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Band 32

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and 13 other authors

# Future biofuel research: Technology and climate protection

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Cuvillier Verlag Göttingen



## Future biofuel research: Technology and climate protection





## UFOP Expert Commission

### "Biofuels & Renewable Resources"

#### Future biofuel research: Technology and climate protection

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## **Bibliographical information held by the German National Library**

The German National Library has listed this book in the Deutsche Nationalbibliografie (German national bibliography); detailed bibliographic information is available online at <http://dnb.d-nb.de>.

1<sup>st</sup> edition - Göttingen: Cuvillier, 2022

© CUVILLIER VERLAG, Göttingen, Germany 2022

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[www.cuvillier.de](http://www.cuvillier.de)

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1<sup>st</sup> edition, 2022

eISBN 978-3-7369-6555-3



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# 1 Introduction

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The combustion of chemicals in engines is much more than a transformation of chemical energy into kinetic energy. Fuel, engine and exhaust gas treatment form a unit with mutual dependencies and optimisation potentials.

While Rudolf Diesel was already using biofuels and vegetable oils in his engines, the breakthrough of biofuels in Germany and in the European Union only occurred at the turn of the last century.

Modern high-tech units today require bespoke fuels, which must also harmonise with exhaust gas treatment and fulfil sustainability criteria.

In Germany, the story of alternative fuels began with the breakthrough of biodiesel around the mid-1900s, which has been endorsed from the beginning by the Union for the Promotion of Oil and Protein Plants (UFOP). Since 2005, UFOP has drawn a portion of its expertise from its Expert Commission "Biotreibstoffe und Nachhaltige Rohstoffe" (Biofuels and Renewable Resources), in which representatives from the motor, mineral oil, biofuel, additive and automotive industries, alongside scientists from universities and research institutions and association representatives, debate the future potentials and challenges for biofuels, as well as discussing strategies and initiating project proposals. When possible, early stage researchers are funded specifically.

Between 2016 and 2018, the future challenges faced by biofuels from an economic and scientific perspective as a pure fuel and a blending component were the focus of intense debate. This paper is the product of those discussions and summarises, from the perspective of the UFOP Expert Commission, the research and action required to ensure research funding for this important economic sector in the coming years, including the acquisition of young scientists.<sup>i</sup>

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<sup>i</sup> The findings of the UFOP Expert Commission are published in reduced form as an international journal article: <https://doi.org/10.1016/j.fuel.2020.117227>



## 2 Motivation and background

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By signing the Paris climate agreement, the states involved agreed to the internationally binding target of limiting the increase in global warming by 2050 to a maximum of two degrees Celsius. The aim should be to limit this increase to a maximum of 1.5 degrees if possible. These objectives mean that the total global "budget" of all greenhouse gases permitted to be emitted into the atmosphere before the deadline is around 750 gigatonnes (for the two-degree target). Currently, the global total of greenhouse gases emitted annually is around 40 gigatonnes. So time is running out. The fundamental goal is to limit the consequences of climate change that are already visible. It is therefore the burden and the particular responsibility of developed countries to speed up this transformation process with ambitious measures and innovative technologies. Considering the global population will likely increase to more than nine billion people by 2050, a key challenge is increased global traffic, which is growing particularly in emerging markets. Climate scientists are sounding the alarm and calling for an urgent transport revolution. At present, transport accounts for more than 14 percent of greenhouse gas emissions globally. In Germany, this figure is even higher at 19 percent, a total of approx. 170.6 million tonnes. According to the International Transport Forum (ITF), CO<sub>2</sub> emissions related to mobility amount to three tonnes per inhabitant in OECD countries. In light of this, the signatory countries of the climate agreement pledged to submit binding national climate action plans by 2019/2020 at the latest. Germany presented its 2050 national climate protection plan at the Climate Change Conference (COP22) in Marrakesh in November 2016. In their coalition agreement, the Federal Government announced that it would finalise the binding sectoral greenhouse gas targets set out in the climate action plan with the climate protection law. In light of these challenges, the natural question is how to design the transformation process, i.e. the changeover to efficient and affordable greenhouse gas-neutral alternative fuels and drives. Politicians and the industries involved are both under intense pressure to act and innovate.

Transition processes, which also affect the usual demand behaviour of consumers as a benchmark for success, are time-consuming and must therefore be organised in a way that is free of ideology and open to new technology with regard to the various challenges in the different action areas. The set deadline of 2050 makes it clear that in order to reach this target, further development of existing technology as well as the testing and use of innovative technology is required for the decarbonisation of global transport. Globally, the combustion engine is and will remain the most important drive in this process. The global process for the defossilisation of fuels, and thus of transportation, begins with biofuels. This process is driven regionally by the potential of resource availability and by legally prescribed national additive specifications. Here, the general principle must be that only greenhouse gas-optimised and certified sustainable biomass raw materials or biofuels are used. In principle, these requirements stipulate the European Renewable Energy Directive (2009/28/EC) and the strengthened subsequent directive (RED II: 2018/2001/EC) as prerequisites for



access to the market in the EU. Therefore, in the case of third-country imports (biomass raw materials or biofuels), also from outside the EU, these statutory requirements must not only be implemented but also ambitiously further developed and monitored in unison.

Above all, the creation of diesel fuels with different biodiesel proportions or biocomponents (Hydrotreated Vegetable Oil, HVO) and raw material provenances is becoming one of the greatest challenges for the petroleum and vehicle industry from a global point of view. Due to ever-increasing and dated legal emissions requirements, engine development and increasingly more complex systems for exhaust gas treatment are the main trendsetters here. At the same time, reduced-consumption, climate-friendly engines are being demanded, not only by statutory requirements, but also by customers.

With its 2050 national climate protection plan, Germany has concretely specified the greenhouse gas reduction target for 2030 in the transport sector. The sector's targets have been legally and bindingly enshrined as a result of coalition negotiations. With the CO<sub>2</sub> limit values for new vehicles prescribed at EU level from 2021 (passenger vehicles: 95 g CO<sub>2</sub>/km and light commercial vehicles: 147 g CO<sub>2</sub>/km), in combination with further (already dated) decreases, the introduction of electrification via hybridisation and purely electric drives is a given. At EU level, a 15% reduction in CO<sub>2</sub> by 2025 and a 30% reduction by 2030 were agreed for heavy commercial vehicles. The reduction percentage refers to CO<sub>2</sub> emissions in 2019. Failure to reach these targets will otherwise lead to financial penalties to be paid to the EU Commission, amounting to billions which will thus no longer be available on a national level for necessary investments. Not least this threat of penalties drives innovation developments in an economic sector which is of such importance for the German national economy.

In order to reach the maximum achievable CO<sub>2</sub> savings potential by 2030, a responsible and proactive environmental policy must be able to differentiate between the technological challenges and what is feasible within the time frame.

The diesel scandal has wrongfully discredited combustion engines as technology carriers. A blend of publicly driven discussion about manipulated exhaust gas treatment systems, pollution in inner cities, driving bans etc. lead to the key question about the outlook for combustion engines and even to discussions about banning them.

The fact that legal emissions requirements must be fulfilled remains undisputed. Therefore, the future of combustion engines will be determined by which processes are needed to make the engines more efficient, even lower in emissions and, depending on the development of alternative fuels, as greenhouse-gas neutral as possible. This is where the potential of mutual optimisation of engine, fuel and exhaust gas treatment assumes an important role. The variety of components needed for this means it will only be successful as part of a wide interdisciplinary approach.



Inner city emission loads must be evaluated against the background of their health effects, but also especially with respect to the different measuring scenarios in Europe. Ideological or technophobic approaches should be rejected. The protection of health and of the climate must be evaluated in view of resource efficiency, workplace safety and social aspects. Reliable engine technologies and climate-efficient fuels contribute to this significantly.

Premature vehicle bans may be politically opportune in certain circles. For many directly and indirectly affected parties (commuters, companies, customers), the consequences cannot be foreseen.

In any case, subjective criticism of the future viability of combustion engines means that young people do not want to study this comprehensive subject. This means that the industry, in the medium term, is lacking junior engineers, who are desperately needed to safeguard the future of Germany as an industry hub.

The authors of this paper are motivated by the question of the feasibility of the combustion engine in the future with the aid of sustainable fuels. In the following, the focus will be on biofuels and identifying the future challenges that exist for them, so that they can contribute to sustainable mobility.

## 2.1 Availability of fossil resources

The Federal Institute for Geosciences and Natural Resources (Bundesanstalt für Geowissenschaften und Rohstoffe - BGR) has formulated the following core statements, among other things, regarding the fossil resources crude oil and natural gas, which are important for fuels:<sup>[1]</sup>

- At approximately 31%, crude oil remains the most significant energy source worldwide for the foreseeable future (Figure 1: Energy consumption, production).
- Supply is considered secure even with moderately increasing demand, reserves and resources are increasing due to non-conventional petroleum (shale oil and heavy oil reserves).
- The conventional reserves important for mineral oil supply remain almost constant.
- Newly-found conventional crude oil deposits are declining significantly (Figure 2).
- A functioning global crude oil market is essential in ensuring supply.
- Natural gas is the third most important energy source.
- Natural gas will be available in sufficient quantities for many decades, even with the increased demand expected in the medium term.
- Europe is one of the largest importers of crude oil and natural gas.

An insufficient supply of conventional fossil fuels is not predicted from a geological perspective and is therefore not a decisive reason to develop alternative fuels. To this end, the country-specific, European and international CO<sub>2</sub> targets, the required reduction in pollution and a lower dependency on imports are crucial.

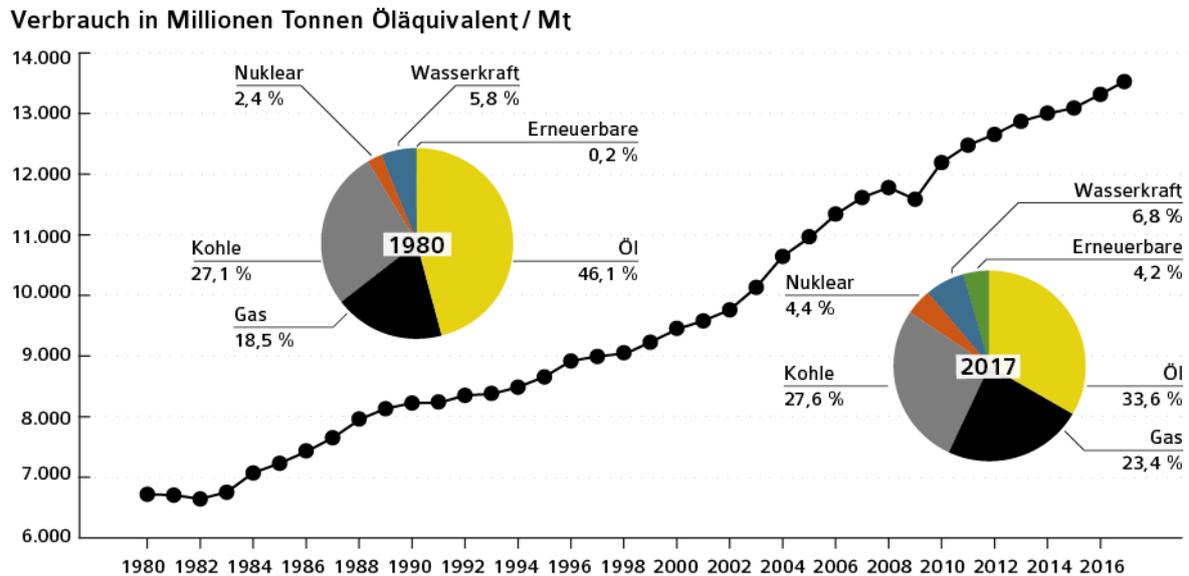


Figure 1: International primary energy consumption from 1980 to 2017 and proportion of all energy and energy sources consumed in 1980 and 2017.<sup>[2][3]</sup>

Renewable energy reaches a consumption percentage of almost 18%, with the classic renewable energy sources such as biogenic energy sources and hydropower dominating in the sector at over 90%. Wind and solar energy meet just under 10% of demand. Biofuels for the transport sector contribute to global energy consumption only slightly at just 0.8%. Production has, however, quadrupled since 2004 from 30 billion litres to 135 litres and is continuing to increase.<sup>[1]</sup>

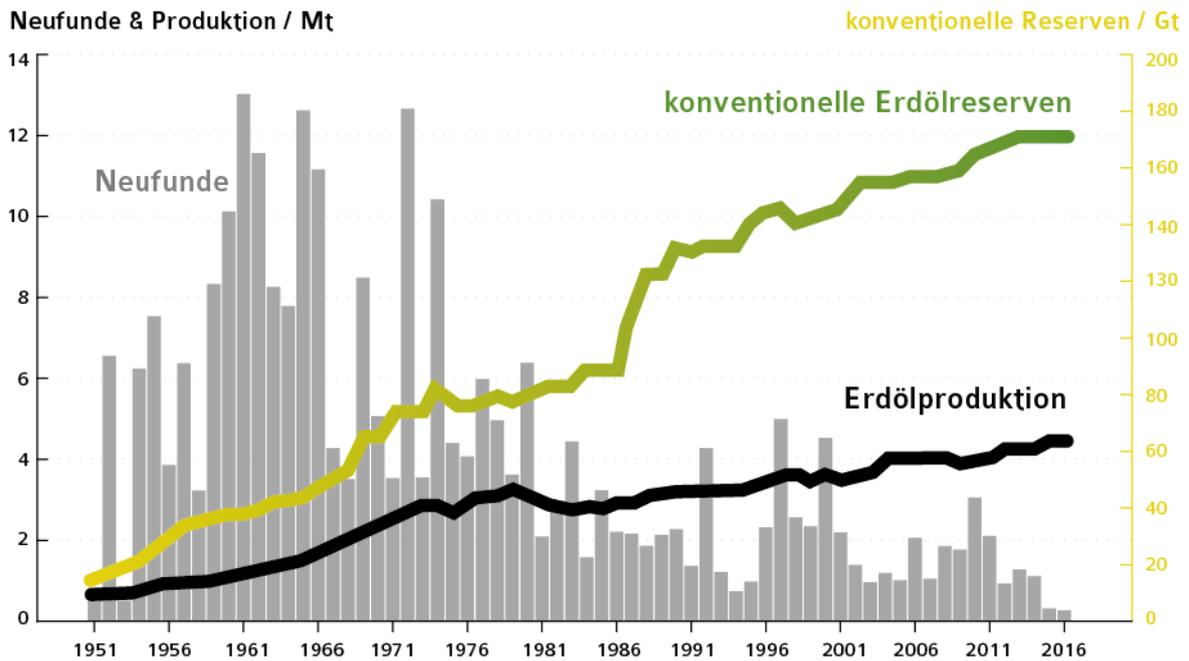


Figure 2: New finds, oil extraction and reserves. [1]

## 2.2 Expected development of mobility

The number of vehicles worldwide (passenger vehicles and light commercial vehicles [ $<6$  t]) will double in the next 20 to 25 years from around 1 billion to 2 billion. In terms of global production, the proportion of clean vehicles or vehicles predominantly powered by combustion engines (48V hybrid) will be approx. 80% in 2030; in total, combustion engines will still be part of approx. 90% of drives, Figure 3. This growth will take place predominantly in developing and emerging countries. Electrically powered vehicles, including hybrids, will make up a proportion of around 15% of the total number of vehicles globally in 2040.

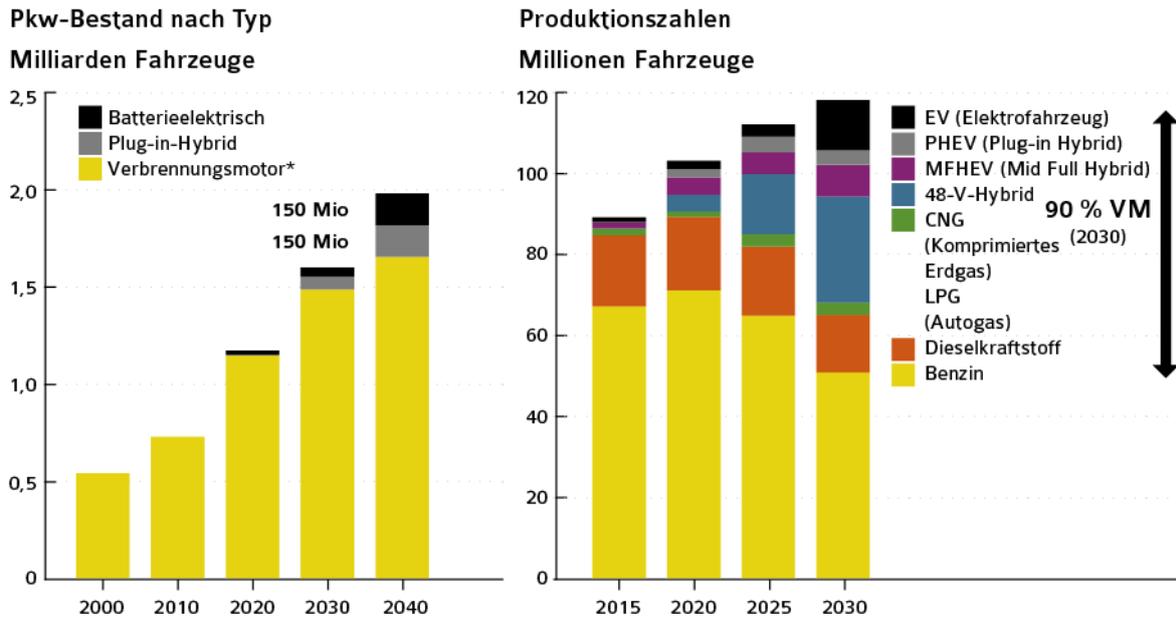


Figure 3: Number of vehicles worldwide and vehicle production (passenger vehicle and LCV).<sup>[4][5]</sup>

Freight transportation is increasing dramatically worldwide. In Germany, an increase of 30-35% is expected between 2000 and 2040, mainly on the roads, see Figure 4.

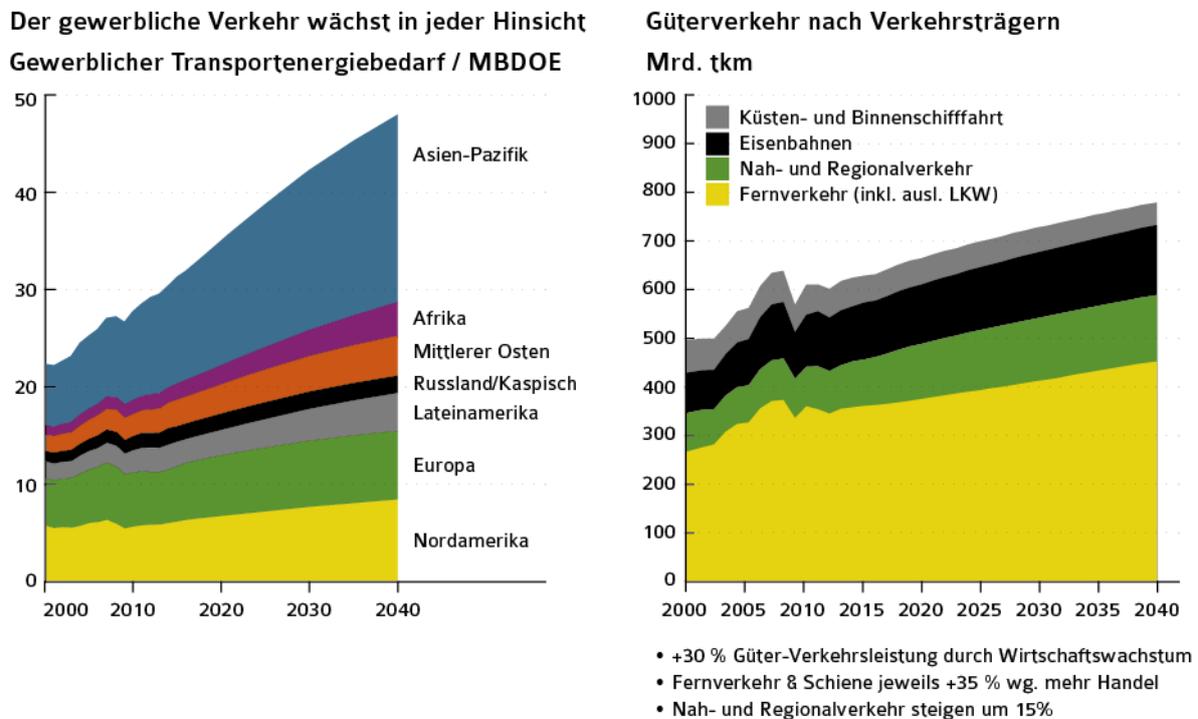


Figure 4: Growth of freight transportation internationally and in Germany.<sup>[6][7]</sup>

Therefore, the energy required for all transportation services increases overall. This is especially dramatic for commercial freight transportation via roads but also in the sea, rail and air transport sectors.

According to this prognosis, 85% of the fuel used for this purpose is still crude oil. This is, however, incompatible with the set CO<sub>2</sub> targets (Figure 5, right).

From this data we can see that with electromobility, even if the electrical energy required is obtained from renewable sources, CO<sub>2</sub>-neutral mobility is not achievable by 2050.

In principle, each drive concept must be evaluated in terms of its climate efficiency from production through to operation and recycling as part of a comprehensive Life Cycle Assessment. The current exclusive CO<sub>2</sub> assessment of the operating phase is not sufficient for a comparison of different concepts.

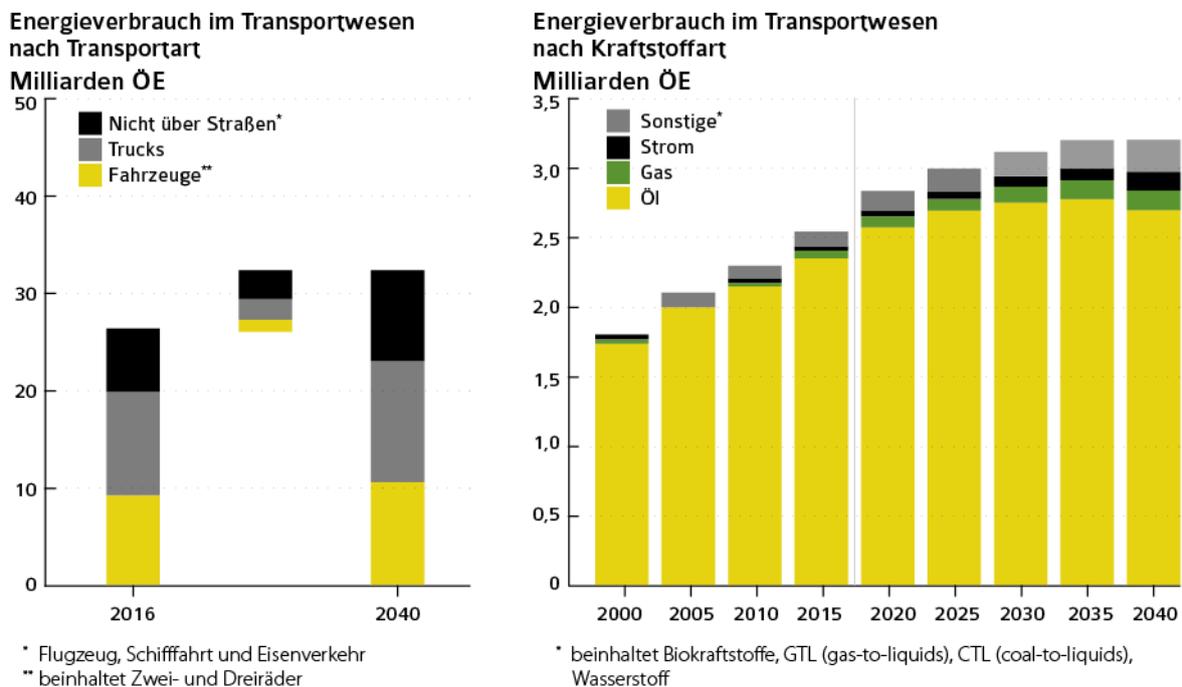


Figure 5: Energy consumption and energy mix for passenger and freight transportation.<sup>[4][6]</sup>

## 2.3 Drives and fuels of the future

The move to electric drives is – depending on the need for mobility and the local air quality – a necessity for a pollution-free environment. But, the use of the internal combustion engine can also be justified. There is no “either/or”, but rather only an optimal drive that is adapted to requirements and regional circumstances.

While an infrastructure for battery charging is, to some extent, economically and logistically conceivable in cities and heavily-populated regions such as Europe, this is



still far from possible in emerging and developing countries. Here, a readily-available, easy-to-use, economical and low-emission fuel must ensure mobility for people and goods, also in the long term. Initially, these will not only be crude oil-based fuels – petrol, diesel fuel and natural gas (CNG, LNG) – but also biogenic liquid and gaseous fuels of the so-called first and second generation. In the medium term, it is likely that new synthetic fuels and so-called e-fuels will also come onto the market.

Due to the long-term availability of a large number of these fuels, infrastructure conditions and, above all, economic aspects, the combustion engine will ensure mobility worldwide for decades to come. Pollutant emissions, specifically nitrogen oxides, can today already be reduced to extremely low levels in petrol and diesel engines. The problem of particle emissions has been solved with the widespread introduction of particulate filters in diesel drives around 2003/2004 and the upcoming implementation of these in petrol engines with direct injection.

Due to the strong growth in mobility, in the next five to ten years, more combustion engines will be produced per year globally than ever before.

Assuming that the electrification of drives overtakes the hybrid drive, passenger vehicles with petrol engines will be “electrified” first. Diesel engines will continue to dominate the freight transportation market segment (truck, sea, rail) and the off-road sector (construction and agriculture machinery and industrial engines), but will be withdrawn from the small and medium-sized passenger vehicle sector for cost reasons. In principle, however, the drive concept will be orientated more than ever towards mobility needs.

Wherever heavy goods are to be transported long distances and the operating costs exceed the investment costs, the diesel motor will still be the first choice. It is the best compromise in terms of cost, CO<sub>2</sub>, durability, flexibility, availability and pollution.

## 3 Biofuels

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Regenerative fuels are commonly referred to as being of different “generations” (fuels of the first and second generations) and certain fuels are considered “advanced”. When assigning fuels to generations, it is often assumed that subsequent generations are superior to the previous generations and are therefore “more advanced”. As no universal definition for the terminology exists, different evaluation criteria, which ultimately produce partly varying classification results, are often used when classifying fuels.

Examples of the evaluation criteria used include:

- The sustainability and ethical safety of raw materials used during fuel extraction (food production competition, spatial efficiency, cultivated biomass versus residual material or excess electricity, direct and indirect land use changes, greenhouse gas emissions, etc.)
- Specific fuel properties (e.g. custom synthetic fuels for innovative combustion processes)

The umbrella of conventional biofuels, i.e. first generation biofuels, encompasses cultivated biomass-based fuels such as vegetable oils, biodiesel from vegetable oils, hydrogenated vegetable oils and bioethanols, which are in competition with food and fodder production. Biodiesel or fatty acid methyl ester (FAME) is produced from the corresponding vegetable oil by transesterification with methanol. Rapeseed oil methyl ester (RME), soya oil methyl ester (SME) and palm oil methyl ester (PME), for example, are formed in this process. Glycerine occurs as a by-product of this process. Hydrogenated vegetable oils (HVO) are produced by hydrogenating vegetable oils with hydrogen, and propane (bioLPG) is also produced. Bioethanol is obtained from raw materials containing starch or sugar such as wheat, corn, sugar beet or sugar cane via a fermentation process.

Advanced biofuels are split into three sub-groups. Biofuels from waste and residual materials, such as biodiesel from used cooking oils (UCOME) or animal fats (TME) are already used to a great extent in Germany and Europe.<sup>[8]</sup>

These also include bioethanols from lignocellulose as well as hydrogenated used cooking oils and hydrogenated free fatty acids (HFFA). Biomethane extracted during anaerobic decomposition of manure, straw and residual materials also falls into this category.

The second group of advanced biofuels encompasses all synthetically produced fuels. This category predominantly includes fuels which are produced using the Fischer-Tropsch process. In a first step, synthesis gas, which then reacts further to paraffinic hydrocarbons with a defined chain length, is produced from a carbonaceous raw material. Alongside coal and natural gas, among others, biomass, agricultural waste



and wood can be used as raw materials. The resulting fuels are predominantly labelled as Biomass-to-Liquid (BtL) and (Bio)Gas-to-Liquid (GtL) or marked with the generic name XtL fuels or Fischer-Tropsch fuels. Fischer-Tropsch fuels (FT fuels) are currently mainly implemented as so-called drop-in fuels for diesel fuels or kerosene, although use as petrol is also possible in principle. As well as these FT fuels, so-called e-fuels also belong to the group of synthetically produced fuels. Carbon dioxide and hydrogen obtained from regenerative electricity are used in the production of e-fuels, in order to synthesise gaseous or liquid combustibles. The process is correspondingly called Power-to-Gas (PtG) or Power-to-Liquid (PtL), or PtX in general. Oxygenous fuels such as dimethyl ether (DME) and polyoxymethylene ethers (OME) are also synthesised in this way. In these fuels, the carbon chain is interrupted by oxygen atoms.

The third group encompasses biofuels obtained from non-agricultural, biological resources, which are also marked as third generation fuels. Biokerosene, biogas and biodiesel from algae in particular, which, depending on the definition, also count as second generation fuels, must be named here.

Despite the classification detailed above, biofuels of all generations exhibit significant commonalities. All biofuels must meet strict sustainability criteria in order to be recognised and used as biofuels. This has had the effect, among others, that not only biofuels themselves must be certified, but also the raw materials used for the biofuels. The potential of greenhouse gas savings has also more than doubled in recent years to over 80%, as measured by the statutory minimum obligation (35%, Renewable Energy Directive 2009/28/EC) (See BLE Evaluation and Progress Report 2019<sup>9</sup>). Special attention is also paid to the fact that modern biofuels can be used in existing applications or with only slight adjustments. This shortens the development time and the financial expense for the use of biofuels with high greenhouse gas savings in existing systems. In order to guarantee safe use, all biofuels must meet the high quality requirements of the fuel industry and of users.

In order to be able to guarantee the quality and operational capability of biofuels and fuel mixtures, requirements and properties are determined by standardisation. The parameters and limit values for this are based on scientific results as well as field experience and observations. The standards are usually developed at a European level as part of a multi-layered process with consensual integration of all affected parties and are subsequently translated into national standards or legislation by the member states.

The most significant standards for the fuel sector are currently EN 590 for the description of test methods and requirements for diesel fuels and EN 228 for the description of test methods and requirements of petrol.

Since the initial introduction of EN 590 in Germany in 1993, the standard has been subject to multiple changes, such as reduction in sulphur content or the introduction of biofuel components. Currently, EN 590 permits an addition of maximum 7% (V/V) FAME, as well as, under compliance with the requirements of the standard, the addition



of further (non petroleum-based) paraffinic hydrocarbons from GtL or BtL processes and HVO in any quantity. A limiting factor here is the lower concentration limit value, so that approx. 26% (V/V) paraffinic diesel fuel (HVO) and 7% (V/V) biodiesel can be mixed with fossil diesel within the framework of EN 590. A fuel with this composition was developed and tested under the name "Diesel R33" and its use would already be possible extensively today.

The biofuels used for admixture are again subject to their own requirements standards. EN 14214 specifies the properties and test methods for FAME (biodiesel) as a pure fuel and a blending component. Due to varying requirements for higher FAME-diesel fuel blends, the specifications for B10 (EN 16734 - Automotive diesel fuel with a proportion of maximum 10% (V/V) FAME) and B20/B30 (EN 16703 - Automotive diesel fuel with a proportion of maximum 20% (V/V) or 30% (V/V) FAME) are recorded in their own standards. With the revision of ISO 8217, FAME may also be implemented in the ship fuel sector, in the so-called DF grades up to a maximum of 7% (V/V).

The requirements for all paraffinic fuels produced by synthesis or hydrogenation processes (BtL, GtL, HEFA) and used as diesel fuels are defined in EN 15940. Paraffinic fuels are, however, most interesting because of their use as kerosene, since other biofuels, such as biodiesel and bioethanols, cannot be used in this way. Paraffinic fuels (HEFA) and FT fuels are already permitted to be used as aircraft fuel according to ASTM D165 and Def Stan 91-91.<sup>[10]</sup>

Biogenic components are also permitted in the heating oil sector. DIN SPEC 51603-6 describes the corresponding requirements for these fuels. As soon as new fuels and biofuels, such as oxymethylene ether or pyrolysis oils, are available, these are checked in terms of their technical and safe applicability. In the second step, the limits and parameters necessary for the technical safety of the application must be specified. Efforts are currently being made to describe OME and pyrolysis oils by way of a requirements standard.

EN 228 specifies similar conditions in the petroleum sector. However, the resulting petrol is classified by octane number here. Several paraffinic fuels (XtL and PtX), as well as different oxygenates (ethanol, ETBE, MTBE, methanol etc.), are suitable as biogenic fuels. The admixture of bioethanols is of greater importance for petroleum fuels. Blends of petrol with a maximum of 5% (V/V) (E5) and a maximum of 10% (V/V) (E10) bioethics are covered by EN 228. EN 51625 (EN 15293 in future) describes the standard requirements of an E85 fuel with a particularly high ethanol content (max. 85% (V/V) ethanol). The ethanol used is again described in EN 15376.

In the agricultural sphere, steps are being made towards self-generated energy supply for vehicles using vegetable oil fuels, which the industry can generate itself and which are especially suitable for use in non-sealed areas, in terms of soil and water protection. Vegetable oil can be used in engines which are suitable for vegetable oils. In Germany, DIN 51605 and DIN 51623 dictate the requirements for vegetable oil fuel, and the requirements for rapeseed oil fuel for use in the corresponding engines are described in DIN 51605.



Hydrogen is not only used as fuel, but is also converted into electrical energy in vehicles using fuel cell technology. Therefore, for standardisation, there is a community body of CEN (European Committee for Standardization) and CENELEC (European Committee for Electrotechnical Standardization) which deals with these characteristics and requirements.

The standards for various fuels and biofuels generate a framework which guarantees the quality and safety of these in accordance with the current state of the art (Table 1). The standards also simultaneously describe the existing technical possibilities for the use of biofuels. An implementation of this operational capability is governed by corresponding political and economic framework conditions.

Further biogenic fuel pathways are possible in principle, although some of these are grouped under the cited standards, such as DIN EN 15940 (for BtL) or EN 590 (R33).



Table 1: Standardisation status. [11]

Standard Number	Title	Edition
DIN 51605	Fuels for vegetable oil compatible combustion engines - Fuel from rapeseed oil - Requirements and test methods	01-2016
DIN 51623	Fuels for vegetable oil compatible combustion engines - Fuel from vegetable oil - Requirements and test methods	12-2015
DIN 51625	Automotive fuels - Ethanol Fuel (E85) - Requirements and test methods	08-2008
DIN SPEC 51603-6	Liquid fuels - Fuel oils - Part 6: Fuel oil EL A, Minimum requirements	03-2017
DIN EN 228	Automotive fuels - Unleaded petrol - Requirements and test methods (to E10)	08-2017
DIN EN 589	Automotive fuels - LPG - Requirements and test methods	03-2019
DIN EN 590	Automotive fuels - Diesel - Requirements and test methods (to B7)	10-2017
DIN EN 15376	Automotive fuels - Ethanol as a blending component for petrol - Requirements and test methods	12-2014
DIN EN 14214	Liquid petroleum products - Fatty acid methyl esters (FAME) for use in diesel engines and heating applications - Requirements and test methods	06-2014
DIN EN 15940	Automotive fuels - Paraffinic diesel fuel from synthesis or hydrotreatment (HVO, GtL, CtL, BtL, PtL)	08-2018
DIN EN 16709	Automotive fuels - High FAME diesel fuel (B20 and B30) - Requirements and test methods	02-2019
DIN EN 16734	Automotive fuels - Automotive B10 diesel fuel - Requirements and test methods	02-2019
DIN EN 15293	Automotive fuels - Automotive ethanol (E85) fuel - Requirements and test methods	10-2018
DIN EN 16723-2	Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network - Part 2: Automotive fuels specification	10-2017
DIN ISO 8217	Petroleum products - Fuels (class F) - Requirements for marine fuels	10-2018



## 3.1 Overview of selected biofuels

### 3.1.1 Biodiesel - Fatty acid methyl ester (FAME)

As it is relatively easy to obtain and is highly compatible with traditional diesel fuels (DF), biodiesel from rapeseed is the biofuel that has been in use in the European Union for the longest time.

Biodiesels are simple conversion products of natural fats and oils (triglycerides = esters from fatty acids with the trivalent alcohol glycerine), which are preferably derived from oil plants from temperate climates, whose main component in the case of rapeseed oil is oleic acid. The glycerine is replaced in what is called a transesterification reaction by the simple alcohol methanol, so that a fat molecule yields three molecules of fatty acid methyl ester (FAME); glycerine is released in this reaction.

Biodiesel is similar to diesel fuel in terms of its resulting properties and is suited for use as a blending component with diesel fuel due to its ability to be mixed as required. Standardised in EN DIN 14214, a consistently good quality is guaranteed for this alternative fuel.

In Central Europe, rapeseed naturally provides the basis for transesterification (RME). However, sunflower oil, soya oil, palm oil (imports) and used cooking oil (designated as UCOME = Used Cooking Oil Methyl Ester) are also used – partly as mixtures – in order to comply with the limits of the standard.

According to DIN EN 14214, biodiesel is also used as a “B100” pure fuel and as a “Bnn” blending component in nn% admixture to diesel fuel according to DIN EN 590. In this case, FAME, as a blending component, must also comply with DIN EN 14214.

In most cases, fossil methanol is used for the transesterification of fats when producing biodiesel. If the proportion of methanol which is derived from fossil sources is also considered, a renewable proportion of approx. 95% remains. In the literature, <sup>[12][13][14][15][16][17]</sup> there are a number of studies which account for all the processing steps in the production of biodiesel in terms of CO<sub>2</sub>. The CO<sub>2</sub> savings potential thus amounts to between 50% and 80%. When producing used cooking oil methyl ester, even higher reduction potentials can be achieved.<sup>[18]</sup>



### 3.1.2 Oxymethylene dimethyl ether (OME)

(Poly) Oxymethylene dimethyl ether are oxygenous oligomers with the chemical structure  $\text{H}_3\text{C-O}-(\text{CH}_2\text{O})_n-\text{CH}_3$ . Components suitable for diesel fuels are the result with repetition factors  $n$  between 3 and 5. OME can, depending on its proportion in the diesel fuel, contribute to the reduction of soot emissions from diesel motors.

OME can be produced using the key substance methanol both petrochemically from synthesis gas, as well as from renewable raw materials via a methanol synthesis. For example, methanol can be produced from methane by a process of enzyme catalysation with methanotrophic bacteria. Furthermore, methanol can be produced using carbon dioxide and water by supplying an electric current as a reversal of the reaction in fuel cells. This production method is described as an example of “Power-to-Liquid”, with which surplus electricity generated by regenerative energy sources (solar, wind) can be used or stored. The energy balance of this process is, however, still not attractive. Perspectively, some studies view the costs for the production of OME as potentially comparable with those involved in the production of diesel fuel.

The influence of OME, particularly blends of OME and conventional diesel fuels, on lubrication has not yet been investigated in detail. The key physical data of OME suggests that the known risk of biodiesel, i.e. the permanent dilution of the engine oil through OME accumulation, should be considered.

### 3.1.3 Hydrogenated Vegetable Oil (HVO)

Fully saturated, broadly paraffinic hydrocarbons can be produced from vegetable oils using full hydrogenation and implementation of special catalysts (hydrotreating with metal catalysts at temperatures around  $400^\circ\text{C}$  and hydrogen pressure up to 150 bar). Their properties are similar to those of petrochemical hydrocarbons. Their evaporation behaviour is particularly comparable. Thus, there are hardly any or only insignificant influences on the engine oil, its functions and its life cycle.

The most famous technology was developed by the Finnish company Neste Oil (NExBTL). Palm oil or residual materials are preferable as feedstock here.

### 3.1.4 Clean vegetable oils

Due to their high biodegradability and low ecotoxicity, as fuels, pure vegetable oils can be viewed as a niche market in environmentally-sensitive sectors, such as the agriculture and forestry industries. Due to the excellent dedication of TFZ Bavaria <sup>[19]</sup>, ASG, Deutz AG, John Deere etc., in 2006, a major step was taken to further expand

on this alternative by creating a pre-standard “Fuels for vegetable oil compatible combustion engines - Fuel from rapeseed oil - Requirements and test methods” (DIN 51605).

### 3.2 Inventory

In 2018, both the production and the consumption of biofuels (ethanol and biodiesel) are not only supported by many countries, but are also legally required by mandates for admixture quotas and partly by tax incentives. An increase in mandates can be seen in biomass-producing countries in particular (Table 2). Especially active here are North and South America, large parts of Asia and also Australia and Europe, though the strategic focus can vary significantly. Various countries in Africa have also already implemented corresponding measures. In contrast to this trend, Russia, a country with a great deal of agricultural land and one of the largest producers of fossil fuels and combustibles, is currently showing only a marginal interest in mandates and can therefore be considered negligible in this regard (Figure 6, Table 3). <sup>[20][21]</sup>

*Table 2: Biodiesel admixture mandates.*

Biofuel mandates %	2018	2019
Indonesia	20	20 (30 is being assessed)
Malaysia	7	10
Argentina	8	12
Brazil	8	10
Thailand	7	10
USA RFS programme	5.8 million t	6.3 million t (2017: 6.7 million t)

Sources: F.O. Licht, Biofuel Digest, FAS, Platts

## Biokraftstoffmandate (global – Stand 2018)

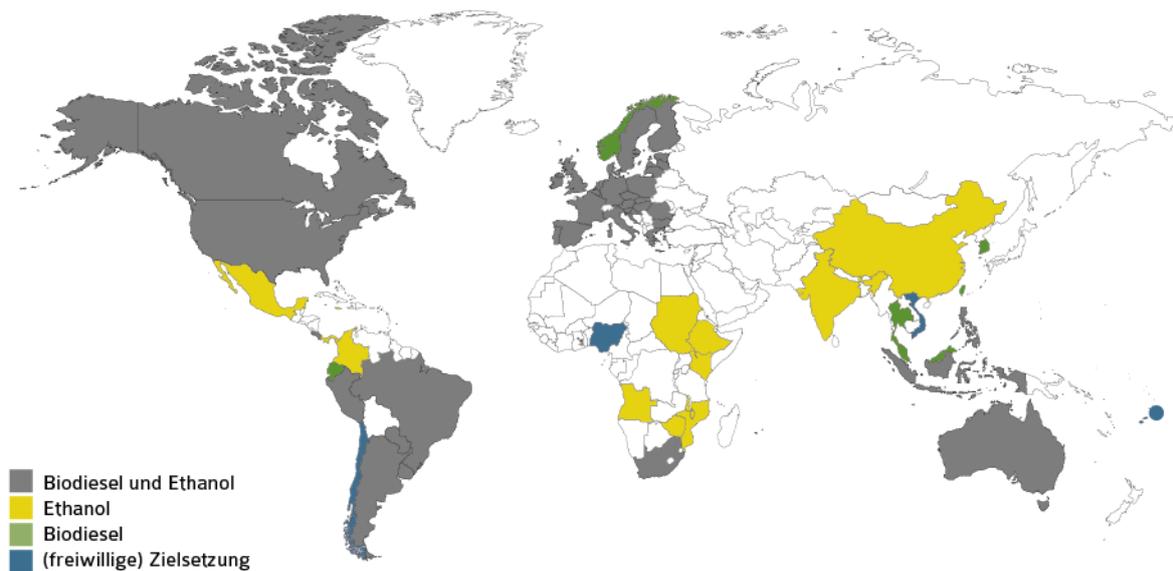


Figure 6: *Biofuel mandates (worldwide – as of 2018).*<sup>[20][21]</sup>

At around 6% in Germany and the European Union, biofuels have been the only comprehensively notable alternative to fossil fuels to date. Access to the market and the maximum admixture level, as well as the renewable energy mix (funding of e-mobility), are regulated by law very differently among the EU member states and account for the greatest differences between the 28 EU member countries. This diversification is the consequence of national authorisations to implement this directive as part of the compromise negotiations of the EU's Energy Council, i.e. between the member states and the standpoint of the European Parliament (co-decision procedure). This means that the proportion of renewable energy in transport in Sweden and Finland is more than 20 percent, whereas in countries such as Spain or Greece this proportion is only 2 percent (2015). The use of biodiesel and bioethanols is "capped" by the respective fuel standards for B7, E5, and E10, while a B30 standard has been specially designed for the use of these fuels in closed commercial vehicle fleets. Additionally, releases for B100 for Euro VI vehicles are individually granted if the fleet operator makes this certified release a condition of purchase. This means that even the most modern vehicle engines can also be operated using B100, under observation of certain maintenance instructions (decreased engine oil replacement intervals etc.). Further extensive data about the German and European market can be found in the report from the Deutsches Biomasseforschungszentrum (German Biomass Research Centre - DBFZ), "Monitoring Erneuerbare Energien im Verkehr" (Monitoring Renewable Energies in Transport)," 1<sup>st</sup> edition.<sup>[22]</sup>

In conjunction with an increasingly global trend, where the raw materials mix of field crops used for the production of biofuels is gradually changed to residual and waste materials, the new edition of the renewable energy directive (2018/2001/EC)



prescribes mandatory minimum quotas in the EU for biofuels made from residual materials e.g. straw. This means that their share of total energy consumption in transport must reach a minimum of 3.5% by 2030. However, this quota can be reached through double allocations for energy content. As a consequence, the physical demand of the biofuel halves. With this measure, the target of a 14% proportion of renewable energies specified in this directive is only virtually achieved. For climate protection, however, a considerably lower contribution is achieved. In the absence of existing production capacities for biofuels from residual materials, it is clear that multiple allocations should trigger investments. In the case that this obligatory quota, which must be demonstrated by the mineral oil companies concerned, is not complied with, corresponding severe fines are a possibility.

As the second largest ethanol producer and third largest biodiesel producer, Brazil has legally stipulated (RenovaBio Programme – 2016) that the mandate for B9, valid since March 2018, will be increased again in March 2019 to B10 and should be retained until 2025. A legally prescribed test phase for B15 (2015 - 2018) should show whether the mandate can be increased further in the future. For ethanol, the mandate for E27 will remain unchanged until at least 2026. Biodiesel production has increased continually in recent years and is based primarily on soya oil (70%) and waste animal fats (16%). For ethanol, the beginnings of production using residual materials have become apparent since 2015. The state also provides tax breaks, which do make palm and castor oil worse options, but still better than fossil fuel alternatives.<sup>[23]</sup>

For China, ranking in ninth place as biodiesel manufacturers and fourth place as ethanol manufacturers, there are major differences between the different provinces. In principle, however, there is a national mandate for E10 until 2020. In contrast, biodiesel has only played a minor role thus far. China is also setting itself major goals with its “13th Five-Year Plan (FYP) (2016)”. The production of ethanol and biodiesel is to be significantly increased again by 2020. There are also efforts to raise waste material-based ethanol production to a commercial level by 2025. The current production share fluctuates around 10%. Only used cooking oil (UCO) is used for FAME production.<sup>[24]</sup>

Table 3: Ethanol and biofuel mandates (worldwide - as of 2018).<sup>[20][21]</sup>

Country	Ethanol	Biodiesel	Country	Ethanol	Biodiesel
Angola	10.0	-	Thailand	-	7.0
Ethiopia	5.0	-	EU	5.0 - 10.0	7.0
Kenya *	10.0	-	Norway	-	3.5 / 5.0 / 7.0
Malawi	10.0	-	Canada *	5.0 - 8.5	2.0 - 4.0
Mozambique	10.0	-	Costa Rica	7.0	20.0
Nigeria **	10.0	-	Jamaica	10.0	-
South Africa	2.0	5.0	Mexico	5.8	-
Sudan	5.0	-	Panama	10.0	-
Zimbabwe	5.0 - 15.0	-	USA *	See Fig. 8	See Fig. 8
Australia *	3.0 / 7.0 / 10.0	- / 2	Argentina	12.0	10.0
China *	10.0	-	Brazil	27.0	9.0
Fiji **	10.0	5.0	Chile **	5.0	5.0
India	5.0	-	Colombia *	6 / 8	8 - 9
Indonesia	3.0	20.0	Ecuador	-	5.0
Malaysia	-	7.0	Paraguay	25.0	1.0
Philippines	10.0	2.0	Peru	7.8	2.0
South Korea	-	2.5	Uruguay	9.0 - 10.0	6.0
Republic of China	-	1.0			

\*Dependent on state/province/region    \*\* (voluntary) targets

The USA is the largest ethanol producer and the second largest biodiesel producer. As regulations are greatly dependent on the individual states, no coherent national data is available. E85 and/or E85 and E15 are common in several states. In biodiesel fuel mixtures, almost the entire spectrum of possible admixtures can be found (Figure 7,8).

## USA – Bundesstaaten (E15 und E85)

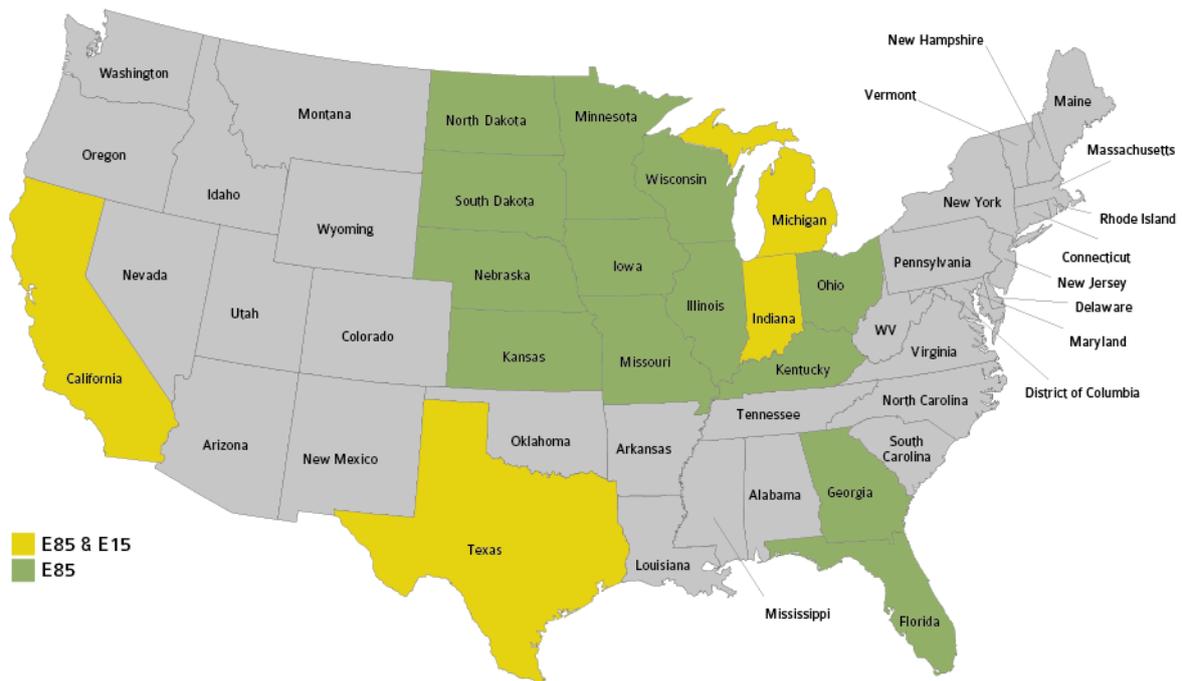


Figure 7: USA – States (E15 and E85).<sup>[20][21]</sup>

## USA – Bundesstaaten (Kraftstoffmischungen mit Biodieselanteil)

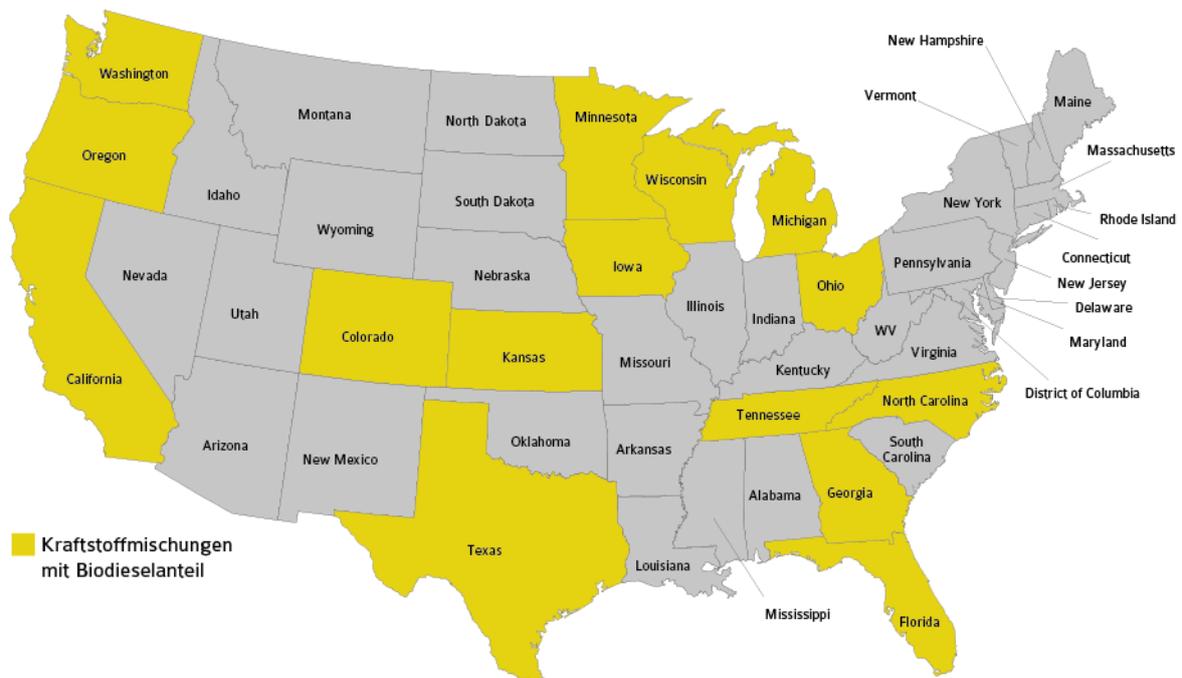


Figure 8: USA – States (Fuel mixtures with proportion of biodiesel).<sup>[20][21]</sup>



### 3.3 Sustainability and acceptance

Biofuels are traded globally and are the subject of an acceptance and availability discussion. In light of this, it should essentially be welcomed that the EU, with the Renewable Energy Directive [2009/28/EC] and the subsequent directive [2018/2001/EC], has introduced and tightened minimum requirements for sustainability, dated acreage origins and greenhouse gas reductions (at least 50%) as a prerequisite for access to the market. The subsequent directive also includes synthetic Fischer-Tropsch fuels (e-fuels). These statutory regulations are the driving force for an increase in the efficiency of transport technology that is open to new technology and driven by competition, but also for increased sustainability requirements, independent of biomass usage, as part of the bioeconomy and defossilisation strategy for the material use of sustainable raw materials. At the same time, the transparent fulfilment of these criteria is a prerequisite for public and political acceptance. Due to its diversity, sustainably produced biomass is one of if not the most important source of energy and revenue in many countries across the world. Today, this resource is “controllable” thanks to satellite technology. Sustainable production of these resources (particularly cultivated biomass) for their later use as alternative fuels is necessary because this biomass potential can be supplied to the food market in a timely manner depending on the supply situation, meaning it acts as a "supply buffer" in the event of increasing food demand. However, the international agriculture commodity markets have determined structural supply surpluses and thus pricing pressure for the agricultural sector for years. This essentially explains the steadily increasing biofuel mandates outside the European Union. An equally challenging discussion with sustainability requirements at its centre about power generation from wind power and raw material extraction for battery production has also long been under way.

## 4 Biofuel mix of the future

In autumn 2017 and into the first half of 2018, numerous studies were published on energy provision and its associated greenhouse gas emissions, taking climate change into account. All studies anticipate that it will be necessary to use climate-neutral fuels - explicitly electricity-based fuels - to achieve the 95% CO<sub>2</sub> reduction required for the "1.5 °C target".<sup>[25,26,27,28,29]</sup> To meet the moderate GHG reduction of 80%, only a fossil fuel share of between 11 and 16% is tolerable.<sup>[25]</sup>

In order for these fuels to be available in sufficient quantities in 2050, the development of appropriate production processes is already necessary now. In particular, paraffinic FT fuels<sup>[30]</sup> and OME<sup>[31]</sup> are currently seen as possible diesel fuels of the future.

However, the composition of regenerative fuels differs greatly from fossil fuels. If this synthetic fuel is to be used in the future because of the disproportionate soot reduction potential of OME, the miscibility must be examined in detail. For an illustration of the polarity and an assessment of the solubility based on the Hansen parameters, an overview of fuels is given in Table 4.

Table 4: Hansen parameters for describing the solubility of selected fuels.

Fuel	$\delta D$	$\delta P$	$\delta H$
HVO	17	0	0
OME	16.5	7.2	4.1
Biodiesel	16.7	5.5	3.0
Toluol	18	1.4	2.0
Diesel fuel	16.3	4.2	3.0

The Hansen parameters describe the influence of non-polar Van der Waals interactions, polar dipole-dipole interactions and the influence of hydrogen bridge bonds on miscibility. In accordance with the principle "like dissolves like", a large difference between HVO and OME can be seen in the contributions of polar and hydrogen bridge bond contributions to solubility. If HVO and OME still mix at room temperature, segregation was observed from 10 °C onwards. Due to the large differences in the density of HVO and OME alone, segregation in the tank inevitably leads to engine damage. However, the HVO/OME mixture represents a maximum polarity difference. If mixtures of fossil fuels with higher blends of regenerative fuels are considered, good miscibility with all fuels can be observed in accordance with Table 4. For example, studies on blending a maximum of 30 % OME with fossil diesel have shown it is an unproblematic substitution. This is due to the miscibility of aromatic compounds, which lies between non-polar n- and iso-alkanes and polar compounds such as OME. An increase in the regenerative fuel share is unproblematic in terms of miscibility if the aromatic concentration is sufficient.



However, if a higher fossil fuel substitution is to take place in the future, the polarity differences must be closely examined. The large polarity differences of HVO and OME result in a strongly temperature-dependent miscibility, which can be improved by biodiesel through its amphiphilic structure, among other things. The amphiphilic properties result from the polar functional ester group and the non-polar residue. Thus, by adding 10% biodiesel, the separation temperature in an HVO/OME mixture can be reduced from 10 °C to -15 °C. This can be estimated in advance using the Hansen parameters.

The different polarities of the regenerative fuels enable optimisation to avoid sedimentation of the ageing products. By admixing OME, the polarity of the fuel mixtures can be selected in such a way that the ageing products are kept in solution. As the proportion of biodiesel increases, the polarity of the fuel mix must be set correspondingly higher because the oxidation products of the ageing of biodiesel bring about a strong increase in polarity. Favourable fuel formulations from regenerative fuels require a balance of good miscibility (down to -20°C) and low or suppressed sedimentation.

## 5 (Bio) Fuels and electromobility

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Electromobility takes precedence over mobility with combustion engines in current political discussion. In Germany and the EU, the CO<sub>2</sub> emissions of these vehicles are counted towards the fleet average at 0 g/km. Thus, it is ostensibly suggested that this form of mobility will be the ideal way forward for the future of mobility. However, two crucial points are neglected here: On one hand, the emissions generated by the production of electricity, and on the other, the provision of energy for consumers (vehicles).

The electricity mix in Germany consists of regenerative sources (wind, solar, water) and fossil sources (gas, oil, coal, uranium) in variable proportions. The regenerative proportion can for example already amount to up to 80 percent in sunny and windy weather (see [www.electricitymap.org](http://www.electricitymap.org)). On the other hand, when there is no wind, the regenerative proportion can fall to under 10 percent at night. If electromobility were to be dramatically increased immediately, the energy required would need to be provided by coal-fired power stations, as the feed-in law gives priority to electricity from renewable resources and this energy is already fully fed-in and consumed. However, even if the average energy mix were to be considered, CO<sub>2</sub> emissions caused by electromobility are still in the same ballpark as emissions caused by combustion engines (UBA, 2016). For the future, however, it can be assumed that the emissions from electricity generation will, or will have to, decrease significantly, especially due to the further expansion of solar energy, because Germany has set itself the goal of having at least 65% of electricity consumption come from renewable energies in 2030.

With the development of renewable energies, however, other problems will arise. The power grid is currently still designed for electricity generation in large power plants. Renewable energies, in contrast, are not centrally generated and the amount of electricity that they provide fluctuates considerably. The capacity of the power grid during distribution is an additional issue. This means that quick-charging stations cannot be offered in certain supply areas due to the infrastructure. Therefore, significant research activity into these problems should be undertaken. It is not expected that the grid expansion will progress quickly enough by 2030 to allow storage facilities for the fluctuating electricity supply to be installed in sufficient quantities.

A third problem is battery technology. Currently, both the storage densities as well as the volume and mass-related densities are too low and the charging time too long to be able to accommodate the mobility needs of today's users. These disadvantages are the biggest obstacles on the consumer side.

One possible solution is the generation of power fuels from CO<sub>2</sub> and electrical excess energy (PtL, Power-to-Liquid fuels), which is also being intensely researched. However, efficiency losses must be expected here in comparison with battery operation. The advantage is that e-fuels are compatible with existing vehicle fleets and



with the infrastructure, and they provide the possibility of the energy generated being stored for a long time.

The research and introduction of e-fuels is primarily a “project” of industrialised countries, who have access to the necessary financial resources to finance relevant development concepts. This is especially true for the construction of large-scale plants, where overcoming “first mover” problems plays an important role.

## 6 Risks and challenges posed by biofuels

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### 6.1 Material compatibility

The variety of possible regenerative fuels results in new requirements for fuel-carrying components. On the one hand, fuel-carrying plastic pipes and seals must be resistant to the fuels used. In the case of liquid fuels, for example, material incompatibilities with OME and tetrahydrofurfuryl alcohol<sup>[32]</sup> are known. With gaseous fuels, for example, material incompatibilities have been found between dimethyl ether and conventional fluorocarbon rubber (FKM) seals. As a result of such material incompatibilities, suitable and cost-effective sealing materials very often have to be developed for the use of new types of fuels.

In addition to fuel-carrying pipes and seals, fuels are also in direct contact with metal components and actuators such as control valves and fuel injectors. Possible mutual influence must also be taken into account in fuel-metal contacts. On the one hand, fuels and their ageing products can attack metallic surfaces and lead to localised corrosion, which can negatively affect the durability and/or functionality of the components. On the other hand, fuel ageing processes can be accelerated on (coloured) metallic surfaces, meaning research must be conducted on both ageing-resistant fuels and fuel-resistant components.

With regard to the contact between fuel and actuators, it should be noted that some components, such as diesel engine injectors on moving parts, are lubricated by the diesel fuel. If fuels with reduced lubricating properties are used at this point, the lubricating properties of the fuels must either be adjusted by admixing additives or the component lubrications must be ensured by design modifications of the components (for example, by external oil lubrication).

### 6.2 Effects on the diesel engine mixture formation process

In conventional diesel engine combustion, the fuel is injected into the combustion chamber under ignition conditions towards the end of compression, with the result that diesel engine injection and combustion occur simultaneously. The result of this simultaneous mixture formation and combustion is high soot formation tendencies under standard conditions, which can lead to a high expenditure in exhaust gas treatment. In this respect, diesel engine alternative fuels offer very great development potential.

At the beginning of the mixture formation process, hydrodynamic and aerodynamic effects initially predominate during fuel injection. In conventional diesel engine combustion, the fuel is generally injected in liquid form under high pressure through a



multi-hole injector into the combustion chamber. The individual fuel jets entering the combustion chamber from the multi-hole injector interact with the compressed air in the combustion chamber, causing the individual fuel jets to break up and atomise. This atomisation process produces individual fuel droplets, upon which stabilising surface tension forces and destabilising air resistance forces act. In this instance, the destabilisation of large droplets is advantageous, as many small droplets have a much larger contact surface with the surrounding air than a few large droplets. For this reason, adapted fuel properties can be used correspondingly to adjust the stabilising surface tension forces and thus improve the mixture formation process. When using gaseous fuels, the effect of adapted surface tension forces is obviously not applicable. In the case of gaseous fuels, however, their disadvantages must also be taken into account, such as the lack of enthalpy of vaporisation within the engine. In the case of liquid fuels, the phase change from the liquid to the gaseous phase can be used for cooling within the engine.

### 6.3 Effects on the diesel engine combustion process

After the injected fuel mixes with the combustion chamber air, auto-ignition effects can occur locally during diesel engine combustion, provided auto-ignition conditions are achieved locally. As a result of the simultaneous injection and ignition, partially premixed combustion reaction zones form at the individual jets of the injection. The combustion kinetic reactions within this flame depend significantly on the local gas conditions in the combustion chamber as well as the burning fuel itself. This is where the really big fuel optimisation potentials arise.

By adjusting the fuel properties in terms of combustibility, molecular oxygen concentration, chain length of intermolecular bond structures, etc., it is possible to directly influence the combustion kinetic processes during combustion. For example, oxygen-containing fuel molecules can be used to reduce the initial soot formation in the combustion chamber. Furthermore, intermolecular bonding structures can be used to adapt fuel self-ignition propensity, whereby a partially reduced self-ignition propensity can be used for a longer ignition delay time and thus for more time for air mixing (mixture formation). An important secondary effect of the reduced soot formation is advantages regarding nitrogen oxide formation within the engine, which primarily takes place during soot oxidation (diesel engine soot-NO<sub>x</sub> trade-off). As many alternative diesel fuels can reduce the initial soot formation and, if necessary, avoid it completely, alternative diesel fuels have the potential to reduce the diesel engine soot-NO<sub>x</sub> trade-off and, if necessary, avoid it completely. Consequently, there is the potential to operate diesel engine combustion with very low soot and NO<sub>x</sub> emissions, which can be used to achieve significant savings in diesel engine exhaust treatment. For this reason, the further development of diesel engine alternative fuels offers great potential to make a cost-effective, efficient and sustainable contribution to mobility,



provided that the fuels are produced from sustainable renewable energy sources. However, the economic viability of new fuels is usually not a given from the outset; rather, procedural upscaling of the production plants and optimisation of the chemical conversion processes are usually required. The examples of metathesis<sup>[33][34]</sup> and solketal production<sup>[35]</sup> illustrate this point.

Challenges arise in the combustion of novel fuels due to partially necessary adjustments in engine operation or engine geometry. Under unfavourable conditions, adjustments in engine operation can lead to an increased introduction of fuel into the engine oil if no further precautionary measures are applied. Oil dilution due to fuel input is also observed with fossil diesel operation. However, fossil diesel has a significantly lower boiling range than biodiesel. By adding fossil diesel or biodiesel to the engine oil, an almost equal decrease in viscosity can be observed. The problem with the mostly high-boiling FAME components is their accumulation in the engine oil without the possibility of removing them by distillation, i.e. the permanent dilution of the engine oil by FAME.

There are two reasons for the differences between FAME and fossil fuel:

1. The creep capability of ester oils is generally very pronounced compared to equiviscous hydrocarbons. This leads to a greater ingress of unburned FAME into the engine oil.

- 2nd Due to the higher boiling temperature (boiling curve) of FAME as opposed to diesel fuel, the proportion of FAME that has leaked into the engine oil remains in the lubricant and leads to a permanent dilution. Figure 9 shows the boiling characteristics of various diesel fuels.<sup>[36]</sup> Engine oil can reach temperatures of 300 °C and higher in the area of the piston rings and cylinder area.<sup>[37]</sup> In the case of fossil diesel, 11% of the content is still unevaporated at 325 °C, whereas biodiesel does not begin to boil until it is above 325 °C. Accordingly, 100 % of the biodiesel introduced remains in the engine oil. In the case of fossil diesel, only 11 % remains at a temperature of 325 °C. These effects can be reduced by adjusting the engine control, for example, by applying multiple injections.<sup>[38][39]</sup>

In addition to oil dilution, the fuel input also causes increased oil ageing. In this respect, the fuel quality has the largest influence.<sup>[40]</sup> In regenerative fuels such as biodiesel, the polyunsaturated FAMEs lead to increased ageing, triggered by the high radical stability of the allylic and bisallylic CH bonds in the molecule. In fossil fuels, it is the share of alkyl aromatics that has the highest radical stability and strongly influences ageing. A distinction is made between the following ageing types:

*Oxidative ageing*, i.e. reactions with atmospheric oxygen, in which organic, oil-soluble, often short-term and therefore relatively strong acids are formed, and

*thermal ageing*, which leads to a substantial increase in viscosity and even resin formation due to the formation of high-molecular structures (polymerisation).

In practice, both processes occur together. The oxidation of oils can be avoided or minimised through so-called antioxidants, however ingressed FAME fuel is especially susceptible to oxidative, thermal and even hydrolytic ageing. Over the ageing period,

the oxidative and thermally initiated reactions lead to an increase in viscosity and a reduction in lubricity.

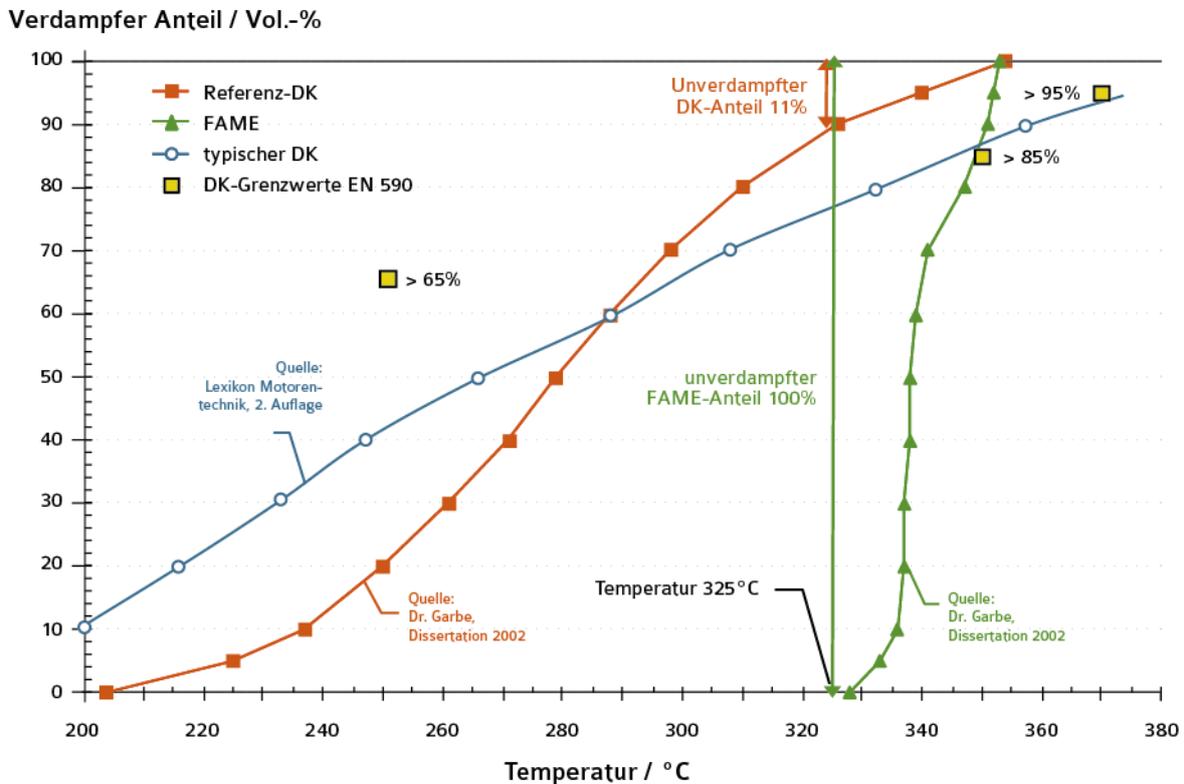


Figure 9: Boiling curves of different diesel fuels.<sup>[36]</sup>

With regard to the engine potential, the compatibility of new fuels with vehicles currently on the market must also be taken into account. This so-called drop-in capability can reduce or limit the possible fuel modifications and thus the theoretically possible development potential. In order to ensure maximum sustainable mobility, it is therefore crucial to conduct research into compatible fuels and engine concepts today. As soon as newly developed concepts can demonstrate economic advantages, such as significantly cheaper exhaust treatment systems, there are realistic chances of economic competitiveness. Schröder et. al were able to show the development potential for improving the combustion properties of biodiesel in particular (lowering the boiling curve) by shortening the chain length of FAME using metathesis.<sup>[34]</sup>

## 6.4 Effects on diesel engine exhaust gas treatment

In addition to oil dilution, the use of biofuels also has an impact on the formation of emissions. The use of biodiesel not only offers the possibility of mitigating climate gases, but it also makes it possible to reduce emissions locally. The biggest chemical differences between biodiesel and fossil diesel are the long-chain unbranched molecules of almost the same chain length, the absence of sulphur and aromatics and the oxygen content. These chemical differences lead to changes in combustion behaviour and thus to different exhaust emissions.

A relative comparison of the emissions of biodiesel versus fossil diesel is shown in Figure 10.<sup>[41][40]</sup> For the figures, only sources were used in which biodiesels were compared with fossil diesel fuels in a standardised test procedure. On average of the evaluated emissions, a reduction of -36 % in hydrocarbon emissions, -25 % in carbon monoxide emissions and -31 % in particulate matter can be observed. Due to thermal effects during combustion of biodiesel in the combustion chamber, NO<sub>x</sub> emissions increase by 13 % compared to fossil diesels, although the energy content of biodiesel is lower than that of fossil diesel by about this amount. Even when using biodiesel blends with fossil diesel, the mode of operation, the design of the engine and the type of injection are important influencing variables that affect the level of emissions.<sup>[42]</sup>

The chemical composition of biodiesel, more specifically its fatty acid pattern, also has an influence on emissions. Highly saturated fatty acid methyl esters have a higher cetane number compared to unsaturated FAME. The higher cetane number leads to a shorter ignition delay and a shorter preheating time, resulting in lower cylinder temperatures. The lower temperature means that saturated FAMEs emit less NO<sub>x</sub>.<sup>[40]</sup>

The use of hydrogenated vegetable oil (HVO) displays a similar emission trend to biodiesel. Figure 11 depicts the emissions of HVO blends, as well as pure HVO, in relation to diesel fuel. The content of HVO in the fuel increases on the X axis (Figure 11).

Limited emissions were measured both on light passenger vehicles in the new European driving cycle (NEDC) as well as on commercial vehicle engines.

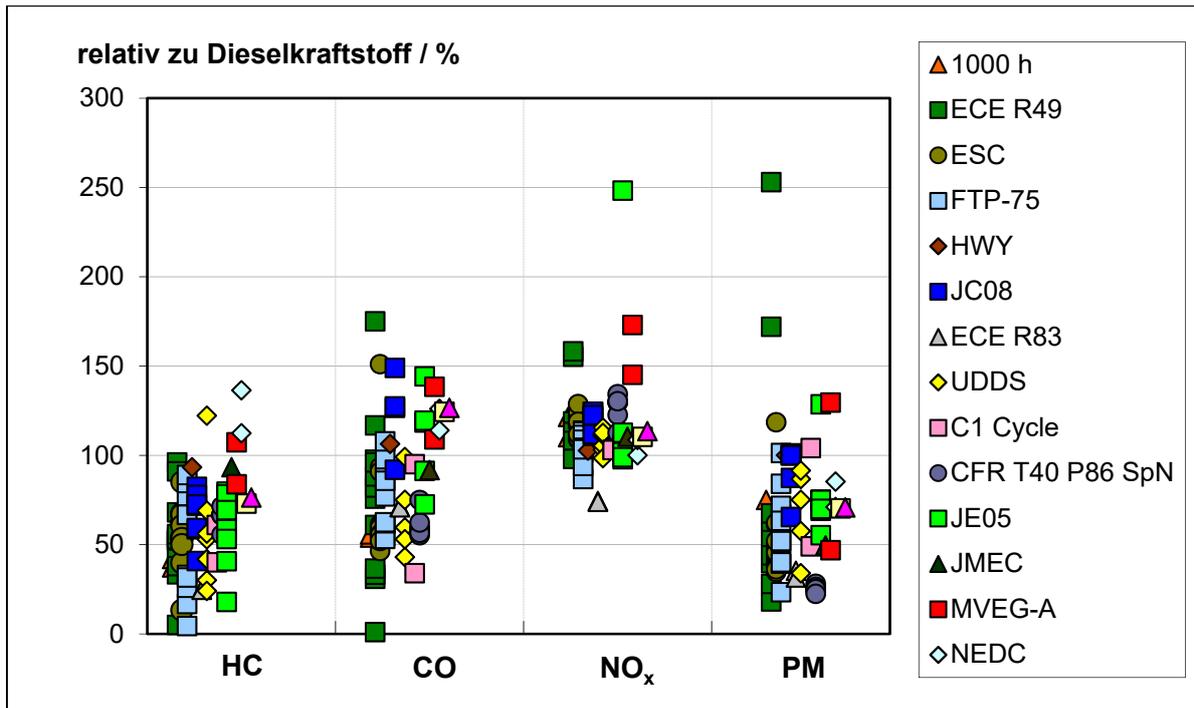


Figure 10: Limited emissions of biodiesel compared to diesel fuel.[41][43-64]

The use of HVO reduces emissions of hydrocarbons (HC), carbon monoxide (CO) and particulate mass (PM) noticeably, relative to diesel fuel. This decrease correlates with the HVO content in the fuel. The more HVO added, the greater the observed effect (Figure 11).

In contrast, nitrogen oxide emissions show an inconsistent trend. In the NEDC, emissions increase by about 10 % due to HVO (Figure 11, NEDC). By way of contrast, the NO<sub>x</sub> emissions from commercial vehicles decrease by approx. 10% due to HVO (Figure 11, all except NEDC, UDC, EUDC and UDDS).

Due to the increased use of exhaust gas treatment systems, which actively react to higher NO<sub>x</sub> concentrations of pollutants, for example, the influence of fuel on the emission behaviour of the engine will decrease somewhat in the future.

relativ zu Dieselkraftstoff / %

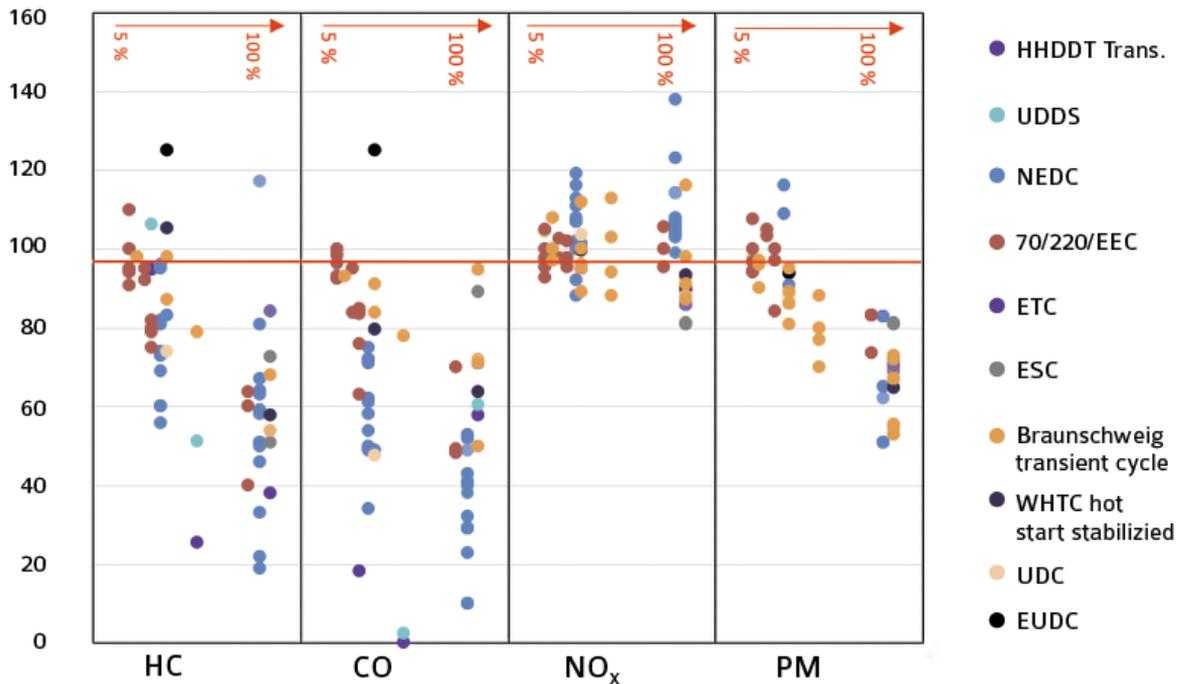


Figure 11: Relative change in limited emissions with different blending of HVO with fossil diesel.<sup>[65][66][67][68][69][70][71]</sup>

Alternative diesel fuels with high oxygen content and as few carbon-carbon bonds as possible offer the potential of significantly simplified exhaust gas treatment systems for particulate and NO<sub>x</sub> emissions. Nevertheless, there are also technical challenges in the area of exhaust gas treatment, such as the possibility of unburnt hydrocarbons leaving the combustion chamber. In this respect, research and development must continue on the development of modern and adapted catalytic converter systems in order to be able to efficiently oxidise unburnt hydrocarbons in new fuel types. Furthermore, it should be noted that current exhaust gas legislation only regulates a part of the theoretically possible emissions, but that this legislation could become significantly stricter in the future. In this context, alternative fuels and combustion processes must be continuously developed and improved, also with regard to future legislation.

## 7 Ageing of fuels

The ageing of organic compounds is the change in physical and chemical properties over time. Ageing processes can be induced by increased temperature, high oxygen input, catalysts such as copper and light irradiation, etc. Ageing products, such as water and acids, in turn lead to increased ageing, as they influence the reaction as catalysts. In DIN EN 14112 and DIN EN 15751, fuel ageing in biodiesel blends is defined by oxidation stability. This must be at least 20 hours and is determined by the Rancimat method. According to the method, 7.5 g of the fuel sample is flown through with 10 L per hour of air at 110 °C. After passing through the sample, the air is directed into distilled water. By measuring the conductivity of the water, highly volatile fuel components and highly volatile ageing products are detected. If the additives are completely used up, this is indicated by an increased conductivity. The length of time that has elapsed before the strong change in conductivity takes place indicates the oxidation stability.

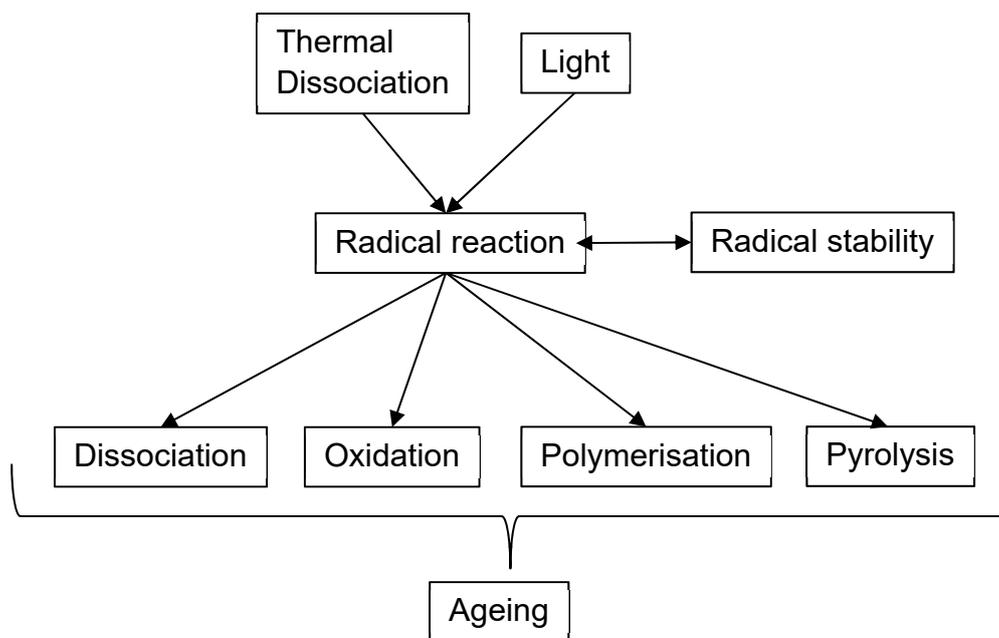


Figure 12: Overview of the ageing of organic compounds.

To inhibit the ageing of biodiesel, it is essential to understand the reaction mechanisms in detail and to identify reaction products. So far, only short-chain reaction products have been identified in the literature by means of gas chromatography with an attached mass spectrometer (GC-MS). However, as a gas chromatographic investigation of long-chain reaction products is not possible, there are no findings on the formation of oligomers.

In the efforts to better understand reaction products, the finding that the effect of antioxidants varies greatly depending on the composition of the fuel is crucial. Thus, it was shown that the different content of doubly and triply unsaturated fatty acid methyl esters effects the efficiency of inhibition by antioxidants.<sup>[72]</sup>



Fuel ageing can be divided into different aspects (Figure 12), which are described in more detail below.

## 7.1 Autoxidation

Autoxidation is the slow oxidation of a chemical compound by atmospheric oxygen. This process is autocatalytic and leads, among other things, to the formation of hydroperoxides. Some examples of autoxidation reactions in everyday life are the formation of acetic acid from alcohols, the fading of colours, fats turning rancid and the browning of cut apples.

The process of autoxidation can be divided into three phases. The first phase is called the start reaction, in which homolytic bond splitting is initiated. If radicals have formed in the initial reaction, chain propagation describes the further reaction with renewed formation of a radical. Chain termination occurs when two radicals form stable products with each other.<sup>[72]</sup>

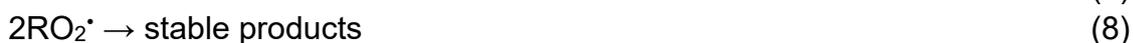
### Start reaction:



### Chain propagation:



### Chain termination:



Through the reaction with atmospheric oxygen, firstly, radicals can be induced and, secondly, existing radicals can react with oxygen to form peroxides. Peroxides are important intermediates in ageing. The varying reactions of hydroperoxides were carried out by gas chromatographic investigations by Frankel et al.<sup>[73]</sup>

The investigated hydroperoxides were obtained during the autoxidation of linolenic acid methyl ester by chromatographic purification. These were thermally cleaved directly at the injection port of the GC-MS at 200 °C, and the thermal cleavage products were identified by mass spectroscopy. Table 5 lists the six investigated hydroperoxides with their respectively obtained thermal decomposition products.

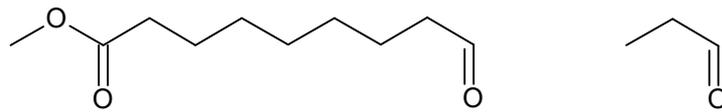


Figure 13: Structural formula of methyl 9-oxononanoate (left) and propanal (right).

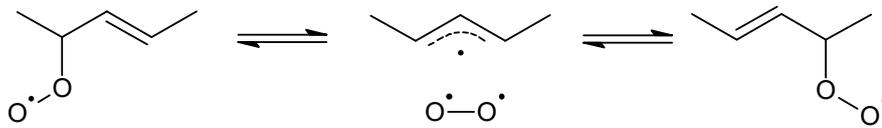
The reaction of hydroperoxides can be described by different reactions. Some of the reactions that took place are indicated in Figure 14. The decomposition products found with the greatest frequency by Frankel et al <sup>[73]</sup> are methyl 9-oxononanoate and propanal, which are formed by bond cleavage initiated by a reaction of a hydroxy radical in the  $\alpha$ -position to the hydroperoxide group. In addition to these decomposition products, further compounds could be identified. Among them are certain aldehydes, which can form further ageing products as intermediates through subsequent reactions.

For the initial formation of hydroperoxides, a radical must be formed at the beginning through thermal dissociation or light irradiation. In the next step, this radical can react with oxygen to form peroxides. Oxygen itself is not able to start the initial reaction. The products obtained from hydroperoxides can then form a whole series of further ageing intermediates or ageing products.

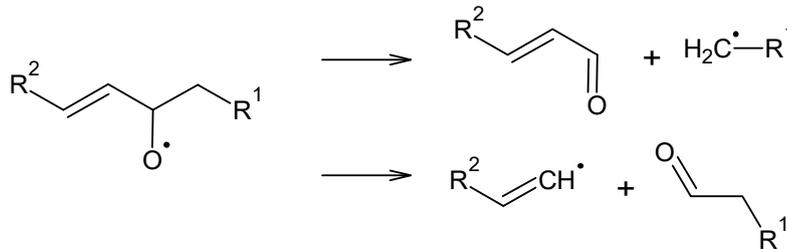
Table 5: Gas chromatographic analysis of the cleavage products of hydroperoxides by thermal decomposition at 200 °C.<sup>[73]</sup>

Volatile compounds							
Acetaldehyde	0.6	0.1	0.9	1.9	0.2		0.3
Ethane	1.0	0.4	1.0		1.2		0.9
Acetone	3.1	4.3	3.8	4.8	5.8		3.1
Propanal	19.4	24.7		2.1	19.9		26.0
Butanal		0.6	1.2		2.4		2.0
2 butanal	1.8	2.0	2.1	29.1	1.7		1.6
1.4 hexadiene			0.9	1.9	3.3		
2.4 hexadienal			0.6	1.0	0.4		
Methyl hexanoate		0.2	0.7	0.1	0.3		
Butylfuran							5.8
2 heptanal					0.7		
2.4 heptanoate	0.2	1.3	4.6	0.7	1.2		5.5
Methyl heptanoate	0.1	1.0	1.9	0.9	1.0		0.2
Methyl octanoate	7.8	0.8	3.5	10.0	10.0		2.5
Methyl 8-oxooctanoate	0.6	1.9	3.0	1.8	2.6		0.3
Methyl 9-oxononanoate	38.8	2.2	7.1	9.2	9.8		30.3
Methyl 10-oxodecanoate	0.6	0.3	6.1	0.8	1.0		2.0
Methyl 10-oxo-8-decanoate	2.7	40.9	35.6	5.1	5.0		2.0
Methyl furanoctanoate				5.0	7.6		1.2
Methyl 11-oxo-9-undecanoate	4.1	4.4	5.5	7.0	6.5		0.9
Methyl 12-oxo-8,10-dodecadienoate			3.7				
Methyl 13-oxo-9,11-tridecadienoate				7.8	5.5		1.8
Not identified	19.2	14.9	17.8	10.8	13.9		13.6

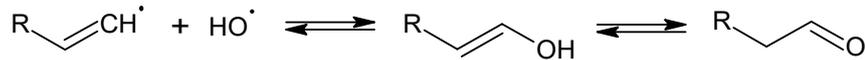
### Thermische Umlagerung von Hydroperoxiden



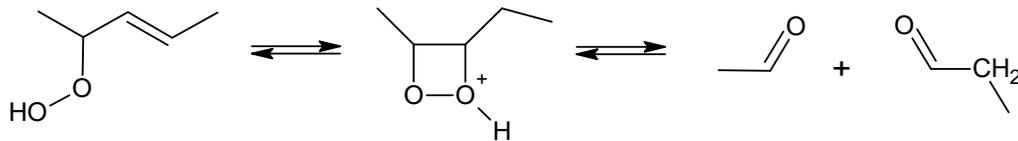
### Betaspaltung



### Keto-Enol-Tautomerie



### Hock-Spaltung



### Intramolekulare Radikalreaktion

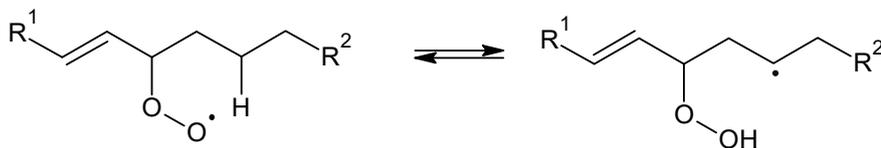


Figure 14: Selection of possible reactions that can occur by autoxidation.<sup>[74]</sup>

## 7.2 Thermal oxidative ageing

The autoxidation is temperature-dependent. The ageing of substances is thus an interplay of radical stability and temperature. According to the Arrhenius equations, the logarithm of the reaction rate constant ( $k$ ) is subject to a linear dependence on the reciprocal absolute temperature.

$$\ln k = \ln A - \frac{E_a}{RT} \quad (9)$$



Where  $R$  is the universal gas constant,  $E_a$  is the activation energy,  $T$  is the temperature in Kelvin, and  $A$  is an empirical constant that incorporates various probability parameters and vibrational constants of molecules<sup>[75]</sup>. Increasing temperature causes greater dissociation and bond weakening, making it easier for homolytic bond cleavage to occur.

### 7.3 Polymerisation

The formation of radicals not only leads to oxidation, but under suitable conditions can lead to polymerisation. During polymerisation, radicals and compounds (e.g. with C-C double bonds) react without the participation of oxygen and form dimers, trimers or oligomers. In this process, already oxidised products can also represent building blocks of oligomers. Some basic requirements must be fulfilled for polymerisation to take place. For voluntary processes to take place, the Gibbs energy of the reaction products must be smaller than the Gibbs energy of the reactants. The Gibbs energy is defined according to equation 10.

$$\Delta G_p = \Delta H_p - T \cdot \Delta S_p \quad (10)$$

The Gibbs energy of a system ( $\Delta G_p$ ) results from its enthalpy ( $\Delta H_p$ ) and the reduction by the system entropy product ( $\Delta S_p$ ) with the absolute temperature. A polymerisation means a decrease in entropy as a large molecule is formed from one or more reactants. For a reaction to occur voluntarily ( $\Delta G_p < 0$ ),  $\Delta H_p$  must be smaller than  $T \cdot \Delta S_p$ . This means that the entropy decrease must be compensated by the formation of energetically favourable compounds.

For a polymerisation to occur, a rapid reaction must also take place between the reactants. In addition, there must be no competitive reactions between the reactants and other compounds. Accordingly, only considerable temperature effects under low concentration of atmospheric oxygen (avoidance of oxidation reactions) leads to the formation of oligomers. Depending on the kinetic course, polymerisation is divided into chain-growth reactions (polymer chain carries reaction-activating functionality) and step-growth reactions (monomers have at least two functional groups). The further differentiation is made according to the following mechanism (Figure 15).

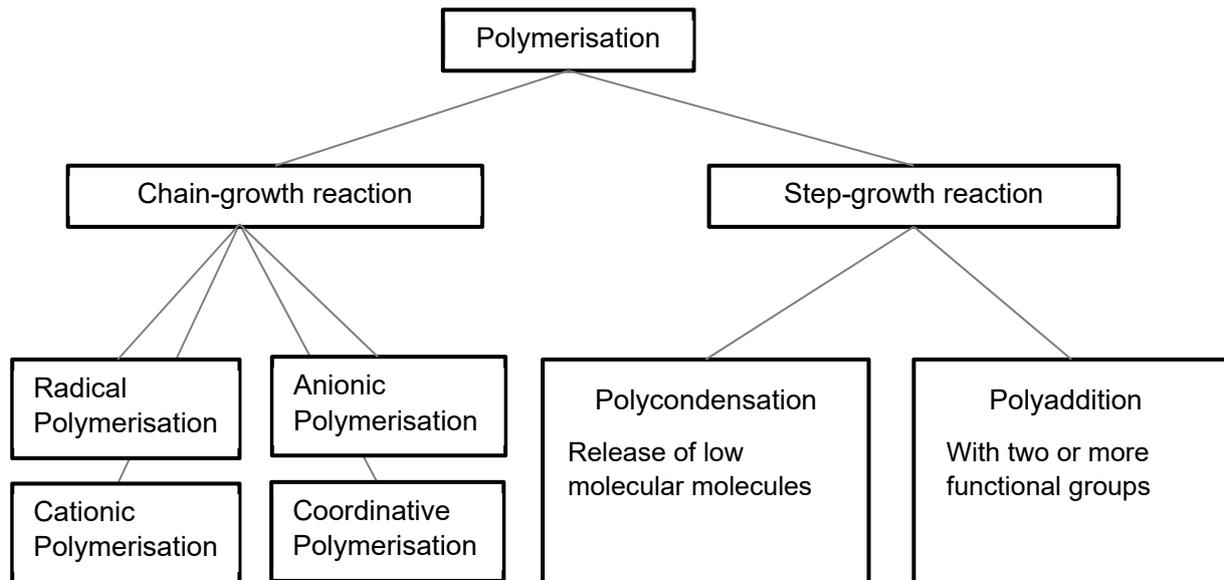


Figure 15: Classification of polymer synthesis by reaction type.

Resonance-stabilised and sterically hindered radicals, as represented by the antioxidants, do not start the polymerisation. The ageing of fuels is subject to the influence of a variety of reactions. Hydroperoxides, for example, which are formed during autoxidation, are very good radical formers at elevated temperatures (thermal radical formation). In addition, reactions such as  $\beta$ -cleavage can lead to the elimination of ethene and the formation of secondary radicals (Figure 16). This results in chain degradation around two carbons with the formation of another alkyl radical.

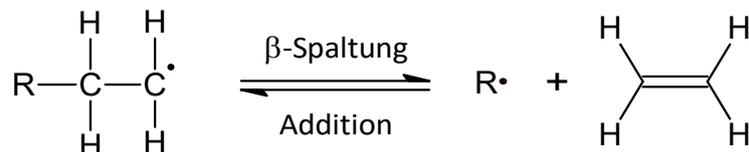


Figure 16:  $\beta$ -cleavage of alkyl radicals.<sup>[74]</sup>

## 7.4 Radical stability

Radical formation depends largely on stabilisation. The more stable a radical, the more easily it is formed, the more the reaction equilibrium shifts to the side of the radicals. Stability is influenced by mesomerism (delocalisation), substituent effects (hyperconjugation), steric effects and the reactivity of the radical centre. In addition, the solvent has an influence on the stabilisation of the starting materials formed as well as products (dimers) or can itself react with the radical. Figure 18 shows the increasing stability of selected organic radicals. The stability increases from primary to secondary to tertiary alkyl radicals (Figure 18). The cause is the hyperconjugation of the binding

electrons of the C–H bond into the half-occupied  $sp^2$  hybrid orbital due to the methyl group. Aryl and benzyl radicals have a significantly higher stability due to mesomerism (Figure 19).

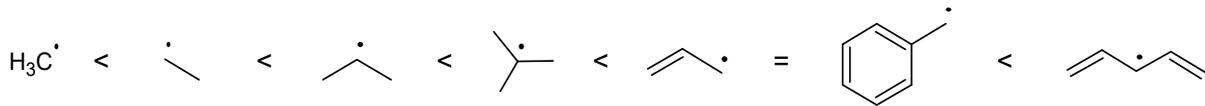


Figure 17: Radical stability.<sup>[76;77;78]</sup>

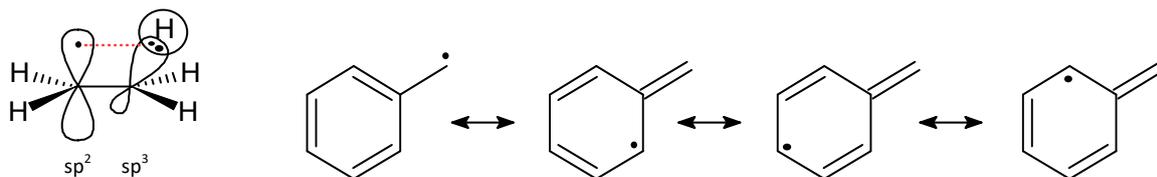


Figure 18: Hyperconjugation and resonance stabilisation.<sup>[79][80]</sup>

## 7.4 Ageing of regenerative fuels

### 7.4 1 Fatty acid methyl ester (FAME)

Biodiesel consists mainly of methyl esters obtained by transesterification of vegetable oils or animal fats with methanol. Depending on the vegetable oil used, biodiesel has a different pattern of fatty acid methyl esters. The compositions of selected oils and fats are summarised in Table 1. The proportion of unsaturated fatty acids is largely responsible for the susceptibility to ageing, as these have allylic and bisallylic positions and lead to the formation of well-stabilised radicals. Thus, in diesel fuel, the biodiesel content is the starting point for fuel ageing.

Fuel ageing can be differentiated into autoxidation and polymerisation. Both reactions are preceded by an initiative radical formation, which is significantly influenced by the radical stability. Besides alkylbenzenes, the most stable radicals are the doubly and triply unsaturated fatty acid methyl esters after homolysis of a CH bond. Hydroperoxides are formed by reaction of the radicals with atmospheric oxygen. The formed hydroperoxides can react further through a variety of possible reactions. The fuel is oxidised by the reaction with atmospheric oxygen. This leads to increased polarity and the associated formation of hydrogen bonds, which in turn results in increased viscosity. The change in polarity changes the solubility of the oxidation products accordingly. If oxidation is too strong, the formation of ageing products leads



to sedimentation or to the formation of a second phase, which consists, among other things, of water that has been formed during oxidation and polymerisation reactions. Sedimentation occurs when the polarity difference between ageing products and fuel matrix becomes too large due to autoxidation. In the case of fatty acid methyl esters, free fatty acids are formed during ageing, which cause an increase in the pH value over the ageing period, which in turn catalyses reactions.

Table 6: Fatty acid composition for different oils and fats.<sup>[81]</sup>

Oil	Fatty acid composition [%]								
	10:0	12:0	14:0	16:0	18:0	18:1	18:2	18:3	22:1
Canola oil				1.5-6	1-2.5	52-67	16-31	6-14	1-2
Corn oil			0-0.3	7-17	1-3	20-43	39-63	0.5-1.5	
Linseed oil				6-7	3-5	13-37	5-23	26-60	
Olive oil		0-1.3	7-20	0.5-5	55-85	4-21			
Palm oil	0-0.4	0.5-2.4	32-48	3.5-6.3	36-53	6-12			
Peanut oil			0-0.5	6-14	2-6	36-67	13-43		0-0.3
Rapeseed oil			0-1.5	1-6	0.5-3.5	8-60	9.5-23	1-13	5-64
Safflower oil				5.3-8	2-3	8-23	68-83		
Soya oil				2-13	2-6	8-31	49-57	2-11	0-0.3
Sunflower oil				3.5-7.6	1.3-6.5	14-43	44-74		
Beef tallow			2-7	25-37	9.5-34	14-50	26-50		

## 7.4.2 HVO

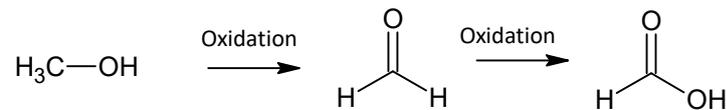
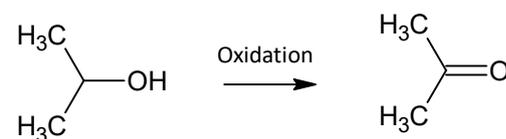
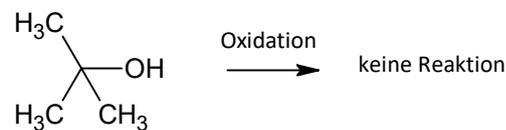
Depending on the production method, HVO consists of a mixture of different n- and iso-alkanes. Alkanes generally have a very low reactivity because the CH and CC bonds have a high bond dissociation energy. In addition, alkanes have no functional groups that can cause a reaction. However, alkanes can enter into redox reactions. In alkanes, the carbon is present in the oxidation states -II (-CH<sub>2</sub>-), -III (-CH<sub>3</sub>) and -IV (CH<sub>4</sub>), which means in the reduced state. Through thermal dissociation of the CH bonds, the carbon can be oxidised by reaction with atmospheric oxygen. Radical formation depends largely on radical stability. N-alkanes can form primary ( $\bullet$ CH<sub>2</sub>R) and secondary radicals ( $\bullet$ CHR<sub>2</sub>), whereas iso-alkanes can form better stabilised tertiary radicals ( $\bullet$ CR<sub>3</sub>). This means that HVOs with a higher iso-alkane content age more rapidly and can form radicals more easily. In addition, a steric tension occurs in the molecule of strongly branched iso-alkanes, which results from the spatial proximity of alkyl groups. This makes these molecules much more reactive.

## 7.4.3 Long-chain alcohols

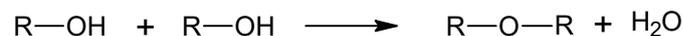
The ageing of alcohols is largely determined by the degree of substitution of the carbon atom. Alcohols are divided into primary (HO-CH<sub>3</sub>), secondary (HO-CH(CH<sub>3</sub>)<sub>2</sub>) and tertiary (HO-C(CH<sub>3</sub>)<sub>3</sub>). Due to the electron-pushing effect of the methyl group, the

electron density of the OH bond increases from primary to secondary to tertiary alcohols. An increased electron density causes an easier splitting-off of the proton of the alcohol group. In addition, the increased electron density has an effect on the formation of hydrogen bonds. The solubility is composed of the hydrogen bonds and the high polarity of the alcohol group. With increasing chain length, the influence of the non-polar (lipophilic) alkyl chain increases, whereby the miscibility with polar (hydrophilic) compounds decreases. Due to the high polarity, alcohols can hold polar ageing products in solution in mixtures with fuel. Due to the two free electron pairs on the oxygen, the alcohol group can cause a variety of reactions (Figure 19). Alcohols can act as a nucleophile or as a base. Protonation of the OH group produces alkyloxonium ions that can cause nucleophilic substitution reactions.

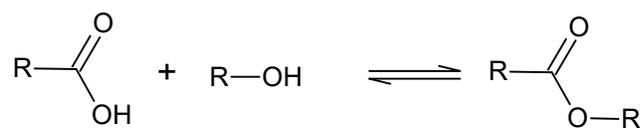
#### Oxidation



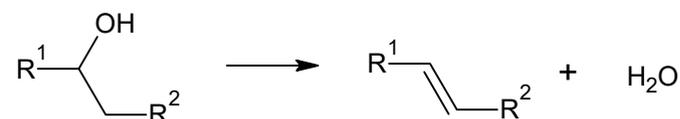
#### Etherbildung



#### Veresterung



#### Eliminierung /Dehydratisierung



#### Protonierung

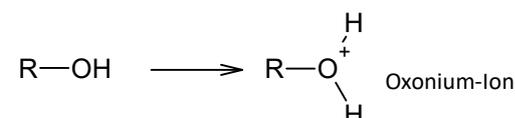
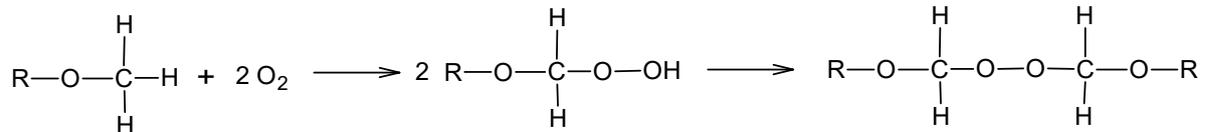


Figure 19: Reactions of alcohols.<sup>[82]</sup>

## 7.4.4 OME

OME is a polyether which is usually present as OME n=3 to 5 when used as a diesel additive. Decomposition can occur by thermal dissociation of the CH bond and subsequent reaction with oxygen (autoxidation). In the process, hydroperoxides are formed, which, through further reaction, form ether peroxides (Figure 20). The formation of hydroperoxides can also be triggered by light irradiation. Another degradation reaction is the protonation of the ether group. Ethers are relatively stable compounds that can only react in an acidic environment.

Bildung von Etherhydroperoxiden



Protonierung

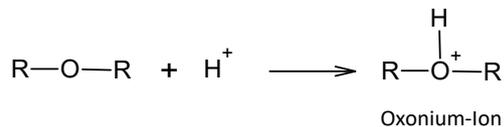


Figure 20: Ether hydroperoxide formation and protonation of ether.<sup>[82]</sup>

The oxonium ion formed can then be attacked by nucleophiles. The synthesis of OME is an equilibrium reaction catalysed by acid (Figure 21). In an acidic environment, the reverse reaction is favoured, producing formaldehyde, which can polymerise to paraformaldehyde. OME in its pure form and in the absence of light is an extremely stable fuel. Only in combination with compounds that form more acids during ageing (e.g. biodiesel and HVO) does OME lose its resistance to ageing.

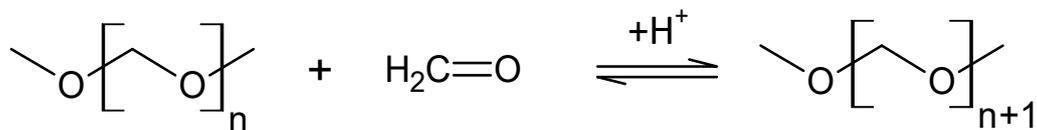


Figure 21: Synthesis of OME.<sup>[83]</sup>

## 8 Polarity effects

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The polarity of fuels and of ageing products which are formed in the thermo-oxidative ageing of fuels have a range of influences on miscibility, solubility and toxicity.

### 8.1 B20 effect

The oxidation of fuels, both fossil as well as synthetic, causes an increase in polarity. With advancing ageing, polar deposition products form. The amount of ageing products which can be diluted in the fuel matrix depends on their polarity. Fang and McCormick<sup>[84]</sup> reported that the formation of deposits is non-linear if the biodiesel proportion in fossil diesel is increased gradually. A maximum deposit formation was found at a proportion of approx. 20% biodiesel in fossil fuel (B20). With an increasing proportion of biodiesel, the polarity of the fuel matrix increases, so that the formed polar ageing products are suspended in solution. With smaller biodiesel admixtures, the amount of formed polar ageing products is smaller. Depending on the composition of the fossil components, the deposit formation maximum shifts. Eskiner et al. reports a maximum of deposit formation with B15.<sup>[85]</sup>

The biodiesel content does not only influence sedimentation. Respective to the amount of sedimentation, an interdisciplinary group of researchers from the Thünen Institute Braunschweig, the Technology Transfer Centre for Automotive Technology of Coburg University and the Institute for Prevention and Occupational Medicine of the Ruhr University Bochum (IPA) were able to report<sup>[86][87][88]</sup> a significant increase in the mutagenicity of emissions in diesel fuel-biodiesel blends, which also shows a maximum at B20 for the first time. Analogous to the formation of deposits, the mutagenicity decreases from a B20 composition up to clean RME and with clean RME reaches a lower value than with clean diesel fuel. Overall, the similarities of the results suggest that there is a correlation between the formation of deposits and the increased mutagenicity of emissions. The interdisciplinary research group coined the term "B20 effect" and carried out further research work on the topic of the polarity of fuels from this finding. The hypothesis for the correlation states that oligomers caused by ageing enter the gas phase more poorly and thus have a greater tendency to pyrolysis than unaged fuel. Investigations on triglycerides strengthened this assumption.<sup>[89]</sup>

### 8.2 Internal diesel injector deposits (IDID)

The introduction of stricter emissions laws requires continuous development of combustion processes of diesel engines and simultaneously, development of the fuels used. Deposits on hot metal surfaces in injectors or other components caused by fuel



components are not a new phenomenon. Due to the increased sensitivity of modern injectors, the increasing variety of fuels and the use of different blended fuels in diesel engines, the deposition problem must be given more attention in future. Internal Diesel Injector Deposits (IDID) can have several causes. They are caused by polar fuel ageing products, certain additives (dodeceny succinic acid) and impurities (saponification agents), among others. Higher injection pressure, in particular, as well as the related higher system temperatures make high demands of the thermal-oxidative fuel stability and additive resistance. For varying fuel polarities, sufficient solubility of all fuel components and the additives used must be ensured.<sup>[90]</sup>

Essential influencing factors for the minimisation of deposition formation are an optimal fuel polarity (e.g. Adjustable using FAME components) and a possibly reduced amount of aromatic nitrogen, oxygen and sulphur compounds.

To be able to reliably and cost-effectively detect critical fuel compositions in advance, the development of new methods of analysis and, where applicable, the inclusion of additional fuel parameters in the fuel specifications is required. For example, a “pre-screening” of fuels can be made possible by a newly developed “Diesel Deposit Formation Test” (DDFT) for testing the tendency of deposit formation of diesel fuels depending on the temperature. Additionally, the test offers potential for stability, compatibility and efficacy tests of fuel additives.<sup>[91]</sup>

Furthermore, it should be examined how useful or meaningful a parameter "polar components" would be for diesel fuels and whether this correlates with the formation of deposits in injection components.

### 8.3 Polarity of synthetic fuels

In order to reach the 2030 climate protection goal for transport, various strategies are being pursued and promoted. In addition to efficiency increases and the use of fully and partly electrical drive (hybridisation), CO<sub>2</sub>-neutral biofuels in particular are currently determining the strategy for defossilising transport in the short term. Due to the increasingly non-polar composition of fuels and longer service lives of fuel mixtures in fuel tanks, an intensification of systematic research is required in this field to avoid negative interaction effects. Measured in terms of global significance, biodiesel in particular, as a polar component in different admixture proportions, poses particular challenges to fuel quality development and safety. However, the share of non-polar biofuels such as Hydrogenated Vegetable Oil (HVO) and longer-term electricity-based renewable fuels (Power-to-Liquid) is rising. The fact that the dwell times of fuel mixtures in the vehicle tank are extending as a result of increasing hybridisation of the drives is challenging, and polar ageing products increase the polarity of fuels. A comparable increase in polarity is also caused by the synthetic PtX fuel, OME. OME creates challenges for miscibility through its higher polarity compared to fossil fuels. Large

differences in polarity between HVO and OME result in a miscibility gap in the case of an admixture of 30% OME to 70% HVO. An admixture of biodiesel plays a central role in this context, as it guarantees lubricity and can also be used advantageously as a solubiliser in fuels. The role of the solubiliser is based on the polarity between HVO and OME and the amphiphilic structure of FAME. In light of this, systematic research needs to be proactively intensified in order to check the functionality of the various fuel mixtures, ideally while the vehicle is running, and/or to combine them in the best possible way during production.

## 8.4 Combustion optimisation using fuel identification

The variety of fuels and fuel compositions present new challenges for automobile manufacturers in optimally designing engines. This will become even more important given future stricter emissions specifications. Fuel composition identification offers the possibility of best optimising engine management to the respective fuel available. Therefore, sensors which can detect various fuel parameters through different measuring processes are subsequently presented.

### 8.4.1 Dielectric relaxation spectroscopy

In plug-in hybrid vehicles, a dwell time of the fuel in the tank that is longer than was previously the case with pure combustion engine vehicles is assumed for purely electrical applications. The ageing process can lead to the formation of polar high-molecular ageing products. The dielectric relaxation spectroscopy can highlight a change in polarity and detect polarisation losses, caused by oligomers, in the imaginary part of the complex permittivity by measuring the relative permittivity. This way, the degree of ageing of a fuel can be determined. Figure 22 shows the increase in relative permittivity for UCOME as an example of ageing detection. The relative permittivity shows a linear correlation between polarity and degree of ageing.

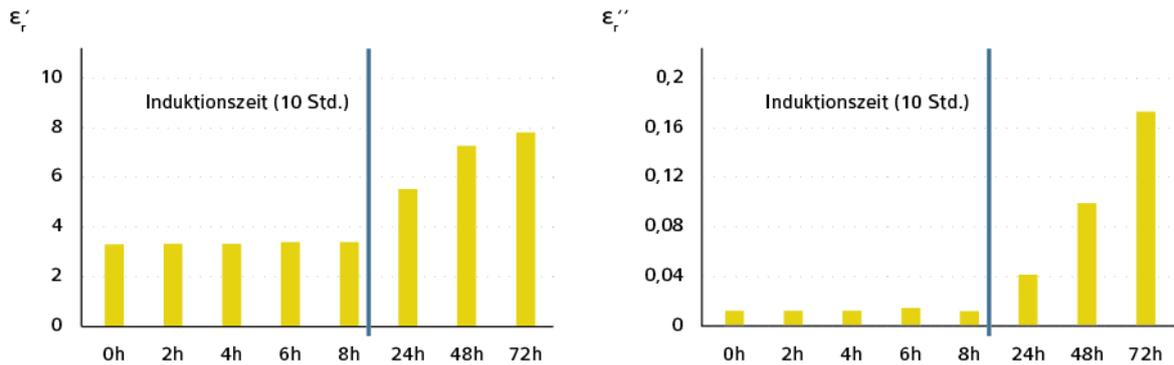


Figure 22: Real part (left) and imaginary part (right) of thermo-oxidatively aged UCOME at 100 kHz and 25 °C (ageing in Rancimat at 110°C). The determined induction time of UCOME is 10 h).

### 8.4.2 Near infrared spectroscopy

Near infrared spectroscopy (NIR) covers the wave length range from 750 to 2500 nm and captures the overtones and combinational vibrations of the molecular groups of IR-active molecules. Thus, fuels can be categorised by the functional groups of their individual components. It is possible, for example, to detect the aromatic content, ester content and degree of isomerisation in order to adapt the engine management accordingly<sup>[92][93]</sup>. Further parameters such as density, heating value and viscosity, which influence the engine combustion, can also be determined.<sup>[94]</sup>

### 8.4.3 Fluorescence spectroscopy

Using excitation with light, valence electrons from occupied molecular orbitals of non-binding and  $\pi$  electrons are energetically excited into excited singlet states. By initially non-radiative transitions from higher vibration states, the relaxation of the electrons, with the emission of fluorescent light, takes place from the first excited singlet state into the ground state. The potential of fluorescence spectroscopy lies in the detection of minute admixtures. Thus, fluorescent additives in the ppm range can be identified. A database-supported evaluation enables the differentiation of fuels from different manufacturers (Figure 23). The degree of ageing by fluorescence can also be tracked by the consumption of antioxidants during the induction phase and the formation of ageing products.

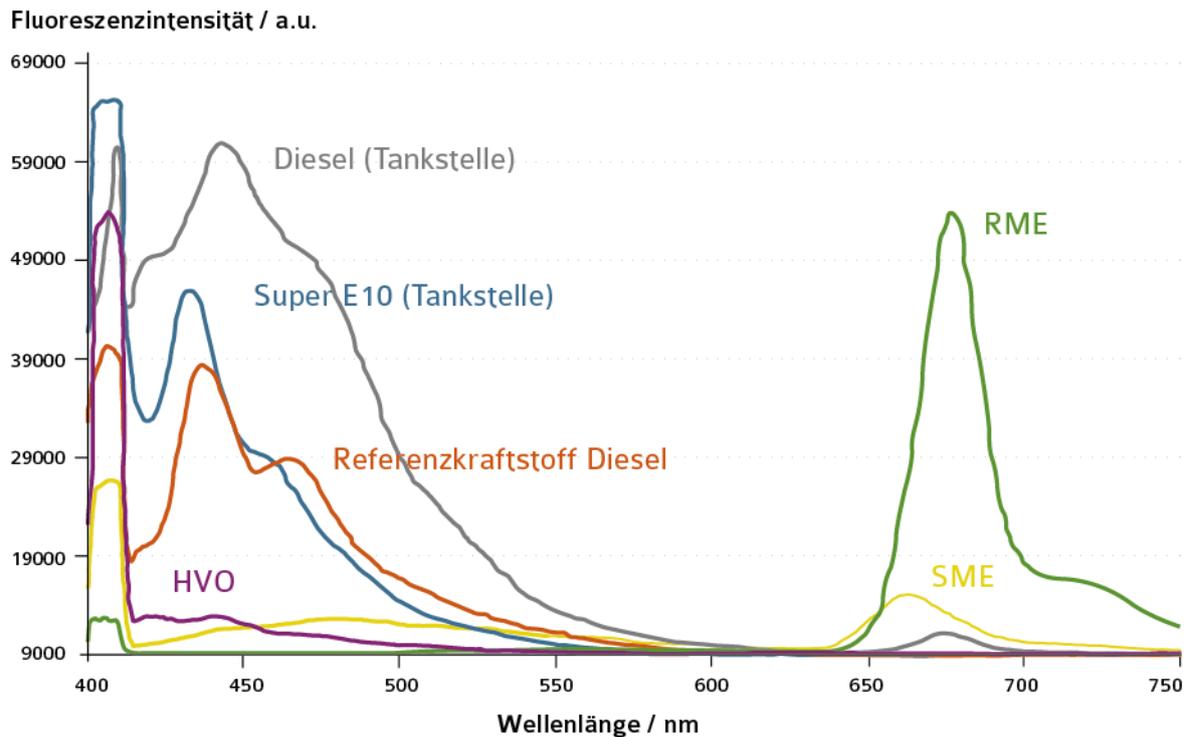


Figure 23: Fluorescence spectra of various fossil and biofuels  
( $\lambda_{excitation} = 405 \text{ nm}$ ).

Overall, these three sensor principles offer a partly redundant option of fuel detection. Coburg University TAC are working on the implementation of such sensors currently.

## 8.5 Additives and possible effects on quality

In addition to criteria such as sustainability, minimisation potential or production costs, the chemical-physical behaviour of modern fuels takes on an essential role in terms of their technical properties.<sup>[95]</sup>

The biofuels presented cover a broad spectrum (the broadest to date) in terms of their solution behaviour (polarity/polarisability), their cold behaviour, their miscibility with each other, their stability, lubricity and many other chemical-physical properties.

Thus, in the middle distillate range, a highly polarised OME faces the non-polar paraffinic HVO, for example; biodiesel and mineral oil-based diesel occupy an intermediate position between these two extremes (with respect to their polarity). The behaviour is similar with petrol – with the extremes of paraffinic XtL fractions and the polar ethanol, as well as the intermediate mineral-oil-derived petrol.

The fuel properties required in the respective standards and in the “Worldwide Fuel Charter” (WWFC)<sup>[95]</sup> must, however, be guaranteed in all cases here. The requirement



of maintaining compatibility with existing (or expected) fuel qualities in wide concentration ranges as a “Drop-in Fuel” must be fulfilled if a significant range of applications is to be achieved in the fuel mix.

However, these types of challenges are nothing new when it comes to fuel development. Over the last 100 years, the health-related, environmental and technical properties of fuels have changed continuously. By adding property-modifying additives, it was always possible to (re)establish the suitability of fuels. Starting with the combustibility correctors and additives to guarantee knock resistance, 100 years ago, new additives – antioxidants, stabilisers, lubricant correctors, deposit reducers, corrosion protection and many other active substances – were continuously developed. In concentrations of only a few ppm, these were able to guarantee the desired fuel characteristics.<sup>[96]</sup>

The regenerative fuel qualities must also guarantee the requirements of technical suitability and also of miscibility with each other, and have been heavily researched in this regard<sup>[97]</sup>. Many research projects are concentrating on these aspects of fuel development and have already developed numerous strategies for adapting the products<sup>[98]</sup>. Technical application problems can usually be avoided by using suitable additive concepts.

Diesel R33 is an example of how blends of completely unpolarisable substances (HVO) with highly polar biodiesel can be combined in mineral oil-based diesel fuel, together with suitable additives, to make a stable “performance fuel”, and even to complement each other with their respective positive properties.



## 9 Combustion optimisation and hybridisation

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Combustion engine drive components will be able to make important contributions to sustainable mobility concepts of the future with the use of regeneratively produced fuels. On the one hand, chemically bound energy sources offer high energy densities, fast refuelling and long operating ranges. On the other hand, the adaptation and optimisation of fuel properties enables new parameters in engine development. Developments to reduce or avoid the conceptual weak points of diesel and petrol engine combustion processes are particularly promising in this respect, as they offer the possibility of achieving great advantages in terms of emissions and efficiency.<sup>[99]</sup> With diesel engines, the possible reduction or avoidance of soot formation within the engine is of great interest, as good soot oxidation within the engine is associated with a high formation of nitrogen oxides and NO<sub>x</sub>. The so-called soot-NO<sub>x</sub> trade-off can be circumvented if the initial soot formation is reduced or avoided. With petrol engines, unwanted self-ignition in the unburnt mixture (knocking and/or pre-ignition) is a technical problem that can lead to efficiency losses and increased emissions, especially in the higher load range. In this respect, alternative fuels offer the possibility of avoiding the unwanted self-ignition in the unburnt mixture and thus of circumventing the emission and efficiency disadvantages.

The market introduction of alternative fuels can be expected to take place in two phases. In the first phase, alternative fuels will have to be compatible with vehicle engines currently on the market. However, this so-called "drop-in capability" means that the properties of the first alternative fuels cannot differ significantly from the properties of current conventional fuels. This comparability also limits the potential of the fuels in terms of combustion process improvements. However, as every efficiency and emission advantage will be important for the development of sustainable mobility concepts, there is a need to develop further potentials.

For a second generation of alternative fuels, it is possible to introduce fuels and combustion processes onto the market that are matched to each other so as to achieve minimal emissions, the highest possible efficiencies and the lowest possible system costs. Partially premixed diesel combustion processes such as the NADI, Unibus or modulate kinetics combustion processes represent a promising technology in this respect, which can completely avoid the formation of soot within the engine at individual operating points by using alternative fuels, adapting the engine design and the engine calibration. As this soot-free combustion can also be achieved at low NO<sub>x</sub> raw emission values, the complete exhaust gas treatment at these operating points can be realised by an oxidation catalyst. However, before the exhaust gas treatment systems for soot and NO<sub>x</sub> emissions can be simplified or omitted, it must be ensured that the formation of soot within the engine can be reliably avoided in large parts of the engine map. However, the use of hybridised drive concepts, in which the combustion engine is phlegmatised and thus the technically relevant engine map range can be significantly reduced, can be of use here. As soon as this is achieved, partially



premixed diesel combustion processes in hybridised drive concepts would have the economic advantage of being able to function with greatly simplified exhaust gas treatment systems, which can provide the necessary financial incentive for the introduction of a second generation of alternative fuels.<sup>[100]</sup>



## 10 Demands of climate policy

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In view of the 2030 and 2050 climate change policy target, time is ticking to fulfil greenhouse gas reduction targets. Sustainable and low-greenhouse-gas biofuels from cultivated biomass are globally available today, marking the beginning of a medium to long-term development strategy to replace fossil fuels and biofuels from cultivated biomass with other alternatives such as biofuels from waste and residual materials, e-mobility and synthetic renewable fuels. Time is needed for the evolutionary development of these options, but how much time is needed and what the future market significance of these options will be is not yet known. These alternatives have for years not been competitive and require an incalculable amount of public funding for infrastructure construction (charging columns, distribution networks), investment promotion, conversion or investment incentives etc. The discussion today is broadly still about research needs and project development when it comes to these alternatives. In order to guarantee the climate protection targets of 2030 and 2050 are met, policy makers must, however, make distinctions between the action areas for funding. In terms of fulfilling the legally dated climate change targets, politicians cannot afford to remove existing options from the market, if it is not yet possible to predict what progress can be made with an approach that is open to new technology.

In order to achieve the 2030 targets, efforts must be aligned with what is currently possible. Especially at this current time, engine and fuel development must not be neglected. In contrast, however, with the hybridisation of drives comes the increase of electrification, which physically reaches its limits with heavy commercial vehicles and off-road machines (construction and agriculture). Creating an infrastructure for overhead lines across Germany and the EU is, judging by the time frame (planning and construction method), likely not achievable. Additionally, shipping and air traffic rely on renewable liquid fuels.

Therefore, the focus must also be on consumption reduction. As a result of the development of engine technology, potential conservation reserves must be enhanced in order to reduce the existing biogenic fuel substitution potential, as measured by the ever increasing total fuel demand.

With the new edition of the Renewable Energy - Directive (REDII), the greenhouse gas reduction specifications are being increased further for biofuels as a prerequisite for access to the market. The GHG reduction efficiency of biofuels can increase in the short term with the goal of competition that is open to raw materials and technologies, and could be strengthened if a GHG reduction obligation based on the German model were introduced throughout the EU with steadily increasing quota requirements, which would drive this competition without "substitution effects". In terms of environmental policy, it makes little sense if waste oil is exclusively used in the EU's most profitable funding areas and if these raw materials are even imported from third countries which themselves, for example, need this raw material for biofuel production. As a



consequence of the GHG reduction requirement, the GHG reduction of biofuels in Germany increased to an average of 81 percent compared to fossil fuels.<sup>[101]</sup>

Competition that is open to technology and raw materials would also promote the site-adapted and most efficient technology for the production of alternative fuels or for the use of renewable electricity. German and European policy is required to support development through corresponding funding policy measures, which must simultaneously aim to accelerate infrastructure development (charging stations), especially in the EU's poorer countries.

## 11 Future requirements of biofuel research

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Both international production and consumption of biofuels (ethanol and biodiesel) are not only ideally supported by many countries, but are also legally required by mandates for admixture quotas and partly by tax incentives. In this context, while there is a global trend of expanding biofuel production to residual and waste materials, traditional raw materials such as vegetable oils, sugar and starch are by far the most important source of raw materials for the onset of global transport defossilisation. The research projects, conducted primarily in Germany, in the area of biofuel are therefore an important scientific source of information for the international exchange of expertise and for the avoidance of duplicating research. However, there is no strategic promotion in the sense of proactive accompanying research. The goal must be to promote existing raw material options such as biodiesel from vegetable oils and also vegetable oil fuels from decentralised processing, because this will also create regional added value.

This approach will lead to more public acceptance. For example, the use of rapeseed oil fuel in diesel engines was subject to many tests in the past and this successful implementation was able to be demonstrated in conjunction with various modifications made to fuel and engine systems. In conjunction with new diesel engines, which are characterised by modern high-pressure injection and exhaust gas treatment systems, even less research has been conducted with rapeseed oil fuel in comparison with fossil diesel fuel or FAME. Therefore, more in-depth information on behaviour in fuel systems, in mixture preparation during injection, on ignition and combustion behaviour, on behaviour in exhaust gas treatment systems, on emission behaviour (even in real operation) and on durability is necessary for the optimisation of engines that are suitable for rapeseed and vegetable oil. Finally, for type approval, the necessary and increasingly strict statutory requirements in the emissions law must be fulfilled.

Analogous requirements and research questions also arise with biodiesel with different fatty acid compositions, chain lengths and admixture proportions of fossil or even renewable aliphatic fuels. Possible interaction effects may impede versatility. The wide variety of potential synthetic renewable fuels makes it necessary to research optimum admixture proportions in order to guarantee the best possible synergy of the respective advantages of individual biofuels within a multi-component mixture. The differences between the polarities of biofuels requires research into miscibility and the use of amphiphilic fuels such as biodiesel, for example, as a solubiliser. In this context, the biofuel mixtures as well as the clean fuels must be examined in terms of their specific properties in order to be able to take advantage of other specific fuel properties in a targeted manner, as well as replacing fossil fuels. Examples here are the use of biologically degradable fuels in environmentally sensitive sectors and the use of cold-stable fuels in aviation.



Additionally, the question is raised as to whether and how biodiesel can be chemically optimised in terms of improved miscibility with fossil and synthetic fuels. The aim is the improvement of the boiling curve by optimising the chain length using metathesis, for example. At this point, it should also be examined as to whether a separation of fatty acids according to the chain length by distillation represents another approach along these lines. For example, natural fatty acid distributions can be separated by distillation after transesterification to the simple alcohol methanol. Thus, fractions of different chain lengths can be represented. If FAME with one, two or three double bonds can be separated using distillation, there is the possibility of taking advantage of different solubility properties in a targeted manner and of thus avoiding miscibility gaps when combining with synthetic fuels. This corresponds to the commercial distillation of pure fatty acids after fat splitting. This idea could be conceivably expanded by a “chemistry based on methyl esters”.

A wide variety of modifications to the fatty acid chain have been described in recent decades, for example selective hydrogenation, dimerisation, co-oligomerisation, Friedel-Crafts alkylation or acylation, ene reaction, radical addition, epoxidation, oxidative splitting/ozonolysis, cyclopropanation, metathesis and more. It must be checked as to which of these reactions is also applicable to the methyl esters of these fatty acids. The resulting reaction products, modified fatty acid methyl esters, can be finally interesterified into other alcohols. This way, base oils, for example high performance lubricants, can be synthesised.

In this way, today’s plants, optimised exclusively for continuous FAME production, would be further developed into bio-refineries with a diverse range of products. As well as the production of fuels, this concept also offers the possibility of substantial use of renewable raw materials.

These new products, but primarily new synthetic fuels or mixtures, have functional groups which do not occur in fossil fuel. Through the ether group, fuels such as dimethyl ester or OME clearly show other solubility properties, which requires considerable research into the material compatibility of fuel-carrying components.

There is also the fact of the functionality test of the fuel additives. With regard to an increasing number of plug-in hybrids which combine the advantages of combustion engine and electrical drive types, the longer dwell time of fuels in the tank must be taken into account and new additives to improve the oxidation stability of biogenic and synthetic fuels, in particular must be researched.

Engines, exhaust gas treatment systems and engine components for biofuels and biofuel blends must be tested in operation under permanent loads as a basis for market introduction (e.g. studies of deposit formation in injectors and measures to avoid this). Therefore, the engines and the exhaust gas treatment system for biofuels and biofuel



blends must be optimised with the goal of improving efficiency and the output of harmful substances, in order to fulfil increasing requirements of emission standards in future.

For various reasons, the ingress of biogenic fuels into lubricant often leads to a reduction of the recommended oil change intervals. To avoid unnecessary early oil changes, oil condition sensors would be necessary. These would continuously detect the specific engine oil load during operation, forward essential information on the oil condition to the operator and send warnings punctually before important limits are exceeded. Oil change intervals can then be set according to need. It should be noted that the overwhelming majority of the reported lubricant problems when using biogenic fuels are due to the fuel quality. Thus it is clear that the (further) standardisation of “new” fuels is of particular importance.

Regarding a future tightening of emissions guidelines in the Euro 7, solutions must be found early on in order to reduce emissions further. The degree of effectiveness of modern engines is already near the upper limit of physical possibility. Optimisation potential exists in the interaction of engine and fuel. If fuel parameters can be shared via sensors, combustion can be optimised using suitable engine management. Not only does the development of sensors play an important role here, but also the adaptation of engine parameters specifically to the fuels. Component detection plays a particular role in the increase of biocomponent quotas in fuels, as this can only be realised through a variety of different raw material sources and, therefore, of different chemical compositions.

Lastly, alongside the scientific research, it is also necessary not to neglect communication with society in order to systematically establish causes for the lack of biofuel acceptance (especially of first generation biofuels) and to be able to take measures against these reservations for all generations of biofuels. New technical developments must be brought into the public sphere in an ideology-free, understandable and explanatory manner, so that both society and politics are able to understand the change and so that it does not actively obstruct it. This is where scientific dialogue takes on an especially important role.

The protection of both the climate and resources is a topic that is still part of positive public discourse and can be accompanied by questions about emissions, in particular in the case of biofuels. The roll-out of sustainable inner city fuels such as diesel R33 shows clearly the great potential of scientific dialogue. This must now be urgently expanded so that the combustion engine, in conjunction with sustainable fuels, can find technical and societal acceptance and a place in the future.



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# FUELS JOINT RESEARCH GROUP



## Fuels Joint Research Group

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This report is the multi-year result of the work of the UFOP Expert Commission „Biofuels & Renewable Resources“ on current and future fields of action in biofuels, which are of great importance in view of climate change.

The expert commission supports the UFOP in all matters relating to biofuel research, with particular emphasis on biofuels from rapeseed oil. The committee acts in an advisory capacity and is made up of experts from scientific research, the vehicle and petroleum industry and trade associations. The expert commission initiates research projects that are funded by UFOP or in cooperation with other institutions. The research reports are published at [www.ufop.de](http://www.ufop.de).



Cuvillier Verlag Göttingen



ISBN 978-3-7369-6555-3



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