced friction is shown (© AVL)



and stable. Features like mass balancing up to second order and different combustions were continually added.

In between cylinder head and crankcase we implemented a so called floating liner system, which is connected to the crankcase over force sensors, **FIGURE 2**. There is no fixed connection between liner and cylinder head but a special sealing ring which is located inside on top of the liner and works like a piston ring. A ring carrier is mounted on the cylinder head. The floating liner system consist of a so called liner carrier, which has liner with water jacket inside.

The floating liner assembly is moveable into liner axis direction according the elasticity of the force sensors. The displacement values we are talking about are in the range of some µm. Thus if there is a force acting at the inner surface of the liner which has a component into liner axis direction this effect is transferred to the force sensors and measured.

The liner has contact to the piston skirt and the piston ring pack. Depending on the current velocity there is more or less lube oil in between what results in time varying friction force signals. On the other hand during fired engine runs we are concerned with pressures that modify the friction force accordingly also over time.

In that way it is possible to measure friction forces in the engine (motored

and/or fired) for different part combinations and also for different lube oils. Of most interest here are distinct surface coatings on the piston skirt and piston rings and different honings on the liner.

In addition, the Frisc also enables us to test the friction behavior of different lube oils like 0W20 and 0W30 and also effects coming from added friction modifiers.

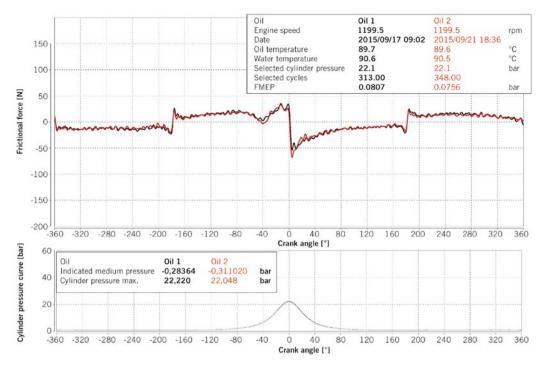
After mounting the engine the Frisc is put onto a test bed and some calibration work has to be done before the real test procedure starts, FIGURE 3. To reach friction stable conditions a break-in run is carried out at defined measurement points. A certain number of cycles that have all the same peak pressure (within defined tolerance) are taken as measurement values and mean values of them are calculated. From raw data to final data dedicated low and high band filters are used and influences like resonance points and crankcase pressure influence are considered as well.

The following figures show some results of a comparison of a defined lube oil with the same lube oil added with a special friction modifier. In general, all figures show in the top placed diagram the friction force FR in [N] over 720 °CA, **FIGURE 4**. The combustion process is gasoline and one can realize from the friction force the four strokes in that order: suction, compression, firing and exhaust.

FIGURE 5, displays the cylinder pressure over the crank angle. There as the table in the top left corner describes Oil specification, indicated mean pressure and maximum cylinder pressure for the two different lubes. The last row of the



FIGURE 3 Frisc engine and test bed (© AVL)



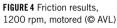


table on top right corner shows the friction mean effective pressure (FMEP) which is an integral value to justify the different lubes. The behavior of the oils shows also differences: Oil 2 shows higher friction losses in the combustion/ compression turn around point but shows less friction at all other points.

DRICON: REPRODUCIBLE MEASUREMENTS ON THE CHASSIS DYNAMOMETER

A prerequisite for emission- and fuel consumption investigation on the chassis dynamometer is the reproducibility of measurements. Emission tests are mostly driven by human drivers who are following the vehicle speed demand trace on a driver's aid monitor. To measure smallest differences in fuel consumption the driven vehicle speed must be the same in all measurements. This also applies to the moment of switching the selector lever from neutral mode to drive mode.

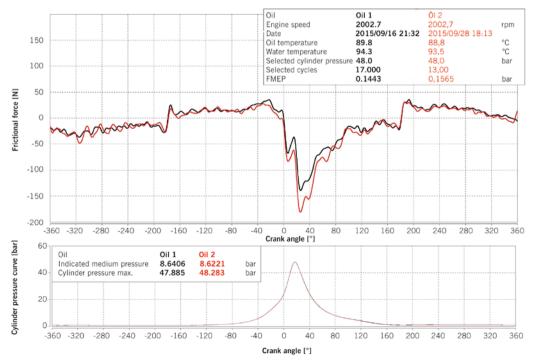


FIGURE 5 Friction results, 2000 rpm, fired (© AVL)



FIGURE 6 Dricon (© AVL)

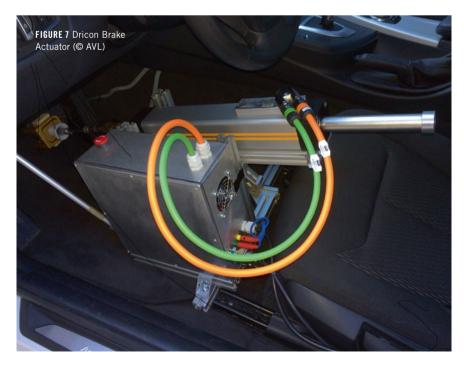
Human drivers are limited in driving reproducible tests. Even at similar driven vehicle speed traces the style of driving has essential influence on the engine torque build up, on gear shifts and therefore on the fuel consumption. To eliminate the human driver's influence the vehicle automation system Dricon, FIG-**URE 6**, can be used. Dricon can perform driving cycles with vehicles with automatic transmission via electrical simulation of the accelerator pedal signals and the usage of a brake actuator, **FIGURE 7**. With this innovative method different ECU datasets, fuels and other fuel consumption influencing parameters can be investigated without the influence of human driving.

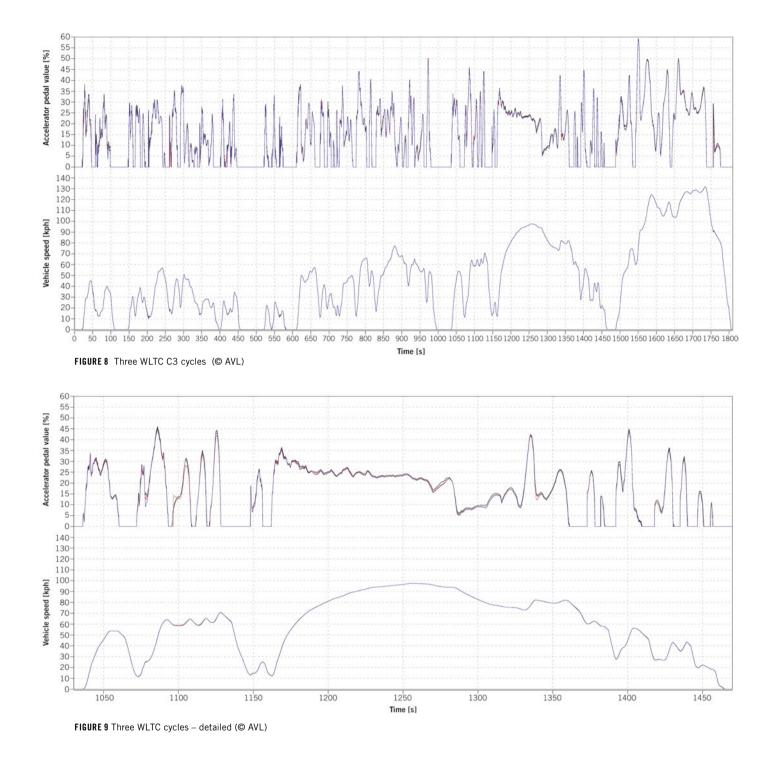
The procedure of an automated fuel consumption or emission investigation test can be separated in into conditioning, emission measurement and post processing.

At both cold start and warm start tests the vehicle has to be in the same initial condition, just the investigated variations (e.g. different fuel, parameterization of fuel consumption- or emission relevant maps of the engine control unit or activated or deactivated power consumers) may be varied. The condition of the exhaust after-treatment has to be the same for each test. Therefore a conditioning cycle is performed where the regeneration of the particle filter, storage catalyst or similar systems is done manually. Afterwards the vehicle has to stay in a conditioning room for a specified time to guarantee the same initial temperatures for each test. During the conditioning the vehicle battery has to be charged to ensure a constant power consumption of the dynamo during the emission test. Additionally the tire pressure has to be at a constant level.

Before the start of the emission measurement it has to be ensured that all mechanical and electrical power consumers such as air condition, light or radio are in the desired state.

At a warm start test a defined warm up program is performed to always ensure the same starting conditions for the measurement program. After that the automated driver is started synchronous with the emission measurement. The engine start and the selector lever positioning also have to be done at a specified time. When the emission measurement is finished a coast down test is performed. In this test, the chassis dvnamometer is in motoring mode and sets the vehicle, which is in transmission mode neutral, to a defined vehicle speed. Afterwards the vehicle coasts down in street simulation mode. All, after the





emission tests, performed coast downs

must show velocity-time- traces with low deviations. Deviations represent different frictions conditions inside the powertrain or a different rolling resistance of the tires.

A basic requirement for the analysis is the same vehicle speed trace for the measurements that are to be compared. During the investigation of the traces it is already possible to determine differences in accelerator pedal values and therefore in fuel consumption. **FIGURE 8** shows three WLTC class 3 emission cycles (cold start) which were performed with the described method. Test 1 (black trace) was performed with activated air condition, at test 2 and 3 the air condition was deactivated. As a result of the high reproducibility of all measurements the driven distance is exactly the same. Despite the almost congruent vehicle speed traces, **FIGURE 9**, shows a difference in the accelerator pedal actuation and therefore a different engine torque request of the engine because of the activated air condition.

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FUTURE FUELS SYNTHETIC FUELS

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Potential of the Synthetic Fuel OME_{1b} for the Soot-free Diesel Engine

One way to reduce greenhouse gas emissions in the transport sector is the substitution of fossil fuels through CO_2 -neutral fuels. Liquid fuels offer advantages compared to gaseous fuels. Fuels from biomass are critically evaluated because the savings in greenhouse gas emissions remain marginal considering the changes in land use and bring significant degradation of fuel quality with it. In contrast to that synthetic fuels with oxygen content (oxygenates) represent a promising way to meet the requirements of future fuels. The contribution of the Institute for Internal Combustion Engines and Powertrains Darmstadt University of Technology shows that OME_{1b} as a pure fuel offers great potential to achieve the long term objectives of eliminating the GHG emissions.

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MOTIVATION

In the long term, a reduction in greenhouse gas (GHG) emissions in the transport sector is inevitable. According to [1] an 80 to 95 % reduction by eliminating these emissions is required until 2050. One possible way to achieve this goal is the substitution of fossil fuels through CO₂-neutral fuels. Liquid fuels have advantages in comparison to gaseous fuels since they are logistically easier to use, have higher energy densities and can use conventional storage technology of current fuels. Fuels from biomass are critically evaluated because the savings in greenhouse gas emissions remain marginal considering the changes in land use and bring significant degradation of fuel quality with it [1, 2]. An EU study including them indirect land use changes (ILUC) shows that Biodiesel leads to a CO₂ increase of 9 to 20 %, compared to using mineral oilbased diesel fuel [2].

The development of current and in particular future drive technologies will be driven by the criteria of CO₂ neutrality and sustainable availability. This fuel should have the potential, together with the internal combustion engine and an "Emission Control System", to improve the ambient air quality in metropolitan areas. In addition, factors such as the economic competitiveness and the functionality follow, for example with regard to range and comfort performance [3].

Synthetic fuels with oxygen content are referred as oxygenates and represent a promising way to achieve the set objectives. Oxygenates show a soot-free combustion, thus avoiding the known NO_x/particulate trade-off. This is achieved by an improved post-oxidation by the presence of oxygen directly at the fuel. At the local rich zones in the combustion chamber the flame zone can be supplied with oxygen. In addition, oxygenates have no direct carbon-carbon bonds (so-called C1-fuels), which complicates the formation of soot. [3] Further, according to [4] the percentage of oxygen in the fuel has a dominant role in the formation of soot or post-oxidation. However, in case of soot developed, the fuel structure is important for the quantification. On this point, C1-fuels show a clear advantage in terms of low-soot combustion.

OXYMETHYLENETHER (OME)

The easiest C1 diesel fuel is DME (34.8 % oxygen), which burns with minimal soot emissions and has a cetane number of 55 to 60 with similar ignition performance as conventional diesel fuel (B7). Because of the low boiling point of DME (about -24 °C) it must be stored in pressurized containers, resulting disadvantages in terms of logistics.

 OME_n is short for oligomeric polyoxymethylene diethyl ether with the general empirical formula $[CH_3O-(CH_2O-)_nCH_3]$. OME is colorless, non-toxic and can be mixed in any amounts of diesel. [3 - 6] Investigations of diesel/OME mixtures show a significant reduction of soot particle emissions, for OME_1 for example in [7] and for $OME_{3/4}$ in [4].

OME burns due to its high oxygen content (OME_{1/5} with n=1/5: 42/50 % oxygen content) and the absence of C-C bonds even with stoichiometric air ratio without the formation of soot particles. This allows the engine operating at higher exhaust gas recirculation rates (decreased fouling of the EGR cooler) in order to reduce the in-engine NO_x formation [4, 8, 9].

The number of oxymethylene groups n influences the properties and thus the usability of the fuel in the diesel engine. OME_1 is volatile (boiling point 42 °C) and the cetane number of about 38 is insufficient low compared to DIN EN 590. OME₁ is produced industrially and used as a mild and non-toxic solvent. OME_{2.5} has a very high cetane number (>90) and diesel-like boiling temperature, but is currently only available in laboratory quantities. The properties, such as cetane number, flash point, kinematic viscosity and heat value can be influenced by the number of oxymethylene groups n. Thus, a specific adaptation of the fuel properties is possible [8, 10].

In addition to the particle reduction and the prevention of the NO_x/particle trade-off the great advantages of higher OME are the high cetane number, the non-toxicity and high flash point, so that the combustion can be improved and handling of the fuel is facilitated. In addition to some studies on a single-cylinder engine the significant reduction of particles by the use of OME₁ has so far also been demonstrated at the six-cylinder full engine [4, 7, 8]. The result is an increased proportion of soluble particles

FUTURE FUELS SYNTHETIC FUELS

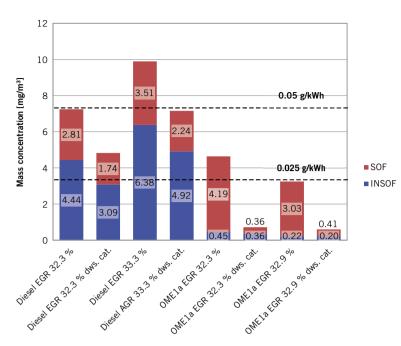


FIGURE 1: Six-cylinder full engine: decrease of the volatile and non-volatile particle components at use of OME_1 [9] (© TU Darmstadt)

(soluble organic fraction – SOF) upon consideration of the total particle mass, which can be converted by oxidizing catalysts, **FIGURE 1**. is of great relevance. CO_2 neutrality is achieved by the industrial processes (e. g. steel and cement production [11]) and power generation [3], where CO_2 is produced as a raw material. In addition to this, regenerative electricity sources

In the production of OME the previously discussed aspect of CO₂ neutrality

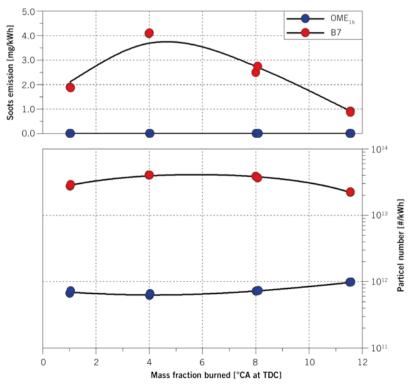


FIGURE 2 Comparison of the specific particulate mass and number B7/OME at $p_{mi} = 3$ bar (© TU Darmstadt)

from offshore wind farms or solar power plants in desert regions for the production of hydrogen can be used (for example by electrolysis). This is used for the reduction of CO_2 for methanol production (CWtL method) and finally by other chemical processes for the production of OME [3, 12, 13].

TEST BENCH

The test results shown are determined by a single-cylinder research engine AVL type FM528. The test engine has a displacement of 0.533 l with a bore of 85 mm and a compression ratio of 16.2. The fuel system is designed as a common rail system with electrically driven high-pressure fuel pump. The injection system has been assembled from series components. Thus there is still further potential for the reduction of emissions by hardware adaptations in future optimization cycles. A further feature of the experimental engine is an electrical supercharger. For the engine control a Protronic Topline of the company Schaeffler Engineering GmbH is used. Thus in addition to the standard calibration tasks own functions using Matlab Simulink can also be implemented.

FUELS

Fuel analyzes of the used fuels are shown in TABLE 1 below. All the tests shown below were carried out with OME_{1b} (additive package "b") and with a conventional diesel fuel (B7, with up to 7 vol.-% FAME) as a basis for the comparison. The change of the fuels was completed in fired engine operating mode at the inlet of the fuel metering system. To avoid formation of vapor bubbles due to the low boiling point of the fuel OME_{1b} it is cooled by fuel conditioning AVL 753C to 20 °C and the whole fuel system is thermally insulated. Because of the volumetrically reduced calorific value of OME_{1b} by about a factor of 1.8 compared to B7 a corresponding increase in the injection time for the same engine load is required. This could be implemented without changes to the injection system.

MEASUREMENT SYSTEMS

Fuel consumption is determined volumetrically by an AVL 735S. For the ther-

Characteristics	Unit	Diesel B7	OME ₁ raw	OME _{1a}	OME _{1b}
Net calorific value	MJ/kg	42.56	22.4* / 23.26 **	22.5* / 23.3**	22.5* / 23.3**
Density at 15 °C	kg/m³	835	863	877	873,4
Boiling point	°C	170-370	42	42	42
Cetane number	-	51.3	37.6	48.3	50
HFRR	μm	202	759	297	278
Kinematic viscosity	mm²/s	2.63 (40 °C)	0.33 (20 °C)	0.58 (20 °C)	0.71 (20 °C)
Oxygen content	% (m/m)	0.8	42.1	41.6	421

TABLE 1 Fuel characteristics *[14, 15] / **[16 - 18] (© TU Darmstadt)

modynamic investigation an indicating system is used with an optical resolution of 0.1 °CA. To quantify the cylinder pressure, a cooled pressure sensor is used with the type AVL QC33C. To analyze the limited gaseous exhaust components an AVL AMA 4000 Advanced is set up. Also not limited components such as methane and unburned OME can be detected with an AVL SESAM i60 FT which was especially calibrated for the application. The particulate emissions are recorded with an AVL 483 Micro Soot Sensor (gravimetric analysis) and a PMP-compliant AVL 489 Particle Counter.

TEST SERIES

As part of the research for this article a variation range is performed. This is performed in the operating points from **TABLE 1**. Basis of the variation range is an engine operating with a single injection and a speed of 1500 rpm. The variation range includes the variation of the injection timing with a resulting mass fraction burned at $mfb_{50} \approx 1$ °CA, 4 °CA, 8 °CA and 12 °CA aTDC.

RESULTS

In the following subchapters some experimental results of the variation series are discussed as examples. Here, as can be seen at the title of the paper, the focus are the emissions of particulate matter in terms of mass and number. **FIGURE 2** shows the variation of the fractional mass burn at low load (3 bar p_{mi}), **FIGURE 3** at an elevated load (7 bar p_{mi}). Throughout the variation the significant reduction of the particulate matter and also particulate number compared to conventional fuel can be seen in two operating points when using OME. The measurement results in terms of particle mass are in operation with OME_{1b} in the field of the detection limit (0.01 to 1 mg/m^3 [6]). At the particulate number a reduction by two (3 bar p_{mi}) or four (7 bar p_{mi}) decades is determined. These is also a decrease of the particulate number in the higher load compared to the low load point with OME_{1b} which is contrary to the behavior of B7. Reasons for this are on the one hand the improved mixture preparation of OME_{1b} compared to B7 in the higher load operation with larger injection volumes and also as already explained in the introduction, the high oxygen content of the fuel itself, which promotes the re-oxidation of the particles, particularly at high combustion chamber temperatures. The measurement results show a clear potential to meet current PN limits (Euro VI: 8.0*1011 #/kWh) without any exhaust

aftertreatment system. For the exhaust gas aftertreatment new requirements are set up at operation with OME_{1b} as well as new potentials, but should not be considered further here.

In addition to the particulate emissions also the nitrogen oxides must be considered. In FIGURE 4 the NO_x emissions are shown. In operation with OME_{1b} the nitrogen oxide emissions are increased for early MFB. This is because of the higher exhaust gas mass flow as well as the increased nitric oxide concentrations. This is due to the increased combustion chamber temperatures (thermal NO) and by the following thermodynamics, the higher efficiency. It can be seen also at the about 15 % lower exhaust gas temperatures in both load points. It should be mentioned here that no exhaust gas recirculation was used in these studies. The typical $NO_x/$ particulate trade-off is avoided with OME_{1b}.

FIGURE 5 illustrates the thermodynamic consideration of the combustion process as an example at the operating point with $p_{mi} = 7$ bar. Based on the heating function with OME_{1b} a more rapid oxidation is visible. This indicates a better mixture preparation and a quicker reaction sequence, resulting in improved emissions in terms of unburned fuel and significantly lower CO emissions when operating with OME_{1b} .

The indicated specific fuel consumption b_i is illustrated in **FIGURE 6** via the normalized NO_x emissions. As already explained in the introduction in operation with an OME_{1b} a higher b_i with a factor of about 1.8 (corresponding to the ratio of the calorific values) is expected. However, as deduced from the ratio of the efficiencies, **FIGURE 6**, OME_{1b} shows a significant increase in the efficiency over the entire

Load point	1		2
Engine revolution in rpm		1500	
Indicated mean pressure in bar	3		7
At mass fraction burned in °CA after TDC		1	
Fuel pressure in bar		500	
Boost pressure in bar absolute		1.4	
Fuel temperature forerun in °C		22	
Variation parameter: fractional mass burn in °CA after TDC		1, 4, 8, 12	

TABLE 2 Load points of the test series (© TU Darmstadt)

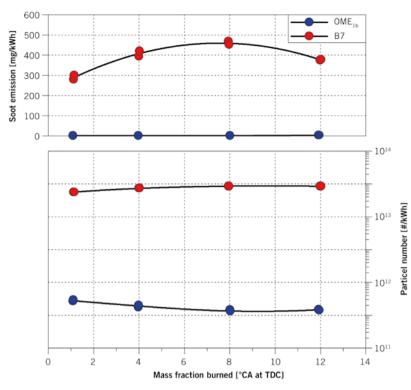


FIGURE 3 Comparison of the specific particulate mass and number B7/OME at p_{mi} = 7 bar (© TU Darmstadt)

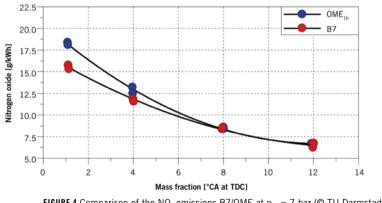


FIGURE 4 Comparison of the NO_x emissions B7/OME at $p_{mi} = 7$ bar (© TU Darmstadt)

range of variation of the fractional mass burn. With regard to this it should be noted that the built up test engine does not need to compensate the additional hydraulic losses due to the higher consumption of OME_{th} since the entire fuel system operates electrically autonomous.

CONCLUSION

Exploration on the single-cylinder car research engine at the Institute for Internal Combustion Engines and Powertrain Systems at Darmstadt University of Technology have shown that OME_{1b}

as a pure fuel has a great potential to achieve the long term objectives of eliminating the GHG emissions. The NO_x/particulate matter trade-off is overridden, so that lowest inner-engine NO_x emissions can be achieved together with simultaneously particulate emissions meeting current emissions legislation levels through appropriate application of the engine controller. As a further result alternative EGR and exhaust aftertreatment systems can be used. Here, for example, a low pressure EGR for achieving high EGR rates, and thus lowest nitrogen oxide emissions at the

same time, soot-free engine operating is conceivable. A precious metal-free oxidation catalyst can be used and the particulate filter is eliminated. Also conceivable is the non-existent soot limit operation with lambda control based on the homogeneously operated gasoline engine and the use of a threeway catalyst. Here the efficiency disadvantage by a stoichiometric engine operation is to be assessed in further work. Higher OME will lower the soot as expected by the higher oxygen content even further, as well as provide further advantages in handling such as a higher boiling point [2].

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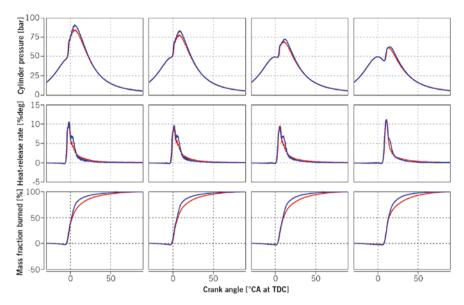
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FIGURE 5 Comparison of the cylinder pressures, heat curves and heat functions B7 (red) / OME (blue) at $p_{mi} = 7$ bar (© TU Darmstadt)

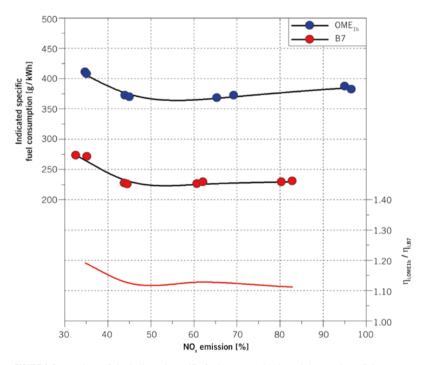


FIGURE 6 Comparison of the indicated specific fuel consumption b_i and the quotient of the efficiencies B7/OME at p_{mi} = 7 bar (© TU Darmstadt)

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Commercialization of Low Carbon Methanol

There are many initiatives worldwide for using methanol as a fuel and taking advantage of its numerous benefits compared to conventional fuels. This article describes how the low-CO₂ production of methanol can already be implemented on a large industrial scale today.





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INTRODUCTION

The European Union (EU) has established targets for carbon dioxide reduction by 2020. Such policies have paved the way for the increase of renewable energy sources (RES) for electric generation, the improvement of energy efficiency, and the decarbonization of fuel for transport. Electrification of mobility is an additional diversification of the fuel mix in the EU. The European Commission recently amended the Renewable Energy Directive to include low carbon fuel of non-biological origin for transport to overcome the challenge of competition between food and fuel resulting from the over-production and over-use of conventional biofuels [1].

Carbon Recycling International (CRI) and Mitsubishi Hitachi Power Systems Europe GmbH (MHPSE) are developing solutions for producing low carbon fuels, using methanol produced from electricity or excess hydrogen (H₂) and carbon dioxide (CO₂). There are many possibilities for the production of low carbon fuels. The hydrogen and carbon dioxide feedstock can be from various sources in the production and power industries. Methanol has multiple energy applications. It is used for fuel blending in Europe and China. It can be directly used in ships and/or upgraded by follow-up processing to high energy density fuels for vehicles, ships, and aviation using the current infrastructure.

POWER TO METHANOL

Conventionally, methanol is produced from synthesis gas generated by steam natural gas (NG) reformation (SMR), coal or residual oil gasification. The common technology is a mega-scale plant of one million t per year, centrally located near the sources of primary energy but at long distances from the points of use. The plants are constructed to maximize economies of scale and can reach capacities of more than 5,000 t of methanol per day output. For fossil feedstock based methanol plants, large amounts of CO₂ are emitted (up to 1 t CO₂ emitted / 1 t methanol produced by NG; up to 3.5 t CO₂ emitted / 1 t methanol produced by coal).

In contrast, the Power to Methanol (PtM) production, pioneered by Carbon Recycling International, is a distributed model. A proposed power to methanol plant is a modular design of 50 to 100 kt/ year and is located near the sources of use. The feedstock consists of basic utility available at a power plant or chemical plant which includes heat, power, hydrogen surplus and carbon dioxide. Each plant is constructed to take advantage of the available infrastructure, by-products, and waste heat. Carbon dioxide is captured and purified on site for use as the main feedstock (1.38 t CO₂ captured / 1 t methanol produced).

For the generation of methanol from carbon dioxide as feedstock, two concepts are available. On the one hand in the PtM concept, hydrogen is generated via water-electrolysis operated by low carbon, low cost electricity. On the other hand, hydrogen is derived from hydrogen-rich off-gases in several industries. Especially in steel and chemical industries, this concept offers an exceptional potential, due to the frequent availability of hydrogen-rich off-gases, such as coke oven gas (COG) and hydrogen as byproduct from ethylene production and chlor-alkali electrolysis. Nowadays, the concept with the utilization of hydrogen-rich process gas is highly promising, whereas hydrogen generation via water-electrolysis will be available with more excess electricity from RES in the future. The combination of both concepts, including excess hydrogen, and the installation of the electrolysis offers an economic advantage if excess electricity is available on site.

In the prospect of a future methanol economy, carbon dioxide is recycled in order to reduce the amount of fossil fuel consumption while decreasing GHG emissions. Methanol is utilized as versatile energy carrier for various applications and further processing to gasoline, diesel or kerosene as fuels for commercial transport.

EMISSIONS TO LIQUID TECHNOLOGY

CRI developed Emissions to Liquid (ETL) technology for PtM and operates an industrial scale plant in Iceland. The George Olah plant is the first PtM plant in the world operating at 6 MWel, capturing 6,000 t of carbon dioxide and producing 4,000 t of CO₂-based methanol per year. The integration with the power generation plant Svartsengi of 75 MWel and 150 MWth provides the necessary power, carbon dioxide and steam.

The plant consists of modularized unit operations for carbon dioxide and synthesis gas compression, post steam turbine carbon capture, electrolytic production of hydrogen (water alkaline electrolyzer), direct CO_2 to methanol synthesis, and distillation for methanol fuel. The modules were designed and fabricated in a controlled manufacturing shop floor environment.

The product has 90 % lower carbon footprint than gasoline, certified by SGS Germany according to the International Sustainability and Carbon Certification (ISCC) standard. The product is used for gasoline blending and biodiesel manufacturing in Sweden, Holland, and Iceland. **FIGURE 1** shows the power to methanol plant of CRI in Iceland.

PRODUCTION OF LOW CARBON METHANOL

In FIGURE 2, the energy balance of a methanol production plant from CO₂ in an integrated steel mill is shown. In case 1, all available H₂ from coke oven gas (COG) on site is utilized with an assumed H₂ capture rate of 90 %. In case 2, electricity from renewable energy sources is used to operate a water-electrolysis for H₂ generation. Case 3 depicts the combination of case 1 and 2. It is shown that the generation of methanol leads to high conversion efficiencies. For the conversion of COGbased H₂, the thermal conversion efficiency (from lower heating value (LHV) of H₂ to LHV methanol, Case1) of 65 % is reached, whereas for the conversion of electrolytic H₂, the conversion efficiency (from electricity to LHV of methanol, Case 2) equals 65 % as well including heat integration measures with the power plant. These concepts are much more commercially competitive than the base case, which includes the combustion of H₂, leading to a conversion efficiency of 42 % [2, 3]. All technologies are state-of-the-art and commercially available in the 100 kt/year Methanol production scale. Similar integrations in other thermal power plants or chemical sites is reaching 60 % conversion efficiency with electrolyzer or up to 70 % when pure hydrogen is available already (e.g. in acetylene/ethylene production).

In **FIGURE 3**, the specific overall balance regarding the greenhouse gas (GHG) emissions as CO_2 equivalent for case 3 are



FIGURE 1 Carbon Recycling International – the world's first commercial power to CO₂ methanol plant, producing 4000 t of methanol and capturing 6000 t of CO₂ (© Carbon Recycling International)

summarized. As the CO₂ is bound within the methanol, emissions are avoided. However, the GHG emissions, which result from the chemical production process by the utilization of steam and conventional & RES electricity, must be considered. This results in an overall reduction of 1.53 t of CO₂ compared to NG-based methanol.

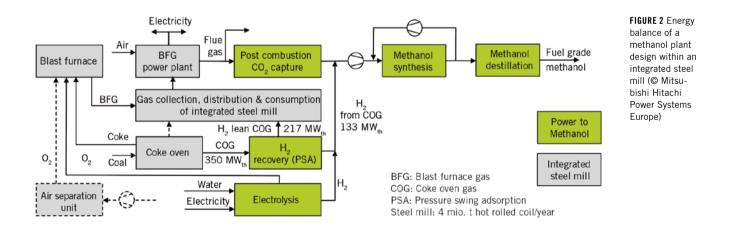
It has to be considered that due to the CO_2 utilisation, additional emissions

tesides CO_2 are avoided, which have not yet been taken into account. The treated flue and exhaust gases as CO_2 and H_2 sources for the methanol synthesis have to be cleaned and pre-treated for the subsequent process steps. Therefore, these gases are extensively more purified due to further processing, leading to less overall emissions such as CO_2 , NO_x , SO_x , dust and hydrocarbons.

METHANOL FUEL FOR TRANSPORT

The utilisation of methanol within the transportation sector is extensive and growing. Regarding the global share of methanol utilization, 27 % of the global methanol production is utilized for transportation: 12 % for fuel blending, 12 % MTBE production and 3 % for Biodiesel production. There are many methanol fuel initiatives around the world. In Europe M3 is standardized in SP95 EN228, whereas in the UK no taxes are applied to M95. In Sweden M100 zero sulfur is utilized as marine fuel. China tests M15 - M100 fuel in eleven major cities. In Iceland, Carbon Recycling International has conducted fleet testing of M50 in Ford's flexible fuel vehicles and anticipate starting testing M100 with Geely vehicles in 2016. In Denmark, methanol-based proton exchange membrane fuel cell vehicles are being deployed by Serenergy, providing all-electric range with zero combustion. The additional costs for the production of an internal combustion engine based fuel flexible vehicle are approximately 100 Euro [4].

Methanol fuel properties offer significant advantages for achieving ultra-high



		_	Power consumption						
Case Import (-	Export (+) Import (-) [MW _{el}]	Power plant [MW _{el}]	Steel mill	H ₂	CO ₂ & MeOH	H ₂	MeOH	MeOH [t/d]	Conversion efficiency
Lela		r617	[MW _{el}]		[MW _{th}]				
Base	20.3	198.9	178.6	-	-	-	-	-	$\eta_{\text{el}}=42~\%$
(1) H ₂ COG	-47.2	148.4	178.6	12.3	4.4	120.0	105.0	451.6	$\eta_{\text{th, th}}=65~\%$
(2) H ₂ Elektrolysis	-87.2	198.9	173.2	110.0	2.9	79.9	69.9	300.6	$\eta_{\text{el, th}}=65~\%$
(3) Both processes	-154.5	148.4	173.2	122.3	7.3	199.9	174.9	752.2	$\eta_{el,\ th}=100\ \%$

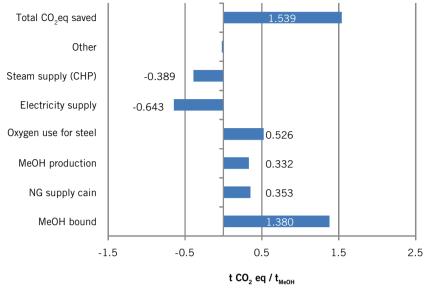


FIGURE 3 Balance of the CO_2 emissions by the methanol production from CO_2 and H_2 in case 3 (© Mitsubishi Hitachi Power Systems Europe)

vehicle engine efficiency, meeting and exceeding diesel engine efficiency [5, 6]. It is also considered feasible to achieve equivalent efficiency of hydrogen fuel cell vehicles through advanced technology of low temperature methanol reforming for high exhaust heat recovery. Methanol's 25 % higher research octane compared to gasoline (109 vs 87) provides the means for utilizing much higher engine compression ratio (CR) without impinging on knock limits [7]. Methanol's nominal octane does not fully reflect its potential, however, as its effective octane is even higher - up to 130 - when methanol is directly injected. Methanol ignition properties also provide significant advantages in enhancing pre-ignition and engine knock control [8].

Methanol provides further efficiency advantages due to its higher latent heat of vaporization compared to gasoline. MIT researchers have found that methanol use in a diesel cycle engine could allow downsizing of a 9 l engine to 5.5 l, while having 30 % more power. Waste heat recovery via methanol reforming allows the use of hydrogen-rich gas, which would allow heavier heat recovery at lower load, compared to current technology diesel engines.

Due to the absence of carbon-carbon bonds in methanol molecule soot formation is virtually zero. The absence of sulfur in the fuel leads to an inherently near-zero sulfur emissions. The lower flame temperature of methanol also results in inherently lower NO_x emissions. Even at higher CR enabled by methanol's wider knock limits, lower levels of NO_x emissions are achievable compared to gasoline. This is resulting from the lower peak in-cylinder temperatures for methanol, as well as its faster combustion response, compared to gasoline. The use of methanol also provides a means of minimizing the tradeoffs associated with the use of higher efficient Atkinson cycle engines rather than Otto cycle engines [9].

CONCLUSION

Low carbon methanol fuel is readily produced from diverse feedstocks, including H₂ from coke oven gas. There are numerous advantages for utilizing methanol and its derivatives, including significant reductions in greenhouse gases, toxic emissions and air pollutants such as SO_x, NO_x and PM. The distribution infrastructure for methanol can be readily expanded to serve diverse transportation market end uses. Methanol fuel vehicle optimizations are feasible at low incremental costs to achieve high efficiency and environmental sustainability benefits. Policy and political support would accelerate the realization of such commercialization.

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Due to European legislation the content of biomass based fuel blends will increase over the next few years. The narrow adaption of ECU functions to fuels conforming to standards may lead to altered operating conditions when using pure biofuels. Within a study funded by Fachagentur Nachwachsende Rohstoffe e. V. (FNR) fuel adapted applications were developed at the University of Rostock to show the potentials at a Euro-6 diesel engine.

Potentials of Biofuels for Passenger Car and Non-road Applications

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THE LONG WAY TO CO₂-NEUTRAL FUELS

Despite currently low crude oil and fuel prices fossil fuels need to be substituted by alternative fuels due to their limited resources and a constantly rising environmental awareness. On the way to CO_2 -free fuels, biomass based fuels offer a CO_2 -neutral and profitable possibility to substitute fossil fuels. According to the EU directive 2009/28/EC the share of renewable energy in the transport sector shall increase at least up to 10 % until 2020. Perspectively, this share is going to further increase in order to contain CO_2 emissions and to secure fuel supply.

The currently valid specification for diesel fuel DIN EN 590 allows an admixture of biodiesel up to a maximum of 7 % to conventional diesel fuel. In contrast to non-road applications, manufacturer approval for biodiesel use in passenger car applications does only exist for cars build before 2005 with a fuel system suitable for rapeseed methyl ester (RME). When exhaust cleaning via diesel particulate filters was introduced in 2006, activities of the car manufacturer for RME approvals were aborted. Besides fatty acid methyl esters (FAME), hydrotreated vegetable oils (HVO) have recently been pushed into the market as blend components. HVO is characterized by its absence of aromatics and a high cetane number [1]. Since the functions of modern engine control units (ECU) are designed for fuels conforming to DIN EN 590 standard, an altered engine behaviour is expected when operating with pure biofuel. Influences on engine behaviour and the potential of a pure FAME respectively HVO operation in modern passenger car and tractor engines is explained below.

EXPERIMENTAL SET-UP

Steady state short term engine experiments were performed with FAME and HVO as pure fuels using a Euro-6 diesel engine at the test bench of the Chair of Piston Machines and Internal Combustion Engines at the University of Rostock. The test engine available for this experiment was a 2.0 l passenger car diesel engine (model CBAC) from Volkswagen. This engine is highly suitable for valuation of biofuel influ-

Engine ID:	CBAC		
Displacement	2.0 I / 1968 cm ³		
Engine type Stroke	Four–cylinder, 16 valves 95.5 mm		
Bore Compression ratio	81.0 mm 16.5:1		
Rated power output Maximum torque	103 kW at 4200 rpm 320 Nm at 1750 – 2500 rpm		
Engine management	Bosch EDC 17		
Injection	Common-rail system (second generation; max. 1,800 bar)		
Exhaust gas recirculation	Cooled high-pressure EGR		
Exhaust turbocharger	installed, with VTG		
Exhaust aftertreatment	DOC – DPF – SCR		

TABLE 1 Test engine specification (© University of Rostock)

ences and their potentials due to its modern second generation common-rail system with injection pressures up to 1800 bar and comprehensive exhaust purification systems consisting of exhaust gas recirculation (EGR), diesel oxidation catalyst (DOC), diesel particulate filter (DPF) and SCR-catalyst (selective catalytic reduction). The regular ECU application is designed for a fuel according to DIN EN 590. A fuel sensor for measurement of FAME contents is not installed. The general engine specifications are summarized in **TABLE 1**.

The valuation of fuel impacts on the combustion behaviour was conducted using measurement of cylinder pressure traces at cylinder 1 via a water-cooled laboratory sensor from Kistler (model 6043). The measurement of injector current feed was done using a clamp ammeter connected to the Kistler indication system for high resolution signal analysis (0.1 °CA). The aim was to investigate the impacts of altered fuel properties on ignition delay, burning intensity and burning position. Using an ETAS interface (model ES 591) values of the engine control unit were analysed to investigate influences on engine control parameters. Gaseous exhaust emissions (O₂, CO, CO₂, NO, NO₂, HC) were measured before and after each component of the exhaust after treatment system using an ABB exhaust analyser (model AO 2020). Smoke opacity was

FUTURE FUELS BIOFUELS

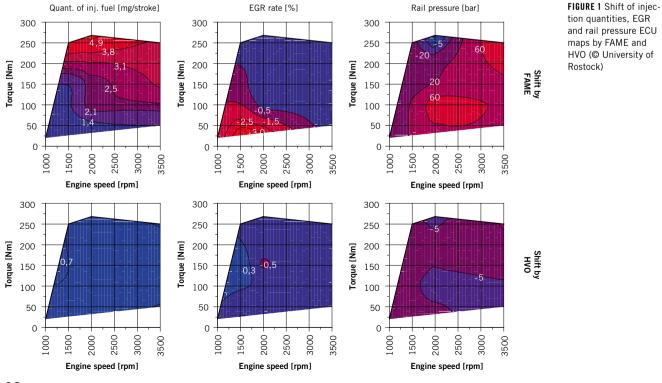
Parameter	Test specification	Unit	DF	FAME	HVO
Density at 15 °C	DIN EN IS012185	kg/m³	842.5	882.2	778.9
Viscosity at 40 °C	ASTM D 7042	mm²/s	3.3	4.1	2.8
Water Content	EN ISO 12937	mg/kg	80	159	29
Flash Point	ISO 2719	°C	67	167	83
CFPP	EN 116	°C	-10	-1	-34
Heating Value	DIN 51900-2	kJ/kg	42,517	37,309	43,846
Cetane Number	AFIDA	-	54	52	77
Lubricity	DIN EN ISO 12156-1	μm	165	119	269
Ash Content	EN ISO 6245	%(m/m)	<0.001	<0.001	<0.001
Total Contamination	DIN EN 12662	(mg/kg)	3.8	0.5	1.7
Carbon Content	DIN 51732	%(m/m)	86.5	77.2	84.4
Hydrogen Content	DIN 51732	%(m/m)	13.4	12.0	14.8
Oxygen Content	calculated	%(m/m)	0.1	10.8	0.8
Sulphur Content	DIN 51400-10	mg/kg	<10	3	0.3
Initial Boiling Point	EN ISO 3405	°C	182	315	203
Final Boiling Point	EN ISO 3405	°C	360	350	299

TABLE 2 Fuel properties (© University of Rostock)

determined via an AVL Smoke Meter system (model 415).

Operation points were selected to be within and outside of the New European Driving Cycle (NEDC) relevant engine map ranges. At first the engine was operated with all fuels using the regular ECU application to measure fuel impacts on control parameters, fuel injection, combustion behaviour and emissions. In a second step variations of control parameters were conducted using a freely configurable engine control unit (model IAV FI2RE). Subsequently, biofuel adapted ECU applications were developed based on these measurements.

Pure fatty acid methyl ester (FAME) and hydrotreated vegetable oil (HVO) were used as biofuels compared to reference diesel fuel (DF). Fuel properties are summarized in **TABLE 2**. HVO shows



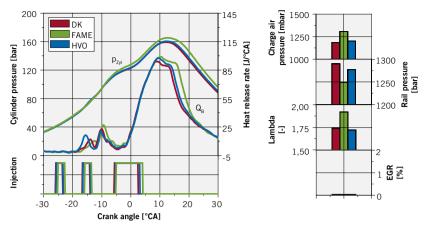


FIGURE 2 Impacts on combustion and boundary conditions at IMEP = 18.9 bar, n = 2000 rpm (© University of Rostock)

properties that are very similar to DF. Its increased cetane number is supposed to lead to shortened ignition delays. The mass based heating value of FAME is below the level of the reference diesel by approx. 12 %. The increased flash point and the higher distillation level in contrast to DF and HVO need to be evaluated as problematic. Both biofuels exceed the specification DIN EN 590 due to their density and are not approved for engine use by the engine manufacturer.

BIOFUEL OPERATION WITH REGULAR ECU APPLICATION

The comparison of the test fuels was conducted at operation points with identical torque and identical engine speed. To realize the same engine torque among the test fuels during engine map measurements the electronic gas pedal signal was adapted accordingly. This signal is connected to the quantity of injected fuel via ECU. The different heating values among the biofuels result in different quantities of injected fuel at the same engine output. The ECU value "quantity of injected fuel" is often used as reference value for several engine control parameters (EGR, fuel rail pressure, charge air pressure) [2]. FIGURE 1 shows the change of the quantity of injected fuel, EGR and rail pressure by the operation of FAME and HVO. It is clearly visible that the heating value of HVO which is similar to the DF heating value leads to negligible shifts of operation points in the EGR and rail pressure maps. However, during FAME operation increased

quantities of injected fuel and thereby shifts of the set values for EGR and rail pressure occur caused by the decreased heating value. These shifts were measured mainly under partial load conditions since engine maps are characterized by high gradients in this region.

Pure fuel impacts on the combustion and altered boundary conditions interfere with each other especially during FAME operation due to the shifts of operation points in the ECU maps shown above. Outside of the NEDC relevant engine map range exhaust gas recirculation is disabled which facilitates the valuation of fuel impacts on the combustion. The combustion process of the test engine is characterized by two pre-injections in all investigated operation points. The resulting pre-combustions at an indicated mean effective pressure (IMEP) of 18.9 bar and 2000 rpm lead to a fluctuation-free main combustion without apparent premix combustion phase for all fuels, FIGURE 2. Based on the high cetane number of HVO, a shortened ignition delay of the first pre-combustion with increased heat release rate is visible. The position, intensity and burning duration of the second pre-combustion as well as the main combustion is similar to the operation with DF. The injection signal of FAME is slightly delayed while the duration of the main injection is increased due to the lower heating value. FAME operation shows a prolonged ignition delay of the first pre-combustion compared to HVO and DF. Thus, the fuel quantity of the second pre-injection is injected into the ongoing first pre-combustion. Caused by the increased duration of the main injection the burning duration increases as well as the maximum heat release rate

Raw emissions of nitrogen oxides (NO_x) were measured using a chemiluminescence detector (CLD) from ABB. A torque variation at constant engine speed of 2000 rpm shows only minor fuel impacts on nitrogen oxide emissions in raw exhaust, **FIGURE 3**. Only during FAME operation NO_x emissions are slightly increased which may result from lower EGR rates and higher fuel rail pressures as shown in **FIGURE 1**. It is clearly visible that NO_x emissions strongly increase for higher torques since EGR is disabled outside of NEDC relevant map ranges.

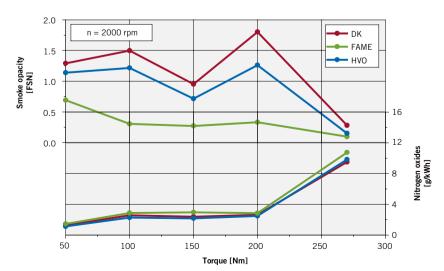


FIGURE 3 Smoke opacity and nitrogen oxides emissions at n = 2000 rpm (© University of Rostock)

HVO and FAME show decreased raw gas opacities compared to reference diesel fuel in the investigated range. HVO is characterized by the absence of aromatics and polycyclic aromatic hydrocarbons (PAH) in the fuel leading to lower soot generation during the combustion process [3]. Furthermore, the low and narrow distillation curve of HVO enhances the vaporization of heavy hydrocarbon fractions [4]. Improvements of soot behaviour by FAME is caused by the fuel-bound oxygen which reduces local zones lacking oxygen ($\lambda < 0.6$) and thereby enhances soot emissions especially in partial load conditions with high EGR rates [5].

POTENTIALS OF A BIOFUEL ADAPTED ECU APPLICATION

The complex influence of the fuel properties on combustion boundary conditions (EGR, rail pressure, etc.) shall be avoided by using a freely configurable engine control unit to investigate the pure fuel impacts. For this purpose, the test engine was operated with the IAV FI2RE application tool to flexibly control injector current feed, throttle position, EGR throttle position, variable turbine geometry (VTG) and fuel rail pressure. Thus, the specific fuel impacts could be observed for a variation of engine control parameters. FIGURE 4 shows the soot/ NO_x-behaviour in raw exhaust gas for variations of injection timing, EGR and rail pressure at 1500 rpm and IMEP of 4.9 bar. Smoke opacity of HVO is below DF-level for all variations, though HVO is showing similar emissions of nitrogen oxides in raw exhaust. These advantages

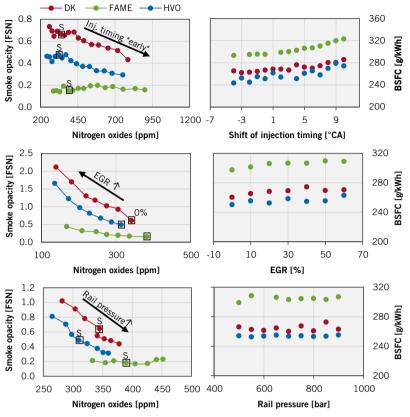


FIGURE 4 Variation of parameters at IMEP = 4.9 bar, n = 1500 rpm (R = regular setting) (© University of Rostock)

in soot behaviour can be used to reduce fuel consumption via shifting the injection timing and increasing the EGR rate to still meet emission limits of DF. Smoke opacity is even lower with FAME and barely changes when control parameters are changed since the effect of the fuelbound oxygen predominates the altered injection and mixture formation conditions. This also offers a FAME application optimized for fuel consumption while meeting DF emissions limits.

The potentials of a biofuel adapted ECU application at two operation points are shown in **FIGURE 5**. For this purpose the quantity of the pre-injections, injection timing, EGR rate, rail pressure and charge air pressure were optimized concerning fuel consumption for each biofuel. Furthermore, raw exhaust

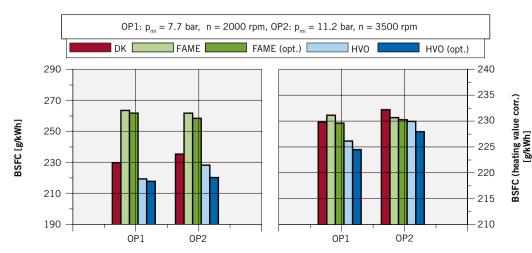


FIGURE 5 Fuel consumption with regular and fuel adapted ECU application (© University of Rostock) emissions were required to not exceed the level of DF emissions with regular ECU in NEDC relevant operation points. The brake specific fuel consumption (BSFC) of FAME at regular ECU application is increased due to its lower heating value, while HVO consumption is slightly decreased compared to DF. Optimized settings for HVO respectively FAME enable a reduction of BSFC of 1 to 3 % compared to the operation with regular ECU application while emission limits still being met. The illustration with corrected heating values shows the combustion impact on fuel consumption isolated from heating values of the test fuels. Especially the early-shift of the combustion position via fuel adapted settings is responsible for the improved fuel consumption.

FAME APPLICATION IN NON-ROAD SECTOR

Pure biofuels are not charged by energy taxes in agriculture and forestry. If diesel fuel prices increase or subsidisation of agricultural diesel stops a short-term demand for non-road mobile machinery capable of running on biodiesel may arise. Hence OEMs are interested in ensuring FAME capability of their engines. Since October 2014 exhaust emission stage Tier 4 final has applied for all non-road applications leading to decreased limits of particulate matter and nitrogen oxides. The stricter emissions limits demand an exhaust after treatment system which is similarly complex as for passenger car applications. Because no approvals for FAME operation exist for engines of the present exhaust stage until now, the impacts of biodiesel and biodiesel blends are currently investigated in steady-state and transient engine tests at the University of Rostock using a Deutz TCD 3.6 final test engine. Similar shifts of the operation points in ECU maps as shown for the passenger car engine are expected due to different fuel properties (heating value, distillation level, flash point). Caused by traces of sulphur, phosphor, potassium and sodium (less than 5 ppm) in FAME, deactivation effects of DOC and SCR catalysts may occur during long-term operation (operating hours of agriculture machines are much higher compared to passenger cars). Thus, long-term engine tests

(1000 and 300 h) will be performed to check if exhaust after treatment systems get poisoned. Similar to the experiments with the passenger car engine variations of ECU parameters will be conducted using a partly opened ECU to develop a FAME adapted application optimizing fuel consumption and emissions. Furthermore the impact of the fuel's oxygen content on soot emissions and required DPF regenerations will be studied.

SUMMARY AND OUTLOOK

Short-term engine experiments were conducted at a Euro-6 passenger car engine to analyse the influences of biofuels on engine and emission behaviour. It was possible to operate the engine with both FAME and HVO without trouble. Shifts of operation points within the ECU maps could be observed for FAME operation. This is caused by different fuel properties (e.g. heating value, oxygen content). Fuel impacts on injection timing and combustion was quantified using cylinder pressure indication. HVO showed a decreased ignition delay for all operation points, while FAME impacts on combustion behaviour was interfered by altered boundary conditions (EGR, rail pressure, charge air pressure). The main combustion was stabilized by two pre-combustions independently of different ignition delays. Both biofuels could reduce raw soot emissions without ECU adaption. The main cause for HVO was the enhanced distillation behaviour and the absence of aromatics and polyaromatics in the fuel. In the case of FAME, mainly fuel-bound oxygen molecules are responsible for the decrease of soot emissions. Raw emissions of nitrogen oxides were similar for HVO and DF, though, increased by approximately 10 % for FAME. A variation of control parameters (injection timing, EGR and rail pressure) with a freely configurable engine control unit could confirm these observations. Biofuel consumption could be reduced using a fuel adapted ECU application without exceeding emission limits of the reference diesel. By the use of sensor systems for the determination of certain fuel properties appropriate ECU settings could be chosen to ensure an operation optimized for each fuel.

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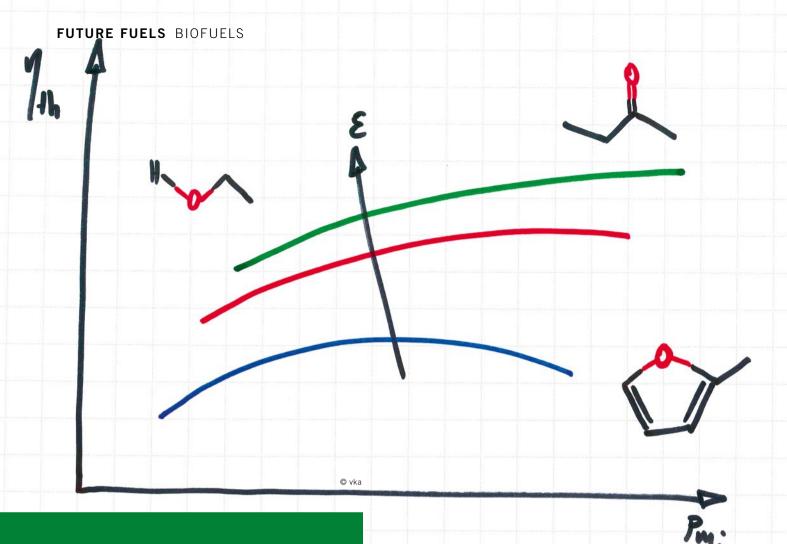
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THANKS

The results shown in this article are part of the research project Use of algae-HVO and eFAME for engine operation (project number 22026012). The authors would like to thank the Fachagentur Nachwachsende Rohstoffe e.V. (FNR) for financial funding.



Tailor-made Fuels for Highly Boosted Gasoline Engines

In the Cluster of Excellence Tailor-made Fuels from Biomass (TMFB) at RWTH Aachen University two alternative fuels were identified as promising fuel candidates to be applied in highly boosted gasoline engines. In thermodynamic investigations the extraordinary properties of the two fuels 2-methylfuran and 2-butanone in comparison to conventional RON95 gasoline and ethanol were demonstrated.

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MOLECULAR STRUCTURE OF THE FUEL AS DEGREE OF FREEDOM

The legislative pressure to decrease CO₂ emissions in the future caused by road transportation is expected to lead to a broader diversification of the applied energy carriers in the transport sector. Hereby, the transition from fossil fuels to biomass-based energy carriers offers the possibility to define new fuel property requirements which possible alternative fuels have to incorporate. In this context, the approach in the Cluster of Excellence "Tailor-Made Fuels from Biomass (TMFB)" at RWTH Aachen University considers the molecular structure of the fuel as a potential additional degree of freedom for an optimized sustainable production and complete usage of the thermodynamic potential of internal combustion engines. Two possible candidates have been identified and were applied in highly boosted gasoline engines: 2-butanone (methyl ethyl ketone) as well as 2-methylfuran. For both fuels, possible synthesis and production routes have been identified [1-5].

FUEL PROPERTIES

Due to its high knock resistance and heat of vaporization, ethanol is known to be very suitable for an application in gasoline engines with high specific loads. By this, a significant efficiency increase in comparison to conventional gasoline fuel can be achieved [6-9]. Hence, ethanol was defined as a base fuel for comparisons in the here presented investigations. Additionally, also conventional gasoline with a research octane number (RON) of 95 (EN228, EN51626-1 respectively) was chosen as a second base fuel as it is the far-most spread fuel for spark ignition (SI) engines in Europe. All relevant fuel properties are summarized in TABLE 1 [7, 10-15]. In comparison to conventional fuels the three alternative fuels feature an increased oxygen content, leading to a decrease of the mass-based heating value of 36 % in the case of ethanol, 28 % in the case of 2-methylfuran and 25 % in the case of 2-butanone.

When considering the volumetric heating value, the order of the biofuels changes since a decrease in oxygen content is accompanied by an increase in density. Conventional gasoline has the lowest density. This leads – with regard to conventional gasoline – to a reduction of the volumetric heating value of 32 % in the case of ethanol, 11 % for 2-methylfuran and 18 % for 2-butanone. Due to their high oxygen content the octane number for the investigated biofuels was determined according to DIN51756-7 [16, 17]. The highest RON was measured for 2-butanone, **TABLE 1**.

The RON of 2-methylfuran is lower than that of ethanol and 2-butanone, but still exceeds conventional gasoline by five units. The higher heat of vaporization of ethanol leads to a more pronounced cooling of the mixture, especially at higher loads. Thereby, the level of knock resistance as described by the RON procedure is increased, especially in direct injection engines.

Disadvantageously, the higher heat of vaporization leads to challenges with regard to cold start operation. For ethanol, the combination of a low vapour pressure and a higher injected fuel mass necessary at lower stoichiometric air requirements leads to a deterioration of the cold-start behaviour [6]. In com-

		RON95 E5 gasoline EN228	RON95 E10 gasoline EN51626-1	Ethanol	2-Methyl-furan	2-Butanone
Molecular structure					ૢૻૢ૽ૻ૾ૺૢ૾ૢ૽ૺૼ૾ૡ૿	Se Se
Sum formula				C ₂ H ₆ O	C ₅ H ₆ O	C ₄ H ₈ O
Carbon mass fraction	%	84.47	83.48	52.14	73.15	66.63
Hydrogen mass fraction	%	13.27	13.24	13.13	7.37	11.18
Oxygen mass fraction	%	2.26	3.28	34.73	19.49	22.19
Density (25 °C)	kg/m³	737	741	787	907.5	799
Boiling temperature	°C	41.5 – 173.5	35.8 - 190.4	78	64	80
Vapour pressure (20 °C)	kPa	-	-	5.8	13.9	10.8
Specific enthalpy of vaporization	$kJ/kg_{air, \lambda = 1}$	~28	-	101.6	35.52	46.10
Stoichiometric air requirement / 1	1	14.14	13.97	8.98	10.08	10.52
Lower heating value	MJ/kg	42.13	41.56	26.84	30.37	31.45
Lower heating value	MJ/I	31.05	30.78	21.09	27.63	25.16
Research octane number (RON)	1	96.3	96.9	109	101.7	117
Motor octane number (MON)	1	85.0	86.4	89.7	82.4	107
Purity	%	_	_	>99.0	>99.8	>99.9

TABLE 1 Relevant properties of the investigated fuels (© vka)

FUTURE FUELS BIOFUELS

Bore	mm	75	
Stroke	mm	82.5	
Stroke/bore ratio	1	1.1	
Displacement	cm ³	364	
Number of valves	1	4	
Maximum absolute boost pressure	bar	3.5	
Compression ratios	1	8.5 and 13.5	
Exhaust valve closing (1 mm)	°CA BTDC	4	
Intake valve opening (1 mm)	°CA ATDC	10	
Maximum peak firing pressure	bar	170	
Maximum fuel pressure	bar	200	
Fuel injector	i. hollow cone, piezo ii. Six-hole, solenoid		

TABLE 2 Technical details of the research engine (© vka)

parison to ethanol, 2-methylfuran and 2-butanone feature moderate heats of vaporization, higher vapour pressures, higher specific heating values and higher air requirements [6, 7]. This allows for an improved mixture formation especially under critical operation boundary conditions like cold-start or cold intake air temperatures [18].

In addition to the heat of vaporization also the boiling temperature is a key criterion for the selection of fuels for SI-type engines. In this work, a boiling temperature of 100 °C was defined as maximum value to still enable the degassing of fuel from the oil pan at typical warm operation temperatures in the range of 90 to 100 °C [8]. For both, 2-butanone and 2-methylfuran this criterion was met.

EXPERIMENTAL SET-UP

The experiments were conducted on a direct-injection single cylinder research engine [8, 19]. Due to the solvent-type properties of 2-butanone and 2-methylfuran, the resistance of different gasket materials were investigated in advance [20]. The materials ethylene propylene diene monomer rubber (EPDM), fluoroelastomer (FKM) and nitrile butadiene rubber (NBR) showed an unacceptable high degree of swelling when brought into contact with 2-butanone and 2-methylfuran. Instead the materials polytetrafluoroethylene (PTFE) und perfluoroelastomer (FFKM) were used

as sealing materials in the fuel system which showed no swelling when in contact with both fuels. The engine is equipped with an external compressor unit to realize a boost pressure of up to 3.5 bar, TABLE 2.

The different compression ratios (CR) were realized by adapted piston geometries, FIGURE 1. The engine features a high peak pressure stability as well as separated, symmetrical intake ports to produce a high degree of tumble motion in the cylinder. The spark plug is located between the exhaust valves, while the injector sits between the intake ports, FIGURE 1. For the thermodynamic investigations two different injectors were used: an outward-opening piezo actuated injector with a hollow cone (cone angle: $90^{\circ} \pm 3^{\circ}$, max needle lift: ~30 µm) and a six-hole solenoid injector

with a spray pattern optimized for lowest wall impingement.

The air was conditioned to reach 25 °C behind the throttle. When operating in throttled mode, the air pressure before the throttle and behind the exhaust port was set to 1013 mbar. In supercharged operation mode the pressure in the exhaust port was raised to the corresponding value in the intake port. The determination of the relative air/fuel ratio (λ) was calculated from the exhaust gas composition based on the formula of Spindt [21] with the extension for oxygenates by Bresenham [22]. The exhaust gas composition was determined from a heated partial flow taken from the exhaust port. The exhaust gas flow sample was analysed using the following systems:

- Hydrocarbons (HC): Flame ionization detector (Rosemount NGA 2000)
- Oxygen (O₂): Paramagnetic oxygen analyser (Rosemount NGA 2000)
- Carbon monoxide (CO): Infrared gas analyser (Rosemount NGA 2000)
- Carbon dioxide (CO₂): Infrared gas analyser (Rosemount NGA 2000)
- Nitrogen oxides (NO_x): Chemiluminescence analyser (Eco Physics 700 EL ht).

The partial exhaust gas flow to detect particle emissions was separated behind the exhaust gas back pressure valve at a pressure level of 1013 mbar. It was transferred to a Smokemeter (AVL 415s) to detect the Bosch Filter Smoke Number (FSN) and to an Engine Exhaust Particle Sizer (EEPS by TSI) to detect the particle number. In order to avoid possible errors when determining the HC emissions by using a flame ionization detector (FID) for the oxygenate fuels, an assumption to equivalent earlier investigations by

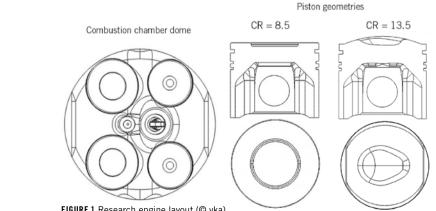


FIGURE 1 Research engine layout (© vka)

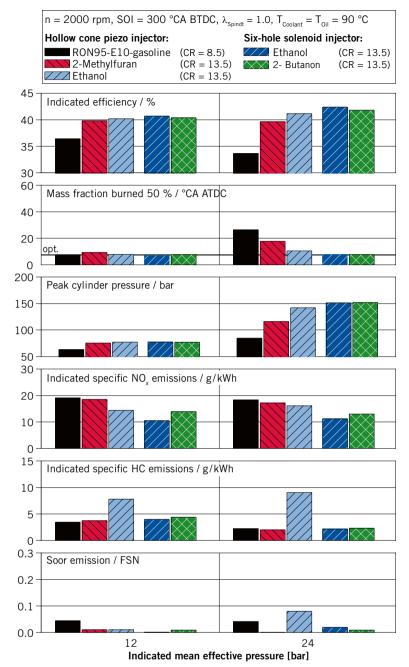
Thewes [7] was made that the HC emissions of all three investigated biofuels exclusively consist of the corresponding fuel molecules. Here, a certain degree of uncertainty remains as the exact composition of the HC emissions cannot be detected.

ENGINE TEST RESULTS

Both TMFB-fuels 2-methylfuran and 2-butanone were investigated as pure substances and compared to conventional RON95 gasoline as well as ethanol. In gasoline engines, the highest possible thermal efficiency depends on the compression ratio, which again is limited by the fuels anti-knock properties. In FIGURE 2 the knock resistance of the investigated fuels based on 50 % mass fraction burned point (MFB 50) in two different load points at an engine speed of 2000 rpm with two different injector configurations (hollow cone and six-hole injector) is shown. Due to their higher knock resistance all investigated biofuels enabled an increase of the engine compression ratio of five units to 13.5 in comparison to conventional RON95 gasoline fuel. A high knock resistance and therefore highest possible thermal efficiency is indicated by a MFB 50 in the optimal range of 7 to 8 °CA after top dead centre (°CA ATDC).

In **FIGURE 2** it can be seen that at an engine load of 12 bar indicated mean effective pressure (IMEP) none of the fuels are knock-limited. With all biofuels the efficiency can be increased by more than 10 % due to the higher compression ratio. In addition the efficiency is affected by gasoline's lower heat of vaporization and the resulting higher wall heat transfer. The differences between the biofuels can be attributed to the differing heats of vaporization as well.

The nitrogen oxide (NO_x) emissions are mainly caused by the temperatures during the combustion [23]. In the case of conventional gasoline the lower compression ratio seemed to compensate the higher enthalpy of vaporization of 2-methylfuran. Ethanol showed the lowest NO_x emissions due to its high enthalpy of vaporization in combination with the lowest adiabatic flame temperature. The decrease of NO_x emissions between the hollow cone and the sixhole injector for ethanol can be attributed to the improved mixture formation

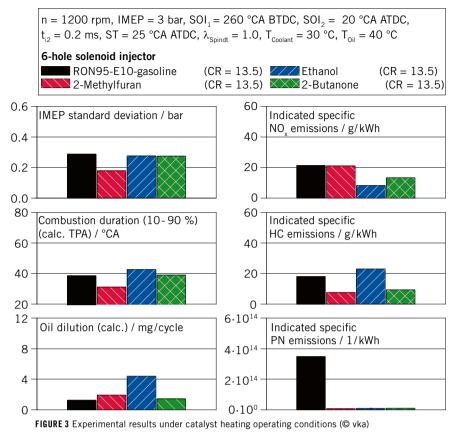




and the resulting cooling of the mixture. This effect becomes even more pronounced when the HC emissions are considered. An increase of HC emissions for ethanol with the hollow cone was observed. This effect is assumed to originate from ethanol evaporating from the cylinder wall oil film which was proven by optical investigations [7].

By changing the injector to a multi-hole type with a narrower spray target the cylinder wall wetting was reduced. This lead to a decrease of HC emissions with ethanol reaching the level of the other fuels. An increase of NO_x emissions of 2-butanone on the other hand can be explained by its lower heat of vaporization and its higher adiabatic flame temperature in comparison to ethanol. The measured soot emissions clearly showed a decreasing trend for all three investigated biofuels in comparison to conventional gasoline.

When the load is raised to 24 bar IMEP the improvement of thermal efficiency for the biofuels increases even



more due to their higher knock resistance. Although operated at a lower compression ratio, the MFB 50 for RON95 gasoline to 26 °CA ATDC, whereas for 2-methylfuran the necessary adjustments only lead to a delay of 18 °CA ATDC. This results in an efficiency increase of approximately 18 % in comparison to conventional gasoline. Regardless of the above mentioned challenges for the combination of ethanol and the hollow cone injector, a MFB 50 of 10 °CA ATDC was reached for this combination due to the high cooling effect and the high RON. This results in an efficiency increase of 21 % in comparison to conventional gasoline.

When using the six-hole injector, ethanol is no longer limited by knocking combustion so an optimum MFB 50 could be adjusted. The higher indicated thermal efficiency of 42.4 % of ethanol with the six-hole injector (compared to 41.1 % with ethanol and the hollow cone injector) can additionally be attributed to the notable reduction of HC emissions which result from the improved mixture formation. Although the heat of vaporization of 2-butanone is lower than that of ethanol, also here no retardation of the MFB 50 was necessary. This can be explained by the very high ignition delay time of 2-butanone which compensates for the higher mixture temperature in comparison to ethanol [18]. The maximum indicated efficiency of 2-butanone of 41.8 % was in the range of ethanol.

In addition to the load sweep measurements at 2000 rpm also catalyst heating operation was investigated with all four fuels in the representative operating point 1200 rpm, 3 bar IMEP to compare them under critical operating conditions. For the engine oil temperature and the cooling water temperature 40 °C and 30 °C were chosen. The investigations were carried out with the six-hole injector and the high compression ratio of 13.5. For all fuels an equal spark timing (ST) and start of injection (SOI) as well as an ignition-coupled injection with constant injection timing (t_{i2}) were chosen, FIGURE 3.

The burn duration of 2-methylfuran which was calculated by a three pressure analysis (TPA) using the software GT-Power results in a good combustion stability, which is also expressed by a low standard deviation of the IMEP [6, 7]. For the other fuels RON95 gasoline, ethanol and 2-butanone comparable combustion stability was observed. In comparison to ethanol benefits with regard to oil dilution could be observed. The oil dilution depicted in **FIGURE 3** was calculated from the relative air/fuel ratio based on exhaust gas components [21,22] and the relative air/fuel ratio determined from the fuel and air flow measurements.

For ethanol - regardless of the optimized six-hole injector spray pattern it is assumed that a high degree of cylinder wall wetting occurs which is due to ethanol's high heat of vaporization, low vapour pressure, elevated fuel flow requirement and higher air requirement. This leads to a higher oil dilution and an increase in HC emissions caused by the following partial desorption of the ethanol from the oil film in the gas exchange phase. The HC emissions of 2-butanone are comparably low as those of 2-methylfuran. Additionally, with all three biofuels a notable reduction in particulate emissions was observed.

CONCLUSIONS AND OUTLOOK

The two fuels 2-methylfuran and 2-butanone were thermodynamically investigated as pure components in a direct injection single cylinder research engine. It could be proven that both fuels feature extraordinary properties when compared to standard RON95 gasoline and ethanol. For both 2-methylfuran as well as 2-butanone lower HC emissions and oil dilution could be observed at low loads and cold boundary conditions in comparison to ethanol.

Under these critical operating conditions especially 2-methylfuran shows an excellent combustion stability behaviour. At the same time, an increase of the compression ratio and hence an efficiency increase of 18 % at high loads could be achieved due to the higher knock resistance in comparison to standard RON95 gasoline. Most notably, 2-butanone combines a high combustion stability at critical (cold) operation conditions with the highest knock resistance at the same level as ethanol which allows for an efficiency increase well above 20 % in comparison to RON95 gasoline in high load points. It can be stated that,

although the compression ratio was increased to 13.5, no knock-limited engine operation area was reached. One disadvantage of 2-butanone and 2-methylfuran in comparison to ethanol are the observed elevated NO_x emissions which only play a role for lean operated gasoline engines. For all three biofuels a notable reduction of the measured particulate emissions can be reported.

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THANKS

This work was performed as part of the Cluster of Excellence Tailor-Made Fuels from Biomass, which is funded by the Excellence Initiative by the German federal and state governments to promote science and research at German universities.

Alternative Fuels in the Well-to-Wheel Debate

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A rearrangement of the fuel care in the mobility from conventional to regenerative energy sources as the basis for fuel in transportation can be guaranteed. This show studies from APL, LBST and FVV. It points towards the contradicting optimization of efficiency and system usefulness. Optimization of different fuel options is directly linked to the energy converter used in the vehicle. Today pure battery electric vehicles (BEV), fuel cell electric vehicles (FCEV) or vehicles with internal combustion engines (ICE) compete. The principal economic feasibility of a sustain-able fuel supply of power-to-gas or power-to-liquid is demonstrated using the example of Germany.

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WHAT IS FUEL?

The wish for mobility of persons and transport of goods is best answered on the level of services, since it cannot be assigned to a classical product category. Fuel, however, is a means to an end; that is in order to judge its importance for mobility one has to take the system environment into account. In the sense of a system boundary one could see the fuel as energy carrier to be stored on board of the vehicle and to be transformed with the help of an energy converter (or a system of energy converters) in the vehicle propulsion according to actual requirements.

The evaluation of a fuel or energy carrier in terms of its sustainability, efficiency, emissions and costs needs to be debated and assessed along the complete chain of supply and use, that means from the primary energy base to the point where wheels are turning (hence "well-to-wheel"). Therefore, upstream energy efforts for fuel production and supply have to be assessed on par with energy demands in the vehicle.

FUELS FROM CONVENTIONAL PRIMARY ENERGY BASE

Fossil-based fuels are mixtures of many different hydrocarbons, which are now mainly produced by refining crude oil. In addition to diesel, kerosene and gasoline more energy carriers have been established, such as methane, liquefied petroleum gas (LPG) and others shown in the left part of **FIGURE 1**. Through dedicated conversion processes liquid and gaseous fuels can also be generated from natural gas and coal.

Through downstream conversion of energy carriers of aconventional primary energy base in the vehicle and by using an internal combustion engine the desired propulsion of the vehicles can be generated. The high storage density of liquid hydrocarbons in particular is reflected in the small tank volumes of vehicle tanks or large range of vehicles with a given tank volume. With battery and fuel cell electric vehicles, the electricity is either temporarily stored in a battery or generated by a fuel cell on board from hydrogen. Today the hydrogen for fuel cell vehicles is either reformed from natural gas or stems from water electrolysis using renewable electricity.

The disadvantage of using fossil primary energy sources is that biogeochemical cycles, notably the carbon cycle, are not closed in reasonable time-scales after the fossil carbon emission occurred. Thus, hydrocarbons from biomass stored over millions of years in the form of fossil reservoirs are now used in a relatively short geological time scale and carbon dioxide is emitted into the atmosphere. The discussions about the climate impact of carbon dioxide are well known.

FUELS FROM REGENERATIVE PRIMARY ENERGY BASE

Regenerative primary energy base either generates hydrocarbons like those from

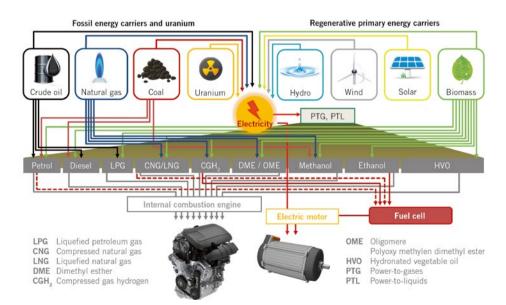
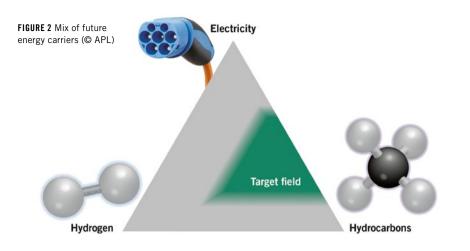


FIGURE 1 Energy carriers derived from fossil and renewable primary energy bases (© APL)

FUTURE FUELS ALTERNATIVE FUELS

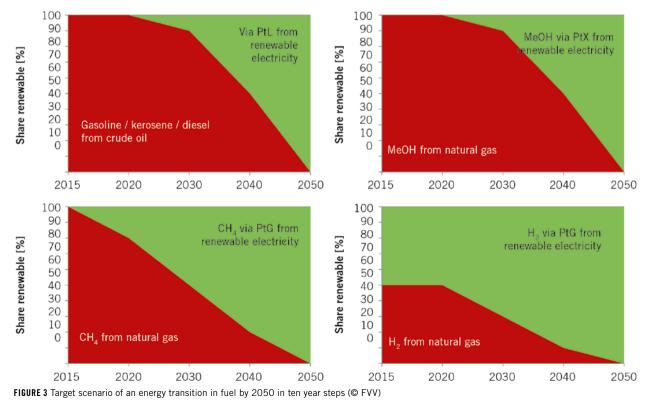


fossil origin basis via the production of biomass and the downstream process engineering or it directly provides electricity of high thermodynamic value (= 100 % energy) as shown in the right part of **FIGURE 1**. Another way is to use renewable electricity to synthesize power-to-methane or power-to-liquids, that means energy-dense fuels for vehicle propulsion with the help of internal combustion engines. The advantage of the use of hydrocarbons from renewable energy sources is the timely closed carbon cycle. In the synthesis process the same amount of carbon dioxide is bound as will be emitted later on in the combustion process. Of course, the electricity gained by the use of regenerative primary base can be directly used in battery electric vehicles or to produce hydrogen for fuel cell vehicles. However, one disadvantage of the battery electric vehicle is that it has no volumetric and gravimetric energy density comparable to hydrocarbons and only limited storage capacity – the vehicle's real operating range is thus limited. The fuel cell vehicle is still in an early stage of commercialization.

TRANSPORT FUEL – THE BIG PICTURE

The portfolio of energy carriers for transport which will be increasingly based on pure regenerative primary energy in the future could be represented as in **FIGURE 2**. The Federal German Environment Agency (UBA) has indicated a mix of electricity, hydrogen and hydrocarbons, the target area with focus on hydrocarbons in its study, published in October 2013.

A fundamental analysis shows that a 100 % regenerative primary energy base is reasonable. The energy balance of our planet shows that the short-wave solar radiation, the direct reflection and the longwave radiation from surface is balanced in a seasonal-on-year average. This is in accordance with the first law of thermodynamics, as otherwise an imbalance would result in either heating or cooling. If one takes the average hourly solar radiation on the earth's surface from about 123,000 TWh and relates it to the global annual primary energy consumption of about 155,500 TWh (IEA 2012), one realizes that solar energy from one hour of global surface solar radiation is the energy equivalent to what mankind consumes in one year.



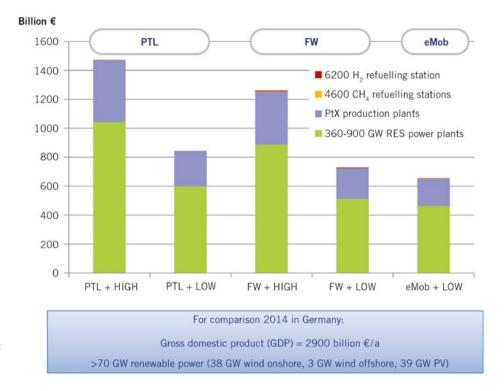


FIGURE 4 Cumulative investment needs for the various scenarios for Germany till 2050 (© FVV)

Conversely, this means that we have no problem of energy shortage in itself, but a challenge of energy conversion, that means transferring the regenerative primary energy into the energy carriers desired as for example future transportation fuels.

In a study, which was conducted by the Ludwig-Bölkow-Systemtechnik (LBST) on behalf of the Research Association for Combustion Engines (FVV) an estimate for the representation of a pure regenerative energy supply of the transport sector in Germany is shown for the year 2050. Based on different demand scenarios for the transport of persons and goods, the resulting power-to-liquids (PtL), power-to-gas (PtG) and electricity for fuel demands were calculated till 2050. In FIGURE 3, a target scenario for the conversion of various fuels into 100 % regenerative primary energy base is sketched. Today, hydrogen (PtH₂) for transport use is already produced with about 50 % renewable electricity, albeit starting from low absolute amounts yet. For synthetic methane (PtCH₄) several demonstration and pilot plants have been put into operation in the last two years. With regards to PtL, first initial demonstration / pilot plants are in operation, too; key components of PtL processes have been established on an

industrial scale in the fossil energy supply; availability of large-scale plants based on renewable electricity can be expected from 2020 to 2030.

To estimate the bandwidth of necessary infrastructure investments more reference scenarios were assumed. The transportation demand has been divided into a high and low variant. The low demand variant is based on the eMobil study scenario "Regional" by Öko-Institut (2014) for the Federal Ministry for the Environment (BMUB). The high demand variant assumes further growth of passenger air and cargo transportation as stipulated by the official traffic forecast 2030 by the Federal Transport Ministry and their extrapolation to 2050 in the context of Fuel and Mobility Strategy (MFS) of the Federal Government.

With regard to the different fuel / powertrain scenarios – that means the assumed vehicle mix and corresponding fuel/energy carriers –for the "PtL" scenario of today's vehicle type composition as well as conservative efficiency improvements through for example mild hybridization was assumed; the "eMob" scenario was derived from above captioned BMUB investigation, anticipating a widely use of electrical drives (BEV and FCEV). The "FVV" scenario assumes an increased conversion to electrified drives with internal combustion engines (REEV), but also takes into account the use of battery and fuel cell electric vehicles.

In **FIGURE 4** the cumulated investment required for PTX production plants, renewable electricity generation plants, methane and hydrogen filling stations are depicted for the entire period up to 2050. Also learning curves have been taken into account in the calculations. It can be seen that all assumed scenarios are dominanted by the share of cumulated investments into power generation plants (some 70 to 80 % of overall cumulated investments). The share of cumulated investments into fuel distribution systems is almost negligible. A transformation of the transport sector to 100 % renewable energy base requires cumulated investments of around 600 to 1400 billion euro, depending on the transportation demand and fuel / powertrain scenario. Considering an average investment of 1000 billion euro cumulated over 35 years until 2050 (that means some 28 billion euro per year in average) against the gross domestic product in Germany (that means some 2,900 billion euro GDP in 2014), it is evident that a full energy transition of the transport sector is in the order of a low single-digit percentage range of GDP. Such an infrastructure

measure is certainly manageable from an economic perspective, even more as a considerable part of the investment contributes to the local value creation. The 360 to 900 GW of renewable electricity generation capacity to be installed for the transportation sector corresponds to about 5 to 15 times of today's installed renewable power plant capacities in Germany. Renewable power plant capacities of this magnitude present no knockout criterion from a technical standpoint in the EU. However, for public acceptance reasons some fuel imports may be desirable, notably of PtL in the high demand scenarios (PtL + HIGH, FVV + HIGH) for its ease of transportation by existing crude oil and minerals products logistics.

COST CONSIDERATIONS

In order to develop an indication of the expected cost levels of different transportation fuels, a cost perspective for 2050 was worked out by Ludwig-Bölkow-Systemtechnik GmbH based on published specifications and technology learning curve extrapolations. Here, all values were converted to the energy content of a liter of diesel equivalent. The summary values are shown in **FIGURE 5**.

For the fossil fuels reference, IEA takes 100 US-Dollar per barrel of oil in 2050 into account which corresponds to about 0.61 euro per liter liquid fuel (diesel equivalent, excluding taxes). The electricity generating costs are conservatively assumed at 8.2 ct/kWh including the costs of transporting electricity. The annual equivalent full load hours of renewable electricity production is considered 4000 hours/a. The carbon dioxide is completely extracted from ambient air (conservative assumption without potential restrictions). From FIGURE 5 it can be seen that the various PtG and PtL products are all in the similar range by 2050 with some 2.5 euro per l of diesel equivalent. The fuel costs are determined by the electricity costs, which account for about 80 % of total costs ex filling station. Further evaluations with the use of renewable electricity power in countries with high solar / wind supply and 6500 hours of equivalent full load production per year including fuel transportation and distribution show a cost saving potential of about 20 % compared to Germany. The difference between fossil and renewable hydrogen

production costs is significantly lower compared to more complex hydrocarbons. Further short- to middle-term cost reducing potentials are thinkable on the basis of business case analyses, for example the usage of concentrated CO₂ (for example from biogas upgrading), or additional revenues from electricity grid services (for example flexible electrolyser operation). Feasible reductions in costs achieved in this way depend on the site selection and the development of regulatory frameworks in the power system.

REVIEW OF THE FUEL PATHS

A transition from presently mostly fossil-based mobility of people and goods to a purely regenerative primary energy base is reasonable. This does not necessarily require pure electric vehicles only. Depending on the modal requirements, model strategies, especially in road transport, may draw from a host of powertrain options including battery-electric components, fuel cell-electric components as well as hybrid systems operated with differently sized internal combustion engine components. All these options have

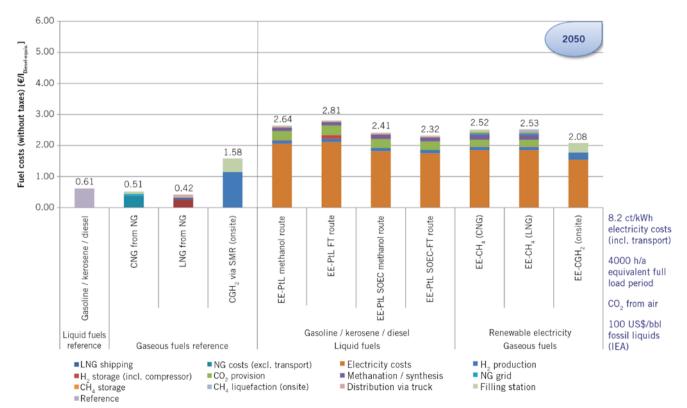
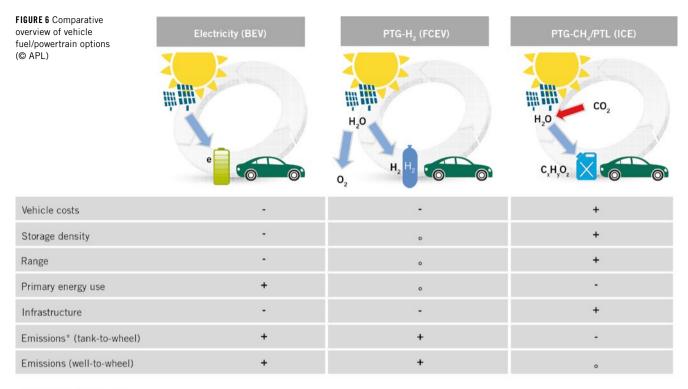


FIGURE 5 Full cost analysis of transportation fuels for the year 2050 with PTX production in Germany (© FVV)



* Criteria air pollutants

in common that they are increasingly operated with renewable electricity, hydrogen or hydrocarbons.

FIGURE 6 shows a summary of the advantages and disadvantages of different fuel / powertrain options. The battery-electric option has significant advantages in the short-distance mobility. The high storage densities of hydrocarbons make them an especially good fit for long-distance and high-performance transport applications. The fuel cell-electric option plays a robust midfield role tapping into small, medium and heavy-duty applications.

The identified cost and investment comparisons show that a transition to a purely regenerative primary energy supply base is not a fast-selling item. As long as the added environmental value (that means sustainability) of renewable fuels is not attributed an economic value, renewable fuels remain more expensive than fossil fuels in the foreseeable future. To make this transition happen, a societal will and facilitating framework is needed in order to achieve the 2050 objectives.

The presented results are based on conservative assumptions for specific

energy needs and costs. Political framework and business-opportunities may allow for lower renewable fuel costs, for example if regenerative electricity could initially be used at reduced tax rates or the use of carbon dioxide from "grey sources", such as cement works or furnaces. Rules for environmental accounting of CO₂ from grey sources would be helpful to this end, thus avoiding CO₂ extraction from ambient air, increasing the fuel production efficiency and preventing carbon leakage between sectors. If the transport sector increasingly requests more regenerative power supply, these requirements are not least to be considered in policy roadmaps and regulatory frameworks for the integration of (fluctuating) renewable electricity generation. The key to business decisions however, is sufficient security of investment. The current 2020-targets (EU FQD, EU RED, German BlmSchG) should thus be further developed with a view to achieving 2050 targets.

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THANKS

The authors would like to thank Dipl.-Ing. Dietmar Goericke for commissioning the study by the FVV and for his cooperation in the writing of this article.



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THE ADOPTION OF LOW VISCOSITY OILS TO REDUCE FRICTION

Low viscosity oil is acknowledged as a key contributor to improved engine efficiency. This has led to the introduction of very low viscosity oils with differing additives, in pursuit of further reduced friction and improved fuel economy. Concurrent with these developments, oil flow reduction has been widely adopted as an effective way to minimize oil pump energy losses.

These actions result in significant challenges for critical engine components. Engine oil has a direct influence on the function and durability performance of sliding engine components, especially bearings and piston rings. Lubrication films between moving parts are getting much thinner; this increases the risk of wear and scuffing and, if the hydrodynamic mode is interrupted and asperity contacts increase, will lead to much higher friction.

The impact of trends in engine oil application on piston rings and bearings can be investigated with analytical tools. To verify the functionality influence of low viscosity oils, Federal-Mogul has developed rig test methods to compare different oils in respect of sliding properties, wear performance and friction reduction.

EFFECT OF LOW VISCOSITY OILS ON PISTON RINGS

In order to evaluate the influence of low viscosity oils on the tribological system of piston rings and cylinder liners, Federal-Mogul uses a rig test that simulates the scuff risk resulting from extreme oil starvation and high contact pressure



How Trends in Lubrication Development Impact Sliding Bearings and Piston Rings

The pursuit of improved fuel economy and lower CO₂ emissions is leading to the viscosity of engine oils continuing to fall, with each new formulation introducing the further complication of a different set of additives. Research at Federal-Mogul shows that while the resulting reduced friction and parasitic losses can significantly improve emissions and fuel economy, changes in operating conditions lead to significant differences in performance. New test techniques have been developed to investigate these relationships and to guide the choice of coating technology.

between a piston ring running face and cylinder bore. These rig tests were carried out with segments from top compression rings and plateau-honed cylinder liners, both manufactured under series production conditions. The used test conditions, which were defined as shown in **TABLE 1**, model the most critical sliding conditions in accordance with the Stribeck curve, **FIGURE 1**.

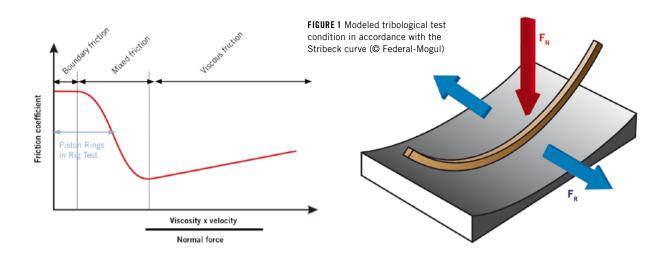
The measurement criteria applied to evaluate the impact of oil viscosity on scuff resistance are based on the time at which the piston ring/cylinder bore system exhibits distinct signs of scuffing from a sharp rise in the coefficient of friction (CoF) over 0.3. Many engine developers are exploring the idea of using lower viscosity oils to assist in meeting future CO_2 and fuel efficiency targets. Much of this work is being carried out with new High Temperature / High Shear (HTHS) viscosity oils, where the HTHS number – which is defined as oil viscosity at 150 °C – is significantly reduced.

One element to consider in relation to this is that low HTHS oils have an inadvertent effect on the tribological mode of the upper compression ring. The use of low HTHS oils, which reduce fluid shear strength, causes a shift in the Stribeck number in the direction of stronger mixed or even boundary, sliding conditions. Therefore, material or coating selection for these upper compression rings must consider the added demand of future application of low HTHS engine oils.

To evaluate the impact of low HTHS oils, investigation of scuff risk with engine oils of HTHS3.5 and HTHS2.9 were carried out using the newly developed rig tests, **TABLE 1**. Using HTHS2.9

Rig test conditions				
Motion	Oscillation			
Normal force [N]	450			
Stroke [mm]	30			
Temperature [°C]	110			
Average speed [m/s]	0,3			
Frequency [Hz]	5			
Duration [h]	μ >0.3 till scuffing			
Oil	HTHS 2.9 HTHS 3.5			

TABLE 1 Rig test conditions for measurementof scuff resistance in the lubricated tribo-logical system piston ring and cylinder liner(© Federal-Mogul)



oil significantly decreases oil film thickness compared to HTHS3.5 oil; calculated according to Hamrock and Dowson [1] the reduction is in the order of 13 %.

TESTING OF PVD-COATED PISTON RINGS IN LOW HTHS OILS

The results for a Physical Vapour Deposition (PVD) coated piston ring, characterized by a 30 µm thick chrome nitride hard layer, using the rig test to evaluate the impact of low HTHS oils on scuffing behavior, can be seen in **FIGURE 2**.

The behavior of PVD coated piston rings in standard oil with HTHS3.5, **FIGURE 2** (a), is characterized by a low CoF of 0.1 with a continuous slight increase over the test time prior to a dramatic increase of CoF at 180 to 220 min. Variances between the single measurements indicate the influences of piston ring barrel shape on contact area and coating morphology. A reduction of HTHS to 2.9, **FIGURE 2** (b), reveals in general the same behavior of the PVD rings, but with a stronger increase in friction coefficient over test time and more importantly, the time period where the tribological system collapsed reduced to 145 to 165 min.

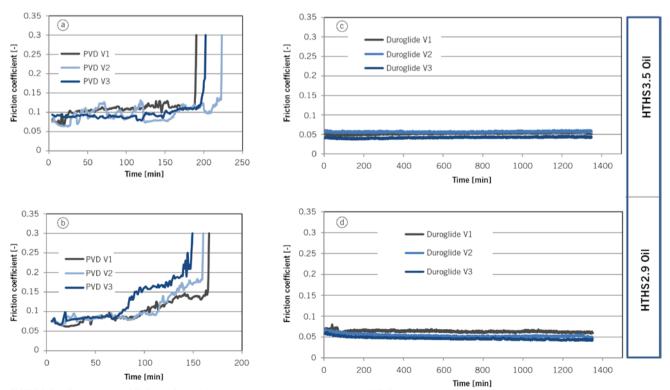
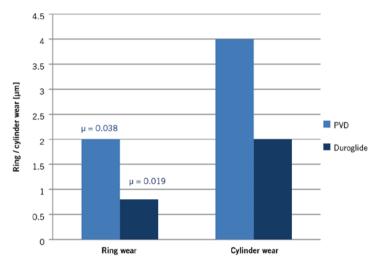
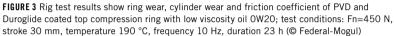


FIGURE 2 Scuff test results of PVD and Duroglide coated piston rings with low viscosity HTHS 2.9 and HTHS 3.5 oil under high contact pressure of 185 MPa (© Federal-Mogul)





TESTING OF DUROGLIDE HYDROGEN-FREE DLC-COATED PISTON RINGS IN LOW HTHS OILS

Diamond-like carbon (DLC) coatings are well known for their robustness under critical tribological conditions. Duroglide, a new generation of hydrogen-free DLC has been developed by Federal-Mogul especially for piston rings in order to achieve lower friction, high robustness, optimized wear resistance and improved cylinder bore protection [2]. The special amorphous carbon-based coating structure of Duroglide has a favorable effect on sliding behavior as well as on wear resistance in poorly lubricated tribological systems.

Results for the tribological behavior of Duroglide coated top compressions rings with engine oils of different HTHS viscosities are shown in FIGURE 2. Under the test conditions shown in TABLE 1, using HTHS3.5 standard oil, the Duroglide coated rings show a significant increase in scuff resistance compared to the PVD coated rings, FIGURE 2 (c). Even after the reduction of the HTHS value down to 2.9, FIGURE 2 (d), resulting in extreme sliding conditions, no signs of scuffing on the Duroglide piston ring running surfaces could be observed. Additionally, after a much longer test duration of up to 1350 min, no sign of collapse could be observed. It was also noticeable that the CoF remained at the very low number of 0.05 with both HTHS oils.

Rig test investigations with further reduced HTHS numbers down to 1.8 confirm the excellent tribological behavior of Duroglide coated piston rings. In comparison to state-of-the-art-PVD coated piston rings, no scuffing marks could be observed.

Additional standard rig tests were carried out using low viscosity oils to validate ring wear, cylinder wear and friction coefficient. The test results underline the importance of surface coating material to achieve the optimal tribological behavior. As shown in FIGURE 3, wear resistance and friction coefficient indicate that DLC Duroglide coated top compression rings have an advantage compared to PVD coated rings tested using the same 0W20 engine oil. The amorphous carbon-based structure of the Duroglide coating, with its superior dry sliding properties, reduces boundary friction and therefore lowers the measured friction coefficient as well as reducing the wear rate.

ANALYTICAL AND EXPERIMENTAL EVALUATION OF LOW FRICTION OIL ON SLIDING BEARINGS

Sliding bearings contribute to about 20 % of friction loss in the base engine [3]. Engine speed, bearing dimensions/ load and oil viscosity/temperature are the main factors that influence friction in the bearing system. It is widely acknowledged that low viscosity oils reduce friction loss in bearings, as long as the system acts under hydrodynamic conditions.

Mixed lubrication conditions during the start phase; asperity contacts due to deformation of mating components; side loads on bearings from belt drives; or oil film thicknesses below a certain level all increase the friction in bearings and may negate the gains from using low viscosity oils. As well as the increase in friction, a high level of mixed lubrication conditions can create wear in the bearing's running surface and negatively influence overall bearing performance.

To evaluate the friction performance of sliding bearings analytical and experimental approaches are combined. The advanced analytical Elasto-Hydro-Dynamic (EHD) tool allows detailed understanding of the bearing's loading mode, based on real cylinder pressure curves, sliding speed and deformation of surrounding components. This includes definition of mixed lubrication behavior and differentiates between pure hydrodynamic friction (shear friction in oil) and friction caused by asperity contacts between moving surfaces.

The experimental approach allows comparison in friction behavior of bearing materials and engine oils under defined test conditions. As classical test procedures for bearings are not able to differentiate between mixed and viscous friction, Federal-Mogul has developed a specific procedure to measure friction in sliding bearings.

The test rig allows friction measurement with separation between boundary friction, mixed friction and viscous friction, FIGURE 1. The system detects transition points in the Stribeck-Curve by determining the change in contact voltage using the lubricant as a dielectric medium, FIGURE 4. Tests have been conducted with both bare aluminum shells and coated versions to measure boundary friction and viscous friction at shaft speed >200 rpm up to 3500 rpm with engine oils acc. SAE 5W-30 with HTHS3.5 and SAE 0W-20 with HTHS2.9. As expected, the low viscosity oil achieves a smaller coefficient of friction for boundary friction and under hydrodynamic conditions (shaft speed >200 rpm). The more interesting result is the fact that a specific coating has a higher impact on friction reduction in bearings than the shift from 5W-30 to 0W-20 oil. At a shaft speed of 3500 rpm



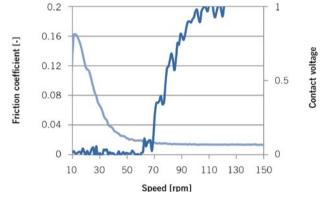
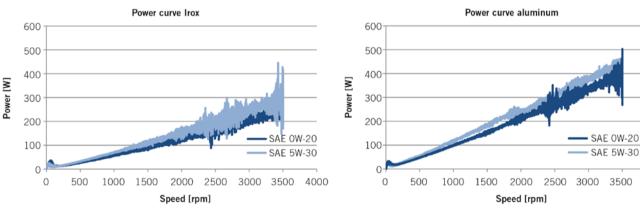


FIGURE 4 Bearing friction test rig; Stribeck curve and contact voltage curve indicating transition points from boundary, mixed and viscous friction (© Federal-Mogul)

the bare aluminum shells achieved a CoF of 0,016 with 5W-30 oil and CoF of 0,014 with 0W-20 oil. The Irox coated bearings achieved a CoF of 0,009 (5W-30) and CoF of 0,008 (0W-20) under same test conditions. This is also reflected in the power curve in **FIGURE 5**, which shows that with the same lubricant, Irox coated shells consume less power than bare aluminum shells. In the period between start and the hydrodynamic regime, both bearing types show higher CoF while using the lower viscosity oil, which indicates conditions of mixed lubrication.

The analytical approach confirms the friction behavior for low to medium engine speeds. The EHD calculation for a 1.6-l-l4-Gasoline engine shows different behavior at different bearing loads when the oil type was changed from 5W-30 to 0W-20. At 1000 rpm the 30 % lower oil viscosity of the 0W-20 oil reduces the power loss by only 6 %, but the 27 % lower viscosity at 3500 rpm generates a 20 % reduction of power loss compared to 5W-30 oil. These results show clearly the strong

4000



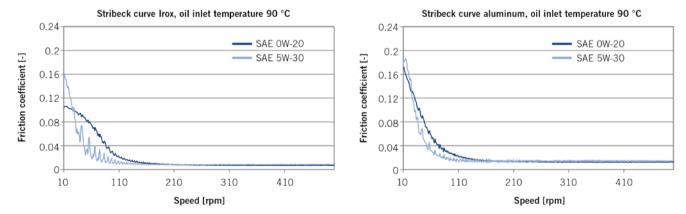


FIGURE 5 Power and Stribeck curves from friction measurement with bare and Irox coated Aluminum shells using 5W-30 HTHS3.5 and 0W-20 HTHS2.9 engine oil (© Federal-Mogul)

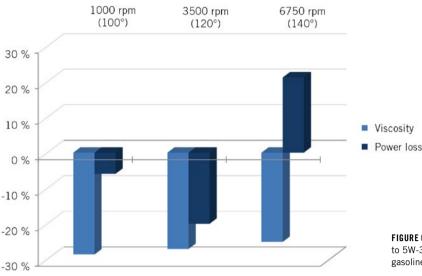


FIGURE 6 Change of viscosity and power loss of OW-20 compared to 5W-30 oil for three different crankshaft revolutions in a 1.6 I gasoline engine (© Federal-Mogul)

influence of the lower shear strength in 0W-20 oil with increasing sliding speed.

When the bearing's behavior at higher speed is calculated, the positive effect of low viscosity oil is reversed. At 6750 rpm, **FIGURE 6**, the low viscosity oil demonstrates a comparable reduction in friction but now with a 20 % increase in power loss compared with the 5W-30 oil. This is linked to the significant increase of asperity contacts; housing deformation, shaft bending and higher oil temperature do not allow the build-up of a sufficient oil film capacity and under these conditions the risk of high wear and finally seizure may increase dramatically.

To further evaluate the impact of low viscosity oils on bearing function, both oil types have been tested for wear rate and seizure on bare aluminum and Irox coated shells. The different tests did not show any deviation in performance using both oil types. While bare aluminum shells show an expected wear rate >200 µm with both oils, the Irox coated parts had only very little wear in the range of 6 µm. All bearings passed the seizure test with both oils under marginal lubrication conditions and survived the target of 30hrs test duration. This indicates a positive impact of the oil additive packages on wear and sliding properties of bearings.

SUMMARY AND OUTLOOK

Low viscosity oils can have a measurable positive impact on parasitic power

loss in combustion engines, but to fulfill the potential of these oils, the relevant components must be designed to take account of the different tribological conditions, such as reduced film thickness. Tests on the new piston ring coating Duroglide with low HTHS oils show no scuffing, while conventional PVD coated piston rings suffer early failure. The new coating also achieved measurably lower wear rates as well as a lower coefficient of friction.

Specially coated bearings can further reduce viscous friction as long as the bearings work in hydrodynamic mode. The positive effect may be reversed when asperity contacts cause more losses through mixed friction than the gains from lower oil viscosity. The individual behavior is engine specific and can be influenced by system stiffness, shaft- and bearing profile and controlled oil temperature. Performance tests for wear and seizure on bearing materials show comparable performance with both 5W-30 and 0W-20 oil.

The results of research have shown that there is a new imperative to understanding the characteristics of the oil when designing components working under lubricated conditions. In addition to designing for low wear and good scuffing resistance, coatings for use with low viscosity oils must protect surfaces when operating with thinner oil films, if the benefits of durability, reduced fuel consumption and CO₂ emissions are to be achieved.

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FUTURE LUBRICANTS ANALYSIS



SIMULATION OF THE **OLIGOMERIZATION PROCESS**

The regulations of emissions make the usage of an exhaust gas aftertreatment system essential. In diesel engines especially, a diesel particulate filter (DPF) is necessary. Additionally, politics has great interest on biogenic components in fuel. Currently in Germany, the biodiesel content in diesel fuel is limited up to 7 % [1]. Climate change effects and saving fossil resources are the main drivers.

During DPF regeneration, unburned fuel from the piston wall leaks into the engine oil. Due to the high boiling point of biodiesel (circa 360 °C), this fuel does not evaporate from the engine oil. In consequence, autoxidation reactions

leads to a faster degradation of the engine oil resulting in oligomerization.

The aim of this work was the simulation and the chemical understanding of the oligomerization process in the laboratory. Therefore, base oil without additives and squalane as well as their defined mixtures with different fuels were examined. To simulate the chemical stress during the aging in a real engine, an oil stability index apparatus (OSI) was used.

Besides the aging studies, measurements of the acid value of total acid number (TAN) and viscosity as well as investigations with size exclusion chromatography (SEC) and fourier transform infrared spectroscopy (FTIR) were carried out.

MATERIALS AND METHODS

Biodiesel as synonym for fatty acid methyl ester (FAME) is the most commonly used biofuel in Europe. In Germany it is mainly produced from rapeseed oil (rapseed oil methyl ester, RME). The RME used in the study had a density of 884 kg/m³ and a viscosity of circa 4.5 mm²/s [2]. Furthermore, hydrotreated vegetable oil (HVO) was used in this work. It consists of a multitude of paraffinic hydrocarbons. Primarily, isoparaffins (up to 80 %) are included as well as n-paraffins. HVO as well as FAME is free of sulfur and aromatics [3]. The density of the HVO used was 780 kg/m³ and the viscosity 3 mm²/s [4]. Pure RME as well

Base Oil Aging with Contemporary Biofuels

Because of the regeneration of the diesel particulate filter, unburned fuel from the piston wall leaks into the engine oil and leads to oligomerization. For a better understanding of the autoxidation reaction in the engine oil, simulations of the aging process in the laboratory were carried out at the Technology Transfer Center Automotive of Coburg University. To exclude the influence of additives in engine oil, neat base oil as well as squalane as a model substance were used.

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as pure HVO do not conform to the standard DIN EN 590 (density 820 to 845kg/ m³ and viscosity 2.0 to 4.5 mm²/s). The density of RME was above the permissible limit of the standard while that of HVO was below. Therefore a mixture of HVO and RME was made with a view of creating a new fuel which conforms to the standard.

Kuronen and Mikkonen [5] reported that HVO reduces regulated emissions in heavy duty engines. This aspect is especially important for high emission areas such as inner cities in which environmental zones have been instituted to improve air quality. For these reasons a new fuel called Diesel regenerativ was created consisting of HVO and RME without any fossil diesel fuel. In order to obey DIN EN 590, a blend of 93 % HVO and 7 % RME was composed. The aim of the project was to create a city fuel. RME assured the fuel lubricity.

In all tested passenger cars, Diesel regenerativ showed with the exception of nitrogen oxides (NO_x) lower emissions; NO_x increased. However, because of its density of 786 kg/m³, this fuel didn't fulfill DIN EN 590 [2, 6]. The viscosity was 3 mm²/s.

Based on Diesel regenerativ, a new fuel was developed which conformed to the standard. The follow-up project, Diesel R33 aimed at market testing and a subsequent possible market introduction in a controlled manner. Diesel R33 obtains 7 % biodiesel from used cooking oil (UCOME from Tecosol GmbH, Germany), 26 % HVO (from Neste Oil, Finland), a quality high-grade diesel fuel (DF) and a sophisticated additive package (from ERC Emissions-Reduzierungs-Concepte GmbH, Germany). The biogenic content of 33 % led to the lable Diesel R33. The density is between 823 kg/m³ and 831 kg/m³ and the viscosity 3 mm²/s. O'Connor calculated approximately 17 % reduction of greenhouse gas potential for Diesel R33 versus fossil diesel fuel. However, Diesel R33 leads to increased NO_x emissions in passenger cars [7]. From the final report of Diesel R33, the fuel used for this stu-

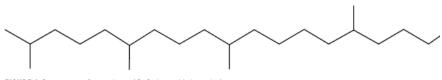


FIGURE 1 Structure of squalane (© Coburg University)

dies consisted of 26 % HVO, 7 % RME and 67 % DF without additives [7].

In this study, pure base oil and pure squalane as well as mixtures with the mentioned fuels with base oil or squalane were used. Neat base oil was used for this investigations to prevent the influence of the additives during the aging. Base oil consists of many hundreds of chemical substances making a detailed analysis impossible. To get a better understanding of the oligomerisation, squalane was used as a model substance for the base oil. In FIGURE 1 the structure of squalane is shown. The usage of squalane was part of the work of Dugmore [8] and Dugmore and Stark [9]. Furthermore, Knorr [10] showed that base oil and squalane have the same aging behavior at the same conditions.

In a fleet project with different biogenic fuels, Volkswagen AG [11] carried out a worst case scenario with a lot of damages using a mixing ratio of 20 % biodiesel and 5 % diesel fuel in engine oil samples. Another publication of Fang and McCormick [12] examined a biodiesel admixture of 20 up to 30 % in diesel fuel. They have proved that these mixtures have the highest tendency for deposit formation [12]. The sample composition for the used base oil and squalane as well as their mixtures with the mentioned fuels is shown in **TABLE 1**.

For all aging tests Oil Stability Index (OSI) measurements according to the standard DIN EN 15751:2014 [13] for FAME was used. The OSI includes a heated reaction vessel. During the thermal aging process, a stream of air (10 l/h) is passed through the sample. The amount of the sample was 7.5 g. Contrary to the prescribed temperature of 110 °C in the OSI, the used apparatus applied a temperature of 170 °C because in this study. This temperature was applied in previous studies [11, 14] as well as by Dugmore and Starke [9]. The duration of each aging process was 40 h.

The TAN indicates the volume of potassium hydroxide required to neutra-

lize all acids present in one gram of sample. For the measurements of the TAN an 888 Titrando with 801 Stirrer from the company Metrohm was used.

The kinematic viscosity of the oil/fuel and squalane/fuel mixtures was measured by Stabinger viscometer SVM3000 from Anton Paar. The sample was measured in a small test tube which is located in a temperature controlled chamber. For the analysis of the liquids a temperature of 40 °C was used.

With the SEC, the molecular weight of the built oligomers could be detected. The SEC measurements were done with an Agilent Technologies 1260 Infinity SEC system. 100 mg samples were mixed with 1000 µl THF. Three columns (PSS SDV 50 Å 3 µl, PSS SDV 100 Å 3 µl and PSS SDV 1000 Å 3 µl) were used for the analysis. The heating temperature of the columns was 30 °C and the eluent was tetrahydrofuran. A sample volume of 100 µl was injected and the flow rate was 0.7 ml/min. For the determination of the size of the molecules, the calibration standard Agilent PL2070-100 (highest molecular mass was 21,300 g/mol) was used.

The molecular vibrations of the functional groups of a molecule can be detected by FTIR. For the analysis, a Nicolet 6700 FTIR from Thermo Scientific was used. An ATR-crystal for ATR spectroscopy was equipped in this instrument. The analysis of molecular vibrations were performed by applying a drop of the sample on the crystal. A deuterated tri glycine sulphate detector and an extended range KBr (XT-KBrTM) beam splitter were included in the apparatus. For the evaluation of the measurements, the Thermo Scientific Omnic Software was used.

RESULTS

FIGURE 2 shows the FTIR-Spectra of base oil and squalane during the aging process. For both substances, an increase of OH-bonds at 3200 to 3600 cm⁻¹ can be observed. These bonds are a result of acid and alcohol generation during the aging process [12]. There were also increasing vibration bonds detected at a wave number of 1650 to 1850 cm⁻¹. The vibrations of squalane are more pronounced than the vibrations of base oil. It can be concluded that more aging products were built with squalane than with base oil.

From Breitmaier and Jung [15] it is known that isoalkanes age faster than n-alkanes because their chemical structure aid a faster autoxidation reaction. The amount of isoalkanes in neat base oil is lower than in squalane which is an isoalkane and this leads to an increased building of radicals with base oil. For the samples in **TABLE 1** the important areas in the spectra were integrated. The results are shown in **FIGURE 3** and **FIGURE 4**.

Base oil	Squalane	RME	HVO	DK	Sample name
100 %					Base oil
80 %		20 %			Base oil + RME
80 %			20 %		Base oil + HVO
80 %		1.4 %	18.6 %		Base oil + Diesel regenerativ
80 %		1.4 %	5.2 %	13.4 %	Base oil + Diesel R33
	100 %				Squalane
	80 %	20 %			Squalane + RME
	80 %		20 %		Squalane + HVO
	80 %	1.4 %	18.6 %		Squalane + Diesel regenerativ
	80 %	1.4 %	5.2 %	13.4 %	Squalane + Diesel R33

TABLE 1 Sample composition (© Coburg University)

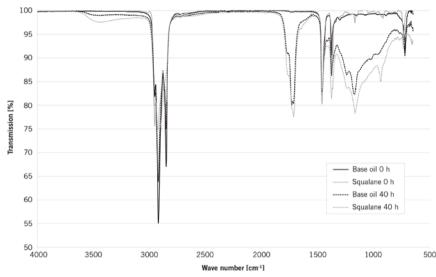
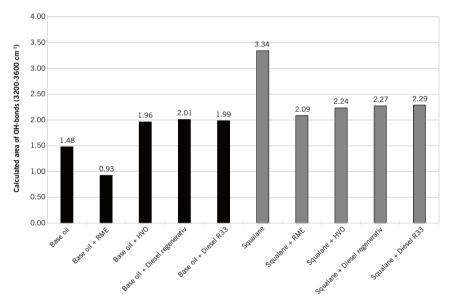


FIGURE 2 FTIR spectrum of base oil and squalane before and after aging (© Coburg University)





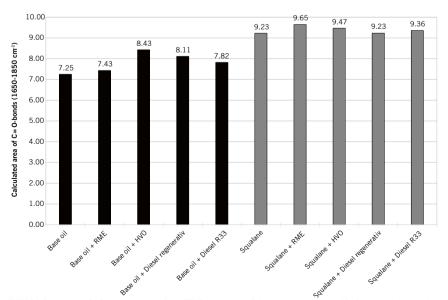


FIGURE 4 Calculated C=O-bonds areas of the FTIR spectrum of the aged substances (© Coburg University)

Variations in hydroxyl vibrations are presented in **FIGURE 3**. Mixtures with RME showed a smaller formation of long chain acids or alcohols after the aging compared to the other mixtures in the same sample series. After the aging process, the differences in the built up of OH-bonds between base oil and squalane with fuels including HVO were negligible though.

The differences in the C=O-bonds are shown in **FIGURE 4**. By comparison of the aged base oil and the squalane mixtures at the carbonyl vibrations (1650-1850 cm⁻¹), squalane and its mixtures showed higher C=O-vibrations. It can be recognized that the mixtures with all fuels showed slightly increased carbonyl vibration bonds compared to the pure base oil as well as the pure squalane.

FIGURE 5 shows the increase of the TAN. It can be observed that the building of acids is higher with squalane mixtures then with base oil mixtures. This observation agrees with the results of the shown areas from the FTIR spectra in **FIGURE 3**. In comparison of RME with HVO, Diesel regenerativ and Diesel R33 a higher TAN could be registered. The reason for this effect is the faster aging of isoalkanes in HVO which are relevant chemicals in the fuels Diesel regenerativ and Diesel R33 [3]. However, it was not expected that a mixture of squalane with RME shows a lower TAN than the pure squalane sample. Furthermore, this sample shows the highest error indicators (34 % higher than the second highest value). Further analysis need to be pursued on the identification of this effect.

The analysis with SEC in **FIGURE 6** presents a higher molar mass for the aged base oil and aged squalane. This building of oligomers could be observed because of the autoxidation of pure substances including isoalkanes and the associated formation of radicals [15].

FIGURE 7 shows the most important area (2000 to 21,000 g/mol) of the chromatogram of SEC of the aged substances. The biggest molecules could only be measured up to a relative molar mass of 21,000 g/mol because of the calibration standards. Higher molecules could not be measured. For better clarity the fuels in **FIGURE 7** are portrayed with markings (RME: X; HVO: squares; Diesel regenerativ: triangles; Diesel R33: dots). The marks are made at three hundred measuring point intervals as a guide for the eye.

For comparison of base oil with squalane, bigger molecules with the base oil as well as with its mixtures were built. A look at the different fuels, mixtures with RME showed much bigger molecules than mixtures with the other fuels. Because of unsaturated esters in RME and the consequently increased autoxidation reaction oligomers were formed. The formation of almost the same molar masses can be observed for squalane mixtures with HVO, Diesel regenerativ and Diesel R33. The mixtures with base oil and HVO, Diesel regenerativ and Diesel R33 showed a small difference. The smaller the amount of HVO in the mixtures, the bigger the molecules which were built. A reason for this effect are the short isoalkane molecules in HVO which possibly lead to the building of smaller polymers [15, 16].

Like the formation of bigger molecules which were detected with SEC, the measurements of viscosity, **FIGURE 8**, showed the same effect. The viscosity of the base oil mixtures is higher than the squalane mixtures. In comparison of HVO, Diesel regenerativ and Diesel R33, the viscosity of RME mixtures is higher. The mixtures of squalane and HVO, Diesel regenerativ and Diesel R33 shows nearly the same viscosity.

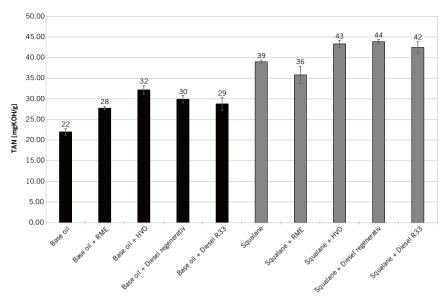


FIGURE 5 Increase of the total acid number of the aged substances (© Coburg University)

CONCLUSION

Up to 20 % fuel in engine oil is realistically reported for diesel fuel powered passenger cars with diesel particulate filter [11]. Under operating conditions, the engine oil degrades and finally has to be changed. For clarification of the aging process in detail and to understand the impact of fuel, neat base oil without additives and squalane as a model substance were used [4, 10]. Squalane represents the isoalkanes in base oil.

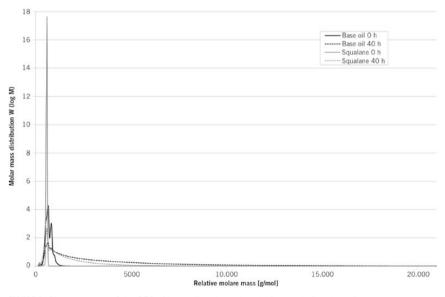


FIGURE 6 Chromatogram of the SEC of base oil and squalane before and after the aging (© Coburg University)

Comparative aging experiments using neat base oil and squalane showed an increased formation of organic acids. A reason for this could be the tendency of isoalkanes taking part in autoxidation reaction [15, 16]. Aged base oil showed a higher formation of undesired macromolecules for base oil than for squalane. Base oil molecules can have more than twice the mass of squalane molecules and so the oligomers from base oil can have a higher mass than those from squalane. This could explain the formation of bigger molecules in unaged base oil than in unaged squalane.

The viscosity showed different effects. Aged squalane obtained a higher viscosity increase than base oil after the aging. The reason for this is currently under investigation.

Additionally four fuels (RME, HVO, Diesel regenerativ and Diesel R33) of 20 % amounts were investigated with regard to their engine oil degradation potency. The result for the formation of acids and alcohols in the RME mixtures were smaller than with HVO, Diesel regenerativ and Diesel R33. These results are a consequence of the evaporation of short-chain and highly volatile compounds which were formed during the aging. With HVO, Diesel regenerativ and Diesel R33 the values of acids and alcohols were in the same range. The viscosity as well as the molecular size showed similar trends.

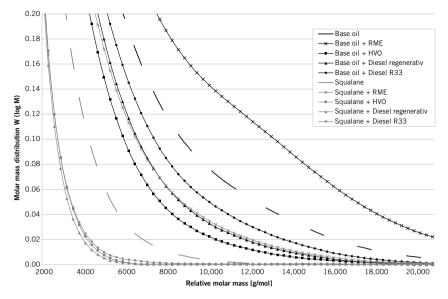


FIGURE 7 Zoom in the most important area of the chromatogram of SEC of the aged substances (© Coburg University)

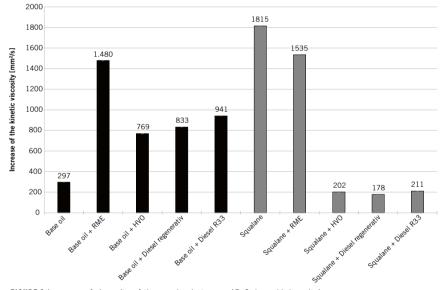


FIGURE 8 Increase of viscosity of the aged substances (© Coburg University)

Finally, it can be stated that diesel fuels with 7% RME content such as Diesel regenerativ and Diesel R33 did not lead to a significantly higher formation of oligomers in base oil or squalane relative to neat HVO.

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THANKS

The authors thankfully acknowledge the funding of the projects Diesel regenerativ and Diesel R33 by the Bavarian State Ministry of the Environment and Public Health and the European Union, funding codes 17029X11 and TEU01EU-62989. Special thanks go to the Union zur Förderung von Oel- und Proteinpflanzen e. V. (UFOP) for financing and support this project.

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AD PRICES Advertising ratecard from October 2015

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PRINT I PROCESSING

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Future Mobility: Physics Will Show the Way

In the world of science, one thing is certain: our world and our lives are described by physics. This opinion is shared by scientists from other disciplines, such as engineering, biology (environment), chemistry (fuels) and even economics (prosperity).

However, physics and its sub-disciplines permit more or less optimised processes and even aberrations. It is a fact that we inevitably consume energy in order to live our lives. Albeit with poor efficiency. But as a result, we are able, for example in the case of mobility, to control large quantities of energy and to perform important work. Therefore, our prosperity today depends essentially on cheap fossil fuels and their economical use.

Mass motorisation and unsustainable urban emissions resulted in today's Euro 6 emissions standards. Thirty years ago, no-one would have considered them to be feasible. And further reductions are also being called for after the forthcoming introduction of RDE legislation. What would then be a sensible target?

The 2015 UN conference on climate change in Paris showed that CO_2 emissions must be drastically reduced if the two-degree climate target is to be met. The transport sector is to expect a 60 % reduction in CO_2 by 2050. And yet, by demanding an end to the use of fossil fuels, environmental politicians and NGOs are setting a nonsensical target. The intention is that no additional fossil-based CO_2 should find its way into the earth's carbon cycle. But even the 2050 targets cannot be met with internal combustion engines and hybridisation. And what does the future hold? EU legislators and NGOs do not believe that the mobility industry and energy providers have the competence to find a solution. In spite of an economically related increase in transport, Brussels focuses on intervention and restrictions.

The solutions it proposes are electric mobility and fuel cell drive systems. However, the carbon footprint must be evaluated from well to wheel and not from tank to wheel. These results would be a sobering wake-up call for politicians. The solution to the dual problem described above may be found in synthetic, carbon-neutral fuels and lubricants. CO₂ recycling (CWtL) can be used to produce carbon-neutral fuels in the form of methane or methanol. OME as an alternative to fossil diesel fuel is already available today from China. Possible sources of CO₂ are coal- and gas-fired power stations and cement factories. Blast furnace gas from steelworks, as a low-cost source of energy and CO_2 , could further reduce the already acceptable price of OME fuel. The FVV has shown that it may even be possible one day to capture CO_2 from the air – but at a higher cost. Such monomolecular C1-OME fuels burn with low emissions in today's diesel engines. And by applying state-of-the-art exhaust aftertreatment technology, it should be possible, in the foreseeable future, to use "sub-zero-emission" vehicles to clean inner-city air. By contrast, electric mobility and the fuel cell will only offer zero emissions. It will be physics that will show the way towards the most sustainable solution.

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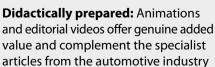
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