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DISSERTATION

Combustion Process Development and Diesel Engine Suitability Investigations for Oxygenated Alternative Fuels

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by

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I confirm that going to press of this thesis needs the confirmation of the examination committee.

Affidavit

I declare, in lieu of oath, that I wrote this thesis and performed the associated research myself, using literature cited in this volume. If text passages from sources are used literally, they are marked as such.

I confirm that this work is original and has not been submitted elsewhere for any examination, nor is it currently under consideration for a thesis elsewhere.

Vienna, 28 June 2019 Aleksandar Aleksandrov Damyanov

Thank You

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I dedicate my work to my recently deceased father, Alexander Damyanov senior.

Abstract

Renewable fuels have the potential to contribute to the reduction of CO_2 emissions of the transport sector. Of particular interest concerning a Diesel engine are oxygen-containing fuels as they can defuse traditional target conflicts such as the particle-NO_x trade-off or the efficiency-NO_x compromise. In the course of the research activities at the *Institute for Powertrains and Automotive Technology* at the *Vienna University of Technology*, the suitability for motor combustion of a series of preselected biofuels was experimentally investigated. The fuels were the short-chained alcohols **ethanol**, **methanol** und **butanol**, one representative of the furans **2-methyltetrahydrofuran**, as well as the ethers **polyoxymethylene dimethyl ether** (POMDME), **di-*n*-butyl ether** and **dimethyl ether**.

On a modified Diesel engine in single cylinder operation, fuel-specific combustion processes were developed and analysed regarding their feasibility, efficiency and emissions. A distinctive feature of the project is the investigation of the fuel introduction into the internal combustion engine in three different ways. In addition to the generally used method of **direct injection** of **neat fuels** or **Diesel-biofuel blends**, the biofuel was also fed via intake manifold injection in combination with parallel direct injection of diesel fuel into the combustion chamber. This method is widely known as “**dual-fuel**” combustion. As a third particularly innovative approach, the operation of the Diesel engine with **synthesis gas** was analysed. The synthesis gas was delivered by the virtual upstream process of bio-fuel reforming with exhaust heat utilisation. The gas is then fed to the engine by means of an injection system into the intake manifold. In this case, the ignition is also effected via diesel pilot injection.

The biofuel potential was evaluated using the three variants of fuel application and the results of the different biofuels were compared. A major part of the content of this thesis originates from the *FFG* funded research project “Oxy-Gen2”. An overall assessment summarizes the partners’ results regarding fuel production analysis, reforming investigations and motor operation, and provides an overview of the fuel potentials for use in a Diesel engine.

Fuels with Diesel-like ignitability proved to be best utilised via **direct injection**. The tested **polyoxymethylene dimethyl ethers** revealed an extreme potential to completely eliminate the diesel typical soot-NOx trade-off since they were found to combust almost free of soot. The slight efficiency disadvantages encountered at the test bench can be dealt with by adapting the injection system. These fuels truly bear the potential to be used as a future Diesel fuel substitute, provided that their production meets the required socio-economical criteria. The high cetane **di-*n*-butyl ether** ranked after the tested POMDMEs regarding both combustion performance and production

feasibility as a fuel of lignocellulosic origin. None of the analysed **2-methyltetrahydrofuran** production processes could deliver positive CO_2 savings and its simulated production resulted in even more CO_2 output than fossil Diesel. It could be concluded that 2-methyltetrahydrofuran is not an appropriate fuel for the combustion process of the conventional compression ignition engine due to its low cetane number. The emission behaviour of the Diesel engine operation with **directly injected blends** of Diesel and alternative fuel was highly sensitive to the alteration of the ignition delay. Alternative fuels with a cetane number higher than Diesel reduced the ignition delay and created combustion conditions that were disadvantageous for the conventional Diesel fuel fraction. Therefore, higher emission levels (especially soot and particle number) were generated. Low cetane fuels like ethanol and methanol extended the ignition delay of the injected blend and enforced better mixture homogenisation, which resulted in less soot emissions. However, the influence of the lower cetane number on the pollutant emission output was significantly reduced at higher load operation, since the ignition delays do not differ so strongly as at low loads.

The **dual-fuel** operation is generally advantageous for low ignitability fuels like short-chained alcohols. The fuels should be of high ignition resistance in order to prevent uncontrolled auto-ignition of the fuel-air charge before the injection of the Diesel jet. The tests of a dual-fuel combustion concept with **ethanol**, **methanol** and **butanol** demonstrated a series of benefits. Significant soot, particle number, NO_x and CO_2 emission reductions were measured together with a noteworthy increase in efficiency. This technique allows high substitution shares and flexible operation depending on the fuel availability. Because of the unsuitable high-pressure hydraulic components, the high vapour pressure and high cetane fuel **dimethyl ether** could be fed only into the intake manifold. This considerably worsened the performance of the engine due to multi-stage auto-ignition in the compression stroke.

The operation of a Diesel engine with **intake manifold injection of synthesis gas** was possible but did not deliver any substantial benefits. The investigations of this operating mode showed that the lean operation of the Diesel engine and the relatively low exhaust gas temperatures make fuel reforming possible only at high loads. The expected advantage of soot mass reduction due to gas combustion was partly proven but generally no significant pollutant emission reduction was figured out and NO_x emissions even tended to increase. The overall efficiency of this non-optimised gas combustion process was lower than in Diesel reference operation, even after the virtual efficiency upgrade through fuel reforming had been considered.

Kurzfassung

Regenerativ gewonnene Kraftstoffe besitzen das Potenzial, einen Beitrag zur Absenkung der CO_2-Emissionen des Transportsektors zu leisten. Von besonderem Interesse beim Dieselmotor sind sauerstoffhaltige Treibstoffe, da sie traditionelle Zielkonflikte wie das Partikel-NO_x-Trade-Off oder den Effizienz-NO_x-Kompromiss entschärfen können. Im Rahmen der Forschungsaktivitäten am *Institut für Fahrzeugantriebe und Automobiltechnik* an der *Technischen Universität Wien* wurde die Eignung zur dieselmotorischen Verbrennung einer Reihe von vorselektierten Biokraftstoffen experimentell untersucht. Diese waren die kurzkettigen Alkohole **Ethanol**, **Methanol** und **Butanol**, ein Vertreter der Furane **2-Methyltetrahydrofuran**, sowie die Ether **Polyoxymethylendimethylether** (POMDME), **Di-*n*-Butylether** und **Dimethylether**.

An einem adaptierten Dieselmotor im Einzylinderbetrieb wurden kraftstoffspezifische Brennverfahren entwickelt und angepasst und in Puncto Umsetzbarkeit, Effizienz und Emissionen analysiert. Eine Besonderheit der Vorhaben war die Untersuchung der Kraftstoffeinbringung in den Verbrennungsmotor auf drei unterschiedliche Arten. Neben dem in der Regel angewandten Verfahren der **direkten Einspritzung** in den Brennraum als **Reinkraftstoff** oder **Diesel-Biokraftstoff-Blend** wurde der Alternativtreibstoff auch über Saugrohreinspritzung in Kombination mit direkter Einspritzung von Dieselkraftstoff dem Motor zugeführt. Diese Methode ist als s.g. „**Dual-Fuel**“-Brennverfahren bekannt. Als dritter besonders innovativer Ansatz wurde der Betrieb des Dieselmotors mit ins Saugrohr eingeblasenem **Synthesegas** analysiert, welches aus dem virtuellen vorgelagerten Prozess der Kraftstoffreformierung mittels Abgaswärme stammte. Die Zündung erfolgte dabei ebenfalls über einen Diesel-Strahl.

Das Potenzial der Biotreibstoffe wurde anhand der drei Techniken des Kraftstoffeinsatzes bewertet und die Ergebnisse der unterschiedlichen Biokraftstoffe miteinander verglichen. Ein Großteil des Inhaltes dieser Arbeit stammt aus dem *FFG*-geförderten Kooperationsprojekt „Oxy-Gen2“. Die Gesamtbewertung der Treibstoffe, in welche die von den Forschungspartnern gewonnenen Ergebnisse bzgl. Herstellungsanalyse, Reformierungs-Untersuchungen und des motorischen Betriebs zusammenfließen, gibt zusammenfassend den Überblick über die Kraftstoffpotenziale beim Einsatz in einem Dieselmotor.

Die **Direkteinspritzung** erwies sich als die beste Einbringungsvariante für Kraftstoffe mit dieselähnlicher Zündwilligkeit. Aufgrund ihrer nahezu rußfreien Verbrennung zeigten die untersuchten **Polyoxymethylendimethylether** ein extremes Potenzial zur vollständigen Abschaffung des dieseltypischen Soot-NOx Trade-Offs. Den leichten

Effizienznachteilen, die am Prüfstand festgestellt wurden, kann durch eine Anpassung des Einspritzsystems entgegengewirkt werden. Diese Treibstoffe können tatsächlich als zukünftige Dieselersatzkraftstoffe eingesetzt werden, vorausgesetzt, dass ihre Produktion den gestellten sozioökonomischen Kriterien gerecht wird. Der hochcetanige **Di-*n*-butylether** weist Nachteile gegenüber den getesteten POMDMEs sowohl beim Brennverhalten, als auch bei der Perspektive zur Herstellung aus Lignozellulose auf. Mit keinem der untersuchten Herstellungsverfahren für **2-Methyltetrahydrofuran** konnte eine CO_2-Einsparung dargestellt werden, im Gegenteil – seine simulierte Produktion ergab sogar einen höheren CO_2-Ausstoß als fossiler Diesel. Es konnte der Schluss gezogen werden, dass sich 2-Methyltetrahydrofuran aufgrund seiner niedrigen Cetanzahl nicht als Kraftstoff für das Brennverfahren des konventionellen Selbstzündungsmotors eignet. Das Emissionsverhalten des Dieselmotorbetriebs mit **direkt eingespritzten Gemischen** aus Diesel und alternativem Kraftstoff, s.g. „**Blends**“, war sehr empfindlich gegenüber der Veränderung des Zündverzugs. Alternative Kraftstoffe mit einer höheren Cetanzahl als Diesel verringerten den Zündverzug und schufen damit nachteilige Verbrennungsbedingungen für die Fraktion an konventionellem Dieselkraftstoff, weshalb höhere Emissionswerte (insbesondere an Ruß und Partikelzahl) erzeugt wurden. Kraftstoffe mit einer niedrigen Cetanzahl wie Ethanol und Methanol verlängerten den Zündverzug des eingespritzten Blends und ermöglichten somit eine bessere Homogenisierung des Gemisches, was zu weniger Rußemissionen führte. Der Einfluss der niedrigeren Cetanzahl auf den Schadstoffausstoß war jedoch im Betrieb mit höheren Lasten deutlich geringer, weil sich die Zündverzugszeiten dort nicht so stark unterscheiden wie bei niedrigen Lasten.

Der **Dual-Fuel-Betrieb** ist im Allgemeinen vorteilhaft für Treibstoffe mit geringer Zündwilligkeit wie die kurzkettigen Alkohole. Die Kraftstoffe sollten einen hohen Entflammungswiderstand aufweisen, um eine unkontrollierte Selbstentzündung des Kraftstoff-Luft-Gemisches vor der Einspritzung des Dieselstrahls zu verhindern. Die Versuche mit dem Dual-Fuel-Brennverfahren mit **Ethanol**, **Methanol** und **Butanol** zeigten eine Reihe von Vorteilen. Es wurden signifikante Ruß-, Partikelzahl-, NO_x- und CO_2-Emissionsminderungen zusammen mit einer bemerkenswerten Effizienzsteigerung gemessen. Diese Methode ermöglicht hohe Substitutionsanteile und einen flexiblen Betrieb in Abhängigkeit von der Kraftstoffverfügbarkeit. Aufgrund der nicht geeigneten Hochdruck-Hydraulikkomponenten konnte der **Dimethylether**, ein Kraftstoff mit hohem Dampfdruck und hoher Cetanzahl, nur in das Saugrohr eingespeist werden. Dies verschlechterte den motorischen Betrieb aufgrund der mehrstufigen Selbstzündung im Kompressionshub erheblich.

Der Betrieb des Motors mit **Saugrohreinblasung von Synthesegas** war möglich, brachte jedoch keine wesentlichen Vorteile. Die Untersuchungen dieser Betriebsart haben ergeben, dass aufgrund des Magerbetriebs des Dieselmotors und der relativ niedrigen Abgastemperaturen die Kraftstoffreformierung nur bei höheren Lastanforderungen möglich ist. Der erwartete Vorteil der Rußmassenreduktion aufgrund der Gasverbrennung wurde teilweise nachgewiesen, es wurde jedoch im Allgemeinen keine signifikante Reduktion der Schadstoffemissionen festgestellt und die NO_x-Emissionen nahmen sogar tendenziell zu. Der Gesamtwirkungsgrad dieses nicht optimierten Gas-Brennverfahrens war niedriger als im Dieselreferenzbetrieb, selbst nachdem die virtuelle Wirkungsgradsteigerung durch die Kraftstoffreformierung berücksichtigt wurde.

> *"The use of vegetable oils may seem insignificant today, but such oils may become in course of time as equally important as some natural mineral oils and the tar products are at the present time. [...] In any case, they make it certain that motor power can still be produced from the heat of the sun, which is always available for agricultural purpose, even when all our natural stores of solid and liquid fuels are exhausted."*[1]

Dr. Rudolf Diesel

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[1] Diesel, R.: The Present Status of The Diesel Engine in Europe and a Few Reminiscences of the Pioneer Work in America; 1912

Contents

Nomenclature

Greek Letters

λ	–	air-fuel equivalence ratio
λ_{BS}	–	air-fuel equivalence ratio calculated according to *Brettschneider*

Chemical Compounds

CH_4		methane
CO		carbon monoxide
CO_2		carbon dioxide
Cr		chromium
H_2		molecular hydrogen
H_2O		water
Ni		nickel
NO		nitrogen oxide
NO_2		nitrogen dioxide
NO_x		nitrogen oxides
O_2		molecular oxygen

Abbreviations

%e.	%	energy share
°CAaTDC		crank angle degree after firing top dead centre
0D/1D		zero-dimensional/one-dimensional
2-MTHF		2-Methyltetrahydrofuran
ACEA		European Automobile Manufacturers' Association
B0		fossil Diesel with 0 % biogenic fuel share
B7		fossil Diesel with 7 % bioDiesel
BuOH		butanol
CEC		certified test Diesel fuel
CEET		Institute of Chemical Engineering and Environmental Technology

CO_{2eq}		carbon dioxide equivalent
DBE		di-n-butyl ether
DME		dimethyl ether
E65		a mixture of 65 vol% ethanol and 35 vol% gasoline
E85		a mixture of 85 vol% ethanol and 15 vol% gasoline
EGR		exhaust gas recirculation
EtOH		ethanol
EU		European Union
FFG		Forschungsförderungsgesellschaft
FFKM		perfluoroelastomers
FSN	–	filter smoke number
GHG		greenhouse gas
HC		hydrocarbons
IFA		Institut für Fahrzeugantriebe und Automobiltechnik
IMEP	bar	indicated mean effective pressure
LHV	J/kg	lower heating value
MEP	bar	mean effective pressure
MetOH		methanol
MFB50%	°CAaTDC	mass fraction burned 50 %
OME		oxymethylene ether
OP		operating point
ÖVK		Österreichischer Verein für Kraftfahrzeugtechnik
P	bar	pressure
POMDME		polyoxymethylene dimethyl ethers
PTFE		polytetrafluoroethylene
PtX		power-to-X
RED		Renewable Energy Directive
T	°C	temperature
TCR		thermochemical recuperation
TPA		three pressure analysis
TU Graz		Graz University of Technology
TU Wien		Vienna University of Technology
U.S.		United States
vol%	%	volumetric share
WKM		Wissenschaftliche Gesellschaft für Kraftfahrzeug- und Motorentechnik e.V.

I. Introductory Chapter

Throughout my studies at the *Vienna University of Technology*, my interest for advanced and sustainable technology development was strengthened and encouraged. The desire to contribute to some of the most important global aspects of our time fortunately found its realisation within the opportunity for a Doctoral thesis at the *Institute for Powertrains and Automotive Technology*. The scientific projects I was involved in or led delivered highly valuable information and results, most of which were consistently made accessible to readers worldwide in the form of conference proceedings, scientific journal articles, book chapters [1], project reports and press releases. Since the quality of the publications was acknowledged by experts and the contributions generally received high recognition in professional circles, I was kindly given the opportunity to compose my thesis as a cumulative dissertation in accordance with the directive of the *Vienna University of Technology* (Appendix 1). The main requirements for this type of thesis are an introductory chapter, including the problem statement, the research objectives, the materials and methods, a summary and the contribution of the scientific publications, and an enclosure of at least three peer-reviewed articles.

Projects

This doctoral thesis shows the academic outcomes of the Diesel alternative fuel projects conducted by me and my esteemed colleagues at the *Institute for Powertrains and Automotive Technology (IFA)* at the *Vienna University of Technology* and at the *Institute of Chemical Engineering and Environmental Technology (CEET)* at the *Graz University of Technology*.

I first started my work on alternative fuels with my master's thesis [3], which was finished in May 2015. Since then I have participated or led projects on potential evaluation of Diesel engine alternative fuels, including combustion process development and fuel production.

The first research project I worked on was funded by the *Austrian Science Funding Agency* (*Österreichische Forschungsförderungsgesellschaft; FFG*), held by the *Austrian Ministry for Transport, Innovation and Technology (BMVIT)* and the *Federal Ministry for Digital and Economic Affairs (BMDW)*. The project partners were the *Institute for Powertrains and Automotive Technology (IFA)* at the *Vienna University of Technology* and the *Institute of Chemical Engineering and Environmental Technology (CEET)* at the *Graz University of Technology* and the companies *AVL List GmbH* and

OMV Refining & Marketing GmbH. *AGRANA Beteiligungs-AG*, Austria's biggest bio-ethanol producer, supported one of the later projects. The *Austrian Society of Automotive Engineers (ÖVK)* also invested in a project handling Diesel substitution fuels.

The names of the non-confidential projects in which I was involved are listed in chronological order together with a short comment on the objectives:

2014-2017	FFG project "Oxy-Gen2"; biofuel production from lignocellulose, fuel reforming, biofuel usage in a Diesel engine and combustion process development for different biofuel supply concepts
2016	Project "Diesel HighBlends", supported by ÖVK; combustion engine investigations of Diesel-biofuel-mixtures with higher biofuel shares
2017-2018	AGRANA-Project "Einsatz von Ethanol und Ethanol-Benzin-Mischungen in einem Dieselmotor mittels Dual-Fuel-Brennverfahrens"; combustion process development and detailed investigations of the dual-fuel operation of a Diesel engine with intake manifold ethanol injection

1 Motivation

Greenhouse Gas Emissions

In the second decade of the 21st century, the world's energy demand is still mainly covered by fossil fuels. Their usage is marked by low costs and wide availability on the one hand, but also by a series of global problems like geopolitical dependency, environmental impairment and emissions of greenhouse gases on the other hand. Carbon dioxide is claimed to be the primary contributor to the greenhouse effect and, therefore, to the observed climate change. The detailed scientific opinion on this topic can be found in the assessment reports of the *Intergovernmental Panel on Climate Change (IPCC)*. Due to increasing environmental awareness among the world's population, the term "CO_2" has become a driving power for an enormous number of research and development activities among industry, science and politics. In 1992, countries across the globe adopted the *United Nations Framework Convention on Climate Change (UNFCCC)* to cooperatively consider options for limiting average global temperature increase and the resulting climate change. The *Kyoto Protocol* was the first international legally binding agreement signed under the *UNFCCC*. It specifies the mitigation obligations of the parties that signed the agreement. It was signed in 1997 and entered into force in 2005. *The Paris Agreement* from 2015 resulted as a successful outcome of the 21st Conference of the Parties (COP 21) in Paris. Governments have agreed on a long-term goal of ensuring that the increase in global average temperature does not exceed 2 °C above pre-industrial levels, aiming to limit the increase to no more than 1.5 °C, as this would significantly reduce risks and the impacts of climate change [4]. As of July 2018, 178 of 197 countries have ratified the Paris Agreement [5]. Each country determines individually the efforts to achieve the set goal within the so-called "Nationally Determined Contributions" (NDCs). The main instrument is the reduction of greenhouse gases originating from human activity, which can be achieved by lowering the usage of fossil fuels.

According to the *International Energy Agency (IEA)*, in 2018, global energy-related CO_2 emissions reached a historic high of 33.1 Gt [2] [2] and the transport sector accounted for approx. one quarter of them [6]. About 96 % of the transport final energy consumption was covered by non-renewables (mainly fossil oil) [7].

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[2] IEA estimates include emissions from all reported energy use of fuels, but exclude emissions from non-energy use of fuels.

The total greenhouse emissions of the European Union in 2016 were 4 441 Mt carbon dioxide equivalent (CO_{2eq}), which is 22 % less than the 1990 levels [5]. The transport sector is a major contributor to the greenhouse gas emissions with a share of about 27 % in 2016. The figure decreases to 20 % if international aviation and maritime emissions are excluded [8]. Road transport accounts for 72 % of the transport GHG emissions and one fifth of the EU's total GHG emissions [8, 9]. 44 % of these total transport GHG emissions were contributed by passenger cars, while 19 % came from heavy-duty vehicles [8]. By 2016, transport emissions (including international aviation but excluding international shipping) were 26.1 % higher in comparison to 1990 and the transport sector remains the only main European economic sector in which GHG emissions have increased, when compared to 1990 levels [10]. The share of energy from renewable sources in the EU's transport sector was 7.1 % in 2016 [11]. Renewable energy in this sector comes mainly from biofuels (close to 90 %), with electricity still playing a limited role [11].

The European Commission's 2011 Transport White Paper sets out an indicative target of a 20 % reduction from 2008 levels by 2030 and a 60 % reduction in transport GHG emissions by 2050 compared to 1990[3] [12]. Specific targets for the transport sector are described in the following legislative EU documents:

- Directive 2009/28/EC on the promotion of the use of energy from renewable sources, also known as RED. It prescribes a 10 % share of renewable energy in transport's final energy consumption for each Member State by 2020. [13]

- Directive (EU) 2018/2001 (known as REDII) is the recently approved recast of Directive 2009/28/EC and handles the period 2020-2030. The directive establishes a binding Union target of at least 32 % renewable energy share in total EU energy consumption in 2030. In order to mainstream the use of renewable energy in the transport sector, each Member State shall set an obligation on fuel suppliers to ensure that the share of renewable energy within the final consumption of energy in the transport sector is at least 14 % by 2030. REDII still caps the contribution crop-based biofuels can make at each Member State's 2020 levels, up to 7 % energy share. So-called "advanced" biofuels (e.g., from straw or non-food cellulosic material) should account for at least 3.5 % energy share and can be double-counted. [14]

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[3] This would correspond to emissions cuts of around 70 % below 2008 levels.

- The regulations on CO_2 emissions from new passenger cars (443/2009) [15] and new light commercial vehicles (510/2011) [16] set average emission limits of 95 gCO_2/km by 2020 / 2021 (new passenger cars) and 147 gCO_2/km by 2020 (new light commercial vehicles). On 17 December 2018, the Parliament and the Commission of the EU tentatively agreed on new CO_2 emission standards for passenger cars and light commercial vehicles in the EU beyond 2020. By 2030, new vehicle emissions will have to be 37.5 % lower than in 2021 and 31 % lower for new light commercial vehicles. Following this political agreement, the Members of the European Parliament and the EU Ministers approved the regulation on 27 March 2019 [17]. The new law demands that the full life-cycle of emissions from cars should be assessed at EU level. The Commission will also have to evaluate whether to have a common methodology for the assessment and consistent data reporting, by no later than 2023. If appropriate, legislation should follow. This message is a very important signal that the lawmakers realise the necessity to address life-cycle emissions and not just the in-use emissions of a vehicle concept. Exactly regarding this point, internal combustion engines operated with regenerative fuels are expected to prove their sustainability.

- The Fuel Quality Directive (98/70/EC) sets out reporting requirements relating to the quality of petrol and Diesel fuels sold for road transport. Member States shall require suppliers to reduce gradually the life cycle GHG emissions per unit of energy from fuel and energy supplied by up to 10 % by the end of 2020. [18]

The 2018 *European Automobile Manufacturers' Association (ACEA)* report on vehicles in use in Europe [19] depicts some very important facts. According to it, 31.5 million vans, 6.3 million trucks and 745 000 buses are in circulation throughout the European Union. Almost 90% of the van fleet and nearly all trucks (96.1%) in the European Union run on Diesel. The EU passenger car fleet grew by 5.7 % over the last five years; the number of vehicles on the road went from 243 to 257 million. In 2016, 53.9 % of passenger cars in the EU ran on petrol, 42.0% were Diesel-driven. The year 2017 saw two new and related trends in EU car registrations: an increase in CO_2 emissions coupled with a rise in petrol sales, according to new data from the *European Environment Agency (EEA)* and the *ACEA* [20]. For the first year (2017) since 2009, petrol cars became the most sold vehicles in the EU, constituting almost 53 % of sales [21]. Diesel cars made up 45 % of the new registrations. The difference between average fuel efficiency of petrol cars (121.6 gCO_2/km) and Diesel cars (117.9 gCO_2/km) started to reduce compared to 2016. The average fuel efficiency of petrol cars has been constant in the last two years; whereas the fuel-efficiency of Diesel cars has worsened compared to 2016 (116.8 gCO_2/km). New cars sold in 2017 emitted on average 118.5 gCO_2/km, a slight increase of 0.4 gCO_2/km compared to 2016. [21]. Sales of plug-in hybrid electric vehicles (PHEV) and battery-electric vehicles (BEV) continued to increase, by 42 % in 2016. However, the share of these categories in the new fleet remains low (1.5 % in 2017). Despite an increase in registrations in recent years, alternatively-powered passenger cars make up only 3.4 % of the total EU car fleet in 2018. A report from the European Commission shows that the EU transport fuel market is still dominated by Diesel, which made up 71.8 % of fuel sold in the year 2016 [22].

Despite the present alternative powertrain development and perceptual trend towards drivetrain electrification, the Diesel engine is predicted to remain crucial for mobility of people and goods in the long term due to its unmatched efficiency, robustness and operational cost and flexibility. The statistics revealed above show that the transport sector is not on track towards its climate goals. Reaching the new passenger cars fleet target of 95 gCO_2/km needs substantial improvements. Only two EU Member States – Austria and Sweden – have already reached the goal of a 10 % share of energy from renewable sources in transport by 2020. Enhancing the usage of greenhouse gas saving alternative fuels in internal combustion engines is a feasible and powerful solution for accelerating the progress of the transport sector towards its climate objectives [23, 24]. Such fuels are already on the market or are ready to use. Additionally, new alternatives are being developed and innovative production methods are being optimised. The range of possibilities is enormous. At the end of the day, the factors GHG savings, availability, environmental acceptability, costs and usability, will determine the fuels of the future.

Emission Legislation

Transport continues to be a source of air pollution, especially of particle emission and nitrogen oxides (NO_x), although these emissions have been significantly reduced in the last decade due to the introduction of fuel quality standards, the Euro vehicle emission standards and the use of cleaner technologies [10]. Especially the Diesel engine has been the focus of criticism due to its generally higher particle and NO_x emissions. The European legislation on exhaust emissions of new cars constitutes a very efficient tool for reducing pollutant emissions and is still developing towards even stricter limits. The current exhaust emission standard Euro 6 has been in force since 2014. For passenger cars equipped with a Diesel engine, it sets a limit of 80 mg/km NO_x, 4.5 mg/km PM (particle mass) and $6x10^{11}$ PN particles/km (particle number) [25]. Commercial vehicles running on Diesel should not emit more than 460 mg/kWh NO_x, 10 mg/kWh PM and $6x10^{11}$ particles/kWh in the World Heavy Duty Transient Cycle

(WHTC) [26]. Alternative fuels have the potential to help achieve further reductions in exhaust pollutants since they can offer advantageous chemical composition and/or enable the development of cleaner combustion processes. A possible fuel derived simplification of the exhaust gas aftertreatment systems will most probably result in higher engine efficiency and lower costs.

WKM Position Papers

Two highly motivating documents for the ongoing research of alternative fuels for internal combustion engines come from the *Wissenschaftliche Gesellschaft für Kraftfahrzeug- und Motorentechnik e.V. (WKM)*[4]*.* Their first position paper was published in June 2017 and formulated three scientific based key messages relating to the future of the combustion engine [27] (Appendix 2). The following statements can be read: *"Combustion engines have been and continue to be the driving force behind mobility, freight transport, and mobile machinery. This role can be complemented, but not replaced, by electrical drives."* and *"The particular advantage offered by combustion engines is the efficient and flexible use of fuels with high energy density and excellent storage and distribution options.* […] *The potential to flexibly use non-fossil and hence* CO_2*-neutral fuels is another guarantee for a long-term and sustainable technology of the future."*

The second *WKM* position paper was published in December 2018 and makes 10 important statements concerning the EU transport CO_2 legislation [28] (Appendix 3). Especially motivating for this dissertation is the appeal to include the potential of synthetic or biogenic fuels (reFuels as generic term for the different CO_2 saving fuels – PtX, E-Fuels, bioFuels) in future EU legislation because they offer far-reaching chances for achieving the CO_2 targets of the Union. Moreover, reFuels can unfold their CO_2 mitigating potential not only in new vehicles but also in vehicles that are already in use. For heavy vehicles, ships and planes, there is no alternative to regenerative fuels.

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[4] WKM e.V. is an association of professors from German, Austrian and Swiss universities who as heads of institutes, heads of departments, or holders of chairs are, or have been, active in the domains of automotive engineering and/or engine technology.

2 Problem Statement

Nowadays, alternative fuels are a popular research topic at many scientific institutions all around the globe. The investigations handle various aspects that are relevant for the ability of a given substance to serve as a future fuel: the production methods and feedstock availability, eco-friendliness and sustainability, socio-economic issues and engine suitability. Hereby, different approaches can be observed – they may be generally defined as “bottom-up” and “top-down”. In the first case, there is a substance that is assumed sustainable and feasible in production and the objective is to test its performance as a fuel for an internal combustion engine. In the second case, the desired properties of the theoretical fuel are predefined for a given combustion concept and the intent is to find or invent a real fuel possessing properties that are as close as possible to the required ones.

An appropriate proposal for a five-point definition of socio-economical compatibility is given by Jacob and Maus in [29], Figure 1.

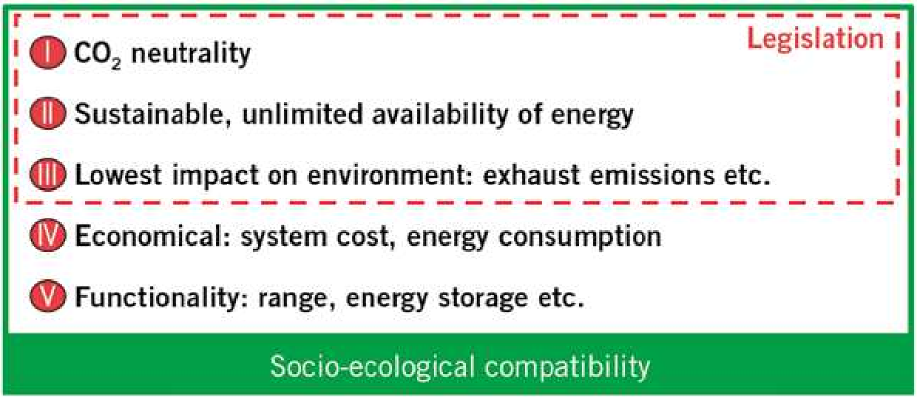

Figure 1: Socio-ecological compatibility criteria of future fuels [29]

The projects, this thesis is based on, followed the bottom-up principle. Most of the investigated possible fuel candidates were preselected in the course of the investigations at the *Institute of Chemical Engineering and Environmental Technology (CEET)* at the *Graz University of Technology* [30, 31, 32]. These investigations examined the conversion of lignocellulosic material to alternative fuels through direct and indirect biomass liquefaction and lignocellulose pulping, and suggested possible fuel alternatives that were worthwhile for engine investigations. At this point, it should be noted that lignocellulosic biomass is a possible, but not the only raw material for the investigated fuels. The fuels may be produced by different methods and from different feedstock, e.g., from starch containing biomass or as synthetic fuels from hydrogen, carbon dioxide and regenerative electricity. Changing the production method, however, would also require a new estimation of the socio-economical compatibility.

This thesis investigates the Diesel engine suitability of several alternative fuels which were found to be possible sustainable fuels within the preselection process.

Ethanol, methanol and butanol belong to the discussed alcohols; the representatives of the ethers are polyoxymethylene dimethyl ethers (POMDME, but also simply “OME_n”), di-*n*-butyl ether (DBE) and dimethyl ether (DME). Additionally, the furan 2-Methyltetrahydrofuran (2-MTHF) was investigated. The focus fell on substances with higher oxygen-content (so-called “oxygenates”), as they were expected to provide advantages due to reduced soot emissions and innovative options for the combustion process. The possibility to use them in a given type of engine depends on the properties provided by their chemical composition. Concentrating only on fuels that are appropriate for the conventional Diesel combustion process would have significantly shortened the list of possible fuel candidates. A required compliance with the current Diesel fuel standard EN590 [33] would also have eliminated substances that are otherwise appropriate as an innovative energy carrier. Since the work is future-orientated, substantial degrees of freedom within the fuel selection were unlocked by altering the combustion process and ignoring the fuel norm.

The problem that is discussed in this thesis concerns the most suitable combustion process for the chosen fuels and their performance and emission behaviour in a Diesel engine. Depending on the fuel properties, generally, two different methods for fuel supply into the Diesel engine are available. On the one hand, the fuel can be directly injected into the combustion chamber of the Diesel engine. This is the commonly used technique for liquid fuels with sufficient ignitability. The same method is applied with fuel mixtures of Diesel and alternative fuel, e.g., the standard B7 Diesel with 7 vol% fatty acid methyl esters (bioDiesel). On the other hand, fuels, which are not suitable for direct injection due to their chemical or physical properties (cetane number, aggregate state, etc.), can be fed into the intake manifold of the engine. The combustion is then started by the ignition of a directly injected Diesel jet. This combustion type is widely known as “dual-fuel” and may be appropriate for a wide range of different fuels. The operation of the engine with a synthesis gas (also called “SynGas”), produced through endothermic reformation of a given alternative fuel, is a highly innovative concept which is still not very popular and at an early research state. Though it is, in general, a dual-fuel process, the SynGas operation is seen as a third method in this work because it consists of the virtual upstream process of the fuel reformation and the gas includes not only a combustible substance but also high amounts of inert components.

2.1 Operation of a Diesel Engine with the Poor-Ignitability Fuels Methanol, Ethanol, Butanol and 2-Methyltetrahydrofuran

Ethanol, methanol and butanol are short-chained alcohols and are not suitable for usage in a Diesel engine via direct injection because their cetane number is very low and ignition cannot be ensured. There are compression ignition engines with direct injection running on ethanol, however, ignitability improvers (so-called cetane boosters) are necessary [34]. This concept is not pursued in this thesis because it is already on the market and would require considerable additive amounts should the even more ignition-resistant methanol be used. These alcohols can be mixed up to a certain ratio with conventional Diesel fuel and then injected directly into the combustion chamber. This is the easiest method to use them in a Diesel engine but the maximum alcohol share in the blended fuel is very limited due to separation issues. In most cases, mixture stabilizing agents like emulsifiers are required. With higher alcohol amounts, ignitability again becomes a problem. Though the method of combusting Diesel-ethanol blends is widely discussed in literature and generally improvements in emissions are reported by most researchers [35-42], a direct comparison of engine performance with blends of Diesel and ethanol, methanol or butanol, conducted under exactly the same conditions, is not known to the author of this thesis.

Perhaps the most promising technique for short-chained alcohol usage in a Diesel engine is the dual-fuel combustion process. The dual-fuel combustion process itself is not a novelty, it has been used in certain applications since the very early age of the internal combustion engine with different fuels, mostly natural gas [43, 44], but also liquefied petroleum gas [43], gasoline [45], hydrogen [43], reformed gases and other alternative fuels [46]. It was in 1901 that Rudolf Diesel obtained a U.S. patent covering the concept of the dual-fuel engine [47]. Similar to the other low reactivity fuels mentioned, alcohols like ethanol or methanol [48-51] can also be very successfully utilized in a dual-fuel designed Diesel engine. There are several possibilities to configure the dual-fuel system depending on the mixture formation method – external or internal. On the one hand, the alternative fuel can be added to the intake air upstream via manifold injection [52], carburettor or evaporator – a method widely known as “fumigation”. On the other hand, the fuel may be directly injected into the combustion chamber through a dedicated injector [53] or a special dual-fuel injector for Diesel and alternative fuel. Several researchers have published articles on investigations of the dual-fuel combustion process with intake manifold injection of alcohols. The findings, however, are not always consistent and differ at some points, as can be concluded from a comprehensive review of many publications on this topic in [54]. It is believed that the discrepancies in the results found in literature have their origin in the differences of the test engines used, investigated load points, operating conditions and ethanol/Diesel ratios. The literature study did not offer satisfactory explanations for the observed efficiency changes with a rising amount of alcohol share. A comparison of the dual-fuel concept performance of the three alcohols discussed in this thesis is not known.

2-Methyltetrahydrofuran (2-MTHF) is also a fuel with a limited ignitability expressed through a cetane number of approx.15. Despite this low value, 2-MTHF still may be used in a Diesel engine under suitable conditions [55]. Janssen et al. [56] showed by investigating pure 2-MTHF via direct injection that the combination of high ignition delay and enhanced fuel oxygen content (18.6 wt% in 2-MTHF) is able to reduce particle emission in the combustion exhaust gas to a great extent, even at the highest EGR rates. As a drawback of the Diesel engine running on 2-MTHF, higher noise, HC and CO emissions are pointed out. It is also reported that 2-MTHF would not ignite at low load testing. Furthermore, combustion of 2-MTHF is found to occur with a rapid heat release and pressure rise, resulting in higher combustion temperature and consecutively higher process efficiency losses. In some cases, this fuel is used in a blend with another (highly reactive) alternative fuel, so that the overall ignitability of the fuel blend reaches appropriate values. Using a mixture of 70 % 2-MTHF and 30 % di-*n*-butyl ether in [57] delivered an extreme particle mass reduction, acceptable noise levels and Diesel fuel-like indicated efficiency.

Similarly to the previously discussed alcohols, 2-MTHF may be added to the conventional Diesel fuel or injected into the intake manifold and then combusted in a dual-fuel operation mode of the Diesel engine. Since the literature survey did not exclude the possibility to use it as a single fuel via direct injection, it is of high interest to analyse this fuel’s performance in comparison to the other investigated fuels. The low cetane number problem could be dealt with by adding a small amount of an ignitability booster additive. The investigations of 2-MTHF parallel to other fuels with similar oxygen content but higher cetane number may constitute an interesting example for the separated influence of ignition delay (mixture formation) and oxygen content on soot emissions.

2.2 Operation of a Diesel Engine with the Highly Ignitable Polyoxymethylene Dimethyl Ethers, Di-*n*-butyl Ether and Dimethyl Ether

Most of the POMDME combustion investigations found in literature discuss dimethoxymethane (OME_1) or mixtures of Diesel and OME_1 because until recently, higher grade POMDMEs were extremely difficult to synthesize. On the one hand, OME_1 possesses a relatively low cetane number of 37.6 and insufficient lubricity properties, therefore, its pure form usage in a Diesel engine is challenging. On the other hand, this fuel is still too reactive for application as a secondary fuel in a dual-fuel combustion process as it would most probably auto-ignite when the air-OME_1 mixture is being compressed during the compression stroke of the engine. An extensive literature survey showed that it is common practice to provide OME_1 with an additive package for enhancing ignitability and lubricity. With an improved cetane number of 48.3, OME_{1a} is supplied to the engine via conventional direct injection and the combustion process behaves analogue to the conventional Diesel process. Exhaust soot emissions are reduced by OME_1 add-on to Diesel [58], the real advantage of OME is, however, demonstrated by using it as a pure substance [59, 60]. In this case, the soot-NO_x trade-off is avoided. The potential of OME_1 combustion to meet current soot and particle emissions limits without any exhaust aftertreatment system is highlighted in [61]. OME_2 is a POMDME with two consecutive oxymethylene units in its molecule structure. It has a very similar soot and particle emission characteristic to OME_1, the combustion process and the performance of both these fuels in a Diesel engine is basically the same.

Generally, $OME_{3\text{-}6}$ are found to have the best suitability for Diesel engine applications, since their properties (boiling point, lubricity and viscosity) are closest to Diesel [59, 62, 63, 64]. The tests with a mixture of the higher $OME_{3\text{-}6}$ and the comparison of combustion results with OME_1 and paraffinic Diesel fuel in [62] confirm the previous findings of extremely low soot and particle emissions for OME combustion. Due to the "newness" of $OME_{3\text{-}6}$ as fuel for compression ignition engines, additional research is required to assess the suitability of the fuel. In particular, the findings of the few previous research investigations on the topic are to be proven and the trends for additional research are to be defined. Since it is more difficult and expensive to produce $OME_{3\text{-}6}$ than OME_1, a direct comparison between these fuels should be undertaken. The possibility to use $OME_{3\text{-}6}$ as a blend with Diesel should also be evaluated.

Di-*n*-butyl ether (DBE) is characterized by a low ignition temperature and, therefore, a very high cetane number of approx. 100 and conventional direct injection is the most promising fuel supply method for this fuel. Due to its high reactivity, DBE shows a very short ignition delay [65] and some researchers use it as an ignition booster in blended fuels [57, 66-68]. Tests with neat DBE in [65, 57] indicate that HC, CO and noise emissions are significantly reduced compared to Diesel in most of the investigated operating points. DBE usage results in almost soot-free combustion according to [65, 67]. The authors explain that DBE and Diesel combustion occurs in a similar way and produces many soot precursors, as a result of which high soot emissions are expected. However, the oxygen content in the molecule and a different soot-oxidizing mechanism overcome the negative influence of the high ignitability and minimize the particulate matter emissions. [69] examines the soot-oxidizing mechanism in the process of DBE combustion and reports missing soot luminescence in the post-oxidation combustion phase, probably resulting from a mechanism unusual for pure hydrocarbons and different particle composition. Additionally, [70] points out the very good mixture formation properties of DBE, which are a consequence of low viscosity, low boiling temperature and low heat of vaporization.

Despite the evidence stated above, the combustion and emission behavior of DBE in a Diesel engine remains of interest because the extremely high ignitability of this fuel combined with its relatively low oxygen fraction of 13.1 % leave space for doubt regarding its particle emission performance. Following this line of thought, the performance of a Diesel-DBE blend is even more questionable.

Dimethyl ether (DME) is the simplest ether and belongs to the so-called C1-fuels since it has no C-C bonds in the molecule. DME boils at -25 °C and possesses a significant vapour pressure of 5.1 bar at standard conditions. Its high cetane number of approx. 65-70 makes it very suitable for compression ignition engines and is known to combust nearly soot free thanks to its oxygen content of 35 wt%, making an avoidance of the soot-NOx trade-off feasible [71]. Some of the properties of DME, however, make its usage in a direct injection Diesel engine challenging. Not only the necessity of a pressure tank but also the low viscosity, the insufficient lubricity properties and the corrosiveness towards conventional sealing materials require an extensive adaptation of the whole fuel system [72]. The high vapour pressure leads to bubble formation and cavitation in warm engine components [73]. This effect can be avoided through pressure increase. Injection timing and strategy also have to be adapted due to the very different mixture formation properties and the low lower heating value of 28.43 MJ/kg. A comprehensive presentation of necessary engine component adaptations and DME performance in a compression ignition engine with direct injection can be found in the work of Ofner, Gill et al. [74–78] as well as in [79–84]. Different OEMs like Volvo, Isuzu, Hino, Nissan, Navistar and Shanghai Automotive have undertaken DME investigations in the last two decades. Especially Volvo built a DME-engine test programme with delivery vehicles in Sweden [85]. The results of the investigations are very promising and bear a high potential for future DME operated Diesel engines, the modifications of the direct injection fuel system, however, are not negligible. For this reason, it is encouraging to introduce another DME utilisation possibility, which is implementable with much less effort: dual-fuel operation with DME manifold injection.

Less research activities dealt with the Diesel engine dual-fuel operation with DME. In Korea, a HCCI dual-fuel engine with different mixing ratios of LPG and DME was examined, optionally with direct and intake manifold injection [86]. The operation mode with DME direct injection and LPG intake manifold injection was found favorable for increasing the mean effective pressure and reducing the emissions. Lim et al. [87] investigated the dual-fuel operation with Diesel direct injection and DME intake manifold injection and reported a 3-stage heat release with cool flame (thermal cracking), pre-mixed and diffusive combustion. The emissions of soot, CO and NO_x are found to be reduced in dual-fuel operation with DME. On the contrary, in [88] an increase in particulate matter emissions is observed with DME intake manifold injection. The increase is attributed to enrichment of the Diesel fuel spray due to displacement of intake oxygen by the fumigated DME, despite the widely observed soot suppressing effect of DME. The self-ignition of the pre-mixed charge increased the cylinder pressure to potentially harmful levels.

The planned engine setup for the projects shown in this thesis allows a viable opportunity to acquire results of the DME operated dual-fuel engine and to compare them with the findings of the other fuel candidates. The examinations can also reveal the behaviour of the atypical combustion process of dual-fuel operation with a highly ignitable intake manifold injected fuel, whereas in conventional dual-fuel applications the supplement fuel is usually of high octane rating.

2.3 Operation of a Diesel Engine with Synthesis Gas Produced through Fuel Reformation

The operation of the engine with a synthesis gas, produced through endothermic reformation of fuels is another possibility to extend the dual-fuel method. The motivation for investigating the combustion process with synthesis gas is provided by the vision of significant engine efficiency enhancement through a thermochemical recuperation (TCR) system based on fuel reformation. In this case, the waste heat of an automotive exhaust gas is used to run additional reforming reactions in a separate reactor. As a feedstock for the reforming process, any hydrocarbons are suitable, however, oxygen-containing substances are expected to enable a more efficient reforming process [89, 90]. The main purpose of the reforming process is to produce a combustible gaseous mixture (SynGas) consisting of H_2, CO, CH_4 and also of CO_2 and H_2O. The reforming process may take place directly in the hot exhaust gas recirculation pipe (EGR), where the reactants for reforming reactions are provided e.g., H_2O, CO_2 and O_2. In addition to EGR, a separate heat exchanger can provide even more heat for the reformer. The TCR system works with Diesel as a primary fuel and also with a second fuel, in this case alcohol as a renewable fuel. The alcohol is fed to the reformer but can also be used for combustion. When the system is running with active fuel reforming and opened EGR valve, the engine will be fed with additional SynGas. If the overall reaction in the reformer is endothermic, waste heat will be converted to chemical energy and the lower heating value (LHV) of the SynGas will be increased in comparison to the LHV of the original biofuel [91]. The increase of LHV and the addition of SynGas to the engine may have positive effects on the overall system efficiency and emissions [92, 93]. The first patent describing the reforming process came from Lindstrom in 1975 [94]. Further research was conducted by Sjöström et al. [95] in the early 1980s and at the *University of Birmingham* since the 1990s, where the first investigations with a Diesel engine originate from [96, 97, 98]. Pettersson et al. [99] report that the ignition of SynGas in a Diesel engine must be supported through an additional Diesel injection since H_2 and CO are not readily ignited by high compression ratio only. Abu-Jrai [92] figured out improvements of soot-NOx trade-off and HC and CO emissions in comparison to conventional Diesel operation with EGR only. At part load operation (25 %), the combustion of SynGas did not improve efficiency in comparison to Diesel fuel but at high load operation, the SynGas combustion was more efficient and efficiency increased with the proportion of SynGas. Tsolakis et al. [97, 98] also reported improved fuel economy at high load engine operation.

It remains unclear whether or not the SynGas operation of the Diesel engine is indeed able to provide benefits towards the conventional combustion process with fuel direct injection (given that the fuel is suitable for it) or the dual-fuel operation with unreformed fuels like ethanol, methanol or butanol is to be favoured. The development of an engine concept with fuel reformer is costly and elaborate and should deliver significant improvements in emission behaviour and efficiency of the Diesel engine if the concept is to be further investigated.

3 Research Objectives

Different preselected alternative fuels had to be analysed regarding the possibility to use them in a Diesel engine. The fuels had to have no usage restrictions, be sustainable and suggest economic feasibility of the production. The tested candidates were ethanol (EtOH), methanol (MetOH), butanol (BuOH), 2-Methyltetrahydrofuran (2-MTHF), polyoxymethylene dimethyl ethers (POMDME or OME), di-*n*-butyl ether (DBE) and dimethyl ether (DME). The objective was to adapt the conventional Diesel combustion process or to develop a suitable one for the fuels that could not be utilised within the conventional Diesel process and to examine the capacity of the fuels to realise potentials for high efficiency, low pollutant and carbon dioxide emissions and justifiable system complexity. These criteria were also the basis for selection of the most suitable combustion process for the different investigated fuels.

4 Materials and Methods

4.1 Materials: Investigated Fuels

The fuels that were investigated within the projects presented in this thesis belong to the groups of alcohols, ethers and furans. Table 1 shows a list of the tested fuels and gives information about the chapters where they are discussed and the form in which they are supplied into the engine.

Table 1: Investigated fuels

Fuel	**Discussed in:**	**Engine fuel-supply form:**
Diesel reference fuel (B0)	Serves as a reference for all investigations	single, blend, dual-fuel basis
Ethanol (EtOH)	Chapter II.1-3; II.7-8	blend, dual-fuel supplement
Methanol (MetOH)	Chapter II.1-3	blend, dual-fuel supplement
Butanol (BuOH)	Chapter II.1-3	blend, dual-fuel supplement
Synthesis gas (SynGas)	Chapter I.5.2 Chapter II.1-3; [100]	dual-fuel supplement
Dimethoxymethane (OME$_1$)	Chapter II.4	single, blend
Mixture of polyoxymethylene dimethyl ethers (OMEmix)	Chapter II.4-6	single, blend
Di-*n*-butyl ether (DBE)	Chapter II.4-6	single, blend
Dimethyl ether (DME)	Chapter I.5.2; [101]	dual-fuel supplement
2-Methyltetrahydrofuran (2-MTHF)	Chapter I.5.2; [102]	single

In the course of the project “Oxy-Gen2”, two Master’s theses were composed. Both were supervised by the author of this dissertation and include complementary information. In the Master’s thesis of Manuel Eckhardt [100], further reading about detailed results of the synthesis gas investigations can be found. The findings of the DME and 2-MTHF tests are not published and, therefore, not a part of the articles forming this cumulative thesis but the most important results will be presented in chapter *I.5.2*. They are also referred to in the “OxyGen2” project reports [102] and DME is a part of Rudolf Krizan’s Master’s thesis [101].

The fuels were supplied to the engine in different forms aiming to achieve best possible utilisation. More information on this topic will be provided in chapter *I.4.2 Methods*. In order to be used as a single energy carrier in a Diesel engine, some of the fuels had to be additivised in order to ensure sufficient ignitability and lubricity. The additives used were:

- polyethylene glycol dimethyl ether 1000 (as cetane booster for OME_1 and 2-MTHF; supplied by *Clariant*)
- poly (ethylene / propylene) glycol alkyl ether (as lubricity enhancer for OME_1 and 2-MTHF; traded as Synalox 40 D700 by *Dow Chemical*)
- monocarboxylic acid (as lubricity enhancer for DBE)
- Fatty Acid Methyl Ester (also known as FAME or BioDiesel; for ethanol-Diesel blend phase stabilisation)
- Emulsifying agent “Tween 60” (for methanol-Diesel blend phase stabilisation, traded by *Sigma-Aldrich*)

4.2 Methods

4.2.1 Analysis Methodology

Investigated Fuel Supply Modes and Engine Operating Conditions

The alternative fuel’s Diesel engine suitability was examined on a combustion engine test bench. It was designed and equipped in accordance with the requirements of the investigation methods. A distinctive feature of the research activities was the analysis of the fuel performance through different ways of fuel supply. In addition to the generally used method of direct injection of Diesel-biofuel mixtures, the alternative fuel was also fed into the combustion chamber via intake manifold injection in combination with parallel direct injection of Diesel fuel. As a particularly innovative approach, the endothermic fuel reforming of the alternative fuel was simulated and experimentally investigated at *AVL List GmbH* in Graz [103]. Hereby, using the exhaust gas enthalpy, the synthesis gas – a combustible mixture of H_2, CO, CH_4, CO_2 and H_2O, is produced from the fuel. Through the thermochemical utilisation of the exhaust gas enthalpy, the heating value of the synthesis gas can be increased with respect to the feedstock. The synthesis gas that resulted at *AVL* was then reproduced on the test bench at the *Institute for Powertrains and Automotive Technology (IFA)* and then fed to the combustion engine by injecting it into the intake manifold.

The scheme in Figure 2 illustrates the procedure for the combustion engine investigation of the fuels. With regard to the fuel characteristics, several possible operating modes resulted. If the fuel could be reformed, the engine could be operated with synthesis gas made from this fuel (Operation mode 1). The ignition of the gas was then initiated by the ignition of the directly injected Diesel fuel. However, the alternative fuel could also be supplied to the intake port as a pure substance (Operation mode 2), if this operating mode appeared to be worthwhile. The ignition was triggered by a Diesel jet in this case as well. The operation with two fuels that are separately fed into the combustion chamber is also called “dual-fuel” operation. If the fuel properties permitted this (lubricity, vapour pressure, cetane number), the alternative fuel was injected directly into the combustion chamber as a pure substance (Operation mode 3 A). A further possibility was the engine operation with a direct-injected fuel mixture, a so-called "blend", if the alternative fuel was mixable with conventional Diesel fuel (Operation mode 3 B).

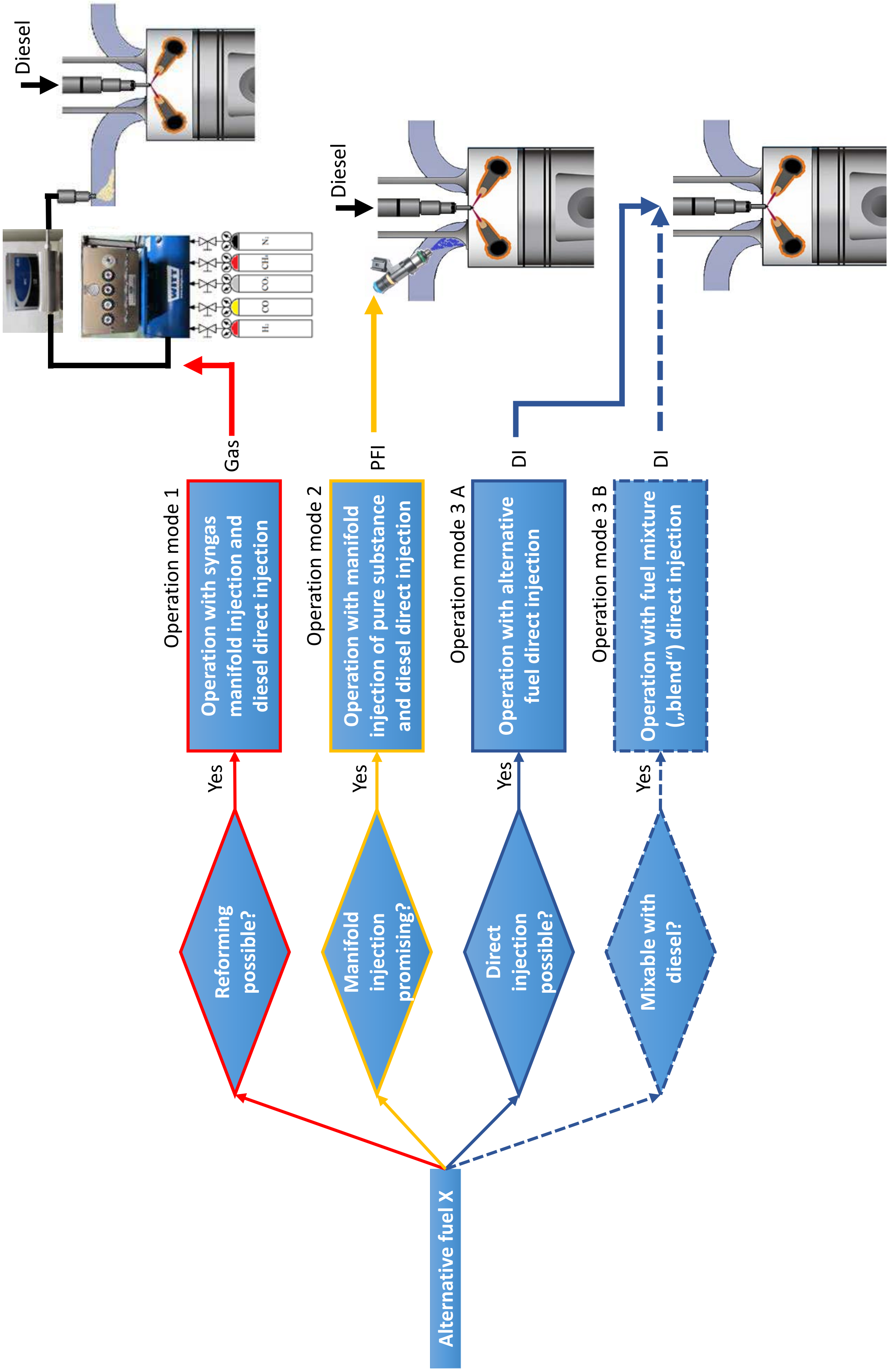

Figure 2: Procedure for the investigations of the alternative fuels (Gas = synthesis gas manifold injection, PFI = port fuel injection (also called “manifold fuel injection”), DI = direct injection)

The investigations were conducted at two or five engine-operating points, depending on the particular project test methodology. The five load points chosen for the detailed diesel-ethanol dual-fuel investigations aimed at covering a typical commercial engine-operating map. The load varied between 5 and 20 bar IMEP, the engine speed between 1500 and 3000 rpm. The most important parameters at these operating points are depicted in Table 2. The Diesel fuel was always injected through a single injection event; multiple injection strategies were not pursued within the scope of the investigations. In the dual-fuel investigations, the manifold fuel injection started at 0 °CAaTDC$_{\text{(firing)}}$. The synthesis gas could not be supplied through a standard gas injector because of its high volume. For this reason, it was continuously injected into the intake charge through a massflow controller unit.

Table 2: Investigated operating points with engine parameters

	All projects		**Only for the detailed diesel-ethanol dual-fuel investigations**		
Operating point	OP-1500/5	OP-1500/15	OP-2000/5	OP-2000/20	OP-3000/20
Speed [rpm]	1500	1500	2000	2000	3000
IMEP [bar]	5	15	5	20	20
Power output [kW]	3.3	10	4.5	17.9	26.8
Rail pressure [bar]	~670	~1040	~800	~1240	~1400
Intake manifold pressure (abs.) [mbar]	1130	2250	1230	2500	2600
Δp exhaust-intake [mbar]	270	500	330	300	300

Figure 3 shows the position of the investigated load points within the load map of the series (not modified) engine.

Variations of different engine operation parameters were carried out in the described operating modes and load points. These were variations of:

- Combustion centre position MFB50% (by adjusting the start of injection)
- Exhaust gas recirculation (EGR) rate
- Air-fuel equivalence ratio (λ)
- Proportion of Diesel fuel to alternative fuel in dual-fuel operation mode (as percent energy share of the alternative fuel in relation to the total fuel energy, [%e.])

The optimum operating parameters for the respective fuel were determined and the results of the variations were compared. The pure Diesel operation with CEC B0 Diesel fuel was the reference for the comparison.

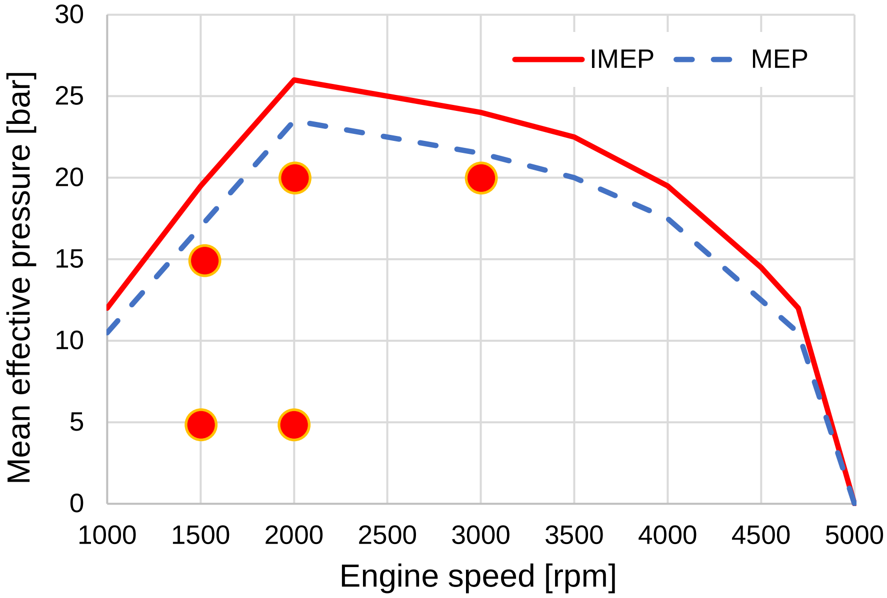

Figure 3: Tested operating points within the load map of the unmodified engine

A representation of the experiment matrices is given in Table 3 and Table 4. Table 3 describes the experiments for the single-fuel investigations. The parameters are varied one at a time. For the dual-fuel investigations, the additional parameter "Diesel-alternative fuel-ratio" was introduced. Since it was found by *AVL* that a low oxygen content in the exhaust gas is required for a high fuel-reforming efficiency, it was necessary to conduct a part of the synthesis gas investigations with an unusually low air-fuel-ratio.

Table 3: Parameter variations for all investigations, excluding the dual-fuel examinations and the tests within the AGRANA-project

OP-1500/5

Variation	EGR [%]	P_{intake} [mbar]	MFB50% [°CAaTDC]	λ_{BS} [-]
MFB50%	30	1130	variable	resulting
EGR p_{intake} const	variable	1130	7.5	resulting
EGR λ_{BS}=1.5	variable	resulting	7.5	1.5
λ_{BS}	30	resulting	7.5	variable

OP-1500/15

Variation	EGR [%]	P_{intake} [mbar]	MFB50% [°CAaTDC]	λ_{BS} [-]
MFB50%	15	2250	variable	resulting
EGR	variable	2250	7.5	resulting

Legend:

OP-X/Y	*Operating point-engine speed [rpm] / load (IMEP [bar])*
MFB50%	*Combustion centre position [°CAaTDC]*
EGR	*Exhaust gas recirculation rate [vol%]*
P_{intake}	*Intake manifold pressure [mbar] (absolute)*
λ_{BS}	*Air-fuel equivalence ratio calculated according to BRETTSCHNEIDER [-]*

Table 4 depicts the experiment design for the detailed investigations of the Diesel-ethanol dual-fuel combustion.

Table 4: Test matrix used for the detailed Diesel-ethanol dual-fuel investigations

OP-1500/5

Variation	EGR [%]	MFB50% [°CAaTDC]	%energ. share of alternative fuel [%e.]
MFB50%	30	variable	0 / 25 / 50 / (60)*
EGR	variable	7.5	0 / 25 / 50 / (60)*
%energ. share of alternative fuel	30	7.5	variable

OP-1500/15

Variation	EGR [%]	MFB50% [°CAaTDC]	%energ. share of alternative fuel [%e.]
MFB50%	15	variable	0 / 25 / (40)* / 50
EGR	variable	7.5	0 / 25 / (40)* / 50
%energ. share of alternative fuel	15	7.5	variable

OP-2000/5

Variation	EGR [%]	MFB50% [°CAaTDC]	%energ. share of alternative fuel [%e.]
MFB50%	30	variable	0 / 25 / 50
EGR	variable	7.5	0 / 25 / 50
%energ. share of alternative fuel	30	7.5	variable

OP-2000/20

Variation	EGR [%]	MFB50% [°CAaTDC]	%energ. share of alternative fuel [%e.]
MFB50%	0	variable	0 / 25 / (40)*
EGR	variable	7.5 / 17.5	0 / 25 / (40)*
%energ. share of alternative fuel	0 / 5	7.5 / 17.5	variable

OP-3000/20

Variation	EGR [%]	MFB50% [°CAaTDC]	%energ. share of alternative fuel [%e.]
MFB50%	0	variable	0 / 20
%energ. share of alternative fuel	0	20	variable

Legend:

OP-X/Y	*Operating point-engine speed [rpm] / load (IMEP [bar])*
MFB50%	*Combustion centre position [°CAaTDC]*
EGR	*Exhaust gas recirculation rate [vol%]*
*	*Not measured with all fuels*

Simulation Software

Besides the experimental investigations on the engine test bench, a 0D/1D-simulation model of the 1-cylinder engine was additionally set up and selected operating points were analysed with it, Figure 4. The software used was *GT-POWER* (v2016) by *Gamma Technologies*. An important feature of the simulation is the optional efficiency loss calculation, which contributes to the understanding of eventual efficiency differences between the discussed operating modes and fuels. The approach used for burn rate calculation was TPA (Three Pressure Analysis) and required three measured pressure curves: intake, cylinder and exhaust. The test bench measurements delivered the input and calibration data for the simulation. The results of the calculations are analysed and visualised with the tool *GT-Post*.

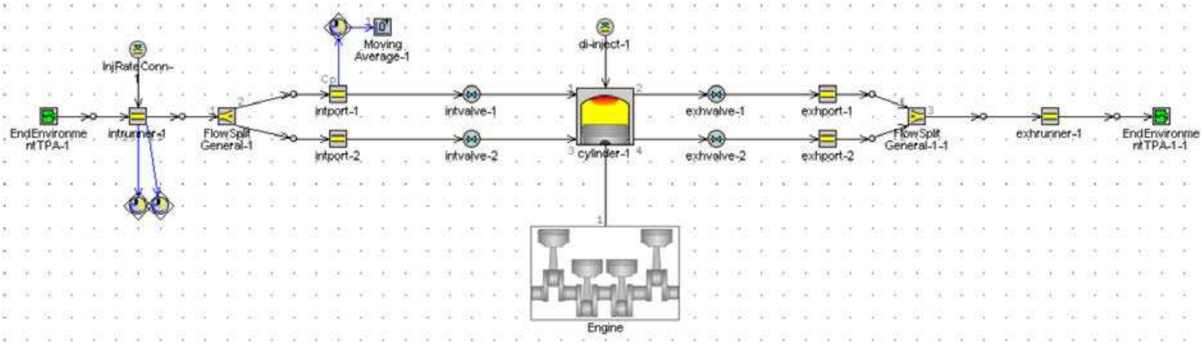

Figure 4: GT simulation model of the 1-cylinder Diesel engine with fuel manifold injection

Comparison

The insights gained from the engine studies clearly showed the trends that can be expected when using the investigated fuels. In order to be able to compare their advantages and disadvantages for Diesel engine use in a quantitative manner, a direct comparison of the results was useful. For this purpose, the optimal operation parameter settings for all fuels at OP-1500/15 were depicted and the results were compared in tabular form.

The overall assessment of the biofuel use was based both on the consideration of the combustion engine suitability and on the fuel production criteria. The assessed categories were engine efficiency, well-to-wheel and tank-to-wheel CO_2 emissions, particle mass and count. For a clearer presentation of the evaluation, characteristic numbers were defined, which represented the percentage change towards the Diesel reference values. The Diesel reference was given the number 100, e.g., a 3 % improvement in engine efficiency when using a biofuel got the number 103, a deterioration of the same value 97. An emission number >100 indicates an increase in the corresponding emissions and vice versa.

The CO_2 savings potential for biofuel production was determined within the framework of the production analysis and is described as “CO_2/energy unit”. It was included in the "CO_2 (well-to-wheel)" criterion.

4.2.2 Test Engine and Experimental Setup

Test Engine

An in-line four-cylinder Diesel engine by *Daimler* was used as a test engine. Table 5 summarizes its most important technical data.

Table 5: Specifications of the unmodified engine [104]

Engine identification	Mercedes-Benz OM 646 Evo
Displacement	2149 cm^3
Cylinders	4 cylinders, 4 valves per cylinder
Bore x stroke	88 x 88.34 mm
Compression ratio	17.5
Injection system	DELPHI high pressure injection with up to 2000 bar; Solenoid injectors with seven-hole nozzle
Exhaust gas recirculation	External, cooled high pressure EGR

The low availability and the high purchase costs of some of the tested fuels made the conversion to single cylinder operation reasonable. Only the first cylinder was fired, the other three were deactivated and their gas exchange was separated from the gas exchange of the fired cylinder. The cylinder had a displacement of 537 cm^3 and a compression ratio of 17.5. Bore and stroke were 88 and 88.34 mm, respectively. The original high pressure common rail Diesel injection system was equipped with seven-hole nozzle solenoid injectors and could handle a pressure of up to 2000 bar. Charging was performed with an external electrically driven supercharger. An electrically adjustable flap valve was used to adjust a turbocharger comparable exhaust gas back pressure. Cooled high-pressure exhaust gas recirculation was applied. The standard exhaust gas aftertreatment system was removed and emissions sampling took place in the raw exhaust gas. The temperatures of the charge air and the fuel were conditioned.

The seats for two intake manifold injectors and various measuring points were adapted in a specially designed intake manifold. The alcoholic fuel was injected with a pressure of 4.5 bar (abs.) into the intake air through a conventional gasoline injector.

Details of the test engine are depicted in Figure 5 – Figure 7.

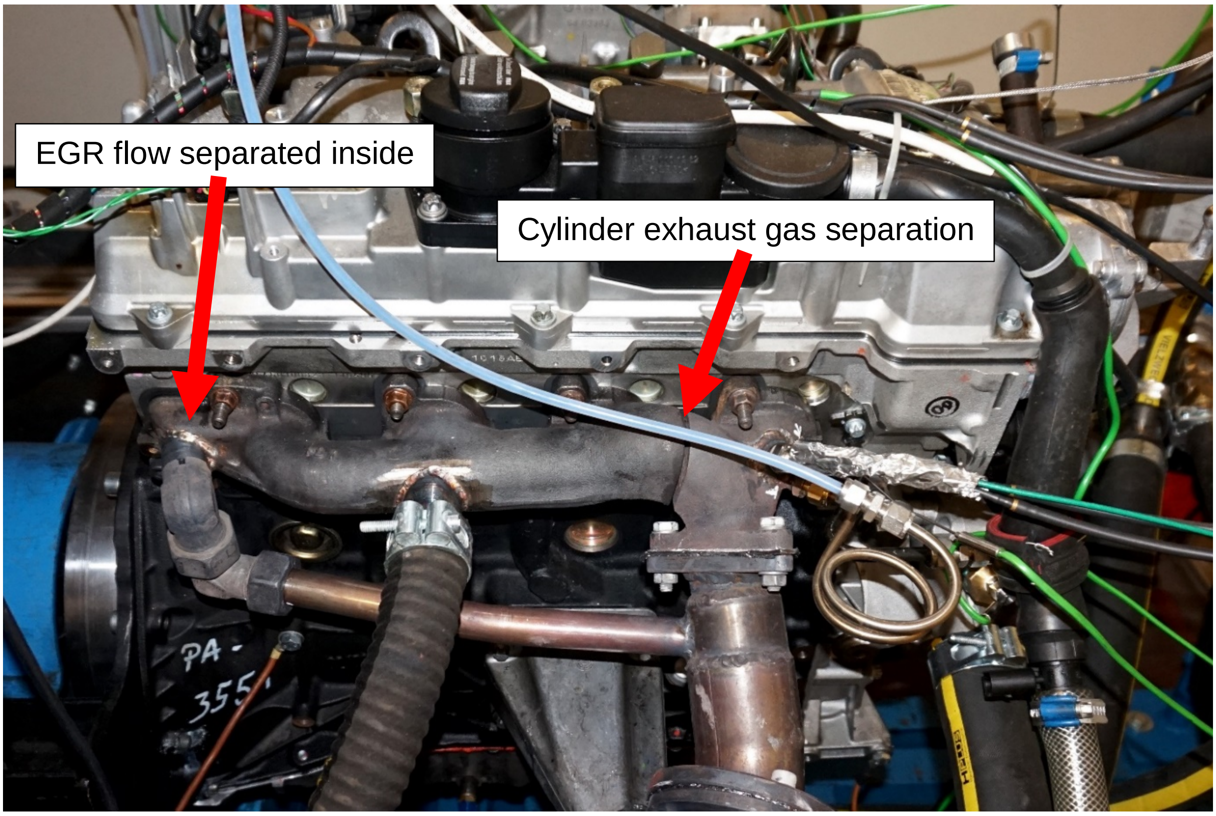

Figure 5: Modified test engine with cylinder gas flow separation

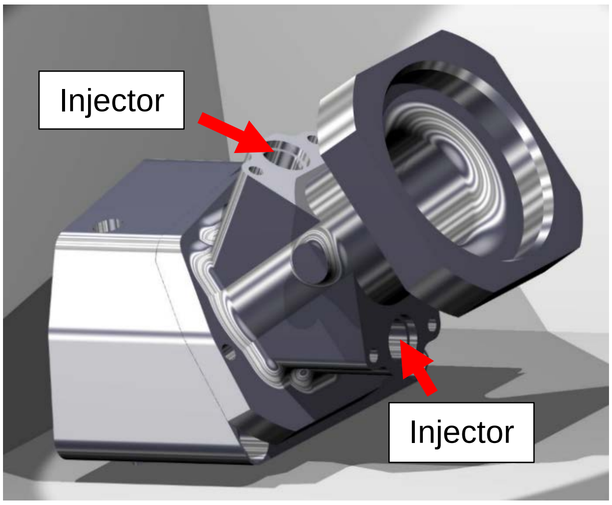

Figure 6: Intake manifold design with two manifold injector seats

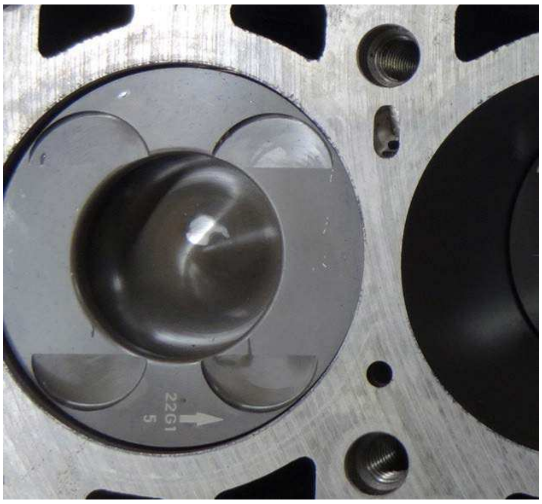

Figure 7: Piston of the test engine with "omega"-bowl

Engine Test Bench

A schematic layout of the test bench is displayed in Figure 8.

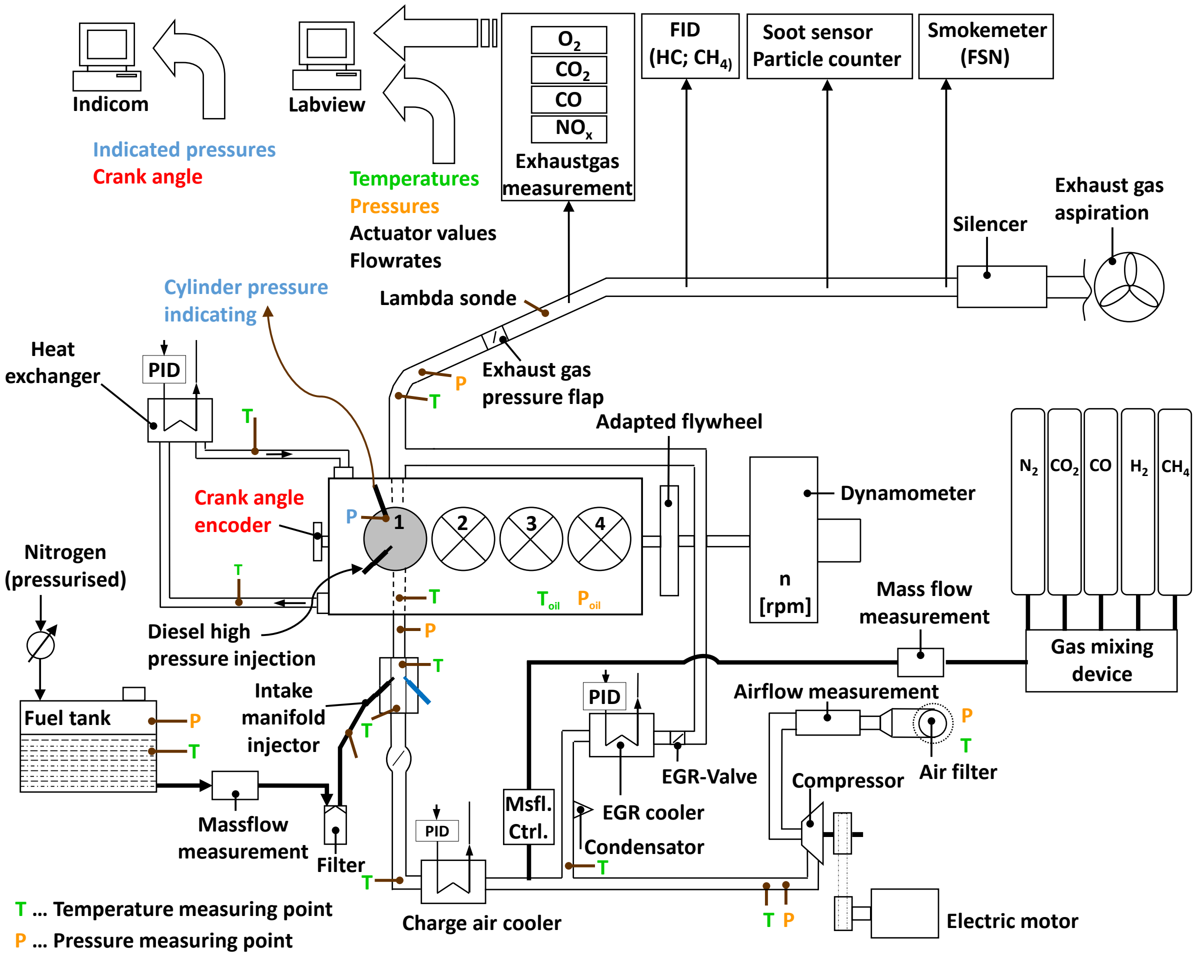

Figure 8: Schematic layout of the engine test bench

The test engine was coupled to a speed-controlled dynamometer. To reduce the vibrations in single-cylinder operation, a flexible disc shaft and an adapted flywheel were used. The engine, fuel and charge air cooling were performed by regulated water-air heat exchangers, the recirculated exhaust gas was cooled by the engine coolant within the standard EGR cooler.

For fuel direct injection, the engine's own common rail system was used. All low-pressure fuel lines were made of PTFE to ensure resistance to chemically aggressive substances. For the same reason, all high-pressure pump seals in contact with the fuel were replaced with parts made of PTFE and FFKM.

The synthesis gas was mixed at the test bench in the desired composition by means of a 5-component gas mixer (Witt KM60-5ME) and injected into the intake manifold upstream of the intercooler. Due to the high volume flow of the synthesis gas, the originally planned natural gas injector could not be used. The flow control was carried out through a mass flow controller MKS IE1000A. A gas analyser was used to accurately determine the synthesis gas composition. Consumption of all fuels was measured with Coriolis massflow meters.

Since the test engine was operated without the original engine control unit, the control and monitoring of the operation was realised via a test bench software (Criistal^{TM} by *Sohatex GmbH*) and external controls. An *AVL LIST GmbH* engine timing unit served for setting the desired injection timings and durations.

Measurement equipment

The test engine was equipped with standard exhaust gas measurement, as well as AVL Micro Soot Sensor^{TM} 483, AVL Particle Counter^{TM} 489 and AVL Smoke Meter 415S. For the exact measurement of the in-cylinder, intake and exhaust pressures, indicating equipment was used. The pressure sensors and the signal amplifiers were *Kistler* products. An IndiModul^{TM} and the software IndiCom^{TM}, both by *AVL LIST GmbH*, served for data processing, visualisation and signal recording. Table 6 gives an overview of the measurement devices and sensors used.

Table 6: Measurement devices and sensors

Category	**Measurement device**	**Category**	**Measurement device**
Fuel consumption (direct injection)	*Siemens* Sitrans FC Mass 2100	Soot mass	*AVL* Micro Soot Sensor 483
Pressure	*Keller* absolute pressure sensors	Soot mass / FSN	*AVL* Smoke Meter 415S
Pressure (indicated)	*Kistler* pressure sensors	Temperature	Ni-Cr-Ni thermocouples
CO_2 and CO	*Siemens* Ultramat 6	Oxygen (O_2)	*Siemens* Oxymat 6
Hydrocarbons and methane	*Testa* FID 1230	Fuel consumption (manifold injection)	*Emerson* CMF010
Air-fuel ratio	*NGK* lambda sonde	Nitrogen oxides ($NO/NO_2/NO_x$)	*Eco Physics* CLD 700 EL ht
Air massflow	*AVL* Flowsonix	Synthesis gas consumption	*Siemens* Sitrans F C 300
Particle number	*AVL* Particle Counter 489	Synthesis gas composition	*Rosemount* NGA 2000

5 Summary of the Research Results

5.1 Summary of the Scientific Publications

Table 7 summarises the topics and the investigated fuels within the presented published work. Peer-reviewed publications, as required for a cumulative dissertation at the *Vienna University of Technology*, are publications 1, 5 and 7 from the list below.

Table 7: Topics and investigated fuels within the published work

1. Damyanov, A.; Hofmann, P.; Derntl, M.; Schüßler, M.; Pichler, T.; Schwaiger, N.: **Operation of a Diesel engine with biogenous oxygenated fuels**; Lenz (Hrsg.); Proceedings of the 38th International Vienna Motor Symposium 2017, Vol. 2, p. 474-500; ISBN 978-3-18-380212-8; 27-28 April 2017, Vienna, Austria *(peer-reviewed)*

2. Damyanov, A; Hofmann, P.; Schüßler, M.; Derntl, M.; Schwaiger, N.; Pichler, T.: **Operation of a Diesel engine with biogenous oxygenated fuels**; Poster presented at the 38th International Vienna Motor Symposium 2017; 27-28 April 2017, Vienna, Austria

3. Damyanov, A.; Hofmann, P.; Derntl, M.; Schüßler, M.; Pichler, T.; Schwaiger, N.; Siebenhofer, M.: **Regenerative Oxygen-Containing Diesel Substitute Fuels as an Ecological Option for Increasing Efficiency and Minimizing Emissions**; Nikolai Schubert (Hrsg.); Proceedings of the 11th International Colloquium Fuels, p. 315-331; ISBN 978-3-943563-32-0; 27-29 June 2017, Ostfildern, Germany

   Topic: Introduction to the methods applied and presentation of the results of the engine investigations with synthesis gas, Diesel-alcohol blends and first experiences with Diesel-alcohol dual-fuel operation.

   Investigated fuels: ethanol (EtOH), methanol (MetOH), butanol (BuOH)

4. Damyanov, A., Hofmann, P., Drack, J., Pichler, T., Schwaiger, N., Siebenhofer, M.: **Operation of a Diesel Engine with Biogenous Oxymethylene Ethers;** Proceedings of the 26th Aachen Colloquium Automobile and Technology, Vol. 1, p. 289-314, ISBN 978-3-00-054182-7; 9-11 October 2017, Aachen, Germany

5. Damyanov, A., Hofmann, P., Geringer, B. et al.: **Biogenous ethers: production and operation in a diesel engine**; Automotive and Engine Technology, Vol. 3, Issue 1-2, p. 69-82; August 2018; https://doi.org/10.1007/s41104-018-0028-x *(peer-reviewed)*

6. Damyanov, A.; Hofmann, P.; Pichler, T. M.; Schwaiger, N.: **Biogenous Ethers – Production and Operation in a Diesel Engine**; MTZ worldwide, Vol. 80, Issue 1, p. 66-71; January 2019; https://doi.org/10.1007/s38313-018-0126-1

   Topic: Analysis of the lignocellulose based production pathways for the highly innovative Diesel substitute fuels polyoxymethylene dimethyl ethers (POMDME, also known as OME) and di-n-butyl ether. Engine performance tests and combustion process assessment and adaptation for these ethers.

   Investigated fuels: polyoxymethylene dimethyl ethers (OME$_1$, OME$_{3\text{-}6}$) and di-*n*-butylether (DBE)

7. Damyanov, A.; Hofmann, P.: **Operation of a diesel engine with intake manifold alcohol injection**; Automotive and Engine Technology, p. 1-12; February 2019; Online ISSN 2365-5135, Print ISSN 2365-5127; https://doi.org/10.1007/s41104-019-00040-2 *(peer-reviewed)*

8. Damyanov, A.; Hofmann, P.: **Biogenous Ethanol: CO$_2$ Savings and Operation in a Dual-Fuel Designed Diesel Engine**; Proceedings of the 14th International Congress Engine Combustion and Alternative Concepts (ENCOM 2019), p. 69-82; ISBN 978-3-945806-15-9; 13-14 March 2019, Essen, Germany

   Topic: Comprehensive investigations of the ethanol-Diesel dual-fuel combustion concept. Discussion of emissions and efficiency loss analysis accompanied by an insight into 1st generation bio-ethanol production gained within a case study of an Austrian bioethanol producer.

Investigated fuels: ethanol (EtOH) and two ethanol-gasoline mixtures with 65 and 85 vol% ethanol (E65 and E85)

Publications (1), (2) and (3)

(1) Operation of a Diesel engine with biogenous oxygenated fuels (paper)

(2) Operation of a Diesel engine with biogenous oxygenated fuels (poster)

(3) Regenerative Oxygen-Containing Diesel Substitute Fuels as an Ecological Option for Increasing Efficiency and Minimizing Emissions

The research project "Regenerative oxygen-containing Diesel substitute fuels as an opportunity for efficiency enhancement and emission reduction - OxyGen2" was first presented 2017 in publication ***(1) Operation of a Diesel engine with biogenous oxygenated fuels (paper)*** in Vienna. The paper described the holistic approach for the biofuel engine suitability investigations, consisting of a sustainability and cost effectiveness analysis (*Institute of Chemical Engineering and Environmental Technology* at the *Graz University of Technology*), the development and investigation of operating strategy and combustion processes (*Institute for Powertrains and Automotive Technology* at the *Vienna University of Technology*) and the investigation of a thermochemical energy recovery in the form of endothermic fuel reforming (*AVL List GmbH*, Graz). The article dealt with the engine operation results of three bio-alcohols – ethanol, methanol and butanol – and with the results of the fuel reforming. Three variants of fuel introduction into the internal combustion engine were discussed: injection of synthesis gas, intake manifold injection and direct injection.

The endothermic fuel reforming[5] using exhaust heat was investigated in experiment and simulation. There was a good consistency between test bench and simulation results. The resulting synthesis gas was used as fuel in a modified Diesel engine and the successful technical feasibility of the combustion process was confirmed. Due to the requirements of the fuel reforming, a low air/fuel ratio was necessary for engine operation with SynGas. Lambda values from 1.1 to 1.4 were investigated, whereby the operation with λ = 1.1 resulted in a very low combustion engine efficiency. Particularly in low load operation, a significant throttling of the intake tract was necessary in order

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[5] Fuel reforming research was conducted by Dr. Michael Derntl and Dr. Martin Schüßler at AVL List GmbH

to reach the low λ-values. The exchange between fuel reforming research and combustion engine investigations showed that real SynGas operation could only be possible at high loads with low air/fuel ratio and high exhaust gas temperatures since low loads with high air excess and low exhaust gas temperatures could not provide the conditions for efficient fuel reforming.

The operation with SynGas showed efficiency disadvantages compared to the reference operation with pure Diesel fuel due to the non-adapted combustion process (piston and combustion chamber design) and high amounts of unburnt fuel but a reduction in soot emissions could be measured. As the SynGas content increased, higher methane and hydrogen emissions were measured in the exhaust gas. The "fuel upgrade" within the generation of synthesis gas could not fully compensate for the efficiency loss in the combustion of the gas at any point. The NO_x emissions at SynGas operation were higher than in Diesel reference operation. The utilisation of a biofuel, of course, resulted in reduced well-to-wheel CO_2 emissions but at the end of the day, it could be concluded that the possibility to operate a Diesel engine with synthesis gas injection is not expected to deliver any other substantial advantages compared to conventional Diesel operation.

Apart from the SynGas manifold injection, the paper also presented the results of a dual-fuel operation with port injection of ethanol, methanol or butanol. By injecting these alcohols into the intake port, depending on the operating point, substitution potentials of up to 85 % could be achieved before unwanted combustion phenomena such as knock and auto-ignition occurred, which prevented further increase of the alcohol amount. At higher loads within this operation mode, the efficiency was increased by up to 2 % points. The observed strong particle emissions decrease allowed a further reduction of the nitrogen oxide emissions. The best results were achieved with ethanol. These outcomes showed that the dual-fuel operation of a Diesel engine with alcohol port injection can be very successful and provoked more comprehensive research within the later detailed Diesel-ethanol dual-fuel investigations.

The direct injection of a Diesel-fuel blend was the third examined method for using alcohols in the Diesel engine. The addition of 10 % by volume of ethanol, methanol or butanol to the Diesel fuel resulted in a significant reduction in soot emissions at low loads. It also represented the special fuel delivery variant realisable with the lowest effort. The use of ethanol was prioritised in this case as well. At high loads, no significant differences to Diesel reference operation could be determined.

Publication ***(2) Operation of a Diesel engine with biogenous oxygenated fuels (poster)*** is the poster presentation accompanying publication 1. However, it added the engine results with Diesel-alcohol blends with 20 vol% ethanol or butanol. Operating the engine at this mode generally produced less soot mass emissions, mitigated the soot-NO_x trade-off and did not affect the efficiency. The soot mass reducing effect became more distinct at higher EGR rates. The effect on particle number in the exhaust gas was contrary at the high load point, leading to a higher number of smaller particles with later combustion centre position. In any case, higher bio-alcohol content in the blend naturally resulted in less well-to-wheel CO_2 emissions.

The poster presentation also revised the tabular method for the comparative analysis because it was found that improved emission results should be better presented through a lower and not through a higher characteristic number in comparison to Diesel reference operation. The characteristic numbers were defined to present the percentage change of a given fuel and operation mode towards the Diesel reference. Therefore, in publication ***(2)***, the characteristic numbers are the reciprocal value of the characteristic number in publication ***(1)*** multiplied by a factor of 10^4.

Publication ***(3) Regenerative Oxygen-Containing Diesel Substitute Fuels as an Ecological Option for Increasing Efficiency and Minimizing Emissions*** added on to publication ***(1)*** but involved the analysis and evaluation of butanol production from cellulosic material (in this case from the energy plant Miscanthus Sinensis)[6]. In this study, an acetone, butanol and ethanol (ABE) fermentation of cellulose was evaluated and two different cases of side stream treatments were compared. The first case (case 1) was an integrated conversion of the hemicellulose fraction into 2-Methyltetrahydrofuran (2-MTHF) and the second case (case 2) was the thermal conversion of hemicellulose for steam and power generation. In case 1, even more CO_2 was produced in comparison to the standard Diesel emissions of 83.8 gCO_2/MJ_{Fuel} (calculated in accordance with the Renewable Energy Directive). In case 2, overall emissions were 32.7 gCO_2/MJ_{Fuel}. The analysis concluded that fuel production is possible and greenhouse gas saving, however, it requires high biomass availability and significant investment costs.

The paper also included more detailed insights into the fuel reforming experiments with ethanol and butanol. The reforming of ethanol and butanol was investigated at 400 °C and 500 °C reformer inlet temperature. The results confirmed that especially low λ values and higher exhaust gas temperatures give a potential to improve the engine's efficiency with butanol or ethanol EGR gas reforming. A chance for further optimisation

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[6] The production analysis and evaluation was performed by Dr. Nikolaus Schwaiger, DI Thomas Pichler and Prof. Matthäus Siebenhofer at the Institute of Chemical Engineering and Environmental Technology (CEET) at the Graz University of Technology

was seen in catalyst improvement with the target of higher biofuel conversion and SynGas selectivity.

Publications (4), (5) and (6)

(4) Operation of a Diesel Engine with Biogenous Oxymethylene Ethers

(5) Biogenous ethers: production and operation in a diesel engine (AAET)

(6) Biogenous Ethers – Production and Operation in a Diesel Engine (MTZ)

Publication ***(4) Operation of a Diesel Engine with Biogenous Oxymethylene Ethers*** belongs to the very first scientific articles investigating the usage of longer-chained polyoxymethylene dimethyl ethers in a Diesel engine. It combined the results of the examinations both of the combustion process development (*Institute for Powertrains and Automotive Technology* at the *Vienna University of Technology*) and of the POMDME production simulation[7] (*Institute of Chemical Engineering and Environmental Technology* at the *Graz University of Technology*). Input feed for the production calculations was spruce wood and it was processed through biomass gasification. Similarly to butanol production analysis in Publication ***(3) Regenerative Oxygen-Containing Diesel Substitute Fuels as an Ecological Option for Increasing Efficiency and Minimizing Emissions***, it was found that POMDME production requires high biomass input and considerable investments but it also offers a fuel product with a very high greenhouse gas saving potential of up to 70.9 % with the boundary conditions set in this study.

The combustion process investigations dealt with the simplest representative of the polyoxymethylene dimethyl ethers – dimethoxymethane (OME_1) and a mixture of the longer chained OME_{3-6} (called OMEmix in the publication). Both fuels were investigated via direct injection as a single fuel and as a Diesel-OME blend with 20 vol% OME share. The study reported no significant differences in combustion quality and emissions between OME_1 and OMEmix. Operating the Diesel engine with OME blends showed improved emission behaviour. The OME properties, however, made hardware and engine application adaptations necessary, even if relatively small OME amounts were to be mixed. Due to the severe corrosiveness of OME, the fuel system sealing materials had to be changed with OME resistant ones. It was stated that if the engine systems are to be modified, the operation with neat OME is highly favourable since it was found to offer an extreme potential to further improve efficiency and pollutant emissions levels of the compression ignition engine, perhaps even to sub-zero levels. In operation with neat OME, the well-known soot-NO_x trade-off was

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[7] POMDME production simulation was performed by DI Joachim Drack, DI Thomas Pichler, Dr. Nikolaus Schwaiger and Prof. Matthäus Siebenhofer at CEET at the Graz University of Technology

eliminated and the soot emissions concentration was at ambient air level even with the maximum possible exhaust gas recirculation rates. Due to the much lower lower heating value of OME compared to Diesel, the direct fuel injection took longer and resulted in an extended main combustion duration, which decreased the thermodynamic engine efficiency. Adjusting the injection pressure was found to be a possible measure to partly reduce this drawback.

Publication ***(5) Biogenous ethers: production and operation in a diesel engine (AAET)*** appeared in “Automotive and Engine Technology” and was based on Publication ***(4)*** while introducing another alternative fuel candidate – di-*n*-butyl ether (DBE). Fuel production simulation was conducted for this new fuel as well. The process was, similar to butanol production in Publication ***(3)***, organosolv pulping. Again, the results showed a high greenhouse gas saving potential by up to 67 % compared to fossil Diesel but also very high investment costs and biomass demand. According to the findings, 5.5 MJ biomass energy input is required for 1 MJ fuel energy. A direct comparison with the calculated values for POMDME suggested that POMDMEs are the better choice for a Diesel substitute.

In this work, POMDME proved to be of higher interest for the Diesel engine than DBE not only because of the production advantages but also due to the results of the combustion investigations. With DBE, the soot mass emissions were slightly improved only at low load testing. Particle number emissions did not decrease; they even significantly increased at higher load. Engine operation with a 20 vol% Diesel-DBE blend showed higher soot mass and particle count emissions than Diesel reference operation at all conditions. The reason for these findings was believed to be the very high ignitability of DBE (expressed through a cetane number of ~100). The article stated that the short ignition delay of DBE reduced the lift-off length of the spray and left less time for its evaporation and mixture homogenisation, thus more local fuel rich zones and more diffusive combustion occurred. Adding 20 vol% DBE to the Diesel fuel had a very negative impact on soot and particle generation because the DBE fraction of the fuel ignited earlier and consequently co-ignited the Diesel portion. Thus, in this way the ignition delay of the blend was shortened compared to pure Diesel operation and less premixed combustion took place. Therefore particle emissions rose. The conducted literature survey suggested DBE to be an effective fuel for soot reduction due to its advantageous chemical structure. The combustion process investigations, however, showed that a fuel can perform differently to expected and its combined properties may influence the in-engine performance in a complex way.

Publication ***(5)*** was republished in a slightly modified form in “MTZ - Motortechnische Zeitschrift”, as publication ***(6) Biogenous Ethers – Production and Operation in a Diesel Engine (MTZ)***.

Publications (7) and (8)

(7) Operation of a Diesel engine with intake manifold alcohol injection

(8) Biogenous Ethanol: CO_2 Savings and Operation in a Dual-Fuel Designed Diesel Engine

Publication ***(7) Operation of a Diesel engine with intake manifold alcohol injection*** was peer-reviewed and published in “Automotive and Engine Technology”. It described the methods and the results of the dual-fuel investigations with ethanol and two ethanol-gasoline mixtures (E65 and E85). The Diesel fuel was directly injected into the combustion chamber and the alcoholic fuel was supplied to the intake air through a conventional gasoline injector, which was installed in a specially designed intake manifold. In contrast to the previously presented publications, in this study the investigations were conducted at five operating points, covering loads from 5 to 20 bar IMEP and engine speeds between 1500 and 3000 rpm.

It was found that the maximum ratio of alcohol to Diesel fuel is limited by irregular combustion phenomena like degrading combustion quality and poor process controllability at low load and knock as well as auto-ignition at high load. At low load testing, up to 70 % of the Diesel energy could be substituted by the alcoholic fuels, whereas at high loads the maximum substitution rate declined to 30 %e. With increasing alcohol amount, a significant reduction of soot mass and particle number of up to 99 % (depending on load point and substitution ratio) was observed. At some testing points, substituting Diesel with ethanol, E65 or E85, led to a reduction of NO_x emissions; however, the real benefit concerning the nitrogen oxides was introduced by the mitigation of the soot-NO_x trade-off. The low soot emissions in dual-fuel operation mode allowed a further increase of the EGR rate, which helped lower the NO_x emissions far below the Diesel reference emission values. The article reported that the indicated engine efficiency was significantly improved with enhanced substitution ratios at medium and high loads (by up to 6 %), whereas it dropped at low loads (by approx. 3 %). Furthermore, it was found that the combustion process tolerance against high EGR rates in dual-fuel mode allows more exhaust gas to be recirculated without affecting engine efficiency the same way as in “Diesel only” operation. Substituting Diesel with manifold injected alcoholic fuels impressively reduced the engine CO_2 emissions at medium and high load operating points. The catalytic conversion of the high HC and CO emissions measured at low load operation would eventually have led to higher tailpipe CO_2 emissions.

At some conditions and higher loads, a cyclic reproducible auto-ignition of the premixed homogenous charge occurred, as in-cylinder temperature and pressure around the end of the compression stroke were sufficient for it. A simulation model was set up for the test engine with *GT-POWER* and selected operating points from the engine test bench measurements were implemented into the model to generate an efficiency loss analysis. The calculations showed that the high amounts of unburnt fuel at dual-fuel operation were the main reason for efficiency degradation, whereas the reduced losses due to real charge composition, real fluid properties, real burn rate and heat transfer enhanced the efficiency of the engine at dual-fuel mode.

Publication ***(8) Biogenous Ethanol: CO_2 Savings and Operation in a Dual-Fuel Designed Diesel Engine*** added to the previous one (Publication ***(7)***) a case study of 1st generation bioethanol by the Austrian bioethanol producer AGRANA. The greenhouse gas saving potential of the bioethanol was analysed and it was reported that the savings might reach up to 98 %, depending on raw feed material and calculation method. For the discussed case, the greenhouse gas savings were between 68 and 72 %. It was also stated that conventional biofuels like European bioethanol have the potential to contribute to the mitigation of the problems surrounding energy supply as well as food and feed production, provided that sustainability and socio-economic criteria are fulfilled and certified.

The knowledge of the greenhouse gas savings of the discussed bioethanol was combined with the results of the combustion engine investigations from publication ***(7)*** into a well-to-wheel analysis of the CO_2 emissions. Here it was shown that by using this bioethanol as a second fuel in the dual-fuel designed engine, the well-to-wheel CO_2 emissions could be reduced by almost 40 %.

5.2 Summary of the Non-Published Research Work

5.2.1 Diesel Engine Operation with Direct Injection of Cetane-Boosted 2-Methyltetrahydrofuran (2-MTHF)

The fuel 2-MTHF was additivised with the same additive package as OME_1 to ensure lubricity and to counteract the low cetane number. Despite the additivation with 3 wt% cetane booster, significant cold start difficulties were experienced. The measured cetane number was 26 and the ignition of the fuel was only possible with a coolant temperature above 70 °C. The combustion took place in the form of a homogeneous or partially homogeneous compression ignition with a long ignition delay and a rapid heat release, Figure 9. In comparison to the Diesel reference, the heat release with 2-MTHFa showed a significantly reduced post oxidation combustion phase. The position of the combustion centre MFB50% could be varied only in a small window due to the particularity of the combustion process. A stable MFB50% could not be set before 5 °CAaTDC even by significantly advancing the start of injection. The attempt to set a combustion centre later than 15 °CAaTDC resulted in misfiring and high cycle variations. Figure 10 shows the cylinder pressure curves for Diesel reference operation and 2-MTHFa operation at low load and equal MFB50% of 7.5 °CAaTDC.

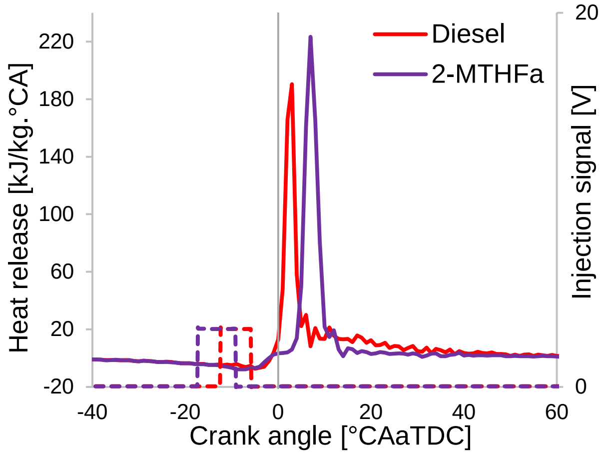

Figure 9: Heat release rate at OP-1500/5 with 30 % EGR and MFB50% 7.5 °CAaTDC

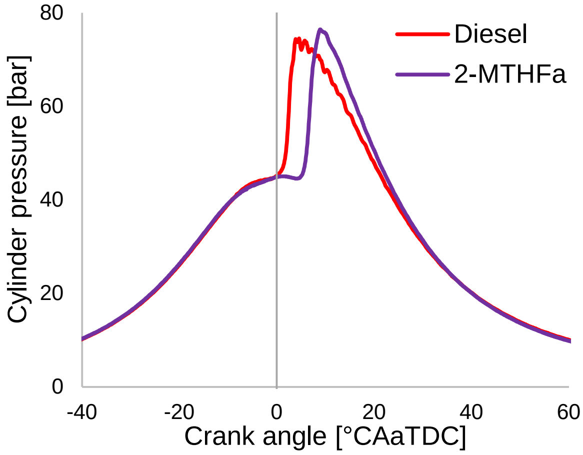

Figure 10: Cylinder pressure at OP-1500/5 with 30 % EGR and MFB50% 7.5 °CAaTDC

Despite the shorter burning duration, the combustion of 2-MTHFa did not emit more noise. It can be seen in Figure 11 that the first derivatives of the cylinder pressures with both fuels deliver very similar pressure gradients. The calculation within the postprocessing tool CONCERTO^{TM} showed a noise level of approx. 96 dB for both cases. The higher heat release and the faster combustion completion with 2-MTHFa, however, result in higher peak cylinder temperatures, Figure 12, which not only lead to a more intense NO_x formation but also to high wall heat losses, reduced isentropic exponent of the charge and consequently also to reduced efficiency, Figure 13 and Figure 14.

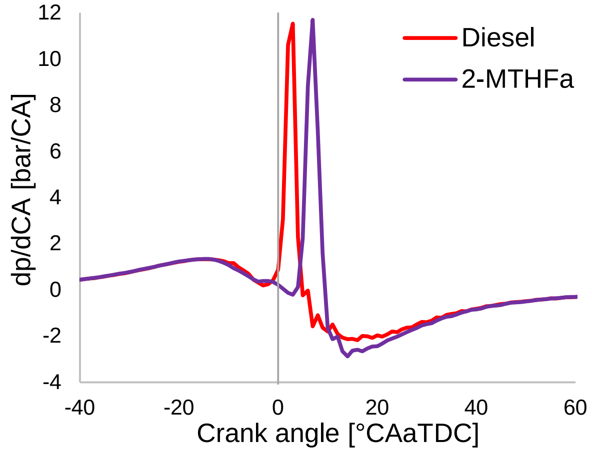

Figure 11: First derivative of the cylinder pressure; OP-1500/5 with 30 % EGR and MFB50% 7.5 °CAaTDC

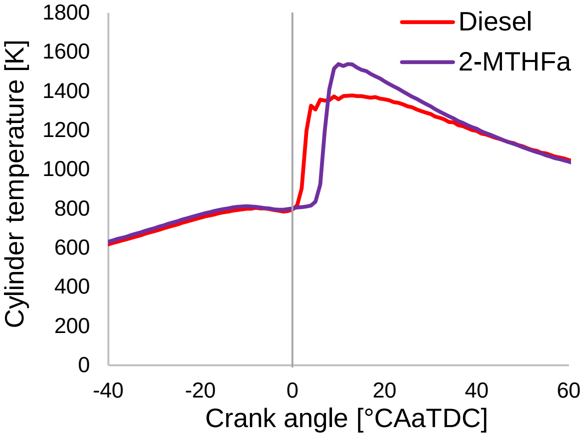

Figure 12: Cylinder temperature at OP-1500/5 with 30 % EGR and MFB50% 7.5 °CAaTDC

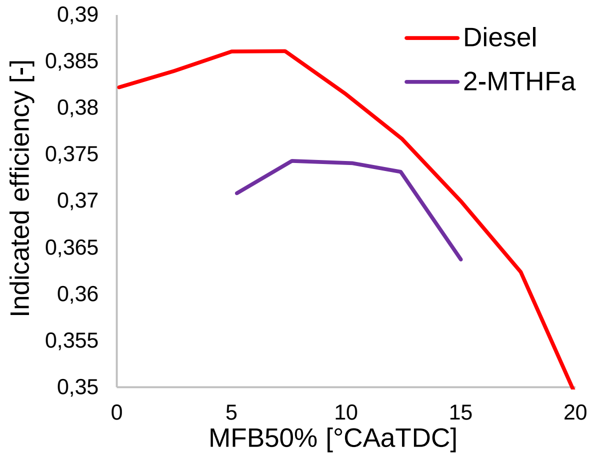

Figure 13: Indicated efficiency as function of MFB50% at OP-1500/5 with 30 % EGR

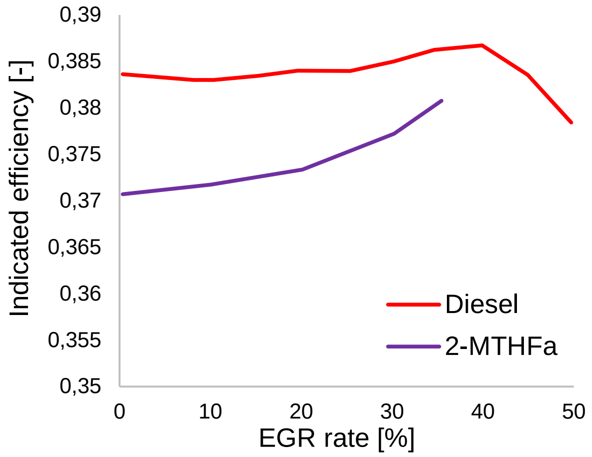

Figure 14: Indicated efficiency as function of the EGR rate at OP-1500/5 with MFB50% 7.5 °CAaTDC

Figure 15 shows that in order to achieve the same NOx level as the Diesel reference, higher EGR rates were necessary with 2-MTHFa, but these were limited by misfirings at the lower load point. As a result, further reduction of the NO_x emissions could only be realised by late shifting the combustion centre position at the expense of efficiency and cycle stability.

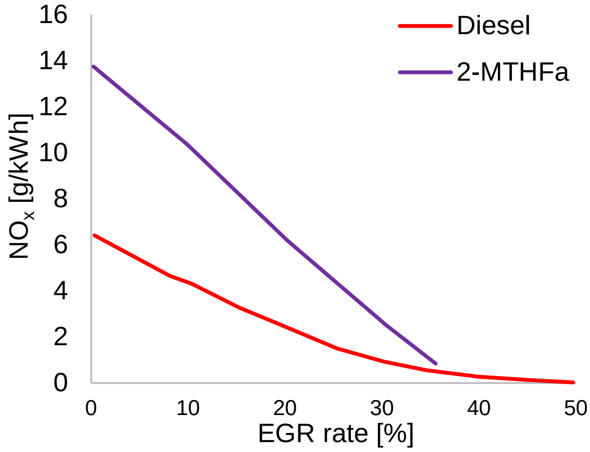

Figure 15: NO_x emissions over the EGR rate at OP-1500/5 with MFB50% 7.5 °CAaTDC

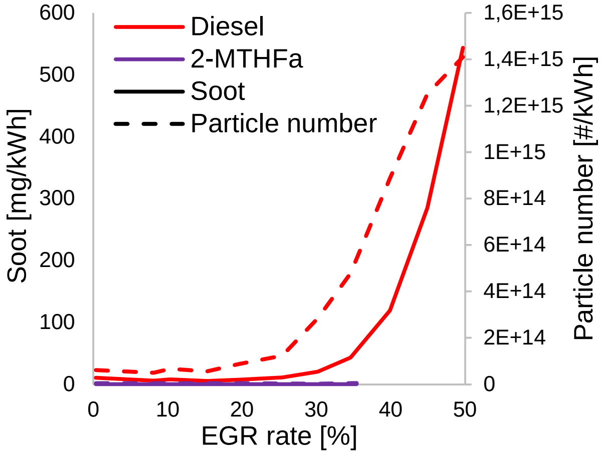

Figure 16: Soot mass and particle number emissions for different EGR rates at OP-1500/5 with MFB50% 7.5 °CAaTDC

As can be seen in Figure 16, the combustion of 2-MTHFa results in significant soot mass and particle number reduction at low load testing. With the scale chosen for the diagram, these pollutants are at near zero levels. The higher oxygen content, the absence of C=C double bonds in the 2-MTHFa molecule and especially the good mixture homogenisation provided by the long ignition delay are the reasons for the observed behaviour.

At higher load conditions, the influence of the low cetane number of 2-MTHFa disappeared. As Figure 17 and Figure 18 prove, the ignition delay was very similar for both Diesel and 2-MTHFa. Moreover, the heat release and its integral do not display any significant differences between the fuels, either.

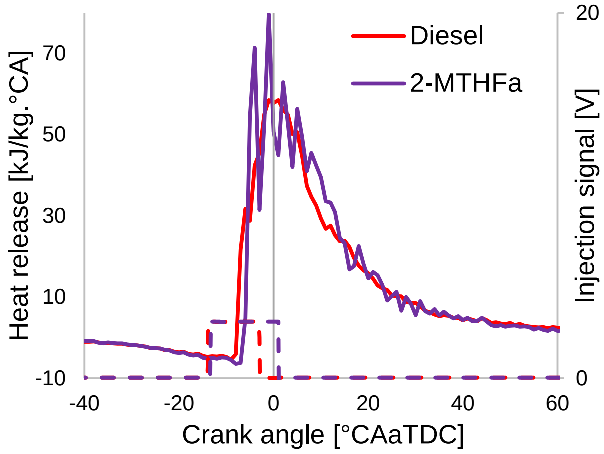

Figure 17: Heat release rate at OP-1500/15 with 15 % EGR and MFB50% 7.5 °CAaTDC

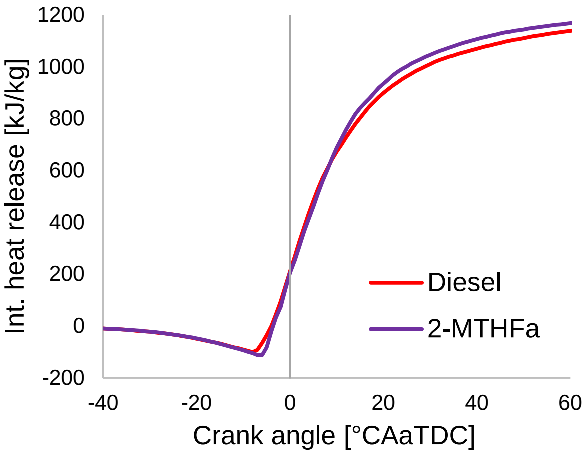

Figure 18: Integrated heat release rate at OP-1500/15 with 15 % EGR and MFB50% 7.5 °CAaTDC

The operation with 2-MTHFa showed a higher EGR tolerance than with Diesel and the soot-NO_x trade-off was mitigated. As can be seen in Figure 19, in the 2-MTHFa case, more exhaust gas could be recirculated before significant efficiency deterioration was encountered. As the diagrams with the indicated data for both Diesel and 2-MTHFa combustion (Figure 17 and Figure 18) suggest, at the same operation point with same MFB50% and 15 % EGR, the measured indicated efficiency is at a very similar level. The advantage of the 2-MTHFa usage appears with higher EGR rates. It is surprising that at the same parameter set, at this load point, 2-MTHFa combustion emits more NO_x emissions than Diesel reference operation, Figure 19. Since the indicated curves and the calculated cylinder temperature (not shown here) do not significantly differ, the origin of the higher emissions should be sought in the reaction mechanisms during the combustion and the role of the enhanced oxygen content. Generally, the 2-MTHFa combustion was soot-poor, but due to the increased nitrogen oxide formation, higher EGR rates were necessary to achieve the same NO_x emission values as at the Diesel reference, which in turn measured more soot in the exhaust gas. Figure 20 depicts the soot and particle number – NO_x trade-off for the alternative fuel and the Diesel reference. Overall, it can be concluded that 2-MTHFa direct injection under higher load can produce less soot mass with the same NO_x emissions and acceptable efficiency.

Basically, however, the fuel in its pure form is not very suitable for the compression ignition engine because of the exhibited cold start difficulties. It should also be noted at this point that the lignocellulosic processes discussed for 2-MTHF production could not reduce the greenhouse gas emissions. In contrast, the bio-2-MTHF considered in this study would produce even more CO_2 than fossil Diesel, as can also be seen in Table 9 (page 57). 2-MTHF may be produced through biomass pulping with Miscanthus Sinensis as raw material. Depending on the process management, the production of 2-MTHF resulted in more gCO_2/MJ emissions (between 53 and 87 %) than fossil Diesel, [31].

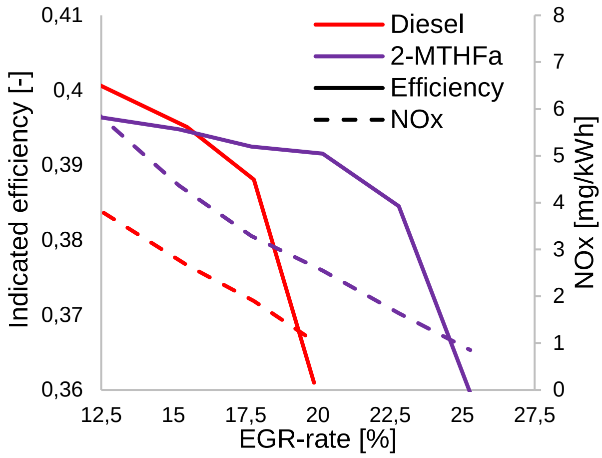

Figure 19: Indicated efficiency and NOx emissions as functions of the EGR rate at OP-1500/15 with MFB50% 7.5 °CAaTDC

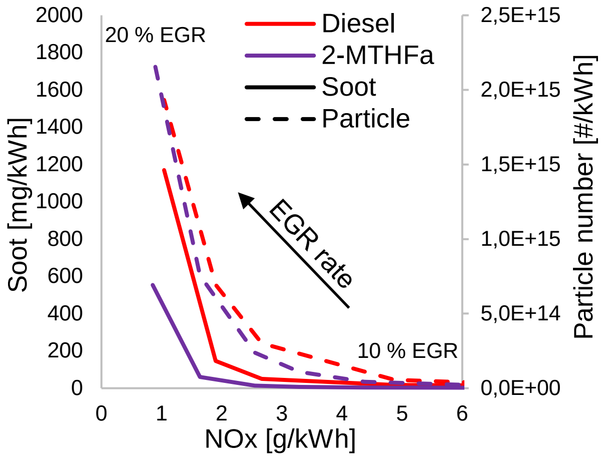

Figure 20: Soot-NO_x and particle number-NO_x trade-off at OP-1500/15 with MFB50% 7.5 °CAaTDC

5.2.2 Diesel Engine Operation with Manifold Injection of Highly Ignitable Dimethyl Ether (DME)

Dimethyl ether is similar to Diesel fuel because of its high ignitability and has the potential to be used directly as a Diesel substitute. Due to the fact that DME is gaseous at ambient conditions and does not liquefy below a pressure of 5 bar, with the available test bench components, it could be fed only into the intake manifold. For this reason, DME was investigated as a dual-fuel supplement via intake manifold injection. The attempts to inject it in liquid aggregate state into the intake air failed because the ether started boiling in the fuel lines near the hot engine components. The pressure of the fuel could not be increased to prevent boiling with the available hardware and the bubble formation in the fuel lines made the Coriolis principle consumption measurement impossible. These considerations led to the decision to inject DME as a gas. The evaporation occurred in the DME bottle, additional evaporation heat was provided by an external heater in order to ensure sufficient gas pressure.

While being fed into the intake manifold, the dimethyl ether auto-ignited twice during the compression stroke of the engine, long before the start of the Diesel direct injection. The rest of the fuel charge was combusted after the ignition of the Diesel fuel. The most important curves of the indicated data are shown parallel for both load points (OP-1500/5 and OP-1500/15) in Figure 21 – Figure 26. This type of combustion has a low thermodynamic efficiency, which is proven by the results shown in Figure 27 and Figure 28.

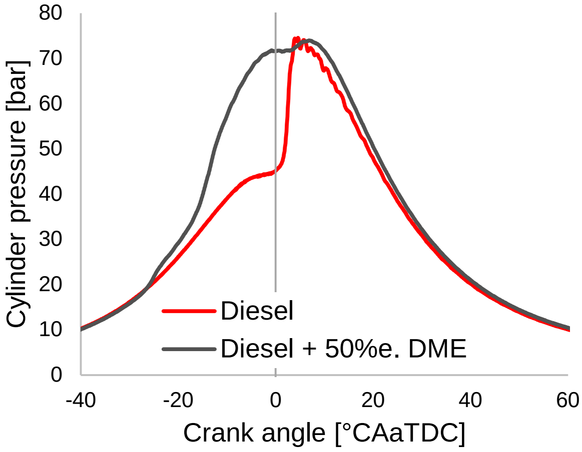

Figure 21: Cylinder pressure at OP-1500/5 with 30 % EGR and MFB50% 7.5 °CAaTDC

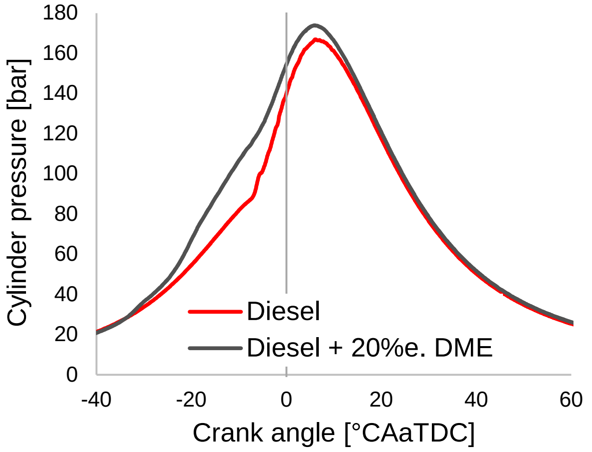

Figure 22: Cylinder pressure at OP-1500/15 with 15 % EGR and MFB50% 7.5 °CAaTDC

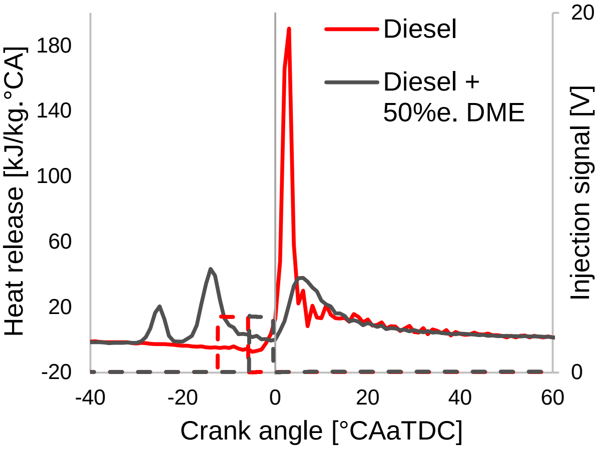

Figure 23: Heat release rate at OP-1500/5 with 30 % EGR and MFB50% 7.5 °CAaTDC

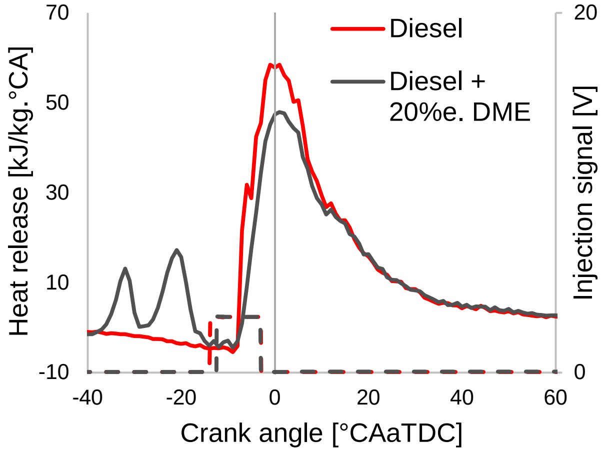

Figure 24: Heat release rate at OP-1500/15 with 15 % EGR and MFB50% 7.5 °CAaTDC

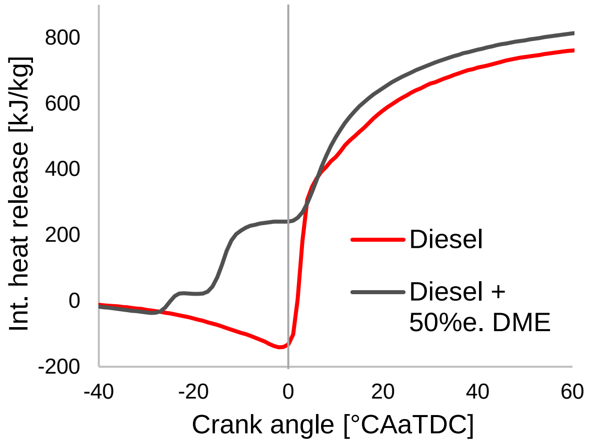

Figure 25: Integrated heat release rate at OP-1500/5 with 30 % EGR and MFB50% 7.5 °CAaTDC

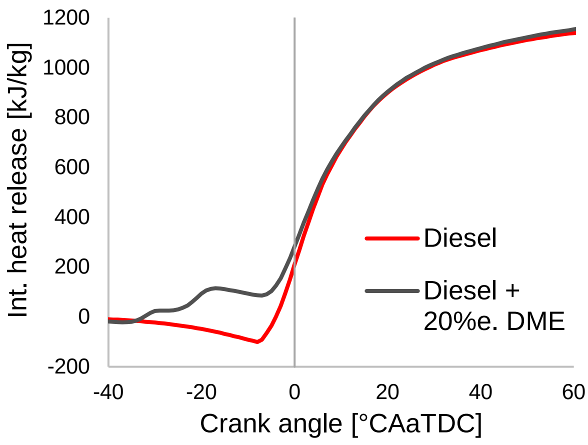

Figure 26: Integrated heat release rate at OP-1500/15 with 15 % EGR and MFB50% 7.5 °CAaTDC

The increase of the DME share at the combustion continuously reduced the efficiency of the process. Higher EGR rates could partially mitigate this drawback mainly due to suppression of the DME amount combusted during the early auto-ignition phases, Figure 29.

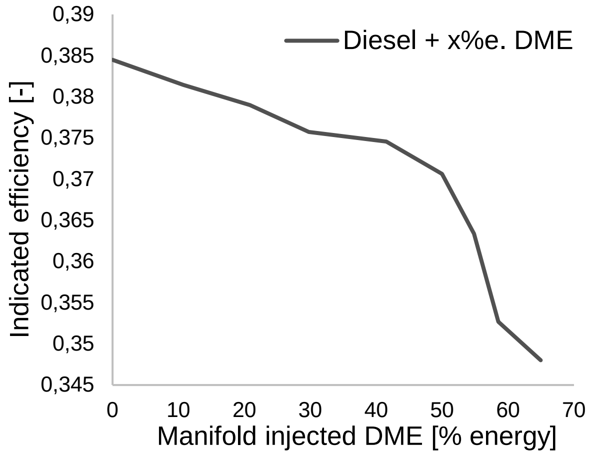

Figure 27: Indicated efficiency as function of the manifold injected DME share at OP-1500/5 with 30 % EGR and MFB50% 7.5 °CAaTDC

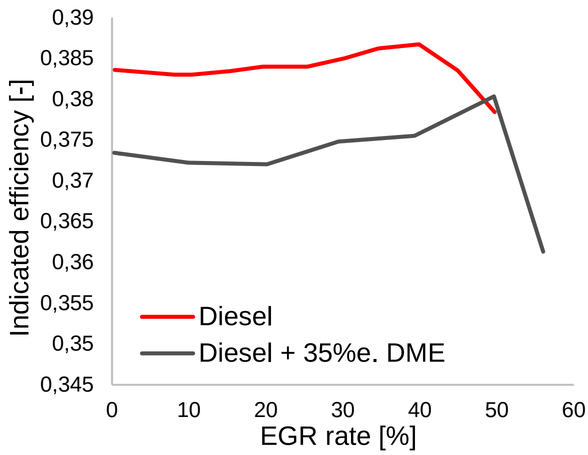

Figure 28: Indicated efficiency as function of the EGR rate at OP-1500/5 with MFB50% 7.5 °CAaTDC

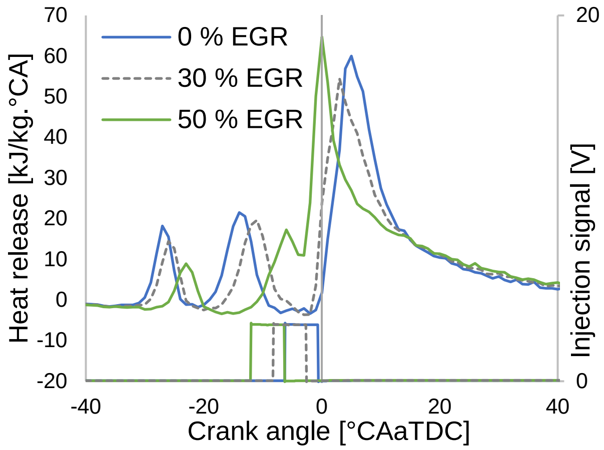

Figure 29: Heat release rate in operation with 35 %e. manifold injected DME at OP-1500/5 with 0, 30 and 50 % EGR and MFB50% 7.5 °CAaTDC

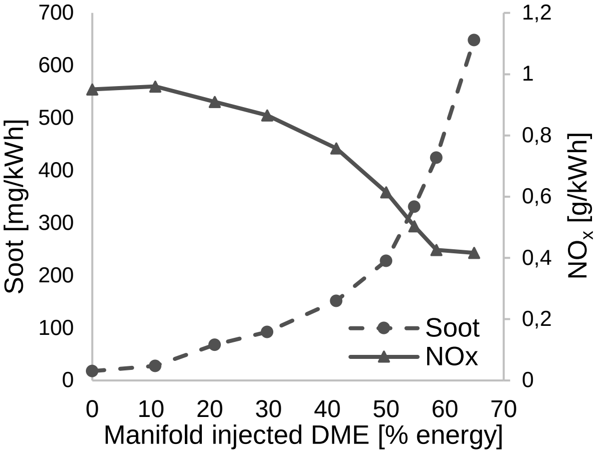

Figure 30: Soot and NO$_x$ emissions as function of the manifold injected DME share at OP-1500/5 with 30 % EGR and MFB50% 7.5 °CAaTDC

Contrary to the expectations presented by the literature review, a very high increase in soot and particulate emissions was observed, as shown in Figure 30 and Figure 31. The reason for this was the combustion of the Diesel jet, which occurred under local air deficiency in the hot burnt gas from the early DME combustion. The directly injected Diesel fraction ignited with a significantly shortened ignition delay, which led to poor homogenisation and reduced lift-off length of the Diesel spray. DME itself is discussed in literature as a fuel with nearly soot-free combustion. Therefore, it is assumed that the reason for the soot and particle emission increase were the disadvantageous conditions during the Diesel fuel combustion.

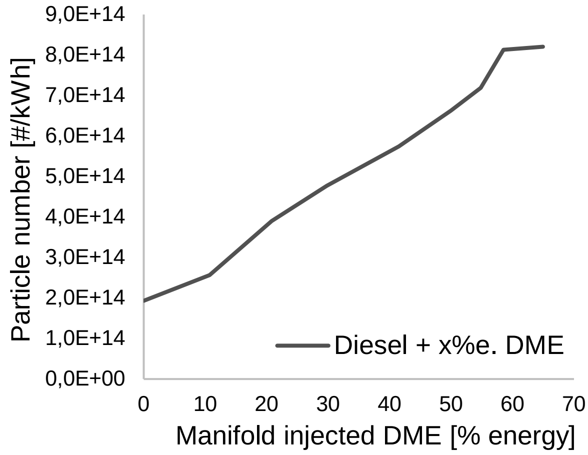

Figure 31: Particle number emissions as function of the manifold injected DME share at OP-1500/5 with 30 % EGR and MFB50% 7.5 °CAaTDC

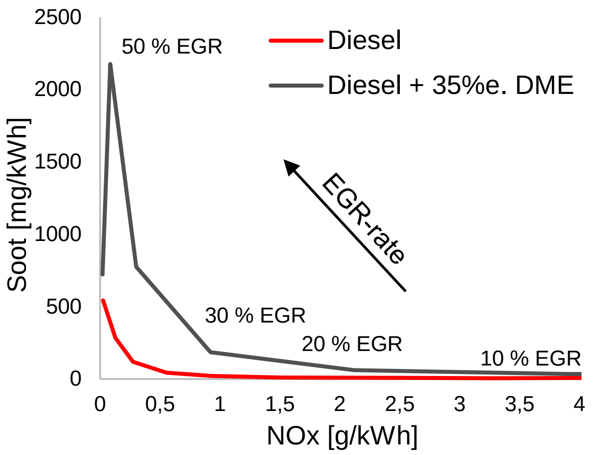

Figure 32: Soot-NO$_x$ trade-off at OP-1500/5 with MFB50% 7.5 °CAaTDC

Figure 30 and the soot-NO_x trade-off depicted in Figure 32 show that the combustion of DME in a dual-fuel mode in the lower load point of 5 bar IMEP emitted less NO_x emissions compared to the Diesel reference, however, at the cost of high soot and particle output. The soot-NO_x trade-off was eventually considerably worsened.

At the higher load point OP-1500/15, the experiments could only be conducted with moderate DME energy shares since higher amounts led to very poor combustion quality of the direct injected Diesel fuel. The main reason is the low air-fuel equivalence ratio at these operating conditions. Figure 33 displays the indicated efficiency over the centre of combustion for different DME energy shares. The combustion with 30 %e. DME was not possible with more than 10 % EGR. It is obvious that increasing DME fractions led to strong efficiency reduction also at the higher load point. The soot and particle emissions were also much higher in comparison to Diesel reference operation, however, the impairment was weaker compared to the differences measured between Diesel reference and DME dual-fuel operation at the lower load point, Figure 34 and Figure 35. At low load testing, the directly injected Diesel fuel in reference operation exhibits a long ignition delay and, therefore, good homogenisation and mixture formation before the ignition occurs. This aspect results in a low level of soot and particle emissions. The introduction of DME disrupts the soot lowering conditions at the Diesel spray and leads to a significant soot production by the Diesel fuel. At the higher load point, the ignition delay is noticeably shortened and the particle generation is enhanced even in the case of reference Diesel operation. Substituting the Diesel fuel by the auto-igniting DME not only additionally increases the soot production at the Diesel spray due to even shorter ignition delay and early oxygen consumption but also simultaneously substitutes the soot producing Diesel fuel by an almost soot-free combusting fuel. Both effects are oppositional.

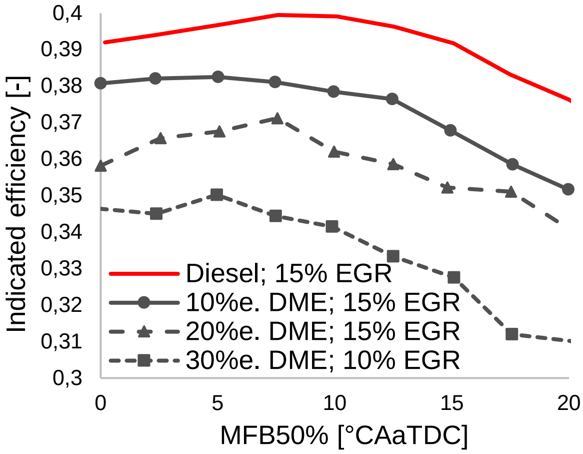

Figure 33: Indicated efficiency as function of MFB50% at OP-1500/15 with different DME shares and EGR rates

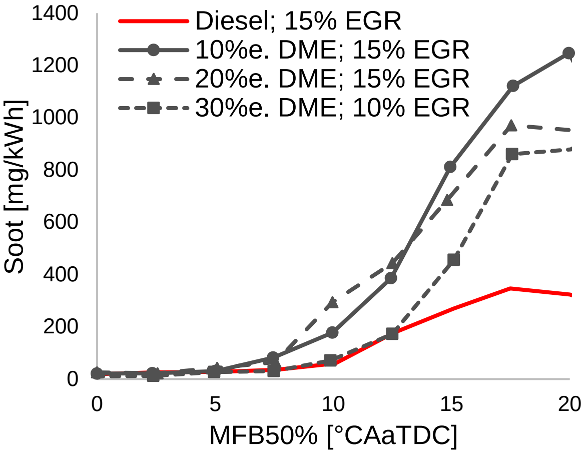

Figure 34: Soot mass emissions as function of MFB50% at OP-1500/15 with different DME shares and EGR rates

At the higher load point OP-1500/15, the NO_x emissions could not be reduced within the dual-fuel operation mode with DME intake manifold injection and behaved as the Diesel reference, Figure 36.

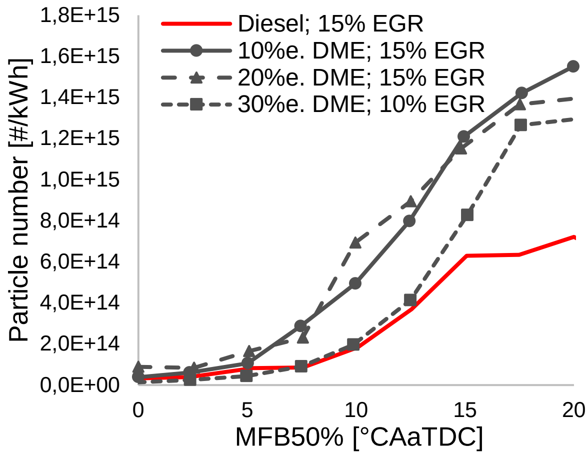

Figure 35: Particle number emissions as function of MFB50% at OP-1500/15 with different DME shares and EGR rates

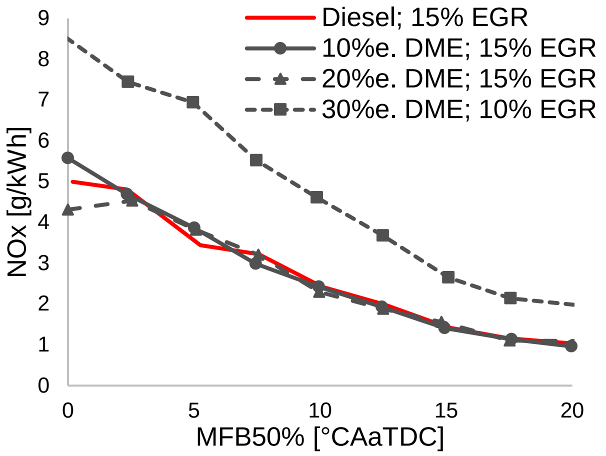

Figure 36: NO_x emissions as function of MFB50% at OP-1500/15 with different DME shares and EGR rates

It could be concluded that DME is a highly attractive Diesel substitute fuel but only in conjunction with direct injection. The dual-fuel experiments with intake manifold injection of DME did not result in any efficiency or emission improvements compared to the conventional Diesel fuel engine operation.

5.2.3 Diesel Engine Operation with Synthesis Gas

The sensitivity of the engine test results to the synthesis gas composition was checked by means of two different concentrations. These showed great differences in the H_2 and CH_4 content and can be understood as extreme cases. Accordingly, the influence of reform mechanisms, reforming fuels and reforming conditions on the performance of the engine could be examined. The values were provided by the reforming investigations at *AVL* and the desired concentrations were set on the engine test bench using a gas mixing device. The two synthesis gas compositions are shown in Table 8.

Table 8: Definitions of both investigated synthesis gas compositions

Vol%	SynGas 1	SynGas 2
H_2	31.5	18
CO	6.2	8.4
CH_4	0	6.4
CO_2	15.2	13.5
N_2	Rest	Rest

Since the endothermic fuel reforming process was found to be efficient only at high temperatures and low air/fuel ratio, the investigations had to be intentionally carried out with low lambda values. The experiments with the two synthesis gas compositions showed that the test results have no significant dependence on the synthesis gas concentration. However, with higher methane content in the synthesis gas, the raw methane emissions increased, as can be seen in Figure 37.

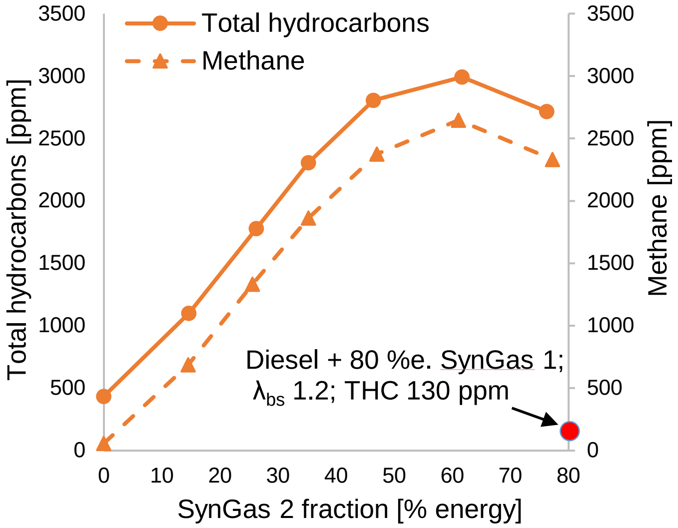

Figure 37: Total hydrocarbons and methane emissions at SynGas operation with "SynGas 2" at OP-1500/5 with MFB50% 7.5 °CAaTDC, λ_{BS} = 1.25, intake manifold pressure p_{intk} = 1030 mbar and variable EGR rate

Figure 38 shows the influence of the synthesis gas fraction on the measured indicated efficiency. The speed in these tests was 1500 rpm, the mean indicated pressure was 5 bar. The yellow curve represents the variation of the energetic SynGas fraction at an operating point with a constant air-fuel ratio of 1.2 and no external exhaust gas recirculation. The orange curve, on the other hand, describes the dependence of the indicated efficiency on the synthesis gas fraction in operation with a constant air-fuel ratio of 1.25 and a variable external exhaust gas recirculation rate. The intake manifold pressure was kept constant at 1030 mbar (abs.). The EGR rate was changed so that the desired air-fuel ratio of 1.25 resulted. As the synthesis gas amount increased, the

EGR rate had to be reduced so that the parameters set at constant remained unchanged.

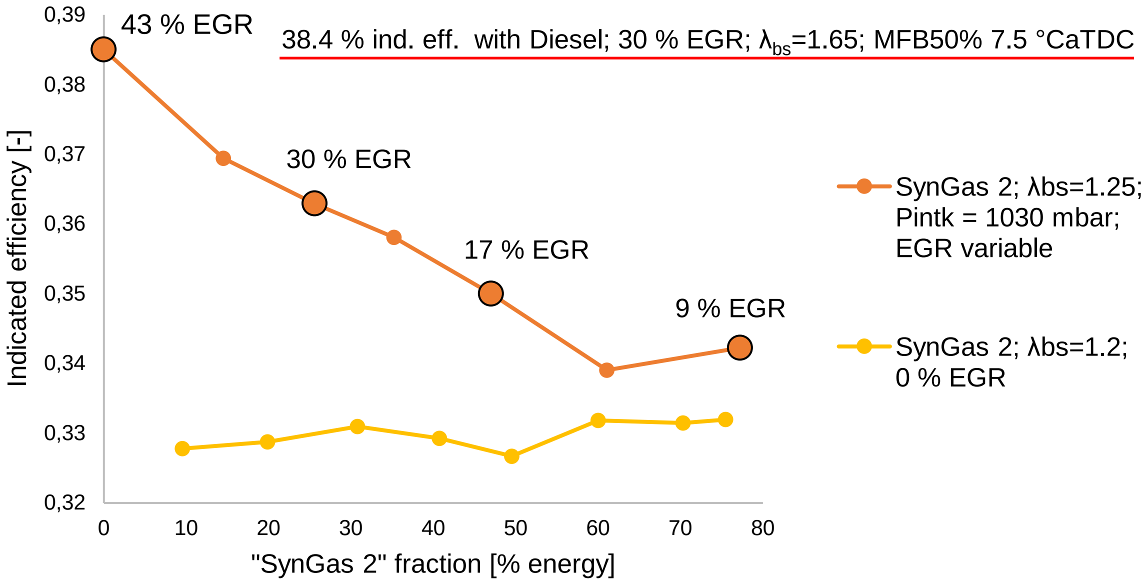

Figure 38: Indicated efficiency as function of the synthesis gas share at operation with "SynGas 2" at OP-1500/5 with MFB50% 7.5 °CAaTDC

In the case without external exhaust gas recirculation, the indicated efficiency was at a low level of about 33 % regardless of the synthesis gas fraction. If the air-fuel ratio was adjusted not by lowering the intake pressure but by recirculating exhaust gas, then there were great efficiency advantages, as can be observed from the orange curve. However, it can be seen that the efficiency decreased sharply and continuously by increasing the synthesis gas amount. For comparison, at a reference point from the operation with pure Diesel fuel, the efficiency was 38.4 % with 30 % external exhaust gas recirculation rate and the air-fuel ratio was 1.65.

Figure 39 shows that the operation without exhaust gas recirculation produces very high NO_x emissions. These could not be reduced to the level of the CEC-Diesel reference point solely by increasing the synthesis gas fraction. As expected, it could be seen that the addition of exhaust gas considerably reduced the nitrogen oxides. In this case, the strong NO_x reduction succeeded at the expense of significantly deteriorated efficiency.

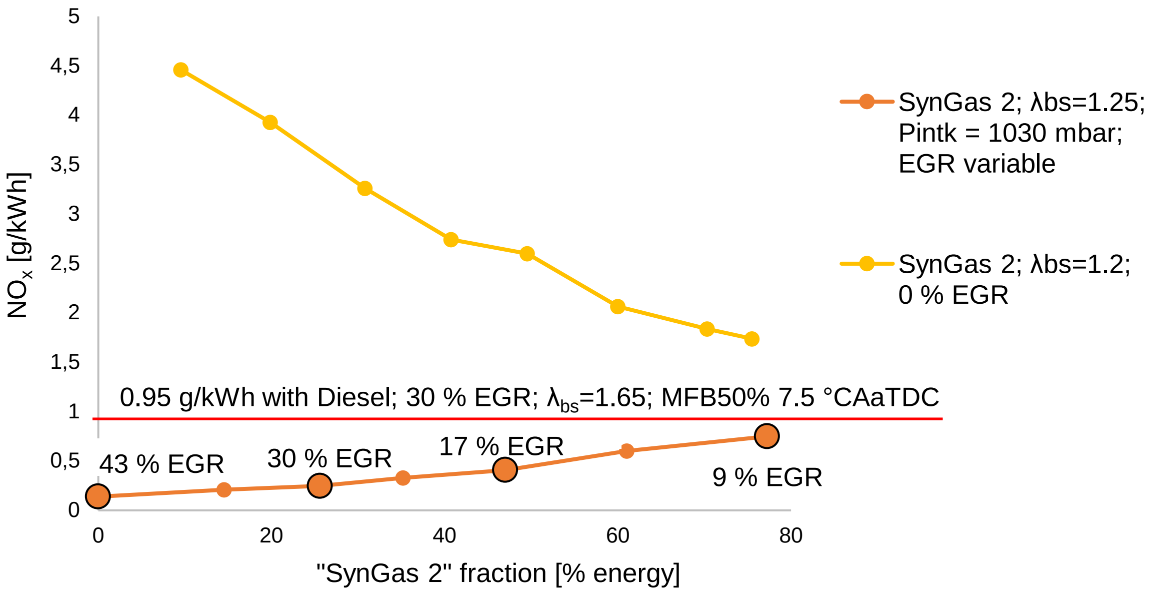

Figure 39: NO_x emissions as function of the synthesis gas share at operation with "SynGas 2" at OP-1500/5 with MFB50% 7.5 °CAaTDC

Compared to the lower load point, at SynGas operation at higher load – 15 bar IMEP and same speed of 1500 U/min, a slight reduction in the efficiency disadvantage towards the Diesel reference operation is observed. Figure 40 shows a variation of the combustion centre position MFB50% at operation with reference Diesel and with the two SynGas compositions already described. Figure 41 depicts the development of nitrogen oxide emissions over the combustion centre position. Both for reference operation and for synthesis gas operation, the set limit value for nitrogen oxide emissions of 2 g/kWh was only achieved at a combustion centre position MFB50% of approx. 12.5 °CAaTDC. Accordingly, the measured indicated efficiency is also read at this MFB50%. The efficiency disadvantage compared to the reference operation could be reduced slightly by taking into account the increase in calorific value due to the endothermic reactions in the virtual reforming process. In the case described, the generation of synthesis gas from ethanol was considered. Despite the efficiency increase of the overall system (reformer and internal combustion engine) in synthesis gas operation by about 0.6-0.7 % points, the disadvantages compared to the reference operation could not be fully compensated.

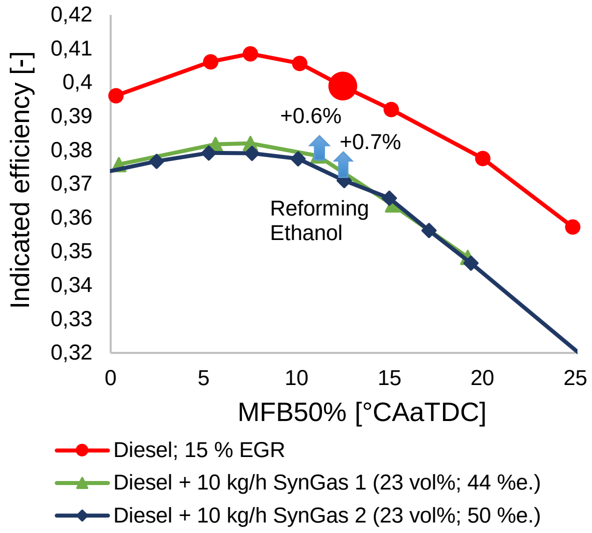

Figure 40: Indicated efficiency as function of MFB50% for reference Diesel operation and dual-fuel operation with two different synthesis gas compositions at OP-1500/15; the lower heating value increase due to endothermic fuel reforming increases engine efficiency

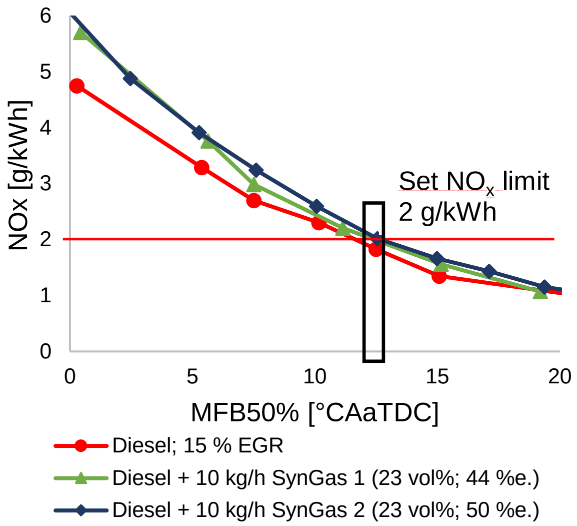

Figure 41: NO_x emissions as function of MFB50% for reference Diesel operation and dual-fuel operation with two different synthesis gas compositions at OP-1500/15

The experiments with two different synthesis gas compositions showed that the performance of the engine was not noteworthily influenced by the concentrations of hydrogen and methane in the feed gas. However, high emissions of unburnt methane were measured in the exhaust gas at operation with the methane-rich “SynGas 2” and the loss analysis showed that such high emissions significantly reduce the measured efficiency. The available measurement apparatus was not appropriate for the reliable measurement of very low hydrogen concentrations (ppm-range such as in the exhaust gas). However, the attempt to determine the emissions of unburnt hydrogen with the existing gas analyser still showed that at operation with synthesis gas considerably more hydrogen is emitted than in Diesel reference operation. It may be concluded that with rising synthesis gas share, the ignition and complete combustion of both hydrogen and methane become challenging.

6 Scientific Contribution of the Dissertation

An important feature of the conducted research is the intended comparability of the fuel investigation results. Specifying a constant set of operating conditions and measurement categories by using the same test engine and the same test methodology allowed the parallel analysis of different combustion processes and fuel performance for tests, which were carried out over a period of four years.

The work of the project partners at *CEET* proved that second generation biofuels from lignocelluloses are a feasible and effective option for greenhouse gas emissions reduction of internal combustion engines. The process engineering simulations, however, imposed the necessity for high biomass feed, which significantly reduces the energy efficiency of the discussed biomass conversion processes. The considerable calculated investment costs for such innovative and sophisticated biofuel production plants are a major obstacle for the market introduction of these biofuels.

Taking a look at the production case study of a first generation biofuel in the middle of Europe sets a reminder that sustainably produced conventional biofuels still have the chance to contribute to the goals of greenhouse gas reduction of the transport sector, while simultaneously supporting food security and local economy. Assessing the socio-economic and environmental impact of alternative fuel production should be carefully approached using acknowledged methods and impartial motivation.

Oxygenated fuels were preferred within the scope of the presented activities since it was expected that their combustion would result in soot and particle emission reduction. Literature reveals different approaches to postulate a relation between soot reduction effect and oxygen mass content of the fuel. These theories certainly have their justification for some fuels; this thesis, however, allows the conclusion that not solely the oxygen content but also the molecule structure, the ignitability and the physical properties of the fuel determine its soot reduction potential. The combustion process and the operation strategy play a crucial role in this aspect and the experimental investigations are the most suitable method for gaining engine suitability insights.

The conducted work proposed three techniques for alternative fuel utilisation in a Diesel engine: direct injection of neat fuel or blend with Diesel, dual-fuel combustion with intake manifold fuel injection and dual-fuel combustion synthesis gas, produced through fuel reforming of the alternative fuel. Such a comprehensive and profound comparison of these variants on the same test bench and for several fuels broadens the current state of knowledge.

6.1 Operation of a Diesel Engine with the Poor-Ignitability Fuels Methanol, Ethanol, Butanol and 2-Methyltetrahydrofuran

Blending Diesel fuel with an alternative fuel is possible but the maximum blending rate depends on the fuel properties. This method is limited by the possible violation of the Diesel fuel norm in force.

The tests of a dual-fuel combustion concept with ethanol, methanol and butanol demonstrated a series of benefits. It was shown that low cetane fuels, unsuitable for direct injection, could be very successfully utilised in a Diesel engine designed to operate in a dual-fuel mode. Significant soot, particle number, NO_x and CO_2 emission reductions were measured together with a noteworthy increase in efficiency. This technique allows high substitution shares and flexible operation depending on the fuel availability. The dual-fuel combustion concept is well-known and commonly used for Diesel-gas engines but the simultaneous examination of the alcohols in this study revives the perception of the advantages of this method. Especially the comprehensive investigations with ethanol and ethanol-gasoline mixtures E65 and E85 add to the knowledge in this field. The results of this research were accredited by a strong media interest, e.g., [105-111]. The literature study before the tests did not offer satisfactory explanations for the observed efficiency changes with rising amount of alcohol share. The conducted engine process simulation and the loss analysis discussion for operation with Diesel only and dual-fuel operation with ethanol gave answers to the questions about the efficiency behaviour of the duel-fuel process with short-chained alcohols.

The production of 2-MTHF was simulated within the project framework of the scientific partners at *CEET, TU Graz*. None of the analysed processes could deliver positive CO_2 savings for this fuel and its production resulted in more gCO_2/MJ output (between 53 and 87 %) than fossil Diesel. The engine investigations of cetane boosted 2-MTHFa proved the fuel to be challenging for utilisation in a Diesel engine due to its low ignitability (cetane number 26). A cold start was not possible with this fuel and the variations of operating parameters were limited. The combustion generally produced less soot but more NO_x emissions. It may be concluded that 2-MTHF is not an appropriate fuel for the conventional compression ignition engine. However, this low ignitability fuel may unfold its potential in a blend with a high reactivity fuel, e.g., DBE. Such experiments were not conducted within the projects on which this dissertation is based but could present a chance for future engine usage of both fuels as their combination could make use of their positive properties and soften the negative ones. In any case, the fuels should emit less well-to-wheel CO_2 saving than their Diesel counterpart.

6.2 Operation of a Diesel Engine with the Highly Ignitable Polyoxymethylene dimethyl ethers, Di-*n*-butyl Ether and Dimethyl Ether

The combustion investigations with di-*n*-butyl ether posed a question concerning the results of the few previously published studies on this topic. With the conditions set for the tests in the current study, the emission behaviour of the combustion process could not be substantially improved. DBE addition to Diesel even worsened the soot and particle emission levels. Given the fact that simulated production from biomass is expensive and inefficient, the possible use of this fuel should be questioned and provoke additional detailed research regarding production techniques and engine application.

The published work on Diesel engine operation with POMDME contributed to the very first investigations of the engine suitability of these highly innovative fuels. Especially the tests with the higher graded OME_{3-6} were a novelty since the fuel had to be imported from China and only a few research groups in Europe had access to it. The tests confirmed the extreme potential of OME to eliminate the soot-NO_x trade-off. In terms of combustion performance, no considerable differences were observed between OME_1 and OME_{3-6} but the low boiling point and high vapour pressure of OME_1 would eventually make OME_{3-6} preferable for Diesel blending, which opens completely new perspectives for the Diesel engine. Together with the production analysis for OME as a second generation biofuel from lignocellulose, the conducted investigations reinforced the basis for future research on this topic.

The only possible way to investigate DME in a Diesel engine without considerable modifications of a series of direct fuel injection system components, was the realisation of a dual-fuel operation mode with DME intake manifold injection. The conducted work showed that such high ignitability fuels are not expected to provide any improvements in efficiency or emission behaviour in dual-fuel mode. The undesired auto-ignition of DME negatively altered the combustion process. Literature reports DME to be a very suitable alternative Diesel fuel in conjunction with direct injection and the current study confirms that future DME investigations should focus on this method.

6.3 Operation of a Diesel Engine with Synthesis Gas Produced through Fuel Reformation

The combustion investigations with synthesis gas, produced by the reforming of the alternative fuel, presented an additional possibility for fuel usage in a Diesel engine. Suggesting this method for alternative fuel evaluation and providing a direct comparison with the dual-fuel method with manifold injection of an unreformed fuel is a novelty. The project partners at *AVL* determined the synthesis gas definition and the virtual upgrade of the fuel's calorific value through the endothermic reforming process. The combustion tests at the *Vienna University of Technology* delivered the boundary conditions for the simulation of the synthesis gas composition. These steps went through several loops and together with the greenhouse gas saving analysis conducted at *CEET* demonstrated efficient and result-oriented scientific cooperation.

The investigations of the synthesis gas operating mode showed that the lean operation of the Diesel engine and the relatively low exhaust gas temperatures make fuel reforming and engine operation possible only at high loads. The expected advantage of soot mass reduction due to gas combustion was partly proven but generally, no significant pollutant emission reduction was figured out and NO_x emissions even tended to increase. The overall efficiency was lower than in Diesel reference operation, even after the virtual efficiency upgrade through fuel reforming was considered.

Despite being disappointing at first glance, these findings were very valuable because they pointed towards a very promising alternative – the SynGas operation of a gasoline engine. The combustion concept of the gasoline engine provides the ultimate conditions for fuel-reforming – stoichiometric air-fuel equivalence ratio and high exhaust gas temperatures. With this motivation, another cooperation project that investigates the potential of a spark ignited gasoline engine to reach 45 % efficiency at SynGas operation with an on-board fuel reformer was started.

6.4 Direct Comparison of Experimental Results

In order to give a succinct summary of the investigation results discussed in this dissertation, all fuels and the corresponding fuel supply methods are listed in Table 9. The assessed categories are efficiency, well-to-wheel and tank-to-wheel CO_2 emissions, particle mass and count. For a clearer presentation of the evaluation, characteristic numbers are defined, which represent the percentage change towards the Diesel reference values. The Diesel reference is given the number 100, e.g., 3 %

improvement in efficiency when using a biofuel would receive the number 103, a deterioration of the same value 97. An emission characteristic number of 70, e.g., means that the emissions add up to only 70 % of the Diesel reference emissions. The table summarises the evaluation for the operation points with the highest indicated efficiency at operating point OP-1500/15 (1500 rpm, 15 bar IMEP) with the arbitrarily set constraint of NO_x emissions ≤ 2 g/kWh. The improvements against the conventional Diesel fuel operation are displayed in green colour, whereas the alarming deteriorations are marked yellow.

Obvious highlights are the efficiency gain and the simultaneous significant soot mass and particle number reduction in dual-fuel operation mode with intake manifold injected alcohols. The other remarkable fuel candidates are the polyoxymethylene dimethyl ethers. These innovative fuels eliminate the soot-NO_x trade-off of the Diesel engine, achieve considerable well-to-wheel CO_2 savings (depending on the production process) and have the potential to even increase the efficiency of the engine if the injection system is appropriately modified.

The operation of a Diesel engine with **intake manifold injection of synthesis gas** is possible but is not expected to deliver any substantial benefits. Future research should focus on the SynGas operation of a $\lambda = 1$ engine concept since it was found that in this case, the conditions for endothermic fuel reforming are favourable for high gas output and reforming efficiency.

The **dual-fuel** operation is generally advantageous for low ignitability fuels like short-chained alcohols. The fuels should be of high ignition resistance in order to prevent uncontrolled auto-ignition of the fuel-air charge before the injection of the Diesel jet. The manifold injection of a high cetane fuel (DME) considerably worsened the performance of the engine due to multi-stage auto-ignition in the compression stroke.

Fuels with diesel-like ignitability proved to be best utilised via **direct injection**. The emission behaviour of the Diesel engine operation with directly injected blends of Diesel and alternative fuel is highly sensitive to the alteration of the ignition delay. Alternative fuels with a cetane number higher than diesel reduce the ignition delay and create combustion conditions that are disadvantageous for the conventional Diesel fuel fraction; therefore, higher emission levels (especially soot and particle number) may be generated. Low cetane fuels like ethanol and methanol extend the ignition delay of the injected blend and enforce better mixture homogenisation, which results in less soot emissions. This behaviour is particularly well pronounced at low load testing. However, the influence of a lower cetane number on the pollutant emission output is significantly reduced at higher load operation since the ignition delay does not differ so strongly as at low loads. In that case, other properties of the fuel blend like oxygen content, spray formation and spray cooling through fuel components with high enthalpy of evaporation determine the generation of the pollutants. For this reason, the soot and particle emission results with the Diesel-alcohol blends and 2-MTHFa were better at the low load point OP-1500/5 than at OP-1500/15.

Table 9: Fuel and method comparison at operating point OP-1500/15 with NO_x emissions ≤ 2 g/kWh

Fuel (combination)	Supply form / injection	Efficiency	CO2 well-to-wheel	CO2 tank-to-wheel	PM	PN#	System complexity
Diesel	single fuel / direct	100	100	100	100	100	~
43%e. SynGas	dual-fuel supplement / manifold	97 1)/97 2)/98 3)	82 1)/69 2)/75 3)	99	43	43	- -
60%e. EtOH	dual-fuel supplement / manifold	103	69	90	9	8	-
40%e. MetOH	dual-fuel supplement / manifold	103	68	92	22	23	-
40%e. Butanol	dual-fuel supplement / manifold	101	74	97	26	43	-
10%vol. EtOH	blended / direct	99	98	101	94	181	~
20%vol. EtOH	blended / direct	100	94	99	48	132	~
10%vol. BuOH	blended / direct	99	96	101	81	163	~
20%vol. BuOH	blended / direct	100	90	99	71	157	~
10%vol. MetOH	blended / direct	99	98	101	119	200	~
OME1a (1600 bar)	single / direct	99	29	107	0	0	~
OMEmix (1600 bar)	single / direct	97	30	114	0	0	~
20%vol. OME1	blended / direct	100	91	101	62	145	~
20%vol. OMEmix	blended / direct	100	91	101	63	141	~
2-MTHFa	single / direct	98	155	100	25	72	~
20%e. DME	dual-fuel supplement / manifold	91	95	105	256	217	-
DBE	single fuel / direct	99	34	101	93	273	~
20%vol. DBE	blended fuel / direct	100	90	101	198	256	~

Legend:

1) Reforming of ethanol; **2)** Reforming of methanol; **3)** Reforming of butanol; **PM** characteristic number for particle mass; **PN#** characteristic number for particle number; **System complexity** complexity for the realisation of a given variant in comparison to the conventional Diesel engine: **~** equal, **-** more complex, **- -** much more complex

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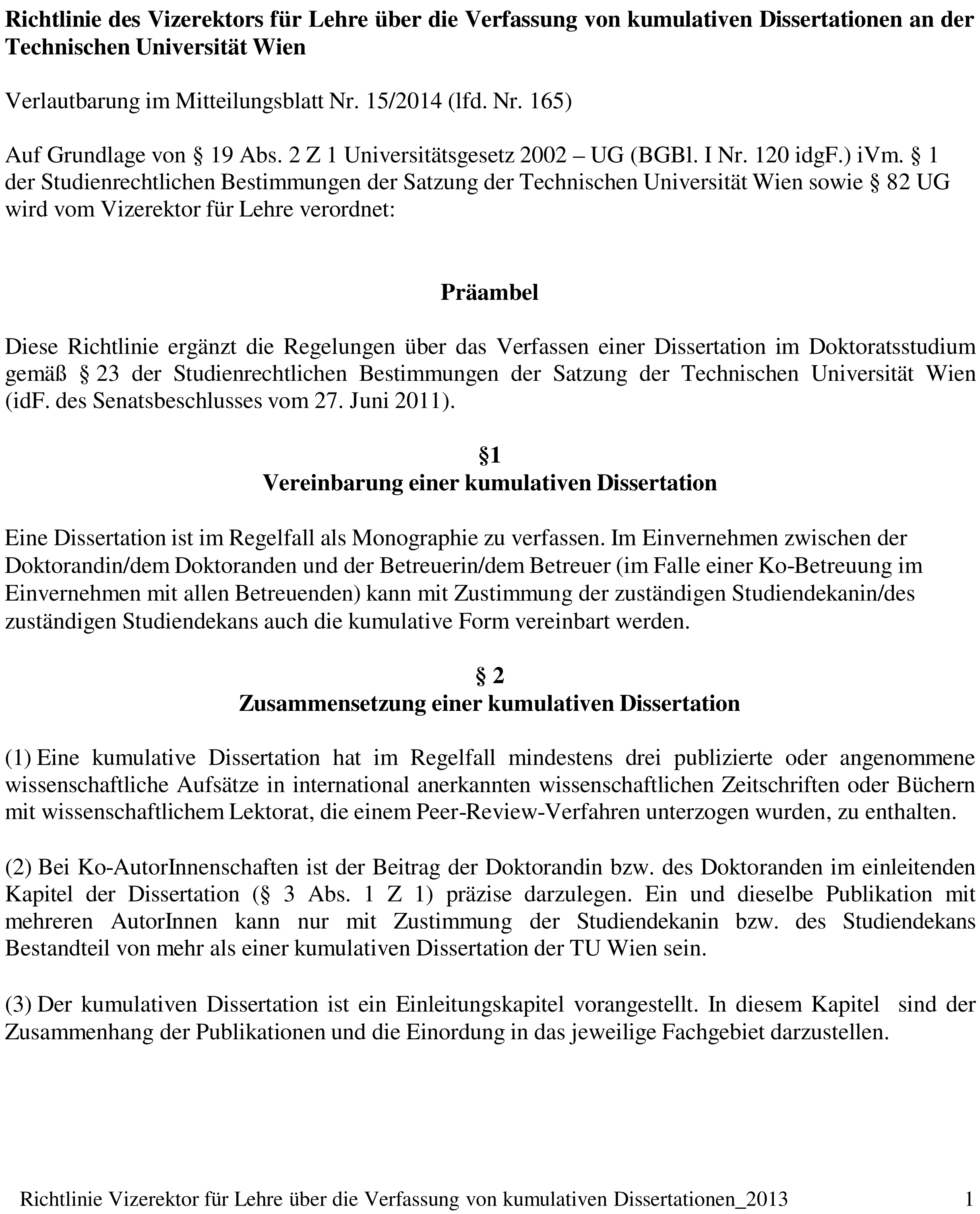
8 Appendices

Appendix 1

Guideline of the Vice Rector for Teaching on the Composition of Cumulative Dissertations at the Vienna University of Technology



Richtlinie des Vizerektors für Lehre über die Verfassung von kumulativen Dissertationen an der Technischen Universität Wien

Verlautbarung im Mitteilungsblatt Nr. 15/2014 (lfd. Nr. 165)

Auf Grundlage von § 19 Abs. 2 Z 1 Universitätsgesetz 2002 – UG (BGBl. I Nr. 120 idgF.) iVm. § 1 der Studienrechtlichen Bestimmungen der Satzung der Technischen Universität Wien sowie § 82 UG wird vom Vizerektor für Lehre verordnet:

Präambel

Diese Richtlinie ergänzt die Regelungen über das Verfassen einer Dissertation im Doktoratsstudium gemäß § 23 der Studienrechtlichen Bestimmungen der Satzung der Technischen Universität Wien (idF. des Senatsbeschlusses vom 27. Juni 2011).

§1
Vereinbarung einer kumulativen Dissertation

Eine Dissertation ist im Regelfall als Monographie zu verfassen. Im Einvernehmen zwischen der Doktorandin/dem Doktoranden und der Betreuerin/dem Betreuer (im Falle einer Ko-Betreuung im Einvernehmen mit allen Betreuenden) kann mit Zustimmung der zuständigen Studiendekanin/des zuständigen Studiendekans auch die kumulative Form vereinbart werden.

§ 2
Zusammensetzung einer kumulativen Dissertation

(1) Eine kumulative Dissertation hat im Regelfall mindestens drei publizierte oder angenommene wissenschaftliche Aufsätze in international anerkannten wissenschaftlichen Zeitschriften oder Büchern mit wissenschaftlichem Lektorat, die einem Peer-Review-Verfahren unterzogen wurden, zu enthalten.

(2) Bei Ko-AutorInnenschaften ist der Beitrag der Doktorandin bzw. des Doktoranden im einleitenden Kapitel der Dissertation (§ 3 Abs. 1 Z 1) präzise darzulegen. Ein und dieselbe Publikation mit mehreren AutorInnen kann nur mit Zustimmung der Studiendekanin bzw. des Studiendekans Bestandteil von mehr als einer kumulativen Dissertation der TU Wien sein.

(3) Der kumulativen Dissertation ist ein Einleitungskapitel vorangestellt. In diesem Kapitel sind der Zusammenhang der Publikationen und die Einordung in das jeweilige Fachgebiet darzustellen.

§3
Struktur einer kumulativen Dissertation

(1) Die kumulative Dissertation besteht aus
1. dem einleitenden Kapitel und
2. den wissenschaftlichen Aufsätzen.

(2) Das einleitende Kapitel hat
1. die Problemstellung,
2. die Ziele,
3. die Methodologie,
4. eine kurze Zusammenfassung der wissenschaftlichen Aufsätze sowie
5. den wissenschaftlichen Beitrag der Dissertation

zu enthalten. Die Nachvollziehbarkeit der Resultate muss aus der Beschreibung der wissenschaftlichen Methodologie eindeutig hervorgehen.

§ 4
Beurteilung und Einreichung einer kumulativen Dissertation

(1) Die Beurteilung einer kumulativen Dissertation erfolgt gemäß § 23 der Studienrechtlichen Bestimmungen der Satzung der TU Wien sowie gemäß den jeweils geltenden Bestimmungen des Studienplans für das Doktoratsstudium der Naturwissenschaften/Sozial- und Wirtschaftswissenschaften/Technischen Wissenschaften an der TU Wien.

(2) Die Einreichung und Abgabepflicht einer kumulativen Dissertation erfolgt nach den Bestimmungen der Richtlinie über die elektronische Abgabepflicht von Hochschulschriften (Mitteilungsblatt 14-2013 idgF.). Die elektronische Version einer kumulativen Dissertation hat das einleitenden Kapitel (§ 3 Abs. 1 Z 1) und abweichend vom gedruckten Exemplar lediglich die Literaturzitate der wissenschaftlichen Aufsätze (§ 3 Abs. 1 Z 2) zu enthalten.

§ 5
Inkrafttreten

(1) Diese Richtlinie tritt nach Veröffentlichung im Mitteilungsblatt der Technischen Universität Wien mit 1. Oktober 2013 in Kraft.
(2) § 1 in der Fassung Mitteilungsblatt 2014, 15. Stück, Nr. 165, tritt mit 1. Oktober 2014 in Kraft.

O.Univ.Prof. Dr. Adalbert Prechtl
Vizerektor für Lehre

Appendix 2

First WKM position paper (excerpt)

WKM Wissenschaftliche Gesellschaft für Kraftfahrzeug- und Motorentechnik e.V. (WKM)

The Future of the Combustion Engine / Assessment of the Diesel Engine Situation

Last year’s fierce debate, with its massive and to some extent justified criticism of diesel engines, has since gained momentum and has even sparked a wider discussion about a potential ban on combustion engines in automobiles.

Wissenschaftliche Gesellschaft für Kraftfahrzeug- und Motorentechnik e.V. (WKM) has viewed these developments with great concern and considers it particularly alarming that biased and rather emotional reporting seems to be replacing matter-of-fact pragmatic information.

Based on the current scientific knowledge, WKM has formulated three key messages related to these issues and to the future of the combustion engine. Additional facts and details are given below.

a. Combustion engines have been and continue to be the driving force behind mobility, freight transport, and mobile machinery. This role can be complemented, but not replaced, by electrical drives. The technological advancement of drive systems is a prerequisite for a successful climate policy in a prospering society. Bans have the opposite effect. [see Facts and Details 1 and 2]

b. Due to very low emissions from internal combustion engines the issue of emissions and pollution concentration in-air will be in future no argument against the diesel or the gasoline engine. Even the current state of technology already ensures that pollution limits can be met without exception. Weak points detected in retrospect are no longer relevant to the future. Thanks to intense research environmentally fully neutral combustion engine drivetrains are completely viable. [see Facts and Details 3 to 7]

c. The particular advantage offered by combustion engines is the efficient and flexible use of fuels with high energy density and excellent storage and distribution options. This basic property has enabled the combustion engine to reinvent itself again and again, and considering the integrated system this enables lower CO_2 emissions in comparison to alternative technologies. The potential to flexibly use non-fossil and hence CO_2-neutral fuels, is another guarantee for a long-term and sustainable technology of the future. [see Facts and Details 7 to 10]

WKM Wissenschaftliche Gesellschaft für Kraftfahrzeug- und Motorentechnik e.V. (WKM)

Additional Facts and Details

1.) WKM condemns all forms of technical manipulation, for example the use of cycle recognition software, to adjust, without physical necessity, special emission reduction measures that are not active under real operating conditions.

2.) WKM strongly supports introduction of the new Real Driving Emission (RDE) regulations in Europe. From September 2017, these regulations will provide clearly defined legal standards in the form of $EURO6d_{temp}$ for recertifications. The RDE Regulations are a great opportunity to help restore lost confidence.

3.) For decades, diesel engine development went hand in hand with finding solutions to the nitrogen oxide problem. Hundreds of research projects have aimed to understand in detail the formation of nitrogen oxides (NO_x) and have sought to reduce emissions, and the NO_x emission problem can now be considered as technically solved.

4.) The development of automotive passenger car diesel engines focused on the fulfillment of regulations relevant to the NEDC (New European Driving Cycle) certification cycle. The resulting discrepancy between certification limits and real emissions has been publicly known and documented for two decades and will disappear as the RDE regulations are applied.

5.) NO_x exhaust gas treatment devices positioned close to the engine is a decisive technological prerequisite in the latest automobile generation, which today already meets the RDE regulations. Numerous measurements on automobiles confirm low NO_x levels.

6.) In terms of mean annual air pollution release rates, the emissions contribution from the most modern diesel automobiles, meeting the new RDE standards, is perceptible, if at all, only on heavily trafficked roads and the Diesel engine's contribution is ensured to amount to only a few percent of the NO_2 pollution limit.

7.) WKM is critical that public reports have repeatedly contained unreasonably judgmental or even false statements. Diesel engines, for example, are not the only source of particulate matter and contribute only a few percent to dust pollution, with the trend pointing downward. Also the contribution of gasoline engines is very low, and will be reduced even further with the introduction of the RDE regulations and the implementation of particulate filters. NO_2 pollution is decreasing already for more than a decade throughout Germany.

8.) WKM is extremely concerned about the trend of discussing a ban on the combustion engine. A ban on combustion engines e.g. from 2030, would have negative effects on fighting climate change. WKM pleads for a holistic and straightforward honest consideration of CO_2 emissions in terms of the supply of energy, and production and disposal of drivetrain systems.

9.) Alternative synthetic and biogenic fuels need to be important elements of further CO_2 reduction. Sustainability ensured through the use of renewable electrical energy is decisive for a successful implementation of the energy turnaround. Combustion engines are ideally suited for supporting this development.

10.) WKM pleads for competition between drivetrain concepts with the aim of reducing emissions to the limit predetermined by the pollution of the intake air (pragmatically zero). According to all predictions, there will be more combustion engines worldwide in 2030 than today. Continued intense research and development and the preservation and holding of technology leadership are appropriate. WKM predicts a long-lasting need for combustion engines and, in particular, also for diesel engines.

Appendix 3

Second WKM position paper

Aktuelle Entwicklungen zur „CO_2- Gesetzgebung im Verkehrssektor“

Die Wissenschaftliche Gesellschaft für Kraftfahrzeug- und Motorentechnik WKM begrüßt die Anstrengungen des Gesetzgebers zur weiteren Reduktion der CO_2-Emissionen.

Zur weiteren Präzisierung der aktuellen und kommenden Gesetzgebungsaktivitäten und zur Erzielung eines bestmöglichen Nutzens für die Umwelt formuliert die WKM zehn Kernthesen.

1.) Jede Gesetzgebung zur Reduzierung der CO_2-Emissionen muss technologieneutral ausgestaltet sein und sich an der tatsächlich wirksamen Minderung von CO_2 aus fossilen Quellen orientieren.

2.) Technologieneutralität ist nur bedingt mit dem aktuell verabschiedeten Gesetz in Einklang zu bringen, welches die elektrische Fahrt, also insbesondere die elektrische Ladung der Fahrzeugbatterien, ohne CO_2-Emissionen abbildet.

3.) Nicht technologieneutrale Gesetzgebungen schädigen die Innovationskraft und unseren Wissenschafts- und Wirtschaftsstandort langfristig. Innovation ist der wirksamste Hebel Mitteleuropas im globalen Klimaschutz.

4.) Die WKM sieht eine Gefahr von Fehlentwicklungen in der Zukunft ohne den gewünschten Mehrwert für die Umwelt. Eine direkte Umsetzung der aktuell geplanten Gesetzgebung wird in der Realität die CO_2-Vorteile kleiner als gewünscht ausfallen lassen.

5.) Die batterie- und brennstoffzellengetriebene Elektromobilität stellt ein wichtiges, wachsendes Element des Mobilitätsangebots der Zukunft dar.

6.) Als Basis vieler Antriebskonzepte bleiben jedoch auch langfristig effiziente und vor allem elektrifizierte Verbrennungsmotoren (Fachbegriff: Hybridisierung) notwendig.

7.) Die WKM plädiert daher für eine umfassende Berücksichtigung von Fahrzeugproduktion, Bereitstellung der Energie und Energiewandlung (Fachbegriffe: Lebenszyklusanalyse, cradle-to-grave sowie well-to-wheel Betrachtung) bei der Bewertung der CO_2-Emissionen. Das verabschiedete Gesetz berücksichtigt im Wesentlichen nur die Analyse des Fahrzeuges im Fahrbetrieb (Fachbegriff: tank-to-wheel Betrachtung).

8.) Effiziente Verbrennungsmotoren sind in der modernen Ausgestaltung immissionsseitig vernachlässigbar und quasi wirkungsneutral (Zero Impact für die Emissionskomponenten NO_x, Partikel PM/PN, Kohlenmonoxid CO, Kohlenwasserstoffe HC).

9.) Die WKM plädiert dafür, das Potential synthetischer oder biogener Kraftstoffe (reFuels als Oberbegriff der verschiedenen CO_2-armen Kraftstoffe - auch PtX-Kraftstoffe, E-Fuels, bioFuels) in der Gesetzgebung zu berücksichtigen. Diese alternativen Kraftstoffe sind in den aktuellen Planungen nur sehr bedingt vorgesehen und bieten weitreichende Chancen, die für eine Erreichung der CO_2-Ziele genutzt werden müssen.

10.) reFuels bieten beispielsweise das Potential, auch bei Bestandsfahrzeugen und nicht nur bei Neufahrzeugen eine signifikante Reduzierung der CO_2-Emissionen zu erzielen. Für schwere Fahrzeuge (Flugzeug, Schiffe, schwere Arbeitsmaschinen, etc.) sind reFuels ohnehin alternativlos.

9 Curriculum Vitae

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05/2015 - present	**Vienna University of Technology** Doctoral Programme in Engineering Sciences Diploma Programme: Mechanical Engineering Institute for Powertrains and Automotive Technology Project Assistant
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II. Published Work

1. Damyanov, A.; Hofmann, P.; Derntl, M.; Schüßler, M.; Pichler, T.; Schwaiger, N.: **Operation of a Diesel engine with biogenous oxygenated fuels**; Lenz (Hrsg.); Proceedings of the 38th International Vienna Motor Symposium 2017, Vol. 2, p. 474-500; ISBN 978-3-18-380212-8; 27-28 April 2017, Vienna, Austria

2. Damyanov, A; Hofmann, P.; Schüßler, M.; Derntl, M.; Schwaiger, N.; Pichler, T.: **Operation of a Diesel engine with biogenous oxygenated fuels**; Poster presented at the 38th International Vienna Motor Symposium 2017; 27-28 April 2017, Vienna, Austria

3. Damyanov, A.; Hofmann, P.; Derntl, M.; Schüßler, M.; Pichler, T.; Schwaiger, N.; Siebenhofer, M.: **Regenerative Oxygen-Containing Diesel Substitute Fuels as an Ecological Option for Increasing Efficiency and Minimizing Emissions**; Nikolai Schubert (Hrsg.); Proceedings of the 11th International Colloquium Fuels, p. 315-331; ISBN 978-3-943563-32-0; 27-29 Juni 2017, Ostfildern, Germany

4. Damyanov, A., Hofmann, P., Drack, J., Pichler, T., Schwaiger, N., Siebenhofer, M.: **Operation of a Diesel Engine with Biogenous Oxymethylene Ethers;** Proceedings of the 26th Aachen Colloquium Automobile and Technology, Vol. 1, p. 289-314, ISBN 978-3-00-054182-7; 9-11 Oct 2017, Aachen, Germany

5. Damyanov, A., Hofmann, P., Geringer, B. et al.: **Biogenous ethers: production and operation in a diesel engine**; Automotive and Engine Technology, Vol. 3, Issue 1-2, p. 69-82; Aug 2018; https://doi.org/10.1007/s41104-018-0028-x

6. Damyanov, A.; Hofmann, P.; Pichler, T. M.; Schwaiger, N.: **Biogenous Ethers – Production and Operation in a Diesel Engine**; MTZ worldwide, Vol. 80, Issue 1, p. 66-71; Jan 2019; https://doi.org/10.1007/s38313-018-0126-1

7. Damyanov, A.; Hofmann, P.: **Operation of a Diesel engine with intake manifold alcohol Injection**; Automotive and Engine Technology, p. 1-12; Feb 2019; Online ISSN 2365-5135, Print ISSN 2365-5127; https://doi.org/10.1007/s41104-019-00040-2

8. Damyanov, A.; Hofmann, P.: **Biogenous Ethanol: CO_2 Savings and Operation in a Dual-Fuel Designed Diesel Engine**; Proceedings of the 14th

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Operation of a Diesel engine with biogenous oxygenated fuels

Einsatz von biogenen sauerstoffhaltigen Kraftstoffen in einem Dieselmotor

Abstract

Second generation biofuels have the potential to contribute to the reduction of combustion engine CO_2 emissions without entering an ethical contradiction to food production. Of particular interest concerning a diesel engine are oxygen-containing fuels as they can defuse traditional target conflicts such as particle-NOx trade-off or the efficiency-NOx compromise. Within the research project “Regenerative oxygen-containing diesel substitute fuels as an opportunity for efficiency enhancement and emission reduction - OxyGen2” („Regenerative sauerstoffhaltige Diesel-Ersatzkraftstoffe als Chance für Effizienzsteigerung und Emissionsminimierung - OxyGen2“), the suitability for motor combustion of a series of preselected biofuels is being experimentally investigated. The most promising fuels include the groups of bio-alcohols, ethers and -furans such as, for example, ethanol, methanol, butanol, dimethyl ether and oxymethylene ethers.

On a modified diesel engine at the Institute for Powertrains and Automotive Technology at the Vienna University of Technology, fuel-specific combustion processes are being developed and analysed regarding their feasibility, cost, efficiency and emissions. A distinctive feature of the project is the investigation of the fuel introduction into the internal combustion engine in three different ways. In addition to the generally used method of direct injection of diesel-biofuel blends, the biofuel is also fed via intake manifold injection in combination with parallel direct injection of diesel fuel into the combustion chamber. As a third particularly innovative approach, the reforming of the biofuel is being investigated experimentally. The resulting synthesis gas is fed to the engine by means of an injection system into the intake manifold. In this case the ignition is also effected via diesel pilot injection.

The biofuel potential is evaluated using the three variants of fuel application and the results of the different biofuels are compared. An overall assessment summarizes the results of the production analysis, reforming investigations and motor operation, and provides an overview of the fuel potentials for the use in a diesel engine.

Introduction

Because of its unmatched efficiency, the diesel engine represents the backbone of road mobility for people and goods. Therefore the search for substitute fuels that are sustainable and have no use restrictions is of high priority. As oxygen-containing biofuels offer advantageous properties in the processes "low-particle combustion" and "endothermal reforming using exhaust gas heat", the research activities in this project focus on these fuels. The selection of the fuels is not limited to the current diesel standard EN590, but also non-standard fuels are to be considered, whereby the usage possibilities are widely expanded by combustion processes, that are unconventional for the diesel engine. The potential within the engine system includes the aspects of efficiency, emission behavior and system complexity, and is to be evaluated based on an expanded observation, including possible exhaust gas heat utilization. The assessment of the selected biofuels of the 2nd generation within the project is carried out in addition to the motor suitability also on the basis of the criteria of sustainability and cost effectiveness of the production. These criteria, however, are not always compatible. The production processes were simulated using process engineering methods and their implementation in large-scale plants was evaluated. For a holistic evaluation, after a thorough literature research a database of biofuels of the second generation was prepared. The most promising fuels belong to the groups of bio-alcohols, ethers and -furans.

Exemplary for the project, the results with alcohol fuels are presented in this paper. Alcohols are currently used almost exclusively in spark ignition engines, because they have a high octane number. However, the use in a compression ignition engine is to be investigated, since an influence of the fuel oxygen on the pollutant emissions can be assumed.

The project considers three variants of fuel delivery. In addition to the generally used method of direct injection of diesel-biofuel blends, the biofuel is also fed via intake manifold injection with parallel direct injection of diesel fuel into the combustion chamber. The third approach consists of the upstream process of "endothermic fuel reforming". Hereby, using the exhaust gas enthalpy the so called synthesis gas - a mixture of H_2, CO, CH_4, CO_2 and H_2O, is being produced from the biofuel. Through the thermochemical utilization of the exhaust gas enthalpy, the heating value of the synthesis gas, can be increased, with respect to the feedstock. The resulting gas mixture is fed to the engine by means of an injection system into the intake manifold. The ignition is effected via diesel pilot injection. Within the scope of the project, both the reforming process and the associated combustion process are examined.

Each of the three methods for utilizing the alcohol fuel (synthesis gas injection, intake manifold injection, diesel blend direct injection) is known and has already been investigated in research. However, such a comprehensive and profound comparison of the three variants on the same engine simultaneously for several fuels, broadens the current state of knowledge. Through the accompanying sustainability analysis, the project is not only limited to the technical feasibility but also consistently assesses the possible use of the respective biofuel in the compression ignition engine.

Fuel-Reforming

Not least because of the thermodynamic cycle of the internal combustion engine, part of the energy that is chemically bound in the fuel is released to the environment in the form of heat [1], [2]. This loss of energy brings a big potential to systems that are able to convert waste heat to usable energy. If the waste heat can be recovered, the efficiency of an internal combustion engine can be significantly improved [3]. Within the OxyGen2 project a Thermo Chemical Recuperation loop system (TCR) [4], [5], [6] is investigated as third variant for the usage of biofuels. The concept is to use the enthalpy of an exhaust gas for the production of a combustible gaseous mixture (syngas). The syngas is derived through biofuel reforming reactions in a separate reactor. Further the loop is rounded off by the additional combustion of the syngas in the engine. The basic flow sheet of the TCR loop system is shown in Figure 1. The investigation of the syngas combustion is done by the Institute for Powertrains and Automotive Technology (IFA), the feasibility of the biofuel reforming is tested by AVL List GmbH on a synthesis gas test bed.

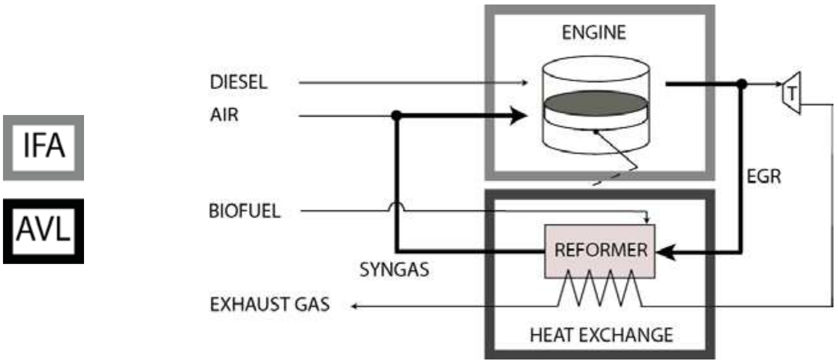

Figure 1 TCR loop System with Biofuel

The main purpose of the biofuel reforming process is to produce a combustible syngas containing mainly H_2, CO and also CH_4, CO_2, H_2O. The reforming reactions may take place directly in the hot exhaust gas recirculation pipe (EGR), where the main reactants for reforming reactions are provided e.g. H_2O, O_2 and CO_2. Only if the overall reaction in the reformer is endothermic ($\Delta H_R > 0$), waste heat is converted to chemical energy and the lower heating value (LHV) of the syngas increases in comparison to the LHV of the injected biofuel [7]. The increase of LHV and the combustion of syngas is expected to have positive effects on the engine's efficiency and emissions [8]. The calculation of ΔLHV is shown in Equation 1.

$$\Delta LHV\ [\%] = \frac{LHV_{SYNGAS}}{LHV_{BIOFUEL}} - 1$$

Equation 1 Gain of Heating Value ΔLHV [%]

The maximum value for ΔLHV can be forecasted with the ideal biofuel reforming reaction, where H_2 and CO are formed predominantly. Table 1 gives an overview of the ΔLHV values of some biofuels. The ratio of formed H_2 to CO equals 2 for all biofuels. Even though this results in different ΔLHV values, because the fuels have a different LHV basis. It can be seen that the highest ΔLHV can be expected for ethanol and butanol reforming, which is further investigated on the syngas test bed.

Table 1 Ideal reforming reactions, ΔLHV

	Ideal Reforming Reactions	LHV [kJ/mol]	ΔLHV [%]
Ethanol	$C_2H_5OH\ (l) + H_2O = 4\ H_2 + 2\ CO$	-1235	24%
Butanol	$C_4H_9OH\ (l) + 3H_2O = 8\ H_2 + 4\ CO$	-2456	25%
Methanol	$CH_3OH\ (l) = 2\ H_2 + CO$	-638	20%

TCR Simulation

In the project the reformer and the engine are situated ex-situ. Therefor a simulation tool was developed, which combines the engine and the biofuel reformer to one system according to Figure 1. Based on ideal engine combustion and ideal reforming in the EGR path, the simulation predicts the characteristics of the syngas at defined engine operating points. For the investigation in the engine test bed two characteristic mean syngas compositions were predicted. One composition favors the formation of H_2, and the second composition also considers CH_4 as a reforming product.

Reforming Results

The reforming of Ethanol and Butanol was investigated with a precious metal catalyst at 500°C reformer inlet temperature. The maximum amount of O_2 in the EGR gas for endothermic reforming is especially of interest, as O_2 determines the heat of reaction as well as the achievable level of ΔLHV. A comparison of experiments and simulation results is shown in Table 2. In the presence of O_2 the reforming experiments showed high biofuel conversions of 67% for butanol and 91% for ethanol. The comparison of the syngas compositions shows that the experiments and the simulation correspond very well. In the experiments a high concentration of H_2 was yielded (14-15%). However, the production of CO_2 was preferred hence the CO concentration was slightly lower. Also small amounts of CH_4 were analyzed in the syngas which further reduces the ΔLHV. As a result the experimental ΔLHV values of 1.8-2.5% are below the values of the ideal simulation (5-6%). Potential in further optimization is seen in catalyst improvement with the target of higher conversion and product gas selectivity.

Table 2 Comparison experiment – simulation, 500 °C reformer inlet

	Conversion	**λ**	**ΔLHV**	**Syngas [mol%]**			
Ethanol				H_2	CO	CH_4	CO_2
Experiment	91%	1.13	2.5%	14.2%	4.9%	1.1%	11.1%
Simulation	100%	1.13	4.6%	13.0%	6.5%	0.0%	10.6%
Butanol							
Experiment	67%	1.2	1.8%	14.9%	3.8%	0.2%	12.7%
Simulation	100%	1.2	6.2%	17.0%	8.3%	0.0%	10.4%

The ΔLHV value is very sensitive to the O_2 concentration in the EGR gas. Higher O_2 levels than 2.2% (λ=1.13) for ethanol and 2.8% (λ=1.2) for butanol change ΔLHV from positive to negative values. A negative ΔLHV indicates exothermic reactions, which are not desired for waste heat recovery. The results confirm, that especially low λ values and high exhaust gas temperatures (500°C) give potential to improve the engine's efficiency with butanol and ethanol EGR gas reforming. At 400°C (or less) reformer inlet temperature the conversion and ΔLHV values of both fuels were insufficient. The interface between the reforming and motor investigations is based on the theoretical reforming results. Thus, the simulation provides the lambda values for the motor operation that are favourable from the point of view of reforming and calculates the efficiency increase on the basis of the theoretical reforming efficiencies. Figure 2 shows the calculated dependency of the heating value increase from the lambda value and the EGR rate for ethanol reforming.

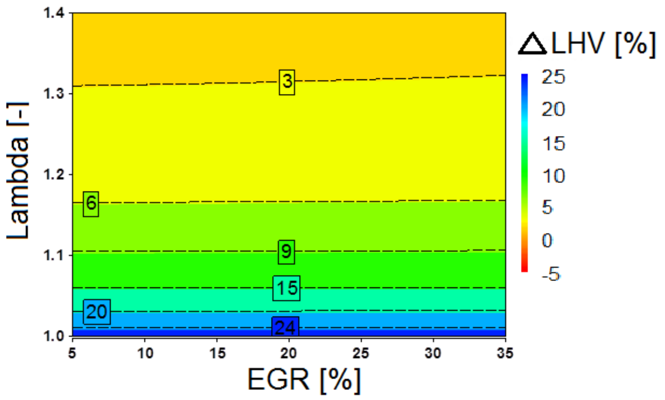

Figure 2 Theoretical increase of heating value for ethanol reforming at 500 °C depending on lambda and the EGR-rate

Investigated fuels and synthesis gas

The tested oxygenated fuels were selected after a comprehensive analysis carried out at the Institute of Chemical Engineering and Environmental Technology at the Graz University of Technology. The production processes of the fuels are simulated with process engineering calculation models and their implementation in large-scale plants is evaluated. The focus is on the cost effectiveness as well as the sustainability of the fuel production. The potential suitability of the substances for combustion engine use is a key criterion for selection. The most promising fuels include the groups of bio-alcohols, ethers and lactones. In the present study the investigation of the use of alcohol in a diesel engine and the potential of synthesis gas as a diesel substitute fuel are treated.

Ethanol, methanol and butanol are the investigated representatives of the alcohol fuels. On the one hand, they are supplied to the engine pure - via intake manifold injection or reforming, on the other hand as alcohol-diesel mixtures. The diesel fuel is a certified test diesel fuel and is briefly refered to as CEC. In the case of the alcohol-diesel blends, a mixture of CEC diesel/alcohol in the volumetric ratio of 90/10 was defined. The fuels used were subjected to full analyzes, the most important properties being summarized in Table 3. Blends are designated by the abbreviation 90CEC10Alcohol.

Table 3 Investigated alcohol fuels and diesel-alcohol blends

	CEC	EtOH	MetOH	BuOH	90CEC 10EtOH	90CEC 10MetOH	90CEC 10BuOH
Chemical formula	$C_{12}H_{23}$ 1)	C_2H_6O	CH_4O	$C_4H_{10}O$			
Cetan number	54,5	8	3	17	49,2	49	50,8
RON		111	114	96			
Ignition temp. [°C]		420	440	325			
Density [kg/m^3]	833,5	789	795	810	828,4	832	831
HFRR [µm]	413				417		428
Heating value [MJ/kg]	42,676	26,677	19,9	32,94	41,25	40,1	41,78
C-Fraction %M	85,4	51,5	37,1	64,6	82,8	81,8	83,7
H-Fraction %M	14,2	13,7	12,8	13,7	14	13,5	14,10
O-Fraction %M	<0,5	34,1	49,2	20,9	3,2	4	2,2
Boiling point [°C]	173-363	78	65	118	64-358	64-354	115-361
$\Delta H_{vaporization}$ [kJ/kg]	300	845	1110	626			
Lst [kg_{air}/kg_{fuel}]	14,5	9	6,46	11,26	13,97	13,73	14,8

1) approximately

While ethanol and butanol can be mixed with CEC without any problem in the given volume ratio, an emulsifier is necessary in the methanol-CEC blend, since otherwise the substances immediately separate into two phases. The emulsifying agent used is named "Tween 60" (Sigma-Aldrich) and allows a short-term stable emulsion.

Since the reforming of the biofuels cannot be conducted directly at the engine test stand at this early stage, it is carried out experimentally on a synthesis gas test bench at AVL List GmbH, whereby the engine exhaust is artificially simulated chemically and physically on the basis of the engine test stand measurements. As a result, a synthesis gas is produced and its composition is analyzed. This gas composition is adjusted by means of a gas mixing system at the engine test rig and is fed back to the suction tract using a gas supply system. The sensitivity of the engine test results to the synthesis gas composition is checked by means of two different concentrations, Table 4. These show large differences in the H_2 and CH_4 content and can be comprehended as extreme cases between which the range of realizable gas compositions can be found. That way, the influence of reforming mechanisms, reforming fuels and reforming conditions on motor operation ca be examined. Since the addition of water vapour represents a disproportionately high effort, the water component is not taken into account in the syngas composition.

Table 4 Investigated synthesis gas compositions

	Syngas(H_2)	**Syngas(CH_4)**
H_2 [Vol%]	31,5	18
CO [Vol%]	6,2	8,4
CH_4 [Vol%]	0	6,4
CO_2 [Vol%]	15,2	13,5
N_2 [Vol%]	Rest	Rest

Table 5 provides information on important properties of the combustible syngas components.

Table 5 Properties of the combustible syngas components

	Hydrogen	**Carbon monoxide**	**Methan**
Heating value [MJ/kg]	120	10,10	50
Vol. heating value [MJ/m3]	10,8	12,6	35,8
Ignition temperature [°C]	585	605	595
Laminar flame speed [m/s]	2,3	0,174	0,42
Ignition limits in air [Vol%]	4,0-75,6	12,5-75	4,9-15,1
Lst [kg_{Air}/kg_{Fuel}]	34,5	2,47	17,3

Test engine and examination methodology

Test engine

A Daimler in-line four-cylinder diesel motor is used as a test engine. Table 6 summarizes the most important technical data of the internal combustion engine.

Table 6 Engine data Daimler OM 646 Evo

Engine identification	Mercedes-Benz OM 646 Evo
Displacement	2149 cm³
Cylinders	4 cylinders, 4 valves per cylinder
Bore x hub	88 x 88,34 mm
Compression ratio	17,5
Injection system	DELPHI high pressure injection with up to 1800 bar; Solenoid injectors with seven-holes nozzle
Exhaustgas recirculation	External, cooled high pressure EGR

The low availability and the high purchase costs of some of the fuels tested make the conversion to single cylinder operation reasonable. Only the first cylinder is fired, the other three are deactivated and their gas exchange is separated from the gas exchange of the fired cylinder. Charging is done with an external electrically driven supercharger. The seats for two intake manifold injectors and various measuring points are adapted in a specially designed intake manifold. An electrically adjustable flap valve is used to produce the necessary exhaust gas pressure. The standard exhaust gas aftertreatment system has been removed and the exhaust system is only used for exhaust gas guidance, sound attenuation and as a measuring point location.

Engine test bench

A schematic representation of the test bench is shown in Figure 3:

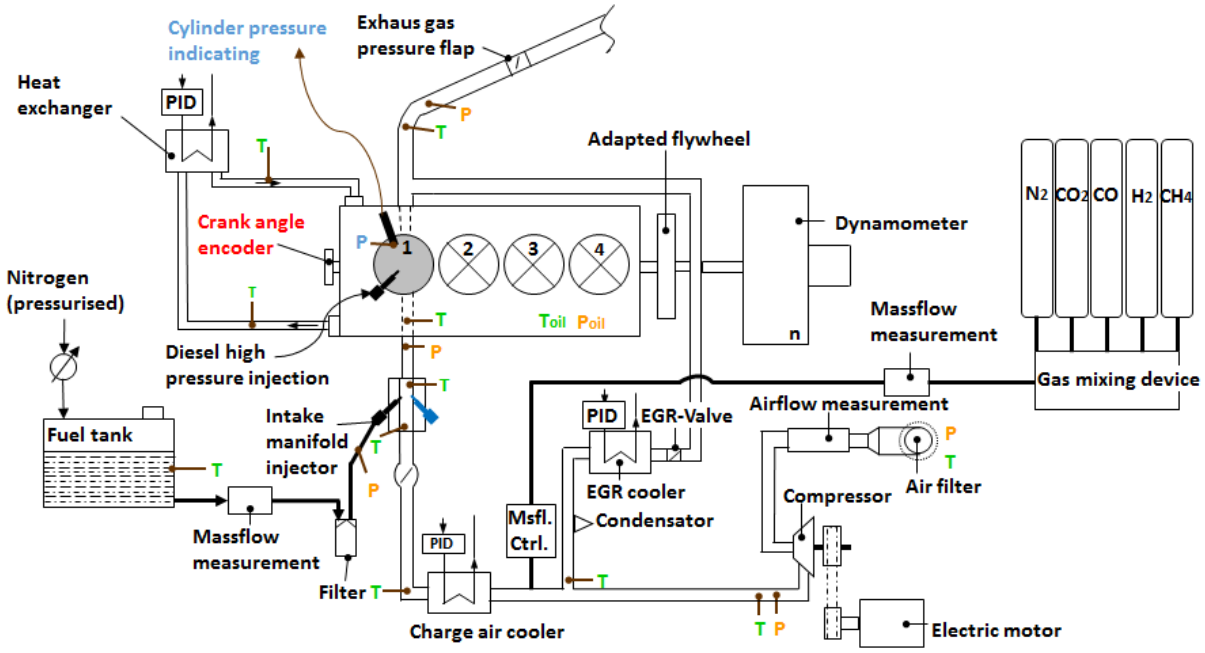

Figure 3 Schematic test bench layout

Examination methodology

The investigations are carried out at two operating points. The first point is defined by an engine load of 5 bar indicated mean effective pressure at 1500 rpm, the second by 15 bar indicated mean effective pressure also at 1500 rpm.

Table 7 Operating points

Name	Speed [min^{-1}]	Indicated mean effective pressure [bar]
BP-1500/5	1500	5
BP-1500/15	1500	15

The scheme in Figure 4 illustrates the procedure for the investigation of the special fuels.

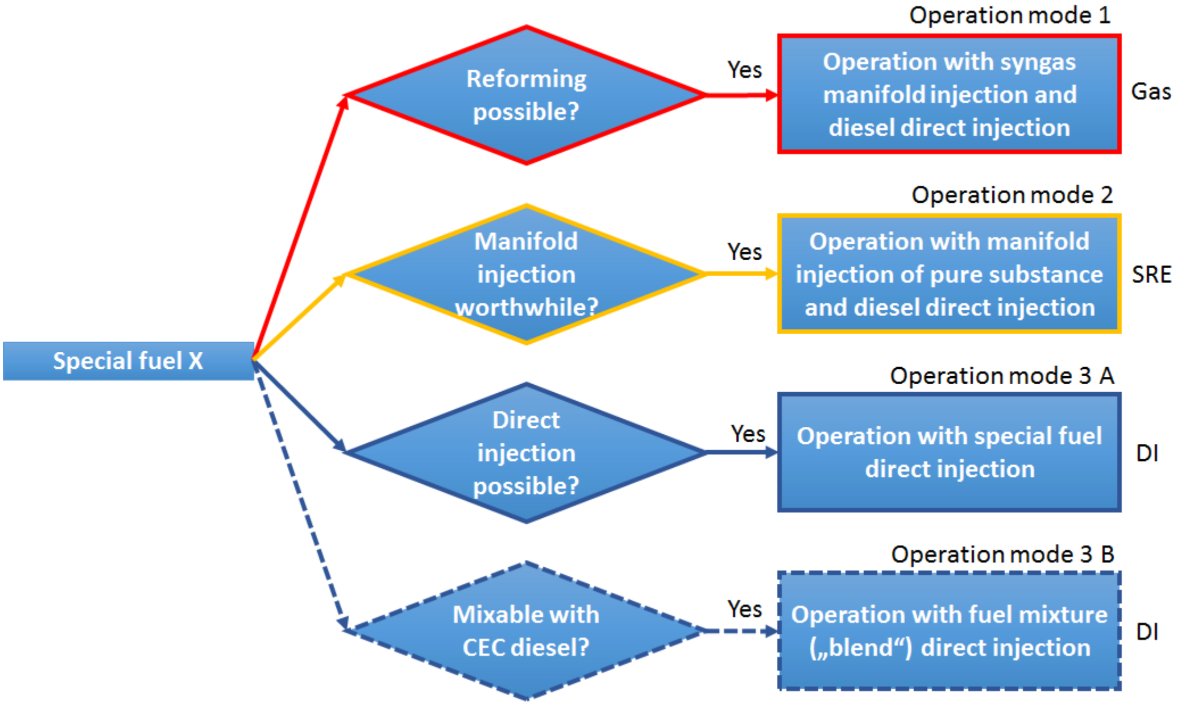

Figure 4 Procedure for the investigations of the special fuels (Gas = synthesis gas manifold injection, SRE = intake manifold injection, DI = direct injection)

With regard to the characteristics of the investigated alternative fuel, several possible operating modes result. If the fuel can be reformed, the engine can be operated with synthesis gas made from this fuel (mode 1). The ignition is then effected by the direct injection of diesel. However, the fuel can also be introduced into the intake manifold (operating mode 2) as a pure substance if this operating mode appears to be worthwhile (no auto-ignition). The ignition is also effected by a diesel jet. If the fuel properties permit this (lubricity, vapour pressure, cetane number), the special fuel is injected directly into the combustion chamber as a pure substance (mode 3 A). A further possibility is the engine operation with a direct-injected fuel mixture, so called "blend", if the alternative fuel can be mixed with CEC diesel (mode 3 B).

Different variations are carried out in the described operating modes, the most important being the variation of the alternative fuel amount, the air ratio, the EGR rate and the center of combustion (AQ50%) conducted by variation of the start of injection. The results of the variations are compared with each other for the investigated fuels and the optimum operating parameters for the respective fuel are determined. The pure diesel operation with CEC diesel fuel is the reference for the comparison. In order to limit the complexity of the exhaust gas aftertreatment, an upper limit for the NOx emissions of 2 g/kWh is set. The maximum charge pressure is limited to 1250 mbar (rel.).

The results of the engine operation provide the boundary conditions for the reforming. Only with this information (exhaust gas temperature and composition, exhaust gas enthalpy) the reforming can be simulated and experimentally investigated. The output is the syngas composition, which is to be set at the engine test stand. The operating parameters for the synthesis gas engine tests deviate from the other examination methodology since a low oxygen content in the exhaust gas is strived for a high efficiency of the reforming. However, this means a disadvantageous engine operation with a low air-fuel ratio.

Results

Synthesis gas – manifold injection

Due to the requirements of the fuel reforming, a low air/fuel ratio is necessary for engine operation with syngas. Lambda values from 1.1 to 1.4 are investigated, whereby the operation with $\lambda = 1.1$ results in a very low combustion engine efficiency. Particularly in BP-1500/5 a significant throttling of the intake tract is necessary in order to reach the low λ-values. The results of the syngas tests for the required air-fuel ratios can only be compared with the realistic diesel reference operation since a deterioration of the pure diesel operation caused by a reduction in the air excess would not be constructive.

The investigations represent a process in which the synthesis gas generation takes place within the exhaust gas recirculation system of the engine. The recirculated gas in the syngas operation is therefore no longer just an inert exhaust gas, but also an energy carrier. Thus, the syngas substitutes a part of the diesel fuel on the one hand and the recycled exhaust gas on the other. Due to the high inert fraction in the syngas composition, the EGR-typical capacity for NOx reduction should still be remained.

The substitution of diesel by syngas results in a reduction of the indicated efficiency both at low and high engine loads. While the EGR rate in the reference mode in BP-1500/5 doesn't affect the indicated efficiency until reaching very high soot formation levels, the efficiency of the diesel engine is continuously reduced with increasing of the syngas quantity and falls by 4.5% points below the efficiency of the diesel reference operation at the maximum possible substitution rate. In the upper load point, the efficiency disadvantage of the syngas operation is reduced, but the efficiency is still below the diesel reference, Figure 5 (on the left).

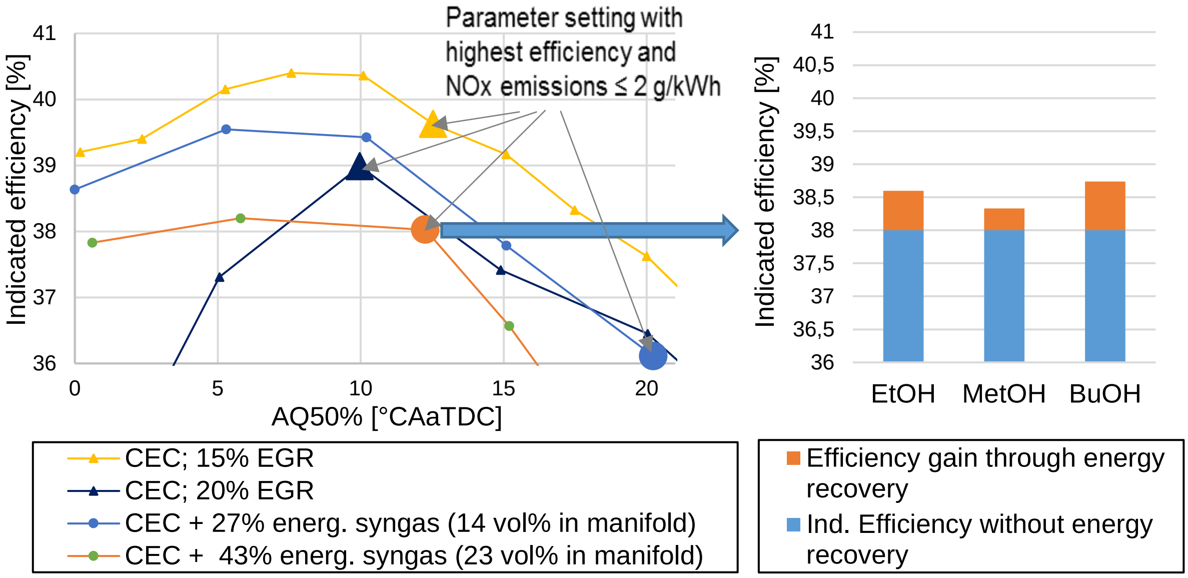

Figure 5 Variation of the combustion centre position AQ50% in BP-1500/15 for diesel reference and syngas operation (left) and efficiency increase by consideration of the energy recovery by the synthesis gas generation (right) based on the three alcohols

The AQ50% variations shown in Figure 5 are carried out at a constant manifold pressure of 2250 mbar (abs.). The air-fuel ratio in BP-1500/15 is already at a low level and no additional measures are necessary to achieve the required λ-values. In the case of the measurement with 43% energetic syngas content, lambda is 1.2. With earlier AQ50%, the temperature in the combustion chamber is higher, which results also in higher NOx emissions. In order to reduce the formation of nitric oxides, the combustion centre position can be delayed and/or the EGR rate can be increased. However, the implementation of these measures must be based on the lowest possible soot emissions and highest efficiency. The enlarged marking points in Figure 5 indicate the optimum point in the respective operating mode, with the NOx emission being below the limit of 2 g/kWh and the efficiency under this condition being as high as possible. It can be seen from Figure 5 that a further increase in the EGR rate in pure diesel operation mode from 15% to 20% results in a reduction in efficiency and thus a further reduction of NOx is at the cost of a strong efficiency loss. In diesel mode with 20% EGR, the NOx emissions are below 2 g/kWh for all combustion positions.

When operating with a 27% energetic synthesis gas fraction, the injected syngas takes up 14% of the total volume of the gas in the intake manifold (air + synthesis gas). For an engine with a real reformer in the EGR system, an operation with 12% EGR would be necessary to display this operating mode. The addition of the fuel to be reformed and its reforming subsequently increase the volume of the reformate in the intake manifold to the above-mentioned 14%. At 43% energetic syngas content, the reformate takes 23% of the volume in the intake manifold and 20% EGR would be necessary to produce this syngas quantity. Thus it is logical to compare the operation with 43% syngas with the diesel operation with 20% EGR. The comparison of the operation with a 27% energetic syngas fraction and the diesel operation with 15% EGR provides information on the differences between the two operating modes when the volumetric ratios of the syngas or exhaust gas to the fresh air in the intake manifold are approximately the same.

As a whole, the fuel reforming is only energetically reasonable if a possible engine efficiency loss is overcompensated by the "fuel upgrading". The actual efficiency of the engine operation is therefore not to be calculated based on the synthesis gas energy used, but on the energy of the fuel used to generate the synthesis gas. With the knowledge of the parameters of the engine operation, the necessary mass of the fuel required for the reforming can be back reckoned. Since the conditions for the reforming change with each change of the engine operation, the calculation has to be carried out separately for selected points. By taking this aspect into account, the efficiency in syngas operation is increased, as Figure 5 (on the right) shows. The synthesis gas used could be produced from either of the three alcohols, but depending on the fuel used, the reforming is effected with different efficiency. The simulation of the process has shown that the upgrade of the calorific value of the syngas generated from ethanol results in an increase of the efficiency of the point shown in Figure 5 by 0.6% points. When reforming methanol, the improvement is 0.33%, that of butanol 0.74%. However, this increase in efficiency is not sufficient at any point to compensate for the higher losses of the reformate combustion.

The comparison of the indicated measurement data of both operating modes shows that the reasons for the efficiency drop in syngas operation are not due to combustion profile, as seen in Figure 6.

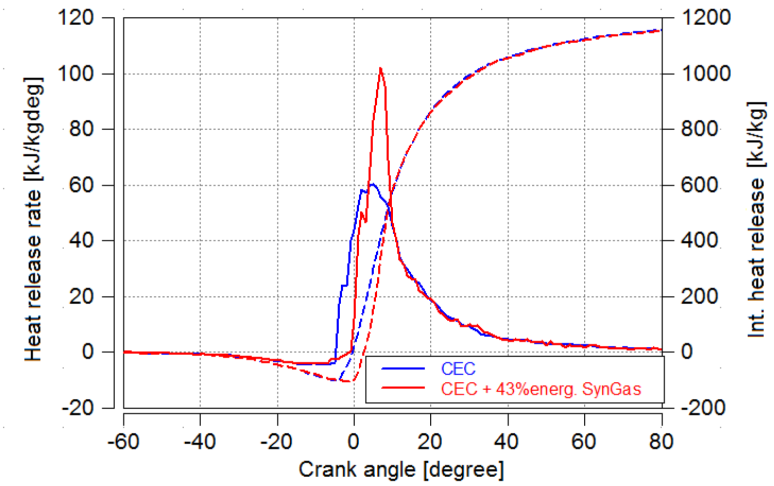

Figure 6 Heat release and integrated heat release of diesel reference operation with 15 % EGR and syngas operation. BP-1500/15; AQ50% = 10 °CAaTDC

The more compact combustion induced by the hydrogen-containing syngas should even lead to a slight efficiency gain at the higher load point compared to the pure diesel operation, since the percentage of constant-volume combustion increases. However, the loss analysis showed that the high emissions of unburnt hydrogen, methane and carbon monoxide lead to the considerable loss of efficiency. Due to the high ignition temperatures of these gases, an incomplete combustion of the syngas occurs. Additional effects are the cooling at the surfaces of the combustion chamber and the combustion chamber shape, which is designed for the conventional diesel combustion process. In BP-1500/5 the indicated curves are almost identical.

The nitrogen oxide emissions in BP-1500/15 increase as a result of the substitution of the recirculated exhaust gas by synthesis gas, Figure 7. This suggests that pure EGR is the stronger measure for NOx reduction. However, more accurate calculations of the specific heat capacities and the absolute heat capacities of the total charge mass in the cylinder have shown that a mixture of air and syngas can absorb even more heat than air and EGR. The reason for this is the high specific heat capacity of the hydrogen in the syngas. Two other aspects seem to be accountable for the stronger NOx reduction in diesel operation mode. On the one hand, the cooling of the cylinder charge by the diesel jet plays an important role. This cooling effect decreases with the substitution of the diesel by the syngas, which results in higher combustion chamber temperatures. On the other hand, in the case of syngas combustion, the ignition delay is prolonged and more premixed combustion takes place with higher heat release rate. Higher local temperatures are associated with this. Both aspects lead to an increase in the combustion chamber temperature and consequently more nitrogen oxides. In order not to exceed the NOx limit of 2 g/kWh, in pure diesel operation 15% EGR is required with an AQ50% at 12.5 °CAaTDC. At the same combustion centre position, 23 vol% syngas are to be supplied into the intake manifold in dual-fuel operation in order to meet the set emission limit.

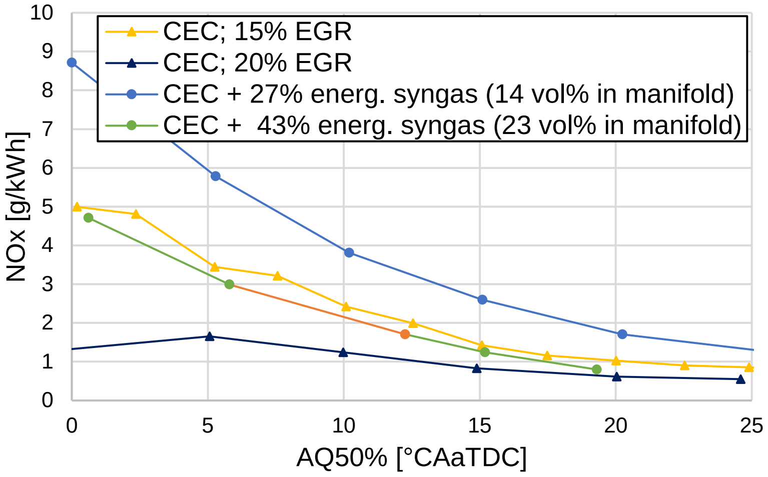

Figure 7 Nitrogen oxide emissions depending on the combustion centre position, BP-1500/15

With syngas operation a strong soot and particle reduction can be achieved in BP-1500/5. While these emissions start exhibiting a strong increase at an EGR rate of about 30% in pure diesel operation, they drop continuously when the syngas amount is increased and reach very low values at high syngas volumes. At this point it must be noted that the observations on the test bench can differ from the results of an engine with a real reformer, since in the present case pure synthesis gas and not real exhaust gas-reformed soot-containing syngas is used. It is, however, expected that the positive influence of the low-particle gas combustion on soot emissions will remain. In addition, the catalyst of the reformer has a precious metal coating, which together with the high prevailing temperatures can promote the oxidation of the particles in the recycled exhaust gas.

Figure 8 shows that the soot reduction effect of syngas operation also persists in BP-1500/15. Compared to the diesel operation with 20% EGR, the syngas operation with 43% energetic syngas content has much lower soot emissions. However, in diesel mode the engine is preferably to be operated with 15% EGR and adjusted combustion centre position (12.5 °CAaTDC) in order to prevent the strong soot formation. In this case, the soot advantage of syngas operation diminishes.

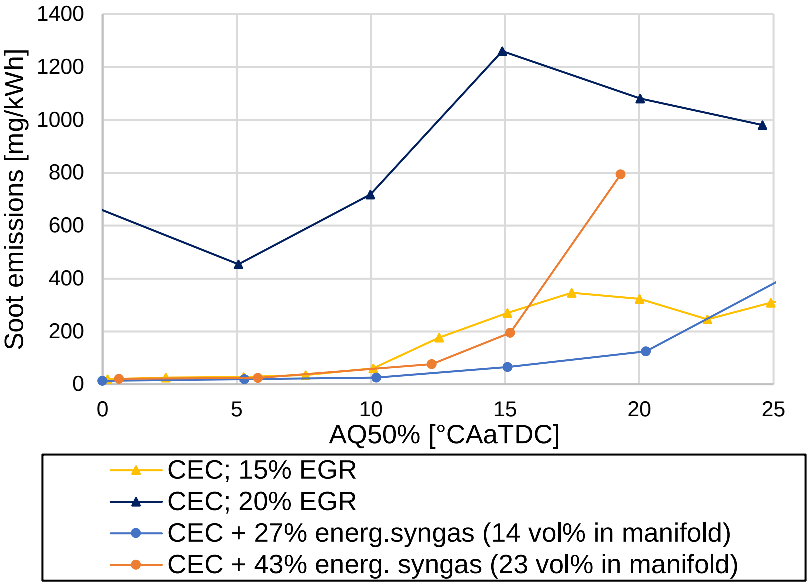

Figure 8 Soot emissions depending on the combustion centre position AQ50%, BP-1500/15

The presented investigations are carried out with both synthesis gas compositions listed in Table 2. The results with both concentrations show no significant differences in efficiency. With the methane-containing composition syngas(CH_4) high methane emissions are measured in the exhaust gas, whereas with syngas(H_2) more hydrogen remains unburnt. The raw methane emissions are converted in an oxidation catalyst at higher temperatures than CO and HC and can become a problem for the exhaust aftertreatment. Moreover, in the upstream process of fuel reforming, the production of a syngas composition without methane is energetically more efficient, which also prioritizes a reforming in terms of high H_2 content.

Fuel manifold injection

The operation of the diesel engine with synthesis gas is one of the three possibilities for fuel introduction into the motor. Using an intake manifold injection or direct fuel injection, the investigated fuel can be supplied to the internal combustion engine without an upstream process. The intake manifold injection can be realized at a lower cost compared to the fuel reforming and offers important degrees of freedom - the tested fuel does not have to be miscible with the CEC diesel, the amount of substitute fuel can be varied within a wide range and the fuel used can have properties, which are contradictory to the requirements for diesel fuels (cetane number, lubricity, etc.). However, a 2-tank system is needed.

The influence of the intake manifold injection of alcohol on the efficiency and the pollutant emission of the diesel engine is best seen when the substitution rate is being gradually increased under otherwise constant conditions. As the alcohol content increases, the directly injected diesel quantity is reduced accordingly, so that the power output of the engine remains unchanged. In the lower load point, for all alcohols a deterioration in efficiency is measured when increasing the substitution rate. This efficiency decrease is stronger for butanol than for methanol and the strongest for ethanol. It is remarkable that the efficiency reaches a minimum before rising again at higher substitution rates. The emissions of unburnt hydrocarbons and carbon monoxide increase approximately equally for all three alcohols, each with an approx. 500 ppm per additional 10% energetic fuel fraction, resulting in a further loss of efficiency. The maximum rate of substitution is limited by an unstable engine run and uncontrollable shift of the combustion centre position. In BP-1500/5 Methanol can be fed to the combustion process with a maximum of 50% energetic fraction, ethanol with 65% and butanol with 85%. It is noticeable that the maximum substitution rates of the three alcohol representatives rank like their auto-ignition temperatures and octane numbers. In a wider sense, the octane number is an indicator for the reactivity of the fuel. The high auto-ignition temperature of methanol leads to combustion misfires already at an energetic portion of 50%, while the lower ignition temperature of butanol permits stable ignition up to a much higher substitution rate.

At the high load point BP-1500/15, this behaviour is partly reversed, see Figure 9.

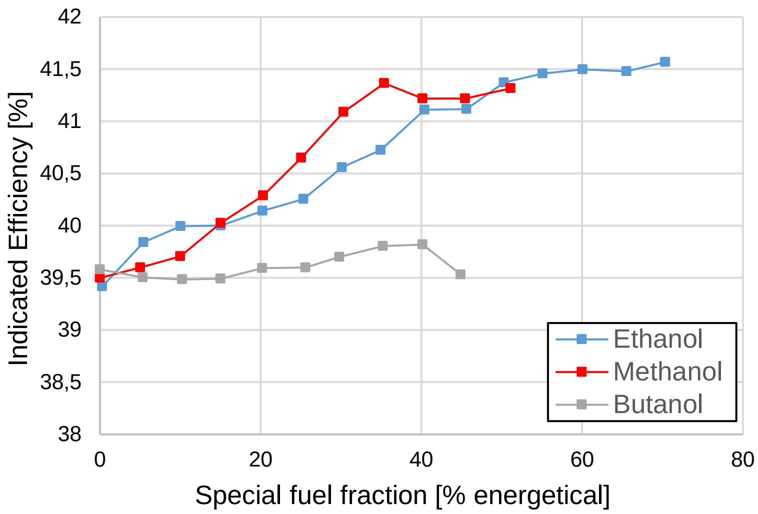

Figure 9 Indicated efficiency depending on the substitution rate for three alcohols in BP-1500/15, 15% EGR

Butanol tends to spontaneous and uncontrolled auto-ignition at the high cylinder pressures and combustion temperatures present at the higher load point, thereby the maximum possible substitution rate is limited to 45%. With up to 70%, Ethanol shows a very similar substitution potential as in the BP-1500/5. The major difference in the efficiency observations at both loads is that at the high load the indicated efficiency always increases with the addition of alcohols (with exception of the last butanol measurement point). By the intake manifold injection of methanol or ethanol with a substitution rate of 50% the efficiency of the engine can be increased by a remarkable 2% points. A slight reduction in CO emissions compared to the diesel reference operation is measured. This means that the oxidation cannot be fully completed in BP-1500/5 due to the cooler charge compared to BP-1500/15. The unburned hydrocarbons also increase in BP-1500/15 with the increase of the injected alcohol, but to a much smaller extent than in BP-1500/5, which is due to the higher combustion chamber temperatures and a more complete combustion.

Figure 10 compares the pressure, heat release and integrated heat release curves of the diesel direct injection operation and the dual-fuel operation with 35% energetic alcohol fraction, the last of which being injected into the manifold. The measurements are carried out at BP-1500/15. The continuous curves represent the CEC diesel reference without any additional fuel. The same boundary conditions apply to all four experiments.

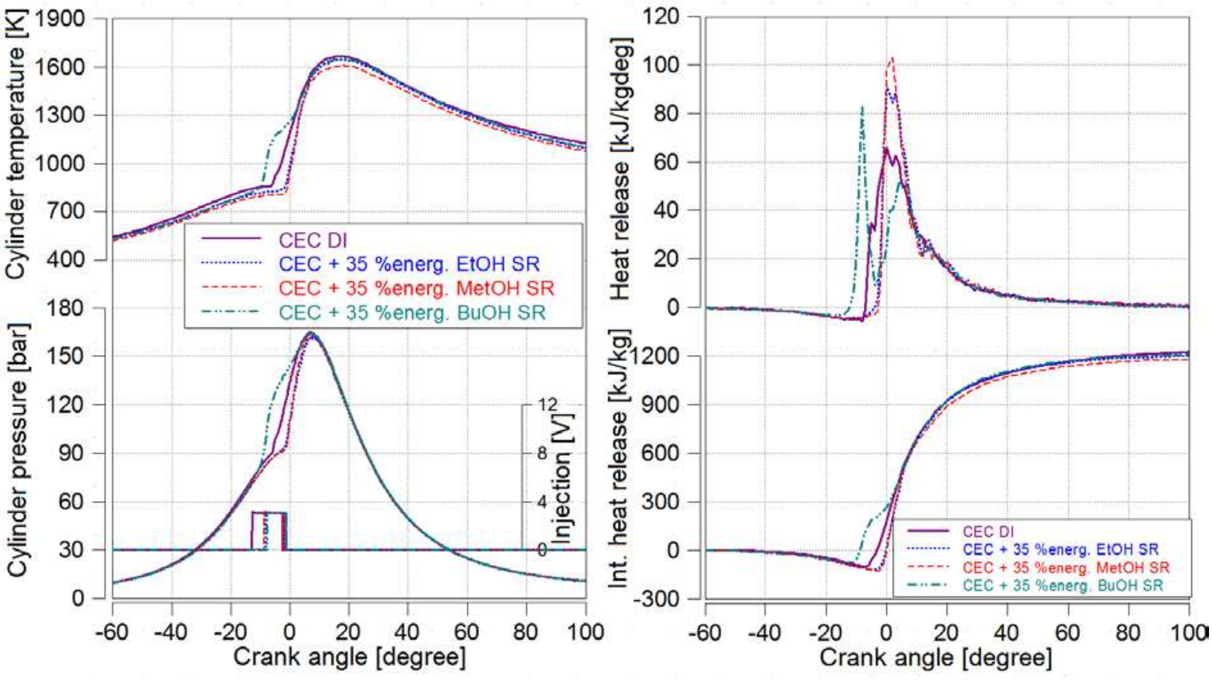

Figure 10 Indicated data of dual fuel operation with alcohol manifold injection in BP-1500/15; AQ50% = 7.5 °CAaTDC; 15% EGR; SR = manifold injection, DI = direct injection

The run of the curves while operating with a 35% energetic butanol content indicates that at the higher load the fuel introduced to the intake manifold auto-ignites before the end of the compression stroke at approx. 10 °CAbTDC and the heat release reaches a local minimum at about 2 °CAbTDC. At this point, about a third of the total energy conversion seems to have been achieved, which is a very good correlation with the energetic butanol content of 35%. The second increase in the heat release is caused by the combustion of the diesel fuel. According to [9] and [10], the fuel properties ignition delay and laminar flame speed are very similar for all three alcohols. The auto-ignition in the butanol combustion is the result of its lower ignition temperature compared to the other two alcohols and causes a strong prolongation of the combustion duration which leads to a reduction in efficiency compared to the very fast combustion in operation with ethanol or methanol.

In order to better understand the reasons for the efficiency increase in alcohol operation, a loss analysis should be carried out, shown in Figure 11. It compares the CEC diesel reference operation in the BP-1500/15 with the operation with 35% energetic methanol content. Both operation modes are shown in Figure 9 (0% and 35% energetic methanol fraction). The calculated losses are deducted in a certain order from the theoretical efficiency maximum (constant volume combustion) of the present internal combustion engine and the remainder represents the measured indicated efficiency. The analysis shows that under otherwise identical conditions, the operation with alcohol intake manifold injection leads to an increased loss due to the charge properties (real charge and mixture properties) as well as due to more unburnt fuel. However, these disadvantages are overcompensated by the lower burning efficiency loss resulting from the faster energy conversion in methanol operation and by the lower wall heat efficiency losses. The reason for the latter is, on the one hand, the lowered temperature level of the charge, on the other hand, the fact that as a whole the energy conversion remains shorter in the region of the top dead centre compared to the CEC diesel reference and the associated loss is thus reduced in percent.

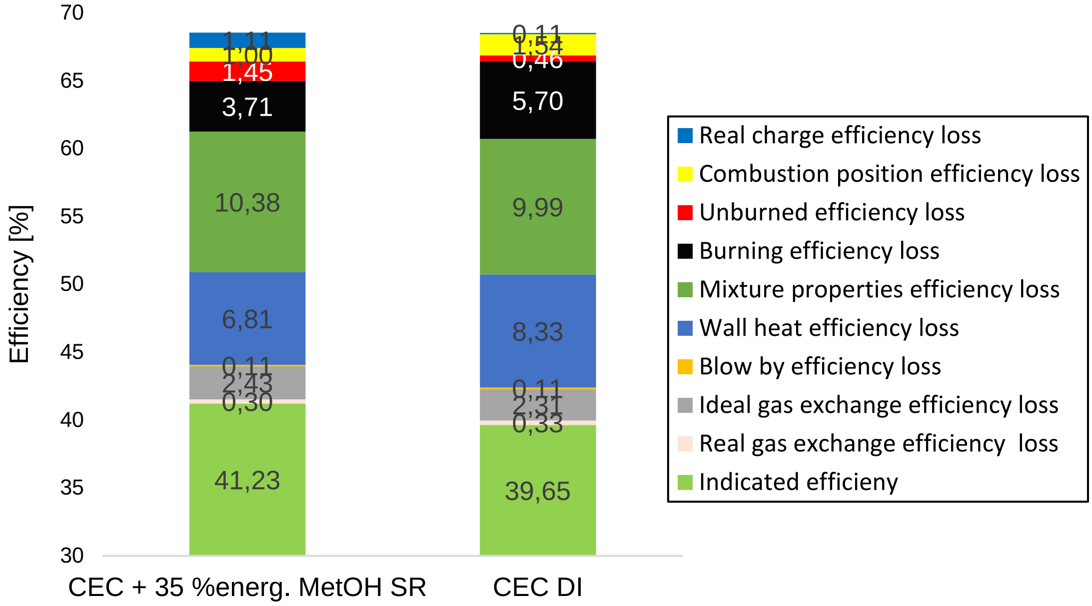

Figure 11 Loss analysis of CEC diesel reference operation and dual-fuel operation with methanol manifold injection in BP-1500/15; 15% EGR

Emissions

In BP-1500/5, the specific NOx emissions increase slightly with an increased amount of additional fuel, but remain in the range of 1 g/kWh. Interesting is the increase in NO_2 emissions with decreasing NO emissions. This fact indicates a shift in the temperature-dependent chemical balance in the formation of nitrogen oxides. In this context, the decomposition of nitrogen dioxide plays an important role:

$$2\ NO_2 \rightleftharpoons 2\ NO + O_2$$

Equation 2 Temperature-dependent chemical balance of the nitrogen oxides formation

At 620 °C, the chemical equilibrium of this reaction is entirely on the right side, and the gas is completely decomposed [11]. At low temperatures (< 250 ° C) the equilibrium shifts to the side of NO_2. Above 450 °C, however, NO is the thermodynamically preferred component [12]. The exhaust gas temperature measured in the BP-1500/5 drops by approx. 15 ° C compared to pure diesel operation. Taking into account the exhaust gas path from the measuring point to the measuring device and the lower exhaust gas temperature, it is possible to conclude that consecutive reactions cause a shift in the product distribution from the right to the left side of Equation 2. The same situation is also found in BP-1500/15, however much more pronounced, see Figure 12. While the total NOx emissions for all three alcohols remain at the diesel reference level of approx. 2.5 g/kWh, regardless of the substitution rate, the emitted NO and NO_2 quantities change noticeably. The operation shown does not fulfil the introduced boundary condition for the NOx emission limit of 2 g/kWh, since the variation is carried out with 15% EGR at the optimum efficiency combustion position. The exhaust gas temperatures shown on the right in Figure 12 correlate with the change in the indicated efficiency (Figure 9) with increasing alcohol content.

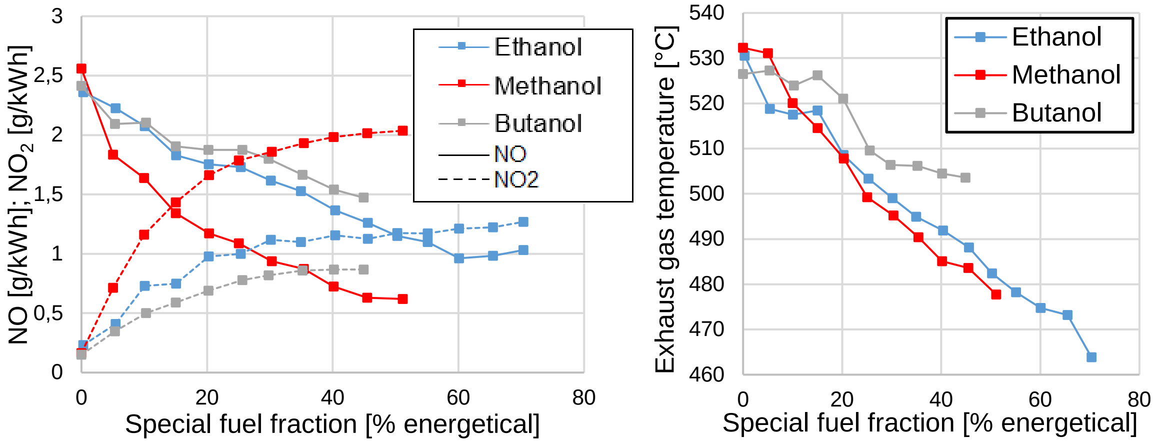

Figure 12 NO and NO_2 emissions (on the left) and exhaust gas temperature (on the right) depending on the substitution rate, alcohol manifold injection in BP-1500/15; 15% EGR

The great advantage of the intake manifold injection of the alcohol fuels lies in the significant reduction of soot and particulate emissions, both for low and high loads. This effect is illustrated in Figure 13 for BP-1500/15.

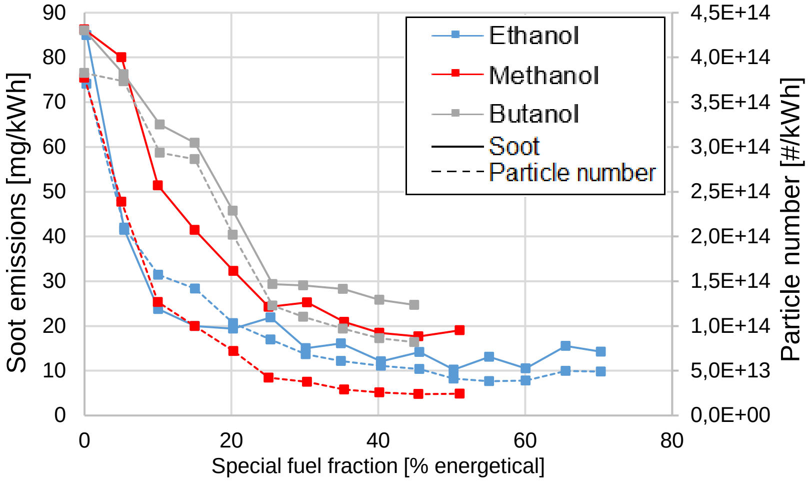

Figure 13 Soot and particle emissions depending on the substitution rate, alcohol manifold injection in BP-1500/15; 15% EGR

The potential for particle reduction increases with the O/C ratio in the alcohol molecule. A significant soot reduction with increasing alcohol content can be detected at both operating loads. In BP-1500/5, the maximum soot reduction appears to be achieved with the maximum energy content of the fuel. In BP-1500/15, on the other hand, a further reduction of particle emissions is hardly observed for energy contents higher than 40%.

By defusing the particle problem, the EGR rate can be increased to further reduce NOx emissions.

In-cylinder reduction of nitrogen oxide emissions

The most effective measure for the in-cylinder reduction of the nitrogen oxide emissions is the increase of the EGR rate. In the case of conventional diesel fuel, this leads to an increase of soot emissions, so that a compromise must inevitably be made when designing the operating parameters. Figure 14 shows the soot-NOx trade-off for the CEC diesel reference in BP-1500/15 and compares it with the behaviour of the dual-fuel operation with alcohol intake manifold injection.

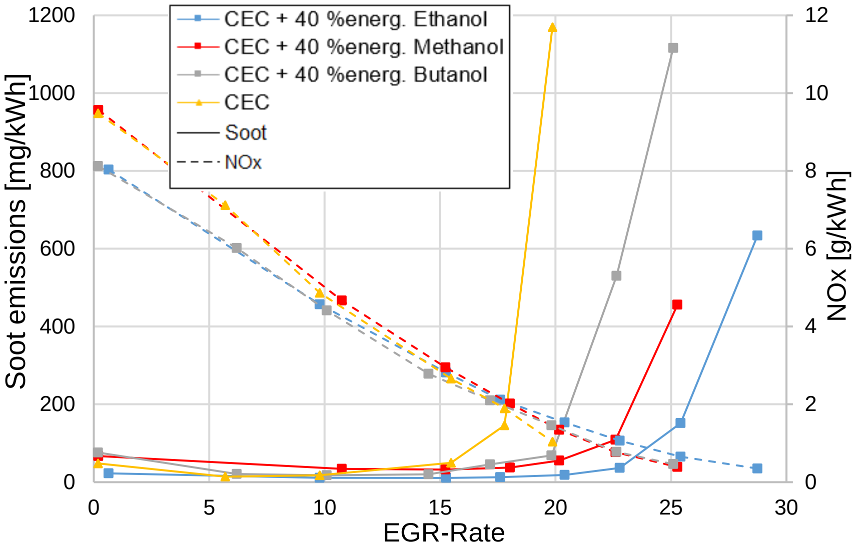

Figure 14 Soot and NOx emissions of diesel reference operation and dual-fuel operation with alcohol manifold injection, BP-1500/15; AQ50% = 7,5 °CAaTDC

The highest soot reduction is achieved with the intake manifold injection of ethanol. With an ethanol content of 40% energetic and an EGR rate of 17%, the particle mass can be maintained at 20 mg/kWh and the NOx emissions at 2 g/kWh with an optimum efficiency combustion position of 7.5 °CAaTDC. In the case of diesel reference, a critical increase of soot emissions and a noticeable reduction in efficiency occurs with more than 15% EGR, as seen in Figure 15. The enlarged marking points indicate the EGR rate, at which the NOx emissions are equal to or below the set limit.

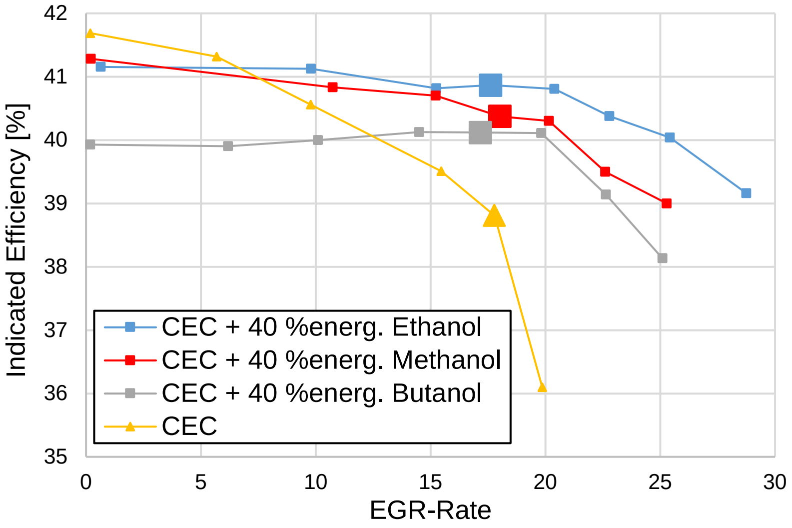

Figure 15 Indicated efficiency of diesel reference operation and dual-fuel operation with alcohol manifold injection, BP-1500/15; AQ50% = 7,5 °CAaTDC

In the case of ethanol or methanol intake manifold injection in BP-1500/5 with 45% energetic alcohol content and 40% EGR, the NOx emissions add up to 0.3 g/kWh with a soot emission of only 2.4 mg/kWh. For comparison, in diesel reference operation, soot emissions of 120 mg/kWh are measured at the same NOx value. Furthermore, the increase in the EGR rate results in a slight improvement of the indicated efficiency in dual-fuel operation.

Direct injection of diesel alcohol blends

In accordance with the Renewable Energy Directive 2009/28/EC fuel mixtures with a 10% volumetric bio-alcohol content are investigated. In the tests carried out, the combustion efficiency is not noticeably influenced by the addition of alcohol, neither at the lower nor at the higher load point.

The use of the alcohol blends at the high load point does not produce noticeable improvements in the exhaust emissions, the measured soot emissions are similar to the diesel reference. For this reason, only the blend results for the lower load point are displayed.

Figure 16 shows the soot-NOx trade-off at the lower load point. At 20% EGR, the NOx emissions of the experiments shown are between 2 and 3 g/kWh, the lowest point of the soot formation in the fuel blends is also observed in this range. However, to further reduce the nitrogen oxides, the EGR rate must be raised, resulting in a significant increase in soot emissions. The addition of 10% by volume of alcohol proves a soot-reducing effect at this operating point, which is particularly pronounced for the ethanol blend at very high EGR rates. At 35% EGR, the NOx emissions with the ethanol blend are 0.5 g/kWh and the soot emissions are reduced by a factor of 4 compared to the diesel reference. At 50% EGR the particle reduction is even higher.

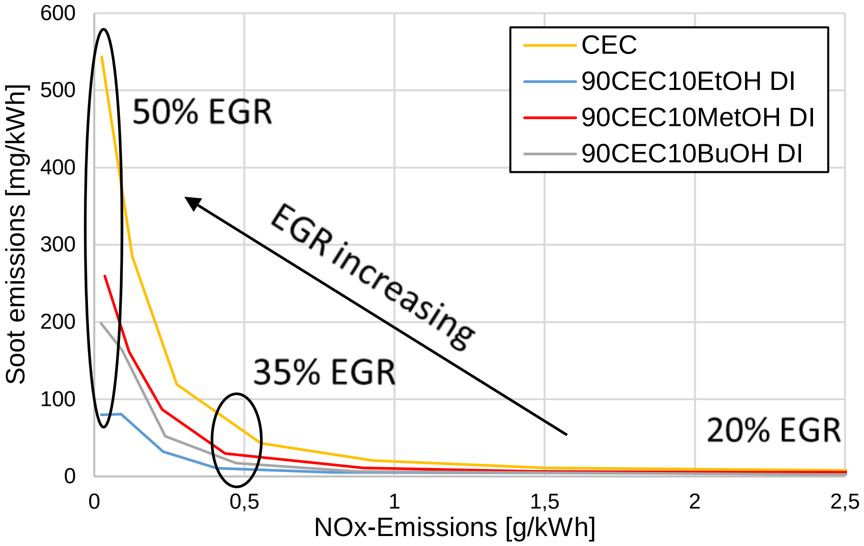

Figure 16 Soot-NOx-trade-off in BP-1500/5

Additional investigations are necessary to explain why the addition of 10% alcohol could not achieve the hoped-for reduction of soot and particulate emissions at the high load point.

Comparative Analysis

The insights gained from the engine studies clearly show the trends that can be expected with the use of the investigated fuels. In order to be able to compare their advantages and disadvantages for the diesel engine use in a quantitative manner, a direct comparison of the best points in the different applications is useful.

The high load point BP-1500/15 is critical for compliance with NOx and soot emission requirements due to the high combustion chamber temperatures and the low air-fuel ratio. The rise of the EGR rate causes a strong increase of soot emissions and a simultaneous reduction in efficiency. However, the strength of the oxygenated biofuels lies precisely in defusing the soot-NOx problem. Additionally, it is expected that the operation of the internal combustion engine at low loads will diminish proportionately as a result of the increasing hybridization of the drive train. These two considerations make it logical to compare the tested special fuels and combustion processes predominantly in BP-1500/15. However, the analysis could also be carried out analogously for the lower load point. The bar chart in Figure 17 shows the highest efficiency and the measured soot emissions while considering the NOx emission limit.

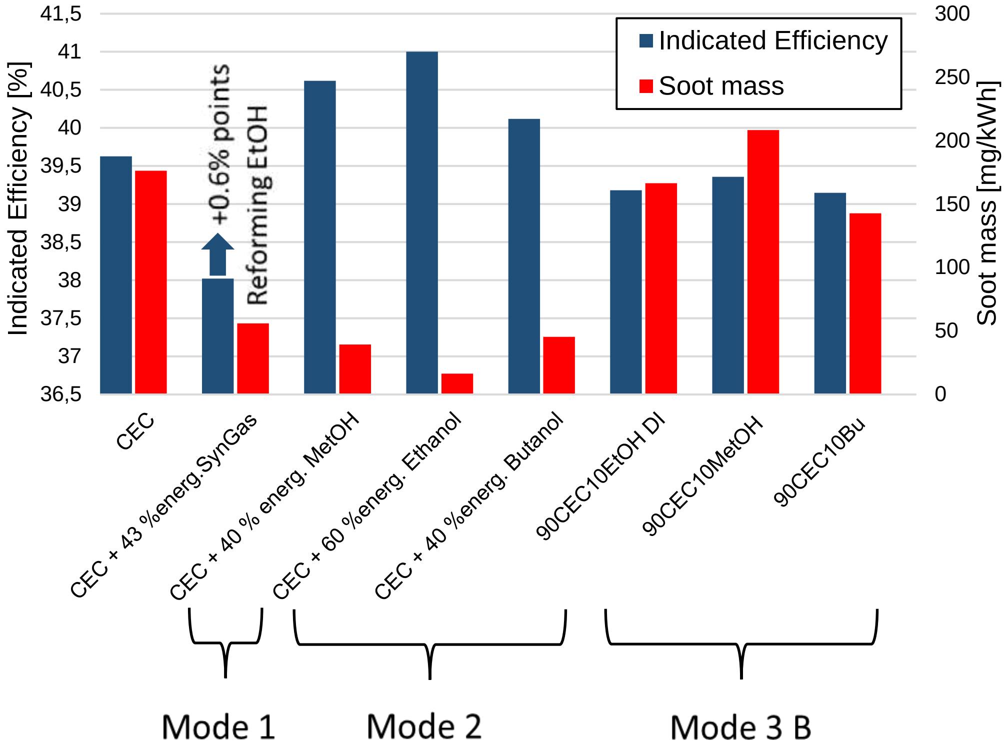

Figure 17 Comparison of the best results of the investigated fuels and operation modes in BP-1500/15 under the condition of highest possible efficiency and NOx emissions ≤ 2g/kWh

The addition of synthesis gas (mode 1) produces an efficiency disadvantage. The raise of the fuel heating value due to the reforming is not enough to compensate for the loss of efficiency during the combustion. However, at this point it is important to emphasize that the combustion chamber is designed for a conventional diesel combustion process and not for gas combustion. The high methane and hydrogen emissions significantly degrade the motor efficiency. By adapting the combustion chamber design, a reduction of the occurring losses is possible.

The intake manifold injection of alcohol (mode 2) allows high substitution rates. In the case of ethanol, the alternative fuel accounts for 60% of the total energy introduced. In this operating mode, significant increases in efficiency at higher loads can be achieved compared to the diesel reference operation. Another significant advantage of the intake manifold injection is the high reduction in soot emissions. It can be seen from the comparison shown that the soot emissions are reduced by a factor of 10 against the reference operation when ethanol is used.

Figure 17 only takes into account the upper load point. In this, the addition of 10% by volume of alcohol does not have any noticeable differences compared to the diesel reference operation. The measured increase in particulate emissions with 90CEC10MetOH is of particular interest. One reason for this measurement result could be the particle formation behaviour of the emulsifier used. At this point, however, this presumption cannot be verified.

Overall view

The overall assessment of the biofuel use is based both on the consideration of the combustion engine suitability and on the fuel production criteria. For a clear presentation of the evaluation, characteristic numbers are defined, which represent the percentage change towards the diesel reference values. The diesel reference is given the number 100, e.g. 2% improvement when using a biofuel would get the number 102, a deterioration of the same value - 98. The assessed categories are efficiency, CO_2 emissions, particle mass. The CO_2 savings potential for biofuel production is determined within the framework of the sustainability analysis carried out by the Technical University of Graz and has already been included in the "CO_2" criterion. Thus, the CO_2 advantage increases with the substitution rate. The CO_2 savings in the production of ethanol from lignocellulosic biomass are assumed to be 47% [13], for methanol 77% [14] and for butanol 63% [15]. The system costs, which increase with the increased complexity of the use of the alternative fuels, are assessed in the column "System Complexity". This assessment criterion accounts for the main component costs of turbocharging, basic engine, fuel system, exhaust gas aftertreatment and exhaust gas recirculation (or reformer for syngas production). Table 8 summarizes the evaluation for the best operation points. The improvements against the conventional CEC operation are displayed in green colour. Significant potentials of the use of biogenic alcohols in the diesel engine are visible. For example, by operation with methanol intake manifold injection 48% CO_2 is saved and the particle mass in the exhaust gas is reduced by a factor of 10.

Table 8 Overall evaluation of the investigated fuels and operation modes; BP-1500/15; charging pressure 1250 mbar (rel); NOx emissions maximum 2 g/kWh

Fuel (combination)	Efficiency	CO_2	PM	System complexity
CEC Diesel DI	100	100	100	o
CEC + 43%energ. SynGas	97$^{1)}$/97$^{2)}$/98$^{3)}$	122$^{1)}$/145$^{2)}$/133$^{3)}$	232	- -
CEC + 40% energ. MetOH SR	103	148	448	-
CEC + 60%energ. EtOH SR	103	144	1071	-
CEC + 40%energ. Butanol SR	101	135	389	-
90CEC10EtOH DI	99	102	106	o
90CEC10MetOH DI	99	102	84	o
90CEC10Bu DI	99	104	123	o

1) Reforming of ethanol considered; **2)** Reforming of methanol considered; **3)** Reforming of butanol considered; **DI** direct injection; **SR** intake manifold injection; **Efficiency** Characteristical number for the efficiency compared to CEC diesel reference operation; **CO_2** Characteristical number for the CO_2-emissions compared to CEC diesel reference operation; **PM** Characteristical number for the particle mass compared to CEC diesel reference operation; **System complexity** Complexity and costs for the respective operation mode; **o** unchanged compared to the original system; **-** more complex than the original system; **- -** much more complex than the original system

Summary

In the course of the research project "Regenerative oxygen-containing diesel substitute fuels as an opportunity for efficiency enhancement and emission reduction - OxyGen2", the suitability of biofuels for diesel engine use is investigated. The holistic approach consists of a sustainability and cost effectiveness analysis (Institute of Chemical Engineering and Environmental Technology at the Graz University of Technology), the development and investigation of operating and combustion processes (Institute for Powertrains and Automotive Technology at the Vienna University of Technology) and the investigation of a thermochemical energy recovery in the form of an endothermic fuel reforming (AVL List GmbH, Graz). In this article the engine operation results are presented for three bio-alcohols - ethanol, methanol and butanol. Characteristic for the project is the investigation of three variants for fuel introduction into the internal combustion engine: injection of synthesis gas, intake manifold injection and direct injection.

The fuel reforming using exhaust heat is investigated in experiment and simulation. There is a good consistency between test bench and simulation results. The resulting synthesis gas is used as a fuel in a modified diesel engine and the successful technical feasibility of the combustion process is confirmed. The operation with syngas shows efficiency disadvantages compared to the reference operation with pure diesel fuel due to the non-adapted combustion process (piston and combustion chamber design), but a reduction in soot emissions can be detected. As the syngas content increases, higher methane and hydrogen emissions are measured in the exhaust gas. The "fuel upgrade" within the generation of synthesis gas cannot fully compensate for the efficiency loss in the combustion of the gas at any point.

By injecting alcohols into the intake manifold, depending on the operating point, substitution potentials of up to 85% can be achieved before unwanted combustion phenomena such as knock occur, which prevent a further increase of the alcohol amount. At higher loads within this operation mode the efficiency is increased by up to 2% points. The observed strong particle reduction allows a further reduction of the nitrogen oxide emissions. The best results are achieved with ethanol.

The addition of 10% by volume of alcohol to the diesel results in a significant reduction in soot emissions at low loads. It also represents the special fuel delivery variant realisable with the least effort. The use of ethanol is prioritized in this case as well. At high loads, no significant differences to diesel reference operation can be determined.

Outlook

The efficiency and emission behaviour of the synthesis gas combustion can be improved by further optimizing the combustion process. In this regard an adaptation of the combustion chamber shape seems to be reasonable. The efficiency of the reforming process can be increased by reducing the oxygen content in the exhaust gas, which is achievable by lowering the lambda value of the combustion. It is necessary to check whether the operation with a very low air-fuel ratio can bring advantages.

The direct injection of diesel alcohol blends is the simplest variant for using an alcohol fuel. With the addition of only 10 percent by volume of bio-alcohol to the diesel, the hoped-for particle emission reduction cannot be completely achieved. The potential of this operating mode will be further investigated by increasing the alcohol amount to 20% by volume.

The list of oxygenated biofuels investigated in this project goes beyond the representatives of the bio-alcohols. Ethers and furans are also in the focus of the scientific activity. In particular, innovative synthetic biofuels such as oxymethylene ethers (OME) promise significant improvements in the emission behavior of diesel engines and have the potential to find a growing application in the future [16], [17], [18]. From today's point of view, the production of biogenic OME has economic disadvantages, since it is associated with high investment costs, system complexity and larger amounts of biomass. However, the advantages of the use in a combustion engine make this fuel group highly interesting and represent a motivation for detailed investigations. These fuels are evaluated with regard to their diesel engine suitability at the Institute for Powertrains and Automotive Technology. The objects of the investigations are the bio-fuel OME1 and a mixture of the higher graded OME oligomers OME2-5. The fuels are used both as a pure substance and as a diesel blend with 10 or 20% by volume of OME.

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2

Damyanov, A; Hofmann, P.; Schüßler, M.; Derntl, M.; Schwaiger, N.; Pichler, T.: **Operation of a Diesel engine with biogenous oxygenated fuels**; Poster presented at the 38th International Vienna Motor Symposium 2017; 27-28 April 2017, Vienna, Austria

Operation of a Diesel engine with biogenous oxygenated fuels

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Regenerative oxygen-containing diesel substitute fuels as an opportunity for efficiency enhancement and emission reduction - OxyGen2

Motivation

Second generation biofuels have the potential to contribute to the reduction of overall CO_2 emissions from traffic without entering an ethical contradiction to food production. Within the presented project the suitability of preselected 2nd generation biofuels for engine combustion is investigated experimentally. Fuels with higher oxygen content are expected to help minimize emissions from diesel engines.

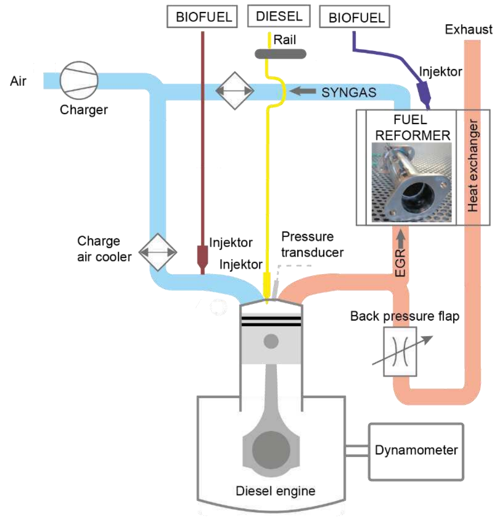
- Investigation of the diesel engine suitability of 2nd Generation Biofuels
- CO_2-Reduction
- Efficiency enhancement
- Emission reduction

Examination methodology

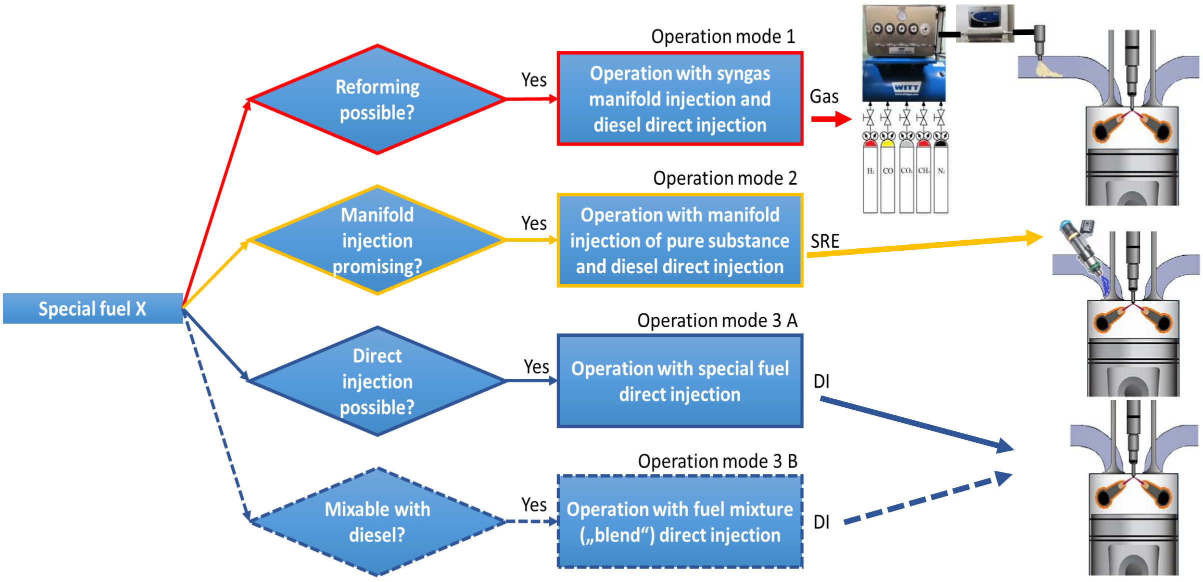
A distinctive feature of the project is the investigation of the fuel supply into the internal combustion engine in three different ways.

- direct injection of diesel-biofuel blends
- intake manifold injection of biofuel parallel to direct diesel injection (Dual-Fuel operation mode)
- intake manifold injection of synthesis gas (as a product of biofuel reforming reactions utilizing exhaust heat)

A boundary condition of 2 g/kWh NOx emissions is set to allow comparison!



Schematic layout of the thermo chemical recuperation system



Special fuel X

Reforming possible? — Yes — Operation mode 1: Operation with syngas manifold injection and diesel direct injection — Gas

Manifold injection promising? — Yes — Operation mode 2: Operation with manifold injection of pure substance and diesel direct injection — SRE

Direct injection possible? — Yes — Operation mode 3 A: Operation with special fuel direct injection — DI

Mixable with diesel? — Yes — Operation mode 3 B: Operation with fuel mixture („blend“) direct injection — DI

Procedure for the investigations of the special fuels (Gas = synthesis gas manifold injection, SRE = intake manifold injection, DI = direct injection)

Thermo chemical recuperation via fuel reforming

- combustible synthesis gas is produced via biofuel reforming utilizing exhaust gas heat
- biofuel reforming reaction take place in a separate reactor, preferably in the EGR path
- if the overall reaction in the reformer is endothermic (ΔHR >0), waste heat is converted to chemical energy and the lower heating value (LHV) of the syngas increases in comparison to the LHV of the injected biofuel.

Comparison of reforming experiment and simulation, 500 °C reformer inlet temperature

	Conver-sion	λ	ΔLHV	Syngas [mol%]			
EtOH				H_2	CO	CH_4	CO_2
Exp.	91%	1.13	2.5%	14.2%	4.9%	1.1%	11.1%
Sim.	100%	1.13	4.6%	13.0%	6.5%	0.0%	10.6%
BuOH							
Exp.	67%	1.2	1.8%	14.9%	3.8%	0.2%	12.7%
Sim.	100%	1.2	6.2%	17.0%	8.3%	0.0%	10.4%

Investigated Fuels

Both pure alcohols and alcohol-diesel blends are subject of investigation. All three alcohols can be used to produce synthesis gas via fuel reforming. In order to cover a wide range of possible synthesis gas concentrations, the combustion characteristics of two different syngas concentrations are tested.

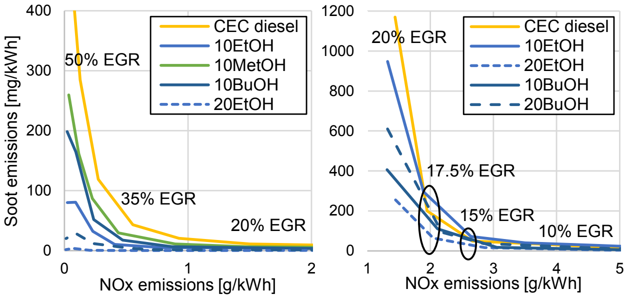
Abbreviations of the investigated fuels

CEC diesel	Reference diesel fuel
EtOH	Ethanol
MetOH	Methanol
BuOH	Butanol
10EtOH	90vol%diesel + 10vol% ethanol
10MetOH	90vol%diesel + 10vol% methanol
10BuOH	90vol%diesel + 10vol% butanol
20EtOH	80vol%diesel + 20vol% ethanol
20BuOH	80vol%diesel + 20vol% butanol
Syngas	Synthesis gas derived from fuel reforming

Results

Direct injection of diesel alcohol blends

At low loads even the addition of only 10 vol% alcohol to the diesel fuel mitigates the soot-NOx trade-off. Increasing the substitute fuel up to 20 vol% enhances the observed soot reduction effect. In the case of ethanol, the traditional conflict between soot and nitrogen oxides is almost eliminated and EGR can be further increased.



Mitigation of the soot-NOx trade-off at low load 1500/5 (left) and at higher load 1500/15 (right) by blending diesel with alcohols

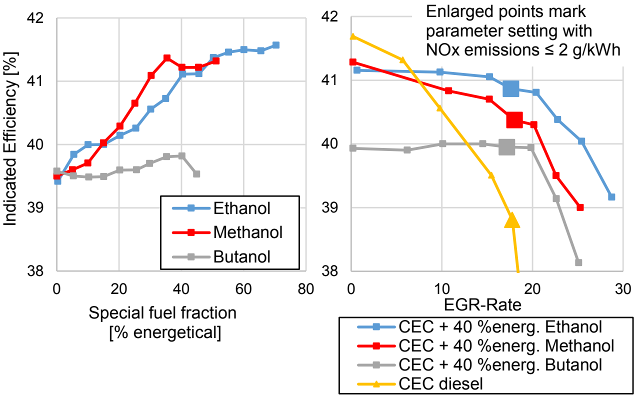
Efficiency is not significantly affected by alcohol addition.

Fuel Manifold Injection

The intake manifold injection can be realized at moderate costs and offers important degrees of freedom:

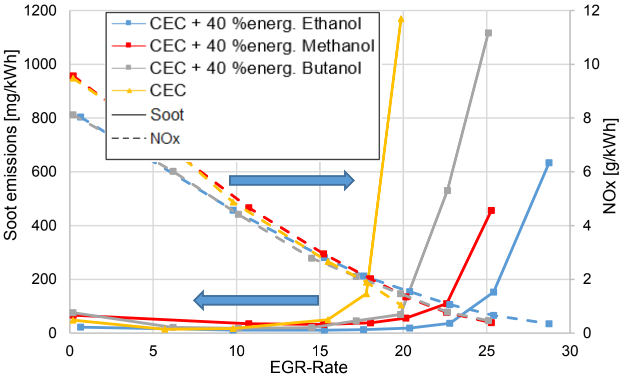
- the tested fuel does not have to be miscible with the CEC diesel
- the amount of substitute fuel can be varied within a wide range
- the fuel used can have properties, which are contradictory to the requirements for diesel fuels (cetane number, lubricity, etc.).

Dual-fuel operation with manifold injection of high alcohol amounts demonstrates a strong increase of efficiency. At high loads butanol tends to auto-ignite, reducing a possible efficiency gain.



Indicated efficiency depending on the substitution rate for three alcohols in OP-1500/15, 15% EGR (left) and indicated efficiency of diesel reference operation and dual-fuel operation at different EGR rates, OP-1500/15; MFB50 = 7.5 °CAaTDC (right)

The efficiency advantage towards reference diesel operation is present especially at high EGR rates.



Soot and NOx emissions of diesel reference operation and dual-fuel operation with alcohol manifold injection at different EGR rates, OP-1500/15; MFB50 = 7.5 °CAaTDC

Operation with high alcohol amounts shows a strong reduction of soot emissions and extended tolerance towards increasing EGR even at high loads. In this way very low NOx emissions can be reached.

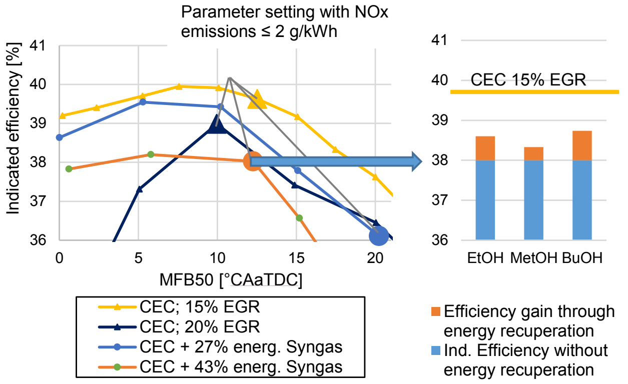
Dual-fuel operation with alcohol manifold injection offers

- strong efficiency enhancement
- soot and NOx reduction
- high substitution potential
- CO_2 reduction

Best results are achieved with ethanol.

Synthesis gas - manifold injection

High exhaust gas temperatures are needed for profitable biofuel reforming, therefor only results of higher load testing are shown below.



Variation of the combustion centre position MFB50 in OP-1500/15 for diesel reference and syngas operation (left) and efficiency increase by consideration of the energy recuperation by the synthesis gas generation based on the three alcohols (right)

The substitution of diesel by syngas results in a reduction of the indicated efficiency. Taking into account the "upgrade" of calorific value due to fuel reforming and heat utilization, the efficiency is being increased. This gain is, however, not sufficient to compensate the higher losses of the reformate combustion. The efficiency of diesel reference operation is not reached.

Emissions of nitrogen oxide are at the level of diesel reference.

Improvement of soot emissions is measured, when operating with syngas.

The potential of biofuel reforming and subsequent syngas combustion is determined by:

- Low air/fuel ratio (necessary for fuel reforming)
- High exhaust temperatures
- The fuel used

Comparison of the investigated variants

The CO_2 savings potential for biofuel production is determined within the framework of the sustainability analysis carried out by the Technical University of Graz and is included in the "CO_2 (well to wheel)" column of the table below. Thus, the CO_2 advantage increases with the substitution rate.

The CO_2 savings in the production of alcohols from lignocellulosic biomass are assumed to be:

- ethanol: 47%
- methanol: 77%
- butanol: 63%

The "CO_2 (tank to wheel)" criterion describes the CO_2 emissions measured in the exhaust gas.

A Reduction of particle mass is observed in almost all variants.

Overall evaluation of the investigated fuels and operation modes; OP-1500/15; charging pressure 1250 mbar (rel); NOx emissions maximum 2 g/kWh

Fuel (combination)	Efficiency	CO_2 (well to wheel)	CO_2 (tank to wheel)	PM
CEC diesel direct	100	100	100	100
CEC+43%energ. SynGas	97¹⁾/97²⁾/98³⁾	82¹⁾/69²⁾/75³⁾	99	43
CEC+60%energ. EtOH manifold	103	69	90	9
CEC+40% energ. MetOH manifold	103	68	92	22
CEC+40%energ. BuOH manifold	101	74	97	26
10EtOH direct	99	98	101	94
20EtOH direct	100	94	99	48
10MetOH direct	99	98	101	119
10BuOH direct	99	96	101	81
20BuOH direct	100	90	99	71

1) Reforming of ethanol considered; **2)** Reforming of methanol considered; **3)** Reforming of butanol considered; PM… particle mass

The results prove the potential of alcoholic fuels to reduce emissions and enhance the efficiency of the compression ignition engine and verify the the suitability of the methods depicted in the project.

3

Damyanov, A.; Hofmann, P.; Derntl, M.; Schüßler, M.; Pichler, T.; Schwaiger, N.; Siebenhofer, M.: **Regenerative Oxygen-Containing Diesel Substitute Fuels as an Ecological Option for Increasing Efficiency and Minimizing Emissions**; Nikolai Schubert (Hrsg.); Proceedings of the 11th International Colloquium Fuels, p. 315-331; ISBN 978-3-943563-32-0; 27-29 Juni 2017, Ostfildern, Germany

Regenerative Oxygen-Containing Diesel Substitute Fuels as an Ecological Option for Increasing Efficiency and Minimizing Emissions

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Summary

Second generation biofuels have the potential to contribute to the reduction of overall CO_2 emissions from traffic without entering an ethical contradiction to food production. Within the presented project the suitability of preselected 2nd generation biofuels for engine combustion is investigated experimentally. A distinctive feature of the project is the investigation of the fuel supply into the internal combustion engine in three different ways. Next to the common direct injection of diesel-biofuel blends, the biofuel is also fed via intake manifold injection parallel to direct diesel injection into the combustion chamber. In addition, a thermo chemical recuperation system is investigated, where hot exhaust gas is used to support biofuel reforming reactions to combustible syngas (H_2, CO). The generated syngas is injected into the intake manifold and is then ignited via diesel pilot injection. The reforming of biofuels is investigated experimentally in a separate reactor on a synthesis gas test bed. In this paper the results with ethanol and butanol as alcoholic biofuels are presented.

1. Introduction

The future supply of fossil fuels is uncertain and accelerates the investigation for sustainable, alternative biofuels with no restrictions in production and combustion engine applications [1]. Biofuels that contain oxygen are particularly of interest for alternative diesel fuels, as they can defuse traditional target conflicts like the particle-NOx trade-off or the efficiency-NOx compromise [2], [3]. Second generation biofuels are derived from lignocellulosic biomass and are exclusively of interest in the project, as they have potential to contribute to the reduction of CO_2 emissions of the transportation sector. They are also expected to have advantageous properties in the processes "low-particle combustion" and biofuel reforming. The selection and evaluation of biofuels for this project is done by the Institute of Chemical and Environmental Engineering (University of Technology, Graz) and is not limited to the current diesel standard *EN590*. The most promising biofuels have oxygen in structure and belong to the groups of alcohols, ethers and furanes. This group of biofuels gives a widely spread potential for combustion processes that are unconventional for diesel engines. Exemplary for the project, the results with ethanol and butanol as diesel substitute biofuels are presented in this paper. Alcohols are currently used almost exclusively in spark ignition engines, because they have a high octane number. However, the use in a diesel engine is investigated, since an influence of the oxygen on the pollutant emissions can be assumed. The combustion investigations are conducted on an engine test bed at the Institute for Powertrains and Automotive Technology (IFA, University of Technology, Vienna)

The investigations consider three main variants of biofuel combustion processes:

1. Combustion of syngas derived from reformed biofuels
2. Intake manifold biofuel injection with parallel direct injection of diesel fuel
3. Direct injection of biofuel and diesel-biofuel blends

In the first variant, a thermo chemical recuperation (TCR) [4], [5], [6] system is investigated. Because of the thermodynamic cycle of the internal combustion engine, a part of the energy that is chemically bound in the fuel is released to the environment as waste heat [7], [8]. This loss of energy brings a big potential to systems that are able to convert waste heat to usable energy. If parts of the waste heat can be recovered, the efficiency of an internal combustion engine can be significantly improved [9].The basic flow sheet of the TCR loop system is shown in Figure 1.

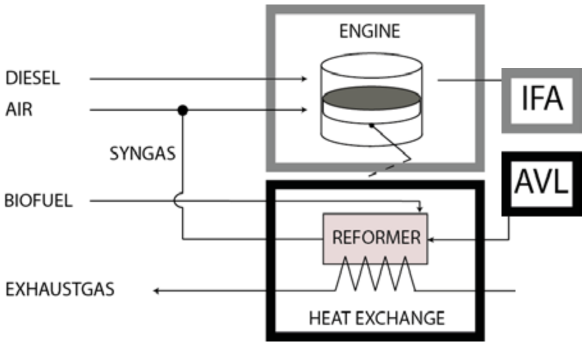

Figure 1: TCR system with a biofuel

The recirculated exhaust gas of the engine is used to produce a combustible syngas derived from biofuel reforming in a separate reactor favorably located in the EGR path. This gas has an increased heating value if compared to the biofuel and is burned in the combustion engine to increase the overall efficiency. The reforming investigations are done on a separate reactor by AVL List GmbH (Graz).

Each of the three investigated biofuel combustion processes is known and has already been mentioned in literature, e.g. [10], [11], [12]. However, the comprehensive and profound comparison of the three variants for a variety of fuels widens the current state of knowledge. Through the accompanying sustainability analysis, the project is not only limited to the technical feasibility study but also consistently assesses the possible use of the respective biofuels in the compression ignition engine. An overall assessment summarizes the results of biofuel production, engine operation and reforming investigations and provides an overview of the biofuel's potential as diesel substitute fuel. The assessment includes the aspects of efficiency, emission behavior, system complexity and sustainability through CO_2 savings.

2. Fuel production simulation

Two second generation biofuels were evaluated based on their production needs and properties. Evaluation criteria were as follows:

Main categories:

- Energetic fuel efficiency: evaluation of the transfer rate of the chemical bound energy into the fuel fraction ($MJ_{Biomass}/MJ_{Fuel}$)
- Process effort: estimation of production costs of fuel production (€/MJ_{Fuel}) (includes biomass price, transport costs, production auxiliaries, energy costs as far as achievable)

Side categories:

- Greenhouse gas reduction: Calculations of greenhouse gas emissions of biofuels based on EU-Directive 2009/28/EG including cultivation and harvest, transport and production processes [13] and a comparison with standard diesel (% CO_2)
- Investment costs: Based on cost estimations and correlations of existing plants (Mio. €)

2.1 Production process

In this study, the pulping process of an ethanol organosolv process was simulated. Main components of lignocellulose (cellulose, hemicellulose and lignin) were separated. Afterwards, hemicellulose and cellulose were converted into fuels by fermentation processes and synthesis routes. Non-converted biomass fractions, such as lignin or hemicellulose were used for steam and power generation. A concept scheme is shown in Figure 2.

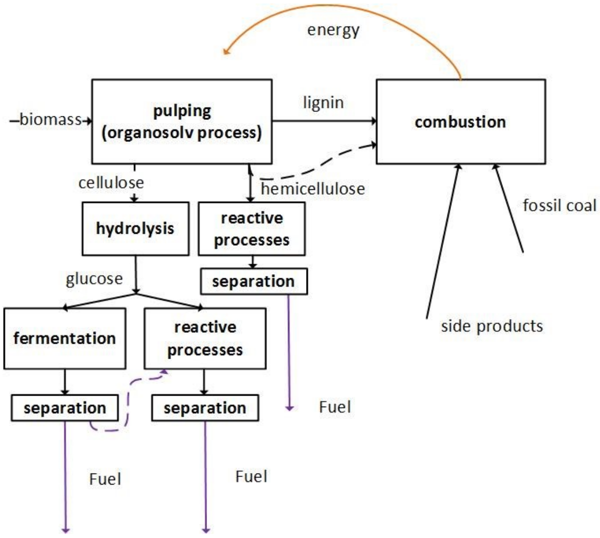

Figure 2: Concept scheme for biomass conversion into fuels using organosolv pulping

In this study an acetone butanol and ethanol (ABE) fermentation of cellulose was evaluated and two different cases of side stream treatments were compared. The first case (case 1) is an integrated conversion of the hemicellulose fraction into 1-methyltetrahydrofuran (MTHF) and the second case (case 2) is the thermal conversion of hemicellulose for steam and power generation.

Plant size was set on an industrial scale with a biomass consumption of 101 t/h. This is the same order of magnitude as proposed in literature [14]. Biomass source was miscanthus sinensis and process operation was based on the work of Alriols [15]. To increase production rates, initial production route was improved. The ethanol organosolv process is auto catalysed by acetic acid, which is formed during the pulping process. A process scheme is shown in Figure 3.

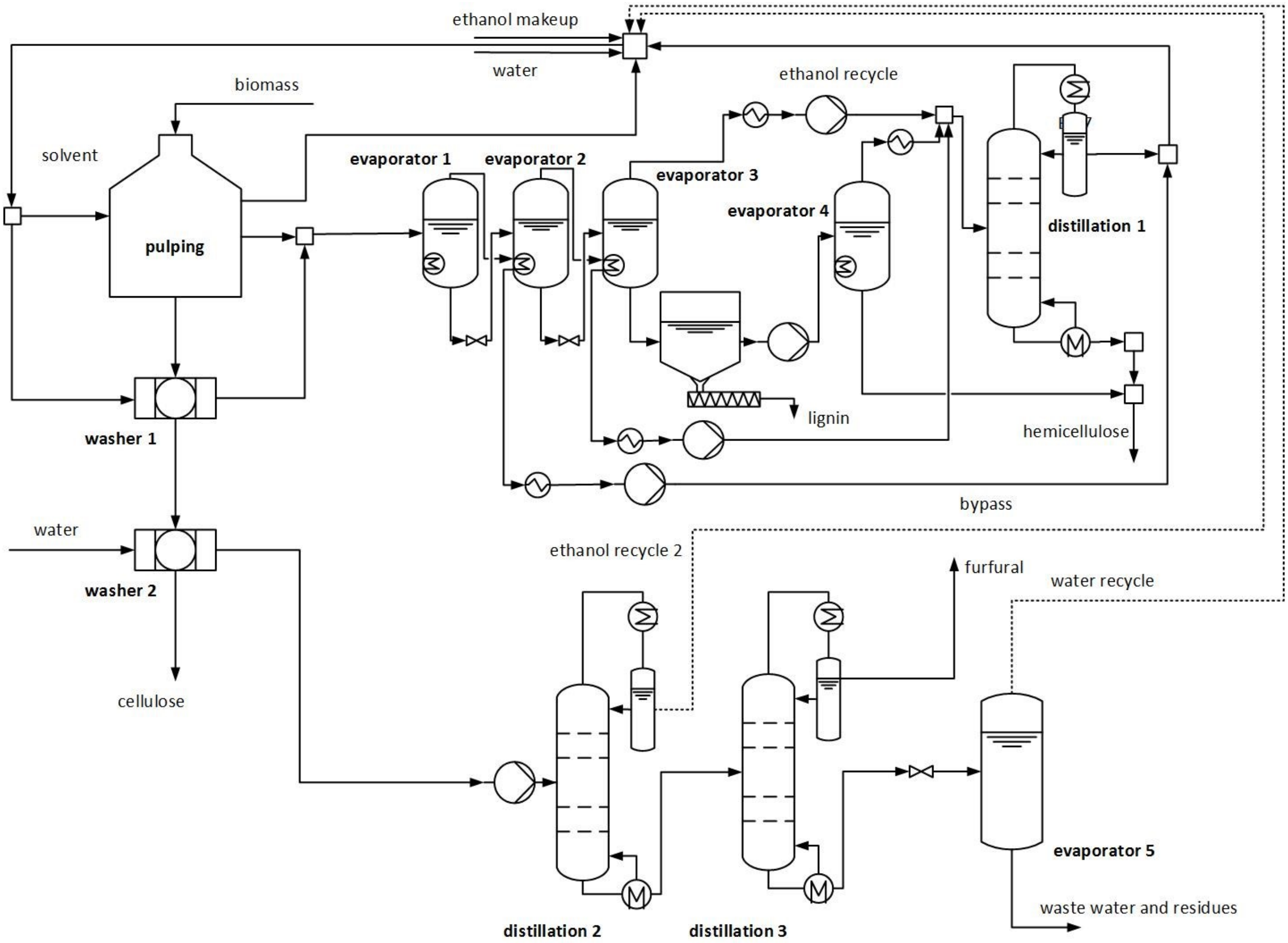

Figure 3: Ethanol organosolv based biomass conversion route for cellulose, hemicellulose and lignin production

During ethanol organosolv pulping 40.7 t/h cellulose are gained. Cellulose is converted into glucose by enzymatic hydrolysation. Subsequent fermentation of glucose yields in acetone, butanol and ethanol. Product separation is performed by distillation. Product separation has to overcome one azeotrope of water and ethanol and additional one azeotrope of water and butanol. The simulated separation process is shown in Figure 4.

With this simulated process route 9.3 t/h butanol are produced and additional 2.9 t/h of acetone are gained. Formed ethanol is used for the pulping process to compensate ethanol losses. Additional need of energy was provided by coal combustion and the calculated CO_2 output was 111.3 g_{CO2}/MJ [16].

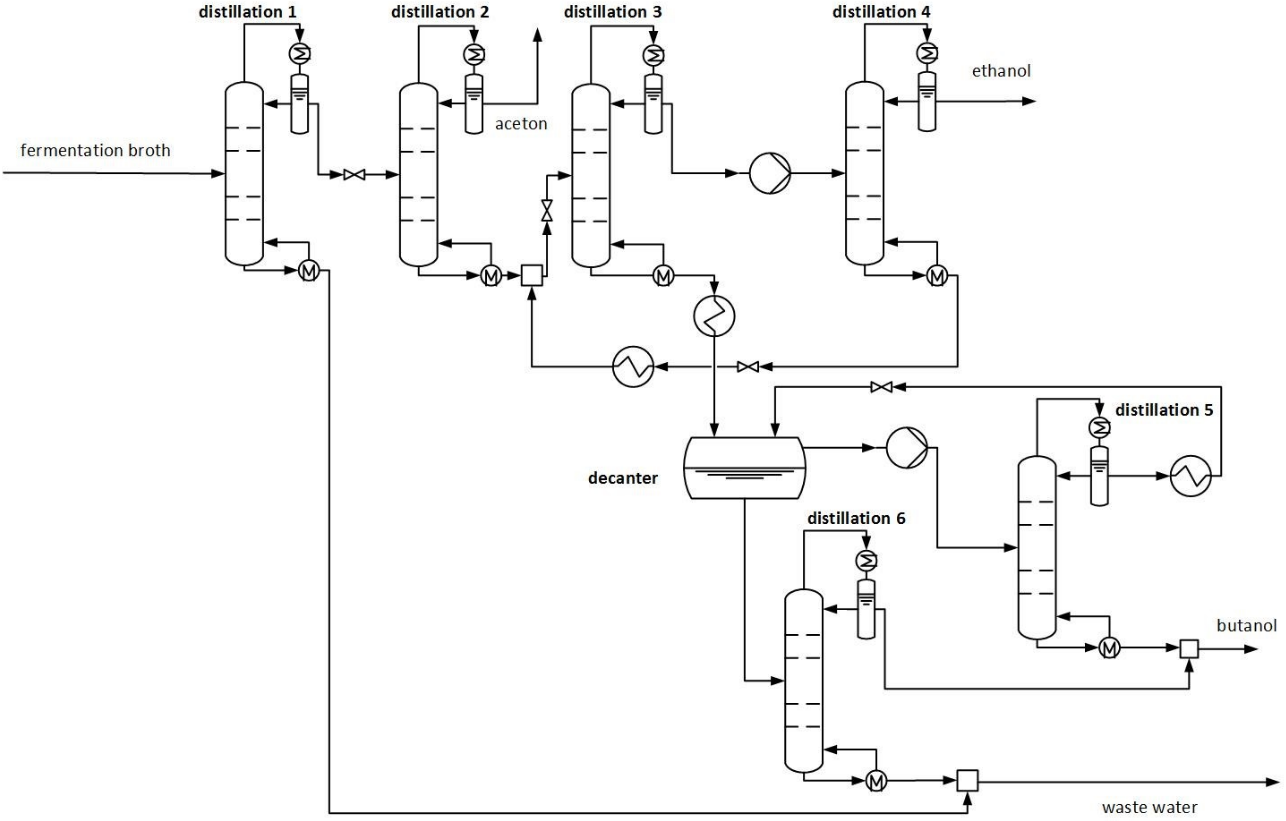

Figure 4: Product separation after ABE fermentation

2.2 Evaluation of butanol production

Based on the process simulation, mass and energy balances of the two cases were compared and results are shown in Table 1.

Table 1: Biofuel production with thermal or chemical conversion of hemicellulose [17]

Case	Cellulose	Hemicellulose	Energetic fuel efficiency [$MJ_{biomass}/MJ_{Fuel}$]	Greenhouse gas reduction [% CO_2]	Process effort [€/MJ_{Fuel}]	Invest costs [Mio. €]
1	A, B	MTHF	3	-53	0.020-0.031	585
2	A, B	combustion.	4.3	63	0.013-0.031	514

Process effort: without taxes, biomass price between 8-80 €/t, without catalyst costs, manpower requirements; 2 persons per unit operation in fully continuous 5 shift operation with wage agreement “chemical industries” Austria, maintenance costs of 2.5% of invest costs per year; Biomass transport of max. 200 km (average distance 93.75 km with an estimated distribution of 75% truck transport and 25% train transport),
Invest costs are based on the correlations of Vasudevan [18] and adapted with a chemical engineering plant cost index of 2014 with 579.8;

Case 1 results in greenhouse gas emissions of 134.2 g_{CO2}/MJ_{Fuel}, which are definitely far above the standard value of diesel, which is 87.64 g_{CO2}/MJ_{Fuel} [16]. This biofuel does not end up in a greenhouse gas reduction and has a negative value in Table 1. In case 2 hemicellulose is used energetically by combustion and reduces additional energy demand. Overall emissions are 32.7 g_{CO2}/MJ_{Fuel}. Moreover, process effort is decreased, but more biomass is needed for biofuel production. To sum up greenhouse gas emission reductions can be gained with an increase of biomass demand with this process.

3. Biofuel Reforming

The main purpose of the biofuel reforming process is to produce a combustible gaseous mixture (syngas) consisting of H_2, CO and also CH_4, CO_2, H_2O. The reforming reactions are considered to take place directly in the hot exhaust gas recirculation pipe (EGR), where the reactants for reforming reactions are present (e.g. fuel, H_2O, CO_2 and O_2). Only when the overall reaction in the reformer is endothermic ($\Delta H_R > 0$), waste heat is converted to chemical energy and the lower heating value (LHV) of the syngas increases in comparison to the LHV of the injected biofuel [19]. The increase of

LHV as well as the combustion of syngas can influence the engine's efficiency and emissions positively [10]. The calculation of ΔLHV is shown in Equation 1, where the biofuel conversion of the reformer is also included, as the conversion may be incomplete in the reforming process.

$$\Delta LHV\ [\%] = \frac{LHV_{SYNGAS}}{LHV_{BIOFUEL} * Conversion_{BIOFUEL}} - 1$$

Equation 1: Gain of Heating Value ΔLHV [%]

The maximum value for ΔLHV can be predicted with the ideal biofuel reforming reaction, assuming 100% conversion, where the products H_2 and CO are formed predominantly. Table 2 gives an overview of the ΔLHV values of selected biofuels. For all biofuels the ratio of formed H_2 to CO is 2. However, this results in different ΔLHV values, because the fuels have a different LHV basis. It can be seen that the highest ΔLHV can be expected for the syngas of ethanol and butanol reforming, which is further investigated experimentally.

Table 2: Ideal steam reforming reactions, ΔLHV

	Reforming Reactions	LHV [kJ/mol]	ΔLHV [%]
Ethanol	$C_2H_5OH\ (l) + H_2O = 4\,H_2 + 2\,CO$	-1235	24%
Butanol	$C_4H_9OH\ (l) + 3H_2O = 8\,H_2 + 4\,CO$	-2456	25%
Dimethylether	$C_2H_5OH\ (g) + H_2O = 4\,H_2 + 2\,CO$	-1328	16%
Methanol	$CH_3OH\ (l) = 2\,H_2 + CO$	-638	20%

3.1 Engine-Reformer Simulation

In this project the reforming process and the combustion engine are investigated separately. Therefore a simulation tool was developed, which combines the engine and the biofuel reformer into a consistent combined system (Figure 1). Based on ideal engine combustion and ideal reforming in the EGR path, the simulation estimates mass and energy balances and predicts the performance of the TCR system.

Calculation of ΔLHV values

Figure 5 shows the influence of the diesel engine EGR rate and λ (air-fuel ratio) value on ΔLHV for the reforming of ethanol. A positive ΔLHV value implies, that the overall reforming reaction is endothermic. With the selected operating conditions an increase of the LHV is possible. The higher the EGR rate, the more heat is provided and the higher is the injected amount of ethanol in the reformer. The overall ΔLHV is almost constant at various EGR rates, whereas λ has a significant influence. With higher λ values more excess O_2 is provided in the EGR path preferring exothermic reactions and hence reducing ΔLHV. The higher the ΔLHV value, the higher is the potential to increase the engine's efficiency with syngas combustion. Therefore, engine operating points at low λ values are recommended.

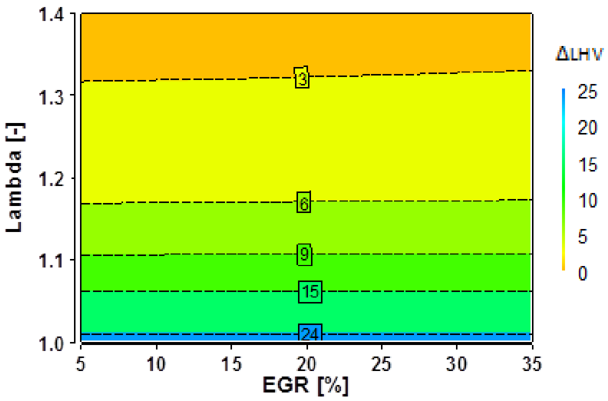

Figure 5: ΔLHV calculation, ethanol

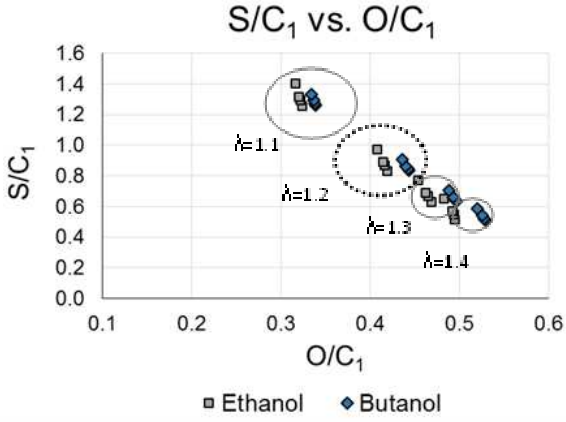

Figure 6: S/C₁ vs. O/C₁

Estimation of the boundary conditions for reforming experiments

To define boundary conditions for the reforming experiments two characteristic numbers at the EGR reformer inlet were extracted from simulation results - the steam to carbon ratio (S/C_1) and oxygen to carbon ratio O/C_1. The letter C_1 refers to the carbon of injected biofuel, S and O refer to steam and elemental oxygen in the EGR path. Figure 6 shows a set of S/C_1 and O/C_1 at various λ values. It can be seen, that S/C_1 can be expected in a range of 0.5-1.4 and O/C_1 in a range of 0.3-0.5 for ethanol and butanol EGR reforming. With higher λ value O/C_1 is increasing while S/C_1 is decreasing. The dotted field of parameters is investigated in the reforming experiments shown here, which is in the range of S/C_1 0.9 and $O/C_1 = 0.4$-0.5.

For the investigations on the engine test bed at IFA two characteristic mean syngas compositions were estimated. One composition favors the formation of H_2, and the second composition also considers CH_4 as a reforming product.

3.2 Reforming Experiments

The aim of the experiments is investigating the potential of biofuel reforming in diesel exhaust gas. The experiments are conducted on a synthesis-gas test bed, where the EGR exhaust gas can be simulated physically in its composition, temperature and volumetric flow. The biofuel is injected directly in the hot gas stream for evaporation and is transported through a mixing section to the reformer catalyst. The reformer consists of a monolithic PGM catalyst sample (d=38mm, L=80mm) in a stainless steel pipe and is operated at a gas hourly space velocity of 15000 [1/h] at standard conditions. At selected operating conditions inlet and outlet concentration of the gaseous species as well as temperature profiles over the catalyst are recorded. The analysis of the gaseous species is done with an *Agilent Micro GC 490*. Figure 7 shows a picture of the reformer and the test bed. Additional insulation minimizes the heat loss of the reformer.

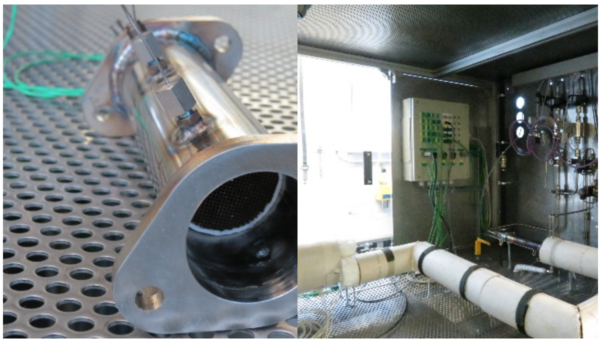

Figure 7: Reformer (left); syngas test bed (right)

EGR reforming of ethanol and butanol, results

The reforming of ethanol and butanol was investigated at 400°C and 500°C reformer inlet temperature. At this exhaust gas temperatures the maximum amount of O_2 in the EGR gas for endothermic reforming is of special interest. The O_2 amount determines the heat of reforming reaction as well as the achievable level of ΔLHV. At constant $S/C_1=0.9$ the amount of O_2 was increased stepwise from $O/C_1=0$ to $O/C_1=0.4$ and 0.5 according to simulation estimation. Figure 8 and Figure 9 show the yield of the main syngas components at 500°C, H_2, CO, CO_2 and CH_4. The syngas formation is influenced significantly by the O/C_1 ratio and H_2 is formed as main component. With increasing O/C_1 ratio the formation of H_2, CO and CO_2 increase, whereas CH_4 remains constant. In general, the ethanol reforming results in higher yields of H_2, CO, and CH_4 when compared to butanol reforming. The difference in reforming products can also be seen in the biofuel conversion and the ΔLHV value calculation of the produced syngas.

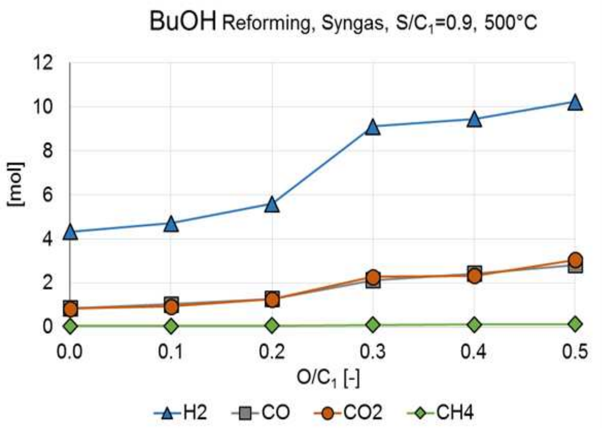

Figure 8: Reforming products butanol

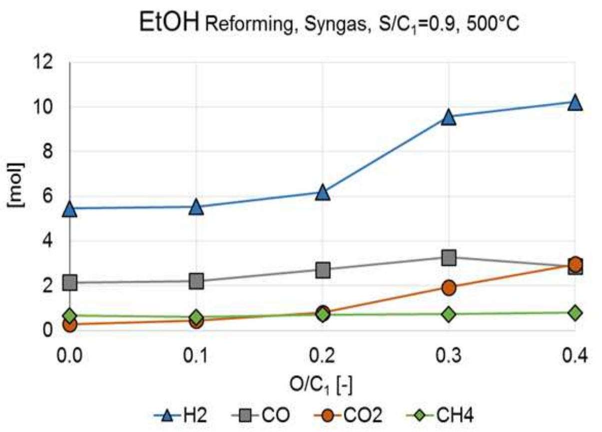

Figure 9: Reforming products ethanol

Figure 10 shows the conversion of ethanol and butanol, Figure 11 shows the corresponding ΔLHV values (Equation 1). The maximum ΔLHV values are approx. 20% at $O/C_1= 0$, like expected from ideal steam reforming (Table 2). In the case of ethanol, 59% converted to syngas, with a 20% increased LHV. In comparison to butanol, ΔLHV of the syngas was 22% but only 25% converted to syngas. This concludes, that incomplete biofuel conversions limits the overall gain of ΔLHV, as unreacted biofuel is fed to the combustion engine.

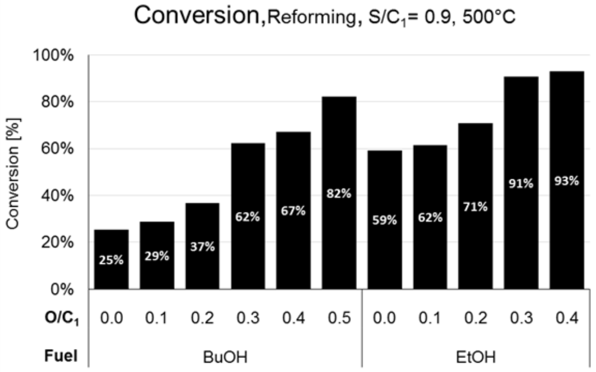

Figure 10: Conversion, ethanol and butanol

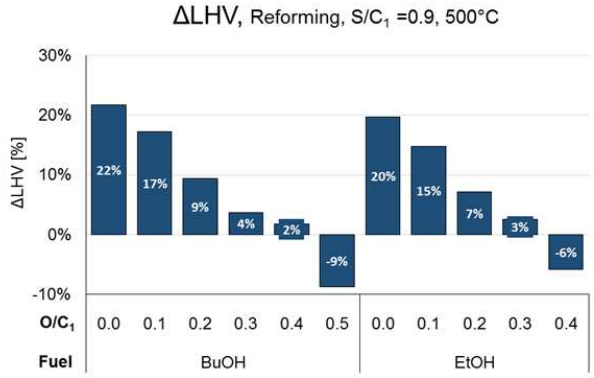

Figure 11: ΔLHV, ethanol and butanol

The conversion of biofuel can be increased from 25% to 82% for butanol and 59% to 93% for ethanol with increasing O/C_1 ratio. In contrary, ΔLHV values are decreasing from 20% to negative values. This transition indicates a change from endothermic to exothermic reaction regime. The O/C_1 limit for endothermic reforming is 0.4 for butanol and 0.3 for ethanol, which is 2.8% O_2 (λ=1.2) and 2.2% O_2 (λ=1.13) in the EGR path.

At 400°C reformer inlet temperature the biofuel conversion and ΔLHV values of both fuels were insufficient and are not presented here.

A comparison of experiments and ideal reforming simulation results at λ=1.13 and λ=1.2 is shown in Table 3. Experiments and simulation correlate very well. In the experiments a high concentration of H_2 was measured (14-15%). However, the formation of CO_2 was preferred, hence the CO concentration was slightly lower than predicted from calculation. Also small amounts of CH_4 were detected in the syngas tests which further reduces the ΔLHV value. As a result, the gained experimental ΔLHV values of 1.8-2.5% are below the values of the ideal simulation results (6-7%).

The results confirm, that especially low λ values and high exhaust gas temperatures (500°C) give a potential to improve the engine's efficiency with butanol or ethanol EGR gas reforming. Potential in further optimization is seen in catalyst improvement with the target of higher biofuel conversion and syngas selectivity.

Table 3: Comparison experiment – simulation, 500°C Reformer Inlet

	Conversion	λ	ΔLHV	syngas [mol%]			
Ethanol				H_2	CO	CH_4	CO_2
Experiment	91%	1.13	2.5%	**14.2%**	**4.9%**	**1.1%**	**11.1%**
Simulation	100%	1.13	7.1%	14.9%	7.2%	0.0%	10.3%
Butanol							
Experiment	67%	1.2	1.8%	**14.9%**	**3.8%**	**0.2%**	**12.7%**
Simulation	100%	1.2	6.2%	17.0%	8.5%	0.0%	10.4%

4. Engine experiments

4.1 Test engine and examination methodology

Test engine

A Daimler in-line four-cylinder diesel motor OM 646 Evo is used as a test engine. The low availability and the high purchase costs of some of the fuels tested make the conversion to single cylinder operation reasonable. Only the first cylinder is fired, the other three are deactivated and their gas exchange is separated from the gas exchange of the fired cylinder. The cylinder has a displacement of 537 cm^3 and a compression ratio of 17.5. The original high pressure common rail injection system is equipped with seven-holes nozzles solenoid injectors. Charging is performed with an external electrically driven supercharger. The two intake manifold injectors and various measuring equipment are adapted in a specially designed intake manifold. An electrically adjustable flap valve is used to produce the necessary exhaust gas pressure. The standard exhaust gas aftertreatment system has been removed and the exhaust system is only used for exhaust gas guidance, sound attenuation and as a measuring point location.

Examination methodology

The investigations are carried out at two operating points. The first point is defined by an engine load of 5 bar indicated mean effective pressure at 1500 rpm, the second by 15 bar indicated mean effective pressure also at 1500 rpm.

The scheme in Figure 12 illustrates the procedure for the investigation of the special fuels. With regard to the characteristics of the investigated alternative fuel, several possible operating modes result. If the fuel can be reformed, the engine can be operated with synthesis gas made from this fuel (mode 1). The ignition is then effected by the direct injection of diesel. However, the fuel can also be supplied into the intake manifold (operating mode 2) as a pure substance if this operating mode appears to be promising (no auto-ignition). The ignition is also effected by a diesel jet. If the fuel properties permit this (lubricity, vapour pressure, cetane number), the special fuel is injected directly into the combustion chamber as a pure substance (mode 3 A). A further possibility is the engine operation with a direct-injected fuel mixture, so called "blend", if the alternative fuel can be mixed with diesel (mode 3 B).

Different variations are carried out in the described operating modes, the most important being the variation of the alternative fuel amount, the air-fuel ratio, the EGR rate and the center of combustion (MFB50). The results of the variations are compared with each other for the investigated fuels and the optimum operating parameters for the respective fuel are determined. The pure diesel operation is the reference for the

Table 4: Operating points

Name	Speed [min^{-1}]	Indicated mean effective pressure [bar]
OP-1500/5	1500	5
OP-1500/15	1500	15

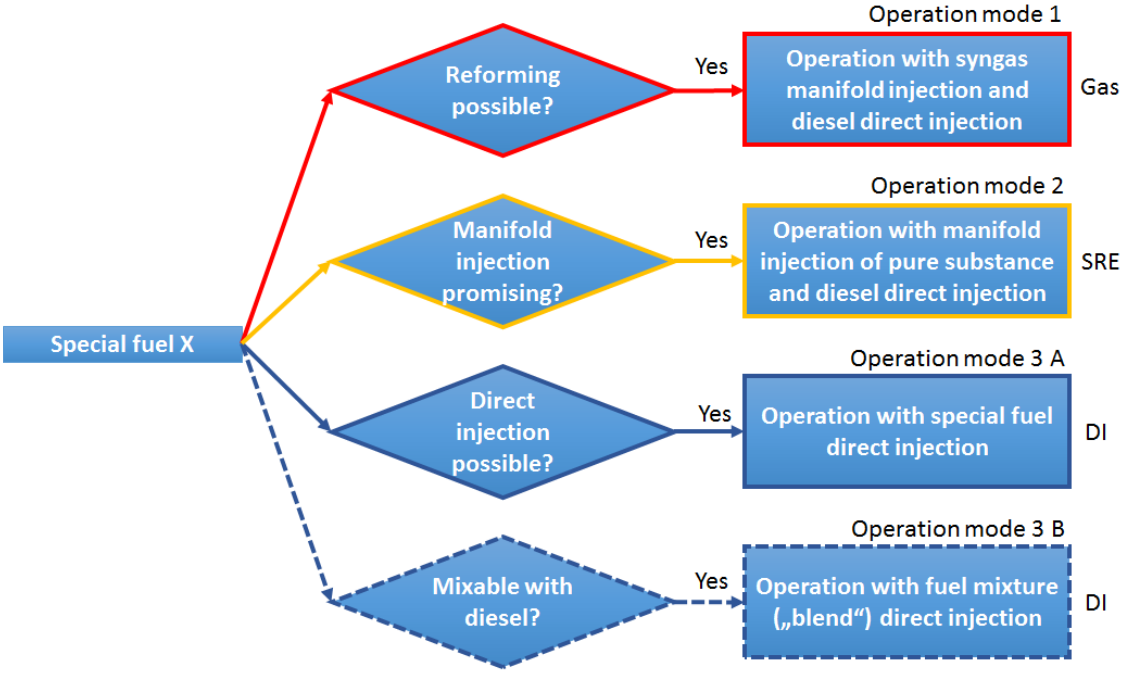

Figure 12 Procedure for the investigations of the special fuels (Gas = synthesis gas manifold injection, SRE = intake manifold injection, DI = direct injection)

comparison. In order to create boundary conditions for the fuel comparison, an upper limit for the NOx emissions of 2 g/kWh is set. The effort for the exhaust gas aftertreatment is also being limited by this constraint. The maximum charge pressure is limited to 1250 mbar (rel.).

4.2 Investigated fuels and synthesis gas

The tested oxygenated fuels were selected after a comprehensive analysis carried out at the Institute of Chemical Engineering and Environmental Technology at the Graz University of Technology. The focus is on the cost effectiveness as well as on the sustainability of the fuel production. The potential suitability of the substances for combustion engine use is a key criterion for the selection.

Ethanol and butanol are two of the investigated representatives of the alcohol fuels. On the one hand, they are supplied to the engine pure - via intake manifold injection or reforming, on the other hand as alcohol-diesel mixtures. The diesel fuel is a certified test diesel fuel and is briefly referred to as CEC. In the case of the alcohol-diesel blends, mixtures of CEC diesel/alcohol in the volumetric ratio of 90/10 and 80/20 were defined. The fuels used were subjected to full analyzes, the most important properties being summarized in Table 5. Blends are designated by the abbreviation X%CECY%Alcohol.

Table 6: Investigated synthesis gas compositions

	syngas(H_2)	syngas(CH_4)
H_2 [Vol%]	31,5	18
CO [Vol%]	6,2	8,4
CH_4 [Vol%]	0	6,4
CO_2 [Vol%]	15,2	13,5
N_2 [Vol%]	Rest	Rest

4.3 Results

4.3.1 Synthesis gas – manifold injection

Due to the requirements of the fuel reforming, a low air-fuel ratio (λ) is necessary for engine operation with syngas. Lambda values from 1.1 to 1.4 are investigated, whereby the operation with $\lambda = 1.1$ results in a very low combustion engine efficiency. Particularly in OP-1500/5 a significant throttling of the intake tract is necessary in order to reach the low λ-values. The results of the syngas tests for the required air-fuel ratios can only be compared with the realistic diesel reference operation since a deterioration of the pure diesel operation caused by a reduction of the air excess would not be constructive. Additionally, at OP-1500/5 the exhaust gas temperature is generally below 500°C, which results in insufficient fuel conversion and ΔLHV values in the reforming process (see chapter 3.2). For this reasons, only the engine results at OP-1500/15 are being discussed here.

Table 5: Investigated alcohol fuels and diesel-alcohol blends

	CEC	EtOH	BuOH	90CEC 10EtOH	90CEC 10BuOH	80CEC 20EtOH	80CEC 20BuOH
Chemical formula	$C_{12}H_{23}$$^{1)}$	C_2H_6O	$C_4H_{10}O$				
Cetan number	54,5	8	17	49,2	50,8	42,4	43,3
RON		111	96				
Ignition temp. [°C]		420	325				
Density [kg/m^3]	833,5	789	810	828,4	831	825	829
HFRR [µm]	413			417	428		
Heating value [MJ/kg]	42,676	26,677	32,94	41,25	41,78	39,323	40,673
C-Fraction %M	85,4	51,5	64,6	82,8	83,7	79,2	81,4
H-Fraction %M	14,2	13,7	13,7	14	14,10	13,6	13,8
O-Fraction %M	<0,5	34,1	20,9	3,2	2,2	6,6	4
Boiling point [°C]	173-363	78	118	64-358	115-361		
$\Delta H_{vaporization}$ [kJ/kg]	300	845	626				
Lst [kg_{air}/kg_{fuel}]	14,5	9	11,26	13,97	14,8	13,44	13,86

1) approximately

The syngas composition, which is defined through the investigations at the AVL, is adjusted by means of a gas mixing system at the engine test rig and is fed back to the intake manifold using a gas supply system. The sensitivity of the engine test results to the synthesis gas composition is checked by means of two different concentrations, Table 6. These show large differences in the H_2 and CH_4 content and can be comprehended as extreme cases covering the range of realizable gas compositions. Since the addition of water vapour represents a disproportionately high effort, the water component is not taken into account in the syngas composition.

The investigations represent a process in which the synthesis gas generation takes place within the exhaust gas recirculation system of the engine. The recirculated gas in the syngas operation is therefore no longer just an inert exhaust gas, but also an energy carrier. Thus, the syngas substitutes a part of the diesel fuel on the one hand and the recycled exhaust gas on the other. Due to the high inert fraction in the syngas composition, the EGR-typical capacity for NOx reduction should still be remained.

The substitution of diesel by syngas results in a reduction of efficiency both at low and high engine loads. Figure 13 (on the left) shows the indicated efficiency measured in combustion centre position variations with CEC and syngas at different EGR and syngas ratios.

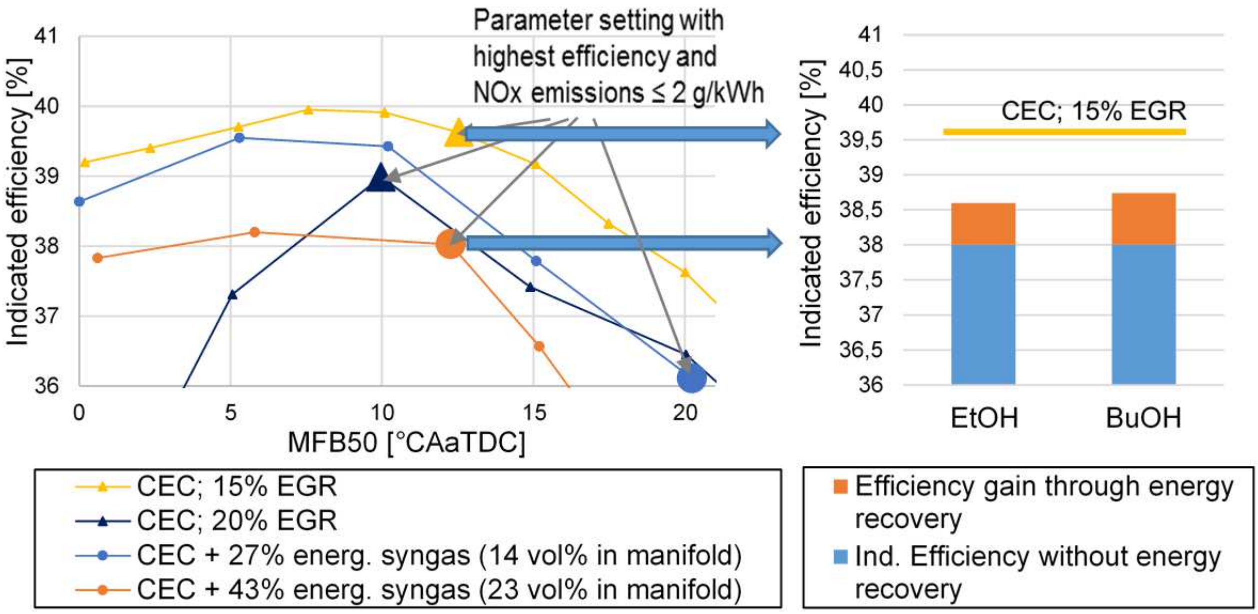

Figure 13: Variation of the combustion centre position MFB50 in OP-1500/15 for diesel reference and syngas operation (left) and efficiency increase by consideration of the energy recovery by the synthesis gas generation (right) based on the two alcohols

With earlier MFB50, the temperature in the combustion chamber is higher, which results also in higher NOx emissions. In order to reduce the formation of nitric oxides, the combustion centre position can be delayed and/or the EGR rate can be increased. However, the implementation of these measures must be based on the lowest possible soot emissions and highest efficiency. The enlarged marking points in Figure 13 indicate the optimum point in the respective operating mode, with the NOx emission being below the limit of 2 g/kWh and the efficiency under this condition being as high as possible. It can be seen that a further increase in the EGR rate in pure diesel operation mode from 15% to 20% results in a reduction in efficiency and thus a further reduction of NOx would lead to a strong efficiency loss.

When operating with a 27% energetic synthesis gas fraction, the injected syngas takes up 14% of the total volume of the gas in the intake manifold (air + synthesis gas). For an engine with a real reformer in the EGR system, a comparable operation with 12% EGR would be necessary to realise this operating mode. The addition of the fuel to be reformed and its reforming subsequently increase the volume of the reformate in the intake manifold to the above-mentioned 14%. At 43% energetic syngas content, the reformate takes 23% of the volume in the intake manifold and 20% EGR would be necessary to produce this syngas quantity. Thus it is logical to compare the operation with 43% syngas with the diesel operation with 20% EGR. The comparison of the operation with a 27% energetic syngas fraction and the diesel operation with 15% EGR provides information on the differences between the two operating modes when the volumetric ratios of the syngas or exhaust gas to the fresh air in the intake manifold are approximately the same.

In general, the fuel reforming is only energetically reasonable if a possible engine efficiency loss is overcompensated by the "fuel upgrading". The actual efficiency of the engine operation has therefore not to be calculated based on the synthesis gas energy used, but on the energy of the fuel used to generate the synthesis gas. With the knowledge of the parameters of the engine operation, the necessary mass of the fuel required for the reforming can be back reckoned. By taking this aspect into account, the efficiency in syngas operation is increased, as Figure 13 (on the right) shows. The synthesis gas could be produced from each of the alcohols, but depending on the fuel used, the reforming is effected with different efficiency. The simulation of the process has shown that the upgrade of the calorific value of the syngas generated from ethanol results in an increase of the indicated efficiency shown in Figure 13 by 0.6% points. When reforming butanol, the improvement is by 0.74% points. However, this increase in efficiency is not sufficient at any point to compensate for the higher losses of the reformate combustion.

The comparison of the indicated measurement data of both operating modes shows that the reasons for the efficiency drop in syngas operation are not due to combustion profile. The more compact combustion induced by the hydrogen-containing syngas should even lead to a slight efficiency gain compared to the pure diesel operation, since the percentage of constant-volume combustion increases. However, the loss analysis showed that the high emissions of unburnt hydrogen, methane and carbon monoxide lead to the considerable loss of efficiency. Due to the high ignition temperatures of these gases, an incomplete combustion of the syngas occurs. Additional effects are the cooling at the surfaces of the combustion chamber and the combustion chamber shape, which is designed for the conventional diesel combustion process.

The nitrogen oxide emissions in OP-1500/15 increase as a result of the substitution of the recirculated exhaust gas by synthesis gas, *Figure 14*. This indicates that pure EGR is the stronger measure for NOx reduction.

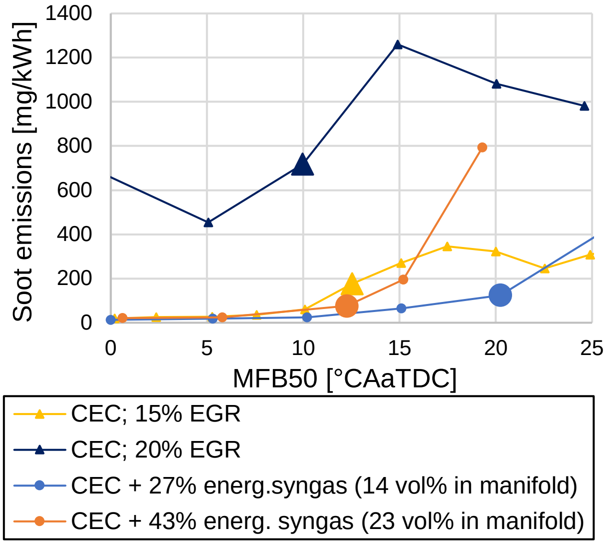

Figure 14: Nitrogen oxide emissions depending on the combustion centre position, OP-1500/15

However, more accurate calculations of the specific heat capacities and the absolute heat capacities of the total charge mass in the cylinder have shown that a mixture of air and syngas can absorb even more heat than air and EGR. The reason for this is the high specific heat capacity of the hydrogen in the syngas. Two other aspects seem to be accountable for the stronger NOx reduction in diesel operation mode. On the one hand, the cooling of the cylinder charge by the diesel jet plays an important role. This cooling effect decreases with the substitution of the diesel by the syngas, which results in higher combustion chamber temperatures. On the other hand, in the case of syngas combustion, the ignition delay is prolonged and more premixed combustion takes place with higher heat release rate. Higher local temperatures are associated with this. Both aspects lead to an increase of the combustion chamber temperature and consequently more nitrogen oxides. In order not to exceed the NOx limit of 2 g/kWh, in pure diesel operation 15% EGR is required with an MFB50 at 12.5 °CAaTDC. At the same combustion centre position, 23 vol% syngas have to be supplied into the intake manifold in dual-fuel operation in order to meet the set emission limit.

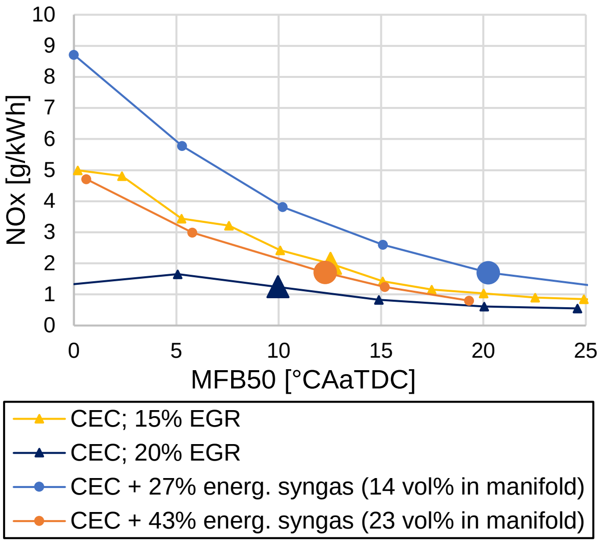

Figure 15: Soot emissions depending on the combustion centre position, OP-1500/15

Figure 15 shows a soot reduction effect of syngas operation at OP-1500/15. Compared to the diesel operation with 20% EGR, the syngas operation with 43% energetic syngas content has much lower soot emissions. However, in diesel mode the engine is preferably to be operated with 15% EGR and adjusted combustion centre position (12.5 °CAaTDC) in order to prevent the strong soot formation. In this case, the soot advantage of syngas operation diminishes. At this point it must be noted that the observations on the test bench can differ from the results of an engine with a real reformer, since in the present case pure synthesis gas and not real exhaust gas-reformed soot-containing syngas is used. It is, however, expected that the positive influence of the low-particle gas combustion on soot emissions will remain. In addition, the catalyst of the reformer has a precious metal coating, which together with the high prevailing temperatures can promote the oxidation of the particles in the recycled exhaust gas.

The presented investigations are carried out with both synthesis gas compositions listed in Table 6. The results with both concentrations show no significant differences in efficiency. With the methane-containing composition syngas(CH_4) high methane emissions are measured in the exhaust gas, whereas with syngas(H_2) more hydrogen remains unburnt. The raw methane emissions are converted in an oxidation catalyst at higher temperatures than CO and HC and may become a problem for the exhaust gas aftertreatment. Moreover, in the upstream process of fuel reforming, the production of a syngas composition without methane is energetically more efficient, which also prioritizes a reforming in terms of high H_2 content.

4.3.2 Fuel manifold injection

The operation of the diesel engine with synthesis gas is one of the three possibilities for fuel supply into the motor. Using an intake manifold injection or direct fuel injection, the investigated fuel can be supplied to the internal combustion engine without an upstream process. The intake manifold injection can be realized at a lower cost compared to the fuel reforming and offers important degrees of freedom - the tested fuel does not have to be miscible with the CEC diesel, the amount of substitute fuel can be varied within a wide range and the fuel used can have properties, which are contradictory to the requirements for diesel fuels (cetane number, lubricity, etc.).

The influence of the intake manifold injection of alcohol on the efficiency and the pollutant emissions of the diesel engine is obvious when the substitution rate is being gradually increased under otherwise constant conditions. As the alcohol content increases, the directly injected diesel quantity is reduced accordingly, so that the power output of the engine remains unchanged. In the lower load point, for all alcohols a deterioration in efficiency is measured when increasing the substitution rate. This efficiency decrease is stronger for ethanol than for butanol. It is remarkable that the efficiency reaches a minimum before rising again at higher substitution rates. The emissions of unburnt hydrocarbons and carbon monoxide increase approximately equally for both alcohols, each with an approx. 500 ppm per additional 10% energetic fuel fraction, resulting in a further loss of efficiency. The maximum rate of substitution is limited by an unstable engine run and an uncontrollable shift of the combustion centre position. In OP-1500/5 ethanol can be fed to the combustion process with a maximum of 65% energetic fraction, and butanol with 85%. It is noticeable that the maximum substitution rates of these alcohol representatives rank like their auto-ignition temperatures and octane numbers. In a wider sense, the octane number is an indicator for the reactivity of the fuel. The high auto-ignition temperature of ethanol leads to combustion misfires already at an energetic portion of 65%, while the lower ignition temperature of butanol permits stable ignition up to a much higher substitution rate. At the high load point OP-1500/15, this behaviour is reversed, see Figure 16.

Butanol tends to spontaneous and uncontrolled auto-ignition at the high cylinder pressures and combustion temperatures present at the higher load point, thereby the maximum possible substitution rate is limited to 45%. The auto-ignition in the butanol combustion is the result of its lower ignition temperature compared to ethanol and causes a strong prolongation of the overall combustion duration which leads to a reduction in efficiency compared to the very fast combustion in ethanol operation. The major difference in the efficiency observations at both loads is that at the high load the indicated efficiency always increases with the addition of alcohols (with exception of the last butanol measurement point). By the intake manifold injection of ethanol with a substitution rate of 60% the efficiency of the engine can be increased by remarkable 2% points. A slight reduction in CO emissions compared to the diesel reference operation is measured. This means that the oxidation cannot be fully completed in OP-1500/5 due to the cooler charge compared to OP-1500/15. The unburned hydrocarbons also increase in OP-1500/15 with the increase of the injected alcohol, but to a much smaller extent than in OP-1500/5, which is due to the higher combustion chamber temperatures and a more complete combustion.

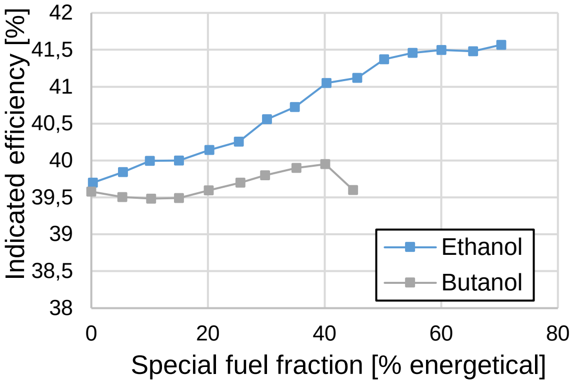

Figure 16: Indicated efficiency depending on the substitution rate in OP-1500/15, 15% EGR, MFB50 = 7.5 °CAaTDC

In order to better understand the reasons for the efficiency increase in ethanol operation, a loss analysis was carried out. It compared the CEC diesel reference operation in the OP-1500/15 with the operation with 40% energetic ethanol content. Both operation modes are shown in Figure 16 (0% and 40% energetic ethanol fraction).The analysis shows that under otherwise identical conditions, the operation with alcohol intake manifold injection leads to an increased loss due to the charge properties (real charge and mixture properties) as well as due to more unburnt fuel. However, these disadvantages are overcompensated by the lower burning efficiency loss resulting from the faster energy conversion in ethanol operation and by the lower wall heat efficiency losses. The reason for the latter is, on the one hand, the lowered temperature level of the charge, on the other hand, the fact that in general the energy conversion remains shorter in the region of the top dead centre compared to the CEC diesel reference and the associated loss is thus reduced.

Emissions

In OP-1500/5, the specific NOx emissions increase slightly with an increased amount of additional fuel, but remain in the range of 1 g/kWh. The exhaust gas temperature measured in the OP-1500/5 drops by approx. 15 ° C compared to pure diesel operation. In OP-1500/15, the total NOx emissions for both alcohols remain at the diesel reference level of approx. 2.5 g/kWh, regardless of the substitution rate. This operating point does not fulfil the introduced boundary condition for the NOx emission limit of 2 g/kWh, since the variation is carried out with 15% EGR at the optimum efficiency combustion position. The exhaust gas temperatures drop with rising alcohol content. In the case of 60% energetical ethanol content e.g., the exhaust gas temperature lies 60 °C below the exhaust gas temperature of the CEC reference operation with 0% alcohol.

The great advantage of the intake manifold injection of the alcohol fuels lies in the significant reduction of soot and particulate emissions, both for low and high loads. This effect is illustrated in Figure 17 for OP-1500/15.

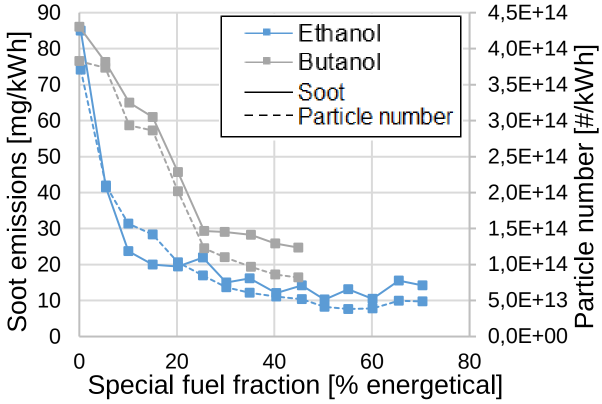

Figure 17: Soot and particle emissions depending on the substitution rate, alcohol manifold injection in OP-1500/15; 15% EGR

By defusing the particle problem, the EGR rate can be increased to further reduce NOx emissions.

In-cylinder reduction of nitrogen oxide emissions
The most effective measure for the in-cylinder reduction of the nitrogen oxide emissions is the increase of the EGR rate. In the case of conventional diesel fuel, this leads to an increase of soot emissions, so that a compromise must inevitably be made when designing the operating parameters. Figure 18 shows the soot-NOx trade-off for the CEC diesel reference in OP-1500/15 and compares it with the behaviour of the dual-fuel operation with alcohol intake manifold injection.

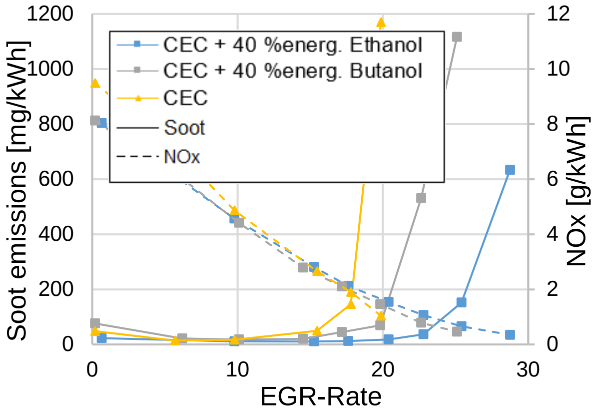

Figure 18: Soot and NOx emissions of diesel reference operation and dual-fuel operation with alcohol manifold injection, OP-1500/15; MFB50 = 7.5 °CAaTDC

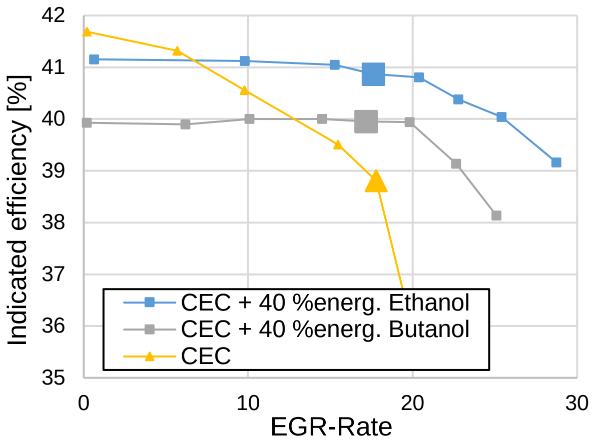

Figure 19: Indicated efficiency of diesel reference operation and dual-fuel operation with alcohol manifold injection, OP-1500/15; MFB50 = 7.5 °CAaTDC

The highest soot reduction is achieved with the intake manifold injection of ethanol. With an ethanol content of 40% energetic and an EGR rate of 17%, the particle mass can be maintained at 20 mg/kWh and the NOx emissions at 2 g/kWh with an optimum MFB50 position of 7.5 °CAaTDC. In the case of diesel reference, a critical increase of soot emissions and a noticeable reduction in efficiency occurs with more than 15% EGR, as seen in Figure 19. The enlarged marking points indicate the EGR rate, at which the NOx emissions are equal to or below the set limit.

In the case of ethanol intake manifold injection in OP-1500/5 with 45% energetic alcohol content and 40% EGR, the NOx emissions add up to 0.3 g/kWh with a soot emission of only 2.4 mg/kWh. For comparison, in diesel reference operation, soot emissions of 120 mg/kWh are measured at the same NOx value. Furthermore, the increase in the EGR rate results in a slight improvement of the indicated efficiency in dual-fuel operation.

4.3.3 Direct injection of diesel alcohol blends

In accordance with the Renewable Energy Directive 2009/28/EC [13] fuel mixtures with a 10% volumetric bio-alcohol content are investigated. This value, however, is only in regard to a mean value of the bio-content in transportation fuels. In order to further explore the potential of alcohol add-on, the substitution rate at the engine tests is subsequently raised to 20%. While butanol can be mixed with diesel at any ratio without a problem, an additive is needed to ensure that the mixture of diesel and 20 vol% ethanol remains a stable one phase liquid. In the presented investigations 3 vol% FAME is used to stabilize the mixture.

At the low load point the addition of 10% by volume of alcohol proves a soot-reducing effect, which is particularly pronounced for the ethanol blend at very high EGR rates. At 35% EGR, the NOx emissions with the ethanol blend are 0.5 g/kWh and the soot emissions are reduced by a factor of 4 compared to the diesel reference. At 50% EGR the reduction is even higher.

The effect of the 10% alcohol blends on soot reduction at the high load point depends on the alcohol used. As can be seen in Figure 20, butanol reduces the soot emissions through all the EGR rates, whereas with ethanol even a slight increase in particulate mass is measured for EGR rates less than 17.5. The positive effect of the small amounts of oxygen in the spray seems to be insufficient to compensate for the cooling effect of ethanol on the diesel spray, thus soot emissions tend to increase slightly. Similar behaviour is also found in literature (e.g. [12] and [20]) and it could be concluded, that the ethanol addition to diesel generally reduces soot emissions, with less exceptions.

At OP-1500/5 the compromise between soot and NOx emissions seems to be completely eliminated when using a blend of CEC and 20% ethanol or butanol. With ethanol, even at 50% EGR the soot emissions remain in the range of 1 mg/kWh while the nitrogen oxides are approaching 0 g/kWh. Under the same conditions, the pure diesel operation results in 500 mg/kWh of soot.

Figure 20 also shows the soot-NOx trade-off for the 20% blends at OP-1500/15. A strong soot mass reduction is observed with the 20% ethanol blend – at 17.5% EGR, NOx emissions are approx. 2 g/kWh and the soot emissions add up to only one third of the soot emissions of CEC reference operation. Mixing 20% butanol to diesel also proves a soot reduction, however surprisingly weaker than the 10% butanol blend.

At this point it must be mentioned, that the effect of alcohol addition on the soot mass emissions is not the same as on the particle number. The reduction of particle number follows the same manner as soot mass reduction in Figure 20, however the influence isn't that pronounced. E.g., the strongest reduction of particle number is achieved with a blend with 20% ethanol and at 20% EGR it is just by a factor of 1.7. At lower EGR rates and with other blends the advantage is even less. An important notice is that with later position of combustion centre the particle number in the exhaust gas raises much stronger for the blends as for pure diesel, whereas the particle mass emissions further behave as in Figure 20. This phenomenon results in a greater number of finer particles. Tschöke et al. [21] report of a particle count rising by 15.6% towards diesel reference, when operating with a diesel blend with 7.7 vol% ethanol at 4000 rpm and 10 bar mean effective pressure. The measured FSN (Filter Smoke Number) number in this case is, however, lower with the ethanol containing diesel. The same article describes a strong rise of the number of very small particles (<15 nm) in blend operation mode at 1800 rpm and 16 bar.

No significant differences in efficiency were measured with the alcohol blends at both load points.

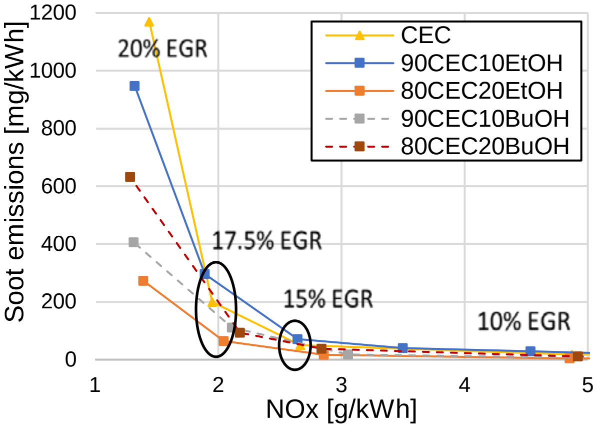

Figure 20: Soot-NOx-trade-off with different blends in OP-1500/15; MFB50 = 7.5 °CAaTDC

Summing up this results, operating the engine with a blend of diesel and alcohol generally produces less soot mass emissions, mitigates the soot-NOx conflict and doesn't affect the efficiency. The soot mass reducing effect gets more distinct at higher EGR rates. The effect on particle number in the exhaust gas is contrary at the high load point, leading to a higher number of smaller particles with later combustion centre position. In any case, the CO_2 benefit when using biogenous alcohols must be mentioned, whereas higher bio-alcohol content in the blend naturally results in less well-to-wheel CO_2 emissions.

5. Comparative Analysis

The insights gained from the engine studies clearly show the trends that can be expected with the use of the investigated fuels. In order to be able to compare their advantages and disadvantages for the diesel engine use in a quantitative manner, a direct comparison of the best points in the different applications is useful.

The high load point OP-1500/15 is critical for compliance with NOx and soot emission requirements due to the high combustion chamber temperatures and the low air-fuel ratio. The rise of the EGR rate causes a strong increase of soot emissions and a simultaneous reduction in efficiency. However, the strength of the oxygenated biofuels lies precisely in defusing the soot-NOx problem. Additionally, it is expected that the operation of the internal combustion engine at low loads will diminish proportionately as a result of the increasing hybridization of the drive train. These two considerations make it logical to compare the tested special fuels and combustion processes predominantly in OP-1500/15. However, the analysis could also be carried out analogously for the lower load point.

The overall assessment of the biofuel use is based both on the consideration of the combustion engine suitability and on the fuel production criteria. The assessed categories are efficiency, well-to-wheel and tank-to-wheel CO_2 emissions, particle mass and count. For a clearer presentation of the evaluation, characteristic numbers are defined, which represent the percentage change towards the diesel reference values. The diesel reference is given the number 100, e.g. 3% improvement in efficiency when using a biofuel would get the number 103, a deterioration of the same value - 97.

The well-to-wheel CO_2 savings potential for biofuel production is determined within the framework of the sustainability analysis carried out by the Technical University of Graz and has already been included in the "WTW CO_2" criterion. Thus, the CO_2 advantage increases with the substitution rate. The CO_2 savings in the production of ethanol from lignocellulosic biomass are assumed to be 47% [22] and for butanol 63% [23]. An emission characteristic number of 70, e.g., means, that the emissions sum up to only 70% of the CEC reference emissions. The system costs, which increase with the increased complexity of the use of the alternative fuels, are assessed in the column "System complexity". This assessment criterion accounts for the main component costs of turbocharging, basic engine, fuel system, exhaust gas aftertreatment and exhaust gas recirculation (or reformer for syngas production). Table 7 summarizes the evaluation for the best operation points. The improvements against the conventional CEC operation are displayed in green colour. Significant potentials of the use of biogenic alcohols in the diesel engine are visible. For example, by operation with ethanol intake manifold injection 31% well-to-wheel CO_2 is saved and the particle mass in the exhaust gas is reduced to only 9% of the particle mass emissions of the diesel reference operation, which makes a reduction of 91%.

It has to be noticed again, that the higher particle count production in blend direct injection operating mode occurs only at high load testing. In OP-1500/5 both particle mass and count are reduced very effectively.

6. Summary and Outlook

Summary

Within the research project "Regenerative oxygen-containing diesel substitute fuels as an opportunity for efficiency enhancement and emission reduction - OxyGen2", the suitability of biofuels for diesel engine use is investigated. This article presents the results for two bio-alcohols – ethanol and butanol. The investigation of three variants for fuel introduction into the internal combustion engine is characteristic for the project: injection of synthesis gas as a product of reforming fuel with exhaust heat, intake manifold injection and direct injection.

The fuel reforming using exhaust heat is investigated in experiment and simulation. There is a good consistency between test bench and simulation results. The resulting synthesis gas is used as a fuel in a modified diesel engine and the successful technical feasibility of the combustion process is confirmed. The addition of synthesis gas produces an efficiency disadvantage. The raise of the fuel heating value due to the reforming is not high enough to compensate for the loss of efficiency during the combustion. A higher efficiency of the reforming process is achieved with low λ values and high exhaust gas temperatures, however both parameters correspond to a decrease of the combustion efficiency of the compression ignition engine. However, at this point it is important to emphasize that the combustion chamber is designed for a conventional diesel combustion process and not for gas combustion. The high methane and hydrogen emissions significantly degrade the motor efficiency. By adapting the combustion chamber design, a reduction of the occurring losses is possible.

The intake manifold injection of alcohol allows high substitution rates, up to 85% depending on the operation point. At higher loads within this operation mode the efficiency is increased by up to 2% points.

Table 7: Overall evaluation of the investigated fuels and operation modes; OP-1500/15; charging pressure 1250 mbar (rel); NOx emissions maximum 2 g/kWh

Fuel(combination)	Efficiency	WTW CO_2	CO_2 (engine)	PM	PM#	System complexity
CEC diesel DI	100	100	100	100	100	~
CEC+43%energ. syngas	97$^{1)}$/98$^{2)}$	82$^{1)}$/75$^{2)}$	98	43	43	- -
CEC+60%energ. EtOH SR	103	69	90	9	8	-
CEC+40%energ. BuOH SR	101	74	96	26	43	-
90CEC10EtOH DI	99	98	101	94	181	~
80CEC20EtOH DI	100	94	99	48	133	~
90CEC10BuOH DI	99	96	101	81	163	~
80CEC20BuOH DI	100	90	99	71	157	~

1) Reforming of ethanol considered; **2)** Reforming of butanol considered; **DI** direct injection; **SR** intake manifold injection; **Efficiency** Characteristical number for the efficiency compared to CEC diesel reference operation; **WTW CO_2** Characteristical number for the well-to-wheel CO_2-emissions compared to CEC diesel reference operation; **CO_2(engine)** Characteristical number for the engine (tank-to-wheel) CO_2-emissions compared to CEC diesel reference operation **PM (#)** Characteristical number for the particle mass (count) compared to CEC diesel reference operation; **System complexity** Complexity and costs for the respective operation mode; **~** unchanged compared to the original system; **-** more complex than the original system; **- -** much more complex than the original system

A significant reduction of well-to-wheel CO_2-emissions is visible in all cases, being higher with higher alternative fuel content and depending on the production process of the biofuel. The use of ethanol or butanol also proves a benefit in tank-to-wheel CO_2 emissions in most of the operation modes. The reduction here results mainly from a higher H/C ratio of the fuel, since engine efficiency doesn't change that much.

A considerable advantage of the alcoholic fuel usage is the high reduction in soot emissions, especially when injecting the fuel into the intake manifold. Alcohol-blended diesel also produces less particulate mass, however it is found that the number of particles may rise under some operating conditions (high load). The reasons for this phenomenon lie within the changes in spray formation and evaporation.

Enhanced tolerance towards higher EGR rates allows a further in-cylinder reduction of nitrogen oxide emissions.

The results in this article prove the potential of alcoholic fuels to reduce emissions and enhance the efficiency of the compression ignition engine and verify the the suitability of the methods depicted in the project.

Outlook

The list of oxygenated biofuels investigated in this project goes beyond the bio-alcohols. Ethers and furans are in the focus of the scientific activity as well. Dibutylether and 2-Methyltetrahydrofuran, for example, are also being investigated. In particular, innovative synthetic biofuels such as oxymethylene ethers (OME) promise significant improvements of the emissions behaviour of diesel engines and have the potential to find a growing application in the future [24], [25], [26]. From today's point of view, the production of biogenic OME has economic disadvantages, since it is associated with higher investment costs, system complexity and larger amounts of biomass. However, the advantages of the use in a combustion engine make this fuel group highly interesting and represent a motivation for detailed investigations.

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Operation of a Diesel Engine with Biogenous Oxymethylene Ethers

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Summary

Fuels from lignocellulosic biomass have the potential to contribute to the target of sustainable future mobility by reducing fossil CO_2 emissions of the transport sector. Of special interest for the diesel engine are oxygenated fuels, since they can help to solve traditional conflicts of objectives like the soot-NOx trade-off or the efficiency-NOx compromise. Oxymethylene ethers (OME) are among the most promising fuel candidates. The diesel engine suitability of these substances is investigated in this study. The fuels used are OME1 and OME2-6, injected in pure form as well as a diesel-biofuel blend with 20% OME share. The combustion tests are combined with an advanced analysis and economical assessment of oxymethylene ethers production as 2nd generation biofuels. OME shortcut production simulation showed a very high greenhouse gas savings potential, accompanied with high plant investment costs.

1 Introduction

Climate change concerns and legislative regulations require adequate measures for reducing the human impact on global warming. Increasing production and usage of renewable energy is seemingly the key to a biocarbon based future and an economical and energetic independence from fossil fuels on a global scale. The transport sector contributes about 23% [1] of the total greenhouse gas emissions in the European Union. Therefore reducing CO_2 from traffic is crucial to achieve the desired climate stabilising objectives. Since no tremendous improvements of the internal combustion engines efficiency can be expected at this late point of technical evolution, the focus is extended to defossilization of fuels. Directive 2009/28/EC of the EU [2] set the framework for the integration of energy from renewable sources and suggested a 10% renewable energy share in transport by 2020. The new Directive 2016/0382 [3], which is currently at a discussion state, introduces a fuel supplier obligation to provide a share of advanced renewable fuels. They have to account for at least 6.8% in 2030, excluding the renewables from 1st generation biofuels. The sub-target for advanced biofuels and biogases is 3.6%. Additionally, the directive describes a member state option for a progressive reduction of energy produced from food or feed crops (1st generation biofuels) to 3.8% in 2030.

The diesel engine with its high efficiency represents the backbone of modern mobility, however its typical exhaust gas emissions make further development inevitable, if future air quality regulations are to be met. Second generation biofuels have the potential to reduce the CO_2 emissions of the transport sector, without being in an ethical contradiction to food production. Oxygenated fuels provide superior combustion properties, since they can help to solve traditional conflicts of objectives like the soot-NOx trade-off or the efficiency-NOx compromise. Among many candidates oxymethylene ethers are discussed to be the most promising alternatives to fossil fuels for future diesel engine powering. They can completely substitute diesel or may be mixed with it and provide an almost soot free combustion. This strategy might wipe out major constraints of diesel engines by improving emissions and efficiency.

Lignocellulosic biomass is a sustainable renewable energy resource which can easily be upgraded to methanol through biomass gasification. Worldwide methanol is a widely used bulk chemical and the production methods are well established. Unfortunately, this toxic alcohol isn't suitable for diesel engine fueling. Further processing can be applied to obtain Dimethylether (DME), an already successfully tested diesel alternative. DME is the simplest ether compound, described by the structural formula $H_3C\text{-}O\text{-}CH_3$. However, DME is difficult to handle, since pressure of 5 bar is necessary to liquefy the gas. By inserting oxymethylene units into the DME molecule, polyoxymethylendimethylethers (POMDME) are synthesized. Their properties depend on the molecule size and therefore on the number of oxymethylene units. The resulting formula is $H_3C\text{-}O(\text{-}CH_2O\text{-})_n\text{-}CH_3$, with n=0 for DME and n=1 for POMDME - Dimethoxymethane. Molecule size with $n \leq 6$ offers combustion properties for alternative fuels. These fuels are simply specified as oxymethylenether or OMEn.

Oxymethylene ethers are colourless liquids, their specific mass, cetan number and kinematic viscosity rise with molecule length. The main factors, responsible for nearly soot-less combustion are the high oxygen content of over 45 wt% and the absence of C-C bonds (C1 oxygenates). The significantly lower calorific value of OMEs can be considered as a disadvantage compared to conventional diesel. Generally, OME3-6 are found to have the best suitability for diesel engine applications, since their properties (boiling point, lubricity, viscosity) are closest to diesel [4], [5], [6], [7]. Many elastomers in present fuel systems are incompatible with OMEs due to their high chemical aggressiveness and construction materials have to be properly chosen [5].

Most of the OME combustion investigations found in literature discuss OME1 or mixtures of diesel and OME1, because until recently higher grade OMEs were extremely difficult to synthesize. Exhaust soot emissions are reduced by OME1 add-on to diesel [8], the real advantage of OME is however demonstrated by using it as a pure substance [6], [9]. In this case the soot-NOx trade-off is avoided. It is proved, that higher methane emissions are produced, when the engine is operated with

OME1 at near stoichiometric conditions. Methane emissions are of great concern for exhaust aftertreatment, because methane has to be valued 25-times the greenhouse effect compared to CO_2 [10] and it can't be sufficiently converted by the oxidation catalyst at temperatures below 500°C [11]. The potential of OME1 combustion to meet current soot and particle emissions limits without any exhaust aftertreatment system is highlighted in [12].

OME2 has a very similar soot and particle emission characteristic to OME1, even at understoichiometric combustion conditions [5]. Particle mass emission was found to remain below 1 mg/kWh regardless of the EGR rate for both OMEs, with an Euro VI limit for heavy duty engines of 10 mg/kWh. Both fuels share a similar CH_4 emission characteristic, when the air-fuel equivalence ratio approaches or undershoots the value of 1.

The tests with a mixture of the higher OME3-6 and the comparison of combustion results with OME1 and paraffinic diesel fuel in [4] confirm the previous findings of extremely low soot and particle emissions for OME combustion. An advanced study on soot formation/oxidation of OMEs in a constant volume chamber was conducted in [13], using both optical and exhaust measurement methods. Again, the core findings are that pure oxygenated fuels are characterized by nearly smokeless combustion and that even small OME amounts in commercial diesel fuel permit significant soot reductions.

The production technology is an essential aspect in every discussion about alternative fuels [14]. Based on preliminary OME production path analysis [15-20], [21] continues the investigations and makes an assessment of OME production costs and concludes, that the production is competitive to conventional diesel fuel production. The feed stock for OME production in the cited study was, however, market available methanol. It may be assumed that the methanol is of fossil origin. OME production routes are also discussed in [22] and [37], but an economic review is not made in this studies.

The present work stands out for the investigation of combustion properties of both OME1 and a mixture of OME2-6, where the fuels are supplied to the diesel engine in pure form as well as in diesel blend with 20 vol% share of OME. A detailed analysis of OME production from lignocellulosic biomass is conducted in order to assess economic feasibility and ecological sustainability of a large scale facility and gives a perspective about the suitability of bio-oxymethylene ethers as future alternative to fossil diesel.

2 Investigated fuels

In this study, a certified diesel fuel is used as reference and is briefly referred to as CEC. Dimethoxymethane (OME1) is the first representative of the investigated oxygenates and is supplied to the engine neat. Due to its low cetan number 37.6 [9] and insufficient lubricity properties (HFRR value of 759 µm [9]), OME1 is provided with an additive. In accordance to literature [9], [5], [7], [23] an additive package of polyethylene glycol dimethyl ether 1000 (Clariant) as cetan booster and a copolymer of poly (ethylene / propylene) glycol alkyl ether (traded as Synalox 40 D700 by Dow Chemical) as lubricant is used. Both additives are added to OME1 by 3 wt% each. The resulting fuel is then called OME1a and is described in a patent [24] as a result of earlier OME investigations. A mixture of the higher OMEs n=2-6 is the second investigated fuel, specified as OMEmix. Its main components are 78.7% OME3 and 19.8% OME4. No additive is used with this mixture, because cetan number and lubricity properties are sufficient for engine use. Additionally, two diesel-OME fuel blends are tested. The Renewable Energy Directive 2009/28/EC suggests a 10% renewable content in the fuel used for transport application. Most of it is assumed to be achieved by fuel blends with biogenous shares. This value, however, is only applicable in regard to a mean value of the bio-content in transportation fuels. In order to further explore the potential of OME add-on, the substitution rate for the engine tests accounts for 20%. In the first case a blend of 80 vol% CEC and 20 vol% OME1 is used and in the second case a mixture of 80 vol% CEC and 20 vol% OMEmix. OME energy content in the blend is 12.6% for both mixtures.

All fuels were subject of analysis, the most import results are presented in Tab. 1. The cetan number of OME1a can't be determined with the standard method due to the low boiling point. Together with HFRR and kinematic viscosity these data were taken from literature [9]. For viscosity of the OME blends is referred to [25].

	CEC diesel	OME1a	OMEmix	20% OME1	20% OMEmix
Cetan number [-]	54.5	48.3	52.8	50.4	52.1
Density (15 °C) [kg/m³]	833.5	880.3	1046	842.8	876
Lower calorific value [MJ/kg]	42.68	23.22	19.4	38.56	37.36
HFRR [µm]	413	297	409		
C-fraction [wt%]	85.4	49.1	43.3	78.7	74.8
H-fraction [wt%]	14.2	10.6	8.7	13.1	12.5
O-fraction [wt%]	-	40.3	47.9	7.9	11.8
H/C-Ratio (atomic)	1.92	2.66	2.416	2.011	1.98
Boiling point [°C]	173-363	42	105-197		
Stoichiometric ratio [kg/kg]	14.5	7.32	5.9	13.06	12.44
Air demand for stoichiometric combustion [kg/MJ]	0.340	0.315	0.304	0.339	0.333
Heat of evaporization [kJ/kg]	358	376			
Kin. Viscosity [mm²/s]	2.4 (40°C)	0.58 (20 °C)	0.96 (40°C)	~1.3 (40°C)	~2 (40°C)

Tab. 1: Characteristical data of the tested fuels

3 Test engine and test methodology

3.1 Test engine

A Daimler in-line four-cylinder diesel motor OM 646 Evo is used as test engine. The low availability and the high purchase costs of the fuels make single cylinder operation reasonable. Only the first cylinder is fired, the other three are deactivated and their gas exchange is separated from the gas exchange of the fired cylinder. The cylinder has a displacement of 537 cm^3 and a compression ratio of 17.5. Bore and stroke are 88 and 88.34 mm, respectively. The original high pressure common rail injection system is equipped with seven-holes nozzles solenoid injectors. Charging is performed with an external electrically driven supercharger. An electrically adjustable flap valve is used to produce the necessary exhaust gas pressure. Cooled high-pressure exhaust gas recirculation is applied. The standard exhaust gas aftertreatment system has been removed. Emissions sampling takes place in the raw exhaust gas. Temperature of the charge air und the fuel are conditioned.

The first experiments with oxymethylene ethers made clear, that the standard materials used in the fuel system are definitely inapplicable. A strong swelling of the seals and the fuel hoses was observed. In the search for suitable materials the perfluoroelastomer FFKM and PTFE (Teflon) seemed to be promising choices. FFKM is however expensive and difficult to obtain, therefore PTFE is successfully used in the whole fuel system, even in the high pressure fuel pump.

3.2 Measurement equipment

The test engine is equipped with high and low pressure indication and standard exhaust gas measurement, as well as AVL Micro Soot Sensor 483 and AVL Particle Counter 489. Additionally an AVL Smoke Meter 415S is used.

3.3 Test methodology

The investigations are carried out at two operating points. The first point is defined by an engine load of 5 bar indicated mean effective pressure at 1500 rpm, the second at 15 bar indicated mean effective pressure also at 1500 rpm, see Tab. 2.

Load point notation	OP-1500/5	OP-1500/15
Speed [min^{-1}]	1500	1500
p_{mi} [bar]	5	15
Rail pressure [bar]	~670	~1000, 1200+ (pure OMEs)
Injection pattern	single injection	single injection
Charge pressure [mbar]	variable	1250
Δpressure exhaust-charge [mbar]	270	500

Tab. 2: Investigated operating points with engine parameters

Different variations are carried out at both operating points, the most important being the variation of the air-fuel ratio, the EGR rate and the MFB50% (by adjusting the start of injection). The difference between charge and exhaust pressure (negative scavenging pressure) is held constant through the variations, however, depending on the load point. This way the effect of the gas exchange on the indicated efficiency is being isolated and the influence of other combustion parameters can be better observed. The results of the variations are analysed and the optimum operating parameters for the respective fuel are determined. The pure diesel operation is the reference for the comparison. In order to create boundary conditions for the fuel comparison, an upper limit for NOx emissions of 2 g/kWh is set, which represents a basis for a possible further reduction with an exhaust gas aftertreatment system. The maximum charge pressure is limited to 1250 mbar (rel.).

All specific emission values in this study are with respect to indicated engine work.

4 Results of the combustion investigations

4.1 Emissions

4.1.1 NOx, Soot and particle emissions

The most effective measure for the in-cylinder reduction of the nitrogen oxide emissions is the increase of the EGR rate. In case of conventional diesel fuel, this leads to an increase of soot emissions, so that a compromise must inevitably be made when designing the operating parameters. Fig. 1 shows the soot-NOx trade-off for the CEC diesel reference in BP-1500/5 and compares it with the behaviour of the diesel-OME fuel blend and the operation with neat OMEs.

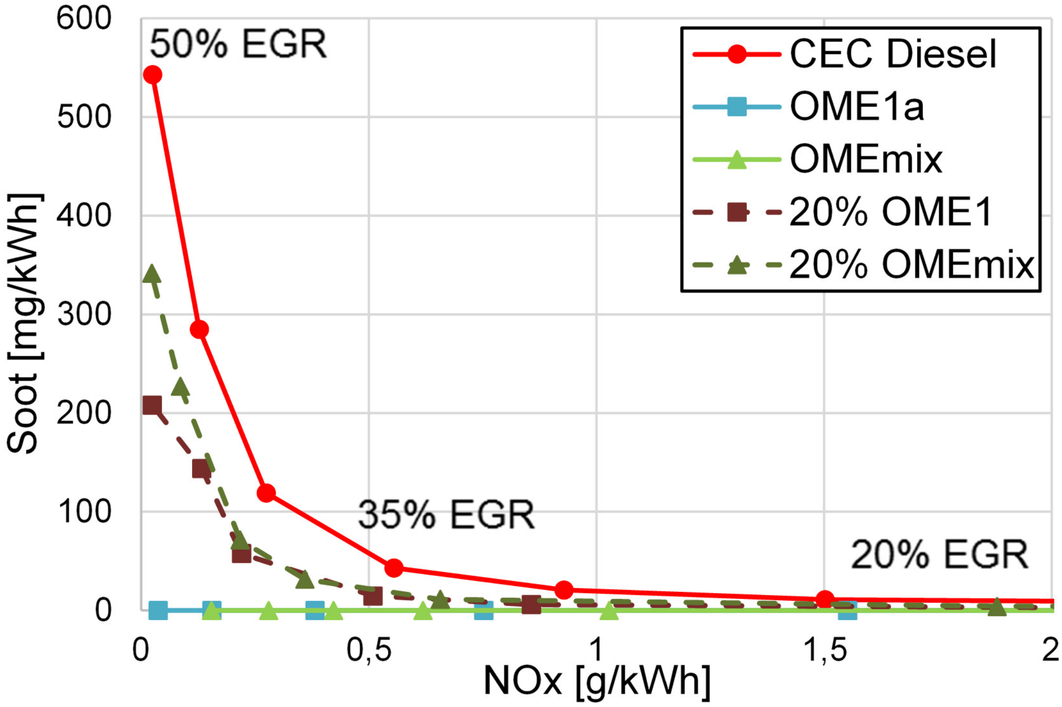

Fig. 1: Soot-NOx trade-off at OP-1500/5; variation of EGR rate; charge pressure const. 130 mbar, MFB50% 7.5 °CAaTDC

The rise of soot emissions is profound in the case of diesel for EGR rates higher than 35%. Blending the fuel with 20 vol% OME proves a soot reduction effect of about 50% at a NOx emission value of 0.25 g/kWh. The advantage is obvious even at higher EGR rates and allows using higher amounts of recirculated exhaust gases in order to achieve further reduction of nitrogen oxides, without exceeding given soot limits. In general, it is found that blending the fuel with OME1 has a slightly higher potential for soot reduction than with OMEmix despite the fact, that OME mix contains more oxygen. The lower boiling point of OME1 contributes to faster spray evaporation and therefore less soot formation. This effect is visible, when the soot formation behaviour of both blends is compared – at very high EGR rates the 20 vol% OME1 blend produces less soot than 20% OMEmix.

As expected, the soot-NOx trade-off is completely eliminated when using neat OME1a or OMEmix. For both fuels the soot emissions remain below 0.1 mg/kWh even at 50% EGR, resulting in an approximate λ-value of 1.2. This results also confirm the suitability of the chosen additive package.

The dependence of the particle number on the EGR rate in Fig. 2 reveals, that the addition of 20 vol% OME to diesel doesn’t provide the same emission reduction effect as on soot mass. The particle number is barely reduced when blending the fuel with OME1 and is almost unchanged with OMEmix. In these blends diesel still accounts for about 87% of the energy content in the fuel. Since OME burns soot free and additionally provides oxygen in the flame that can quickly react with the diesel molecules, the soot mass is reduced. If the evaporation behaviour and viscosity properties however support the formation of finer spray droplets, the number of particles may rise even when the whole soot mass is reduced. The measurements confirm this assumption and suggest that blend operation emits more but finer particles. The origin of these particles must lie in the diesel fuel, as the neat oxymethylene ether substances don’t produce any particle emissions, as can be seen in Fig. 2. The same trend of reducing soot emissions while having no significant influence on particle count is reported in literature with a blend of diesel and 25% OME1 [6], however the indicated mean effective pressure in the reference source is 13 bar and the rail pressure is 1800 bar.

Pure OME1a and OMEmix show the same particle number, even at 50% EGR the value is in the range of $2x10^{11}$ particles per kWh, or $5x10^{4}$ particles per cm^{3}.

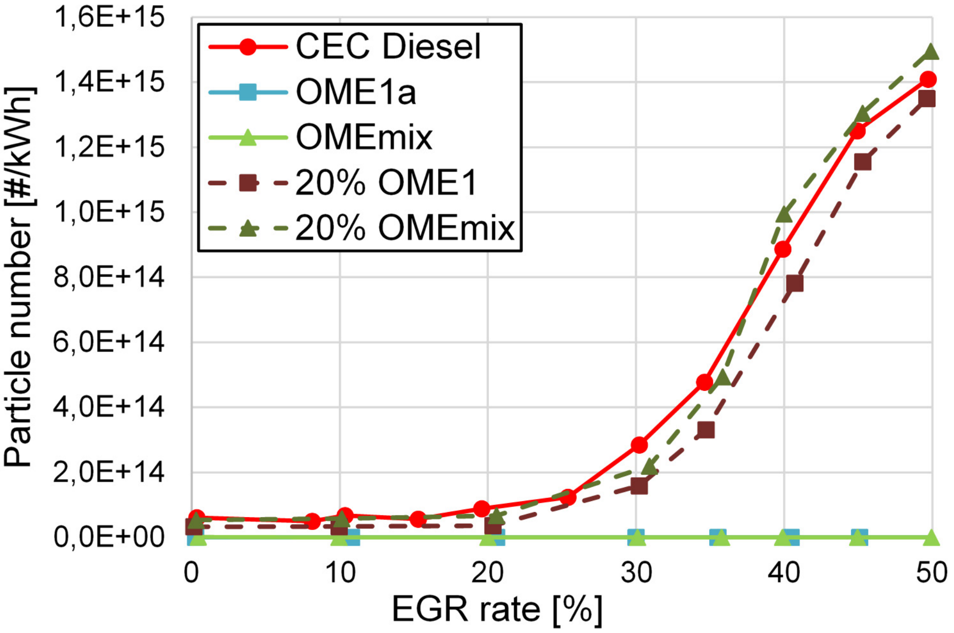

Fig. 2: Particle number as a function of EGR rate at OP-1500/5; charge pressure const. 130 mbar, MFB50% 7.5 °CAaTDC

At the higher load point OP-1500/15 no sufficient soot mass reduction is measured when operating on oxymethylene blends, see Fig. 3. Particle number is very similar for both diesel reference and blend fuel, Fig. 4. Nevertheless, the superior qualities of neat OMEs are present at higher loads as well. Soot mass and particle number are even further reduced with increasing EGR rate. The reason for this phenomenon is assumed to be the 70°C drop of combustion temperature (from 0% EGR to 20% EGR, calculated in a separate combustion analysis) and an associated reduction of soot formation. At neat OME operation with 20% EGR lambda is 1.2, soot mass is below 1 mg/kWh and particle number is measured to be $1\text{x}10^{12}$ particles per kWh or $1\text{x}10^{5}$ particles per cm³. These values are still in the range of pollution concentration of ambient air in big cities [7], [26] and are achieved without any exhaust gas aftertreatment.

The results displayed in figure Fig. 3 show that the emissions of nitrogen oxides at OME operation aren’t reduced in the same way as in reference or blend operation. The analysis of the indicated data of the operation point with 20% EGR revealed, that despite equal maximum cylinder temperature, in the case of OME high temperatures are longer present on a time scale than with pure diesel. Therefore more time is available for NO to form. Additionally, combustion of the OMEs presented here requires less air and more air remains unreacted at constant manifold pressure. As a consequence the lambda value is higher for the OMEs (1.2 at 20% EGR and 1250 mbar charge pressure) than for diesel or the blends (1.1 at 20% EGR and 1250 mbar charge pressure) and more oxygen can react to NO. For both reasons NOx emissions are higher for OME operation than for diesel at the same EGR rate. It is logical to further increase the EGR rate in OME operation, however, combustion quality drops.

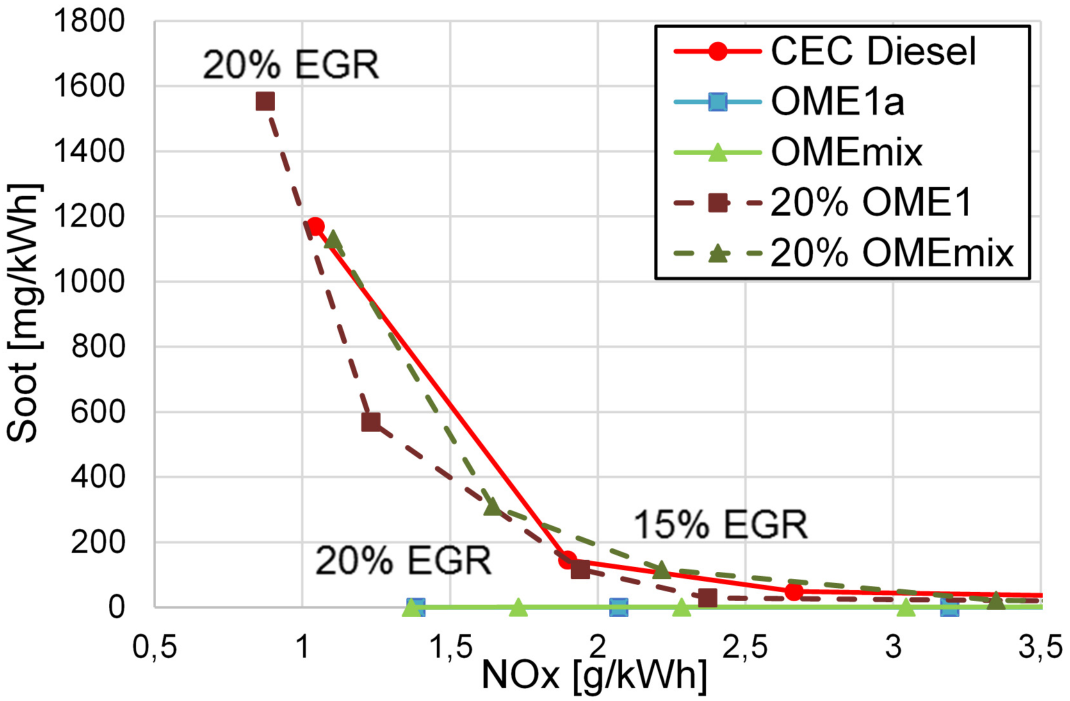

Fig. 3: Soot-NOx trade-off at OP-1500/15; variation of EGR rate; charge pressure const. 1250 mbar, MFB50% 7.5 °CAaTDC

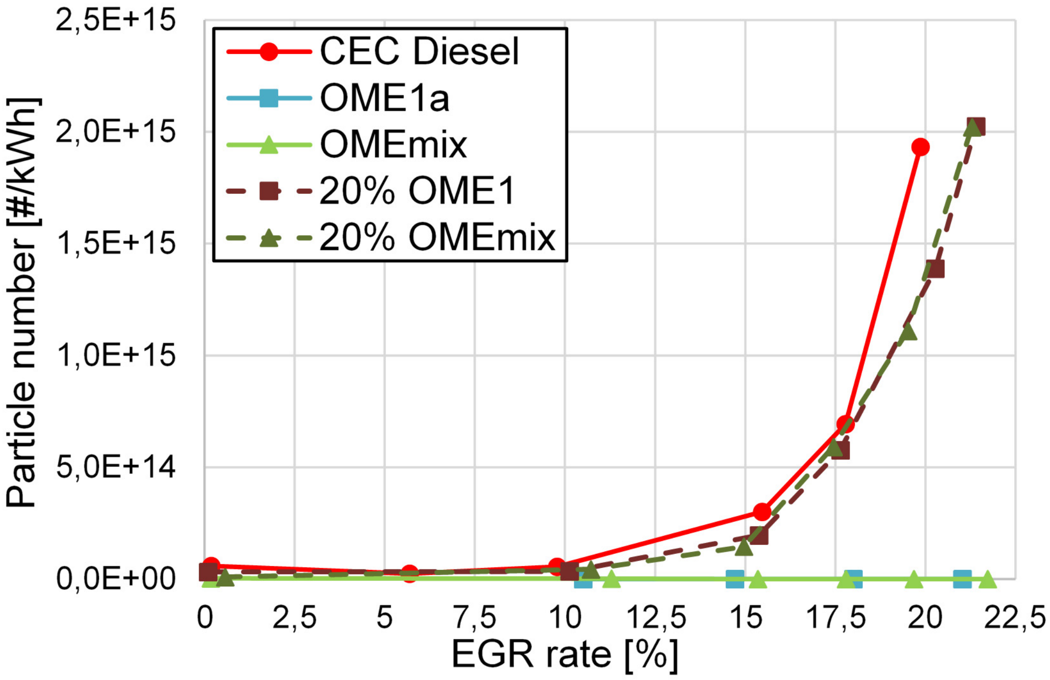

Fig. 4: Particle number as a function of EGR rate at OP-1500/15; charge pressure const. 1250 mbar, MFB50% 7.5 °CAaTDC

Fig. 5 shows the soot concentration in the exhaust gas of diesel engine operation with OME1a and the particle concentration in ambient air. This comparison really allows OME combustion to be called “soot free”, as stated in literature. Compared to OP-1500/5, the values of OP-1500/15 are twice as high, but it should also be mentioned, that the effect of the motor oil can’t be separated, since the oil used isn’t ash-free.

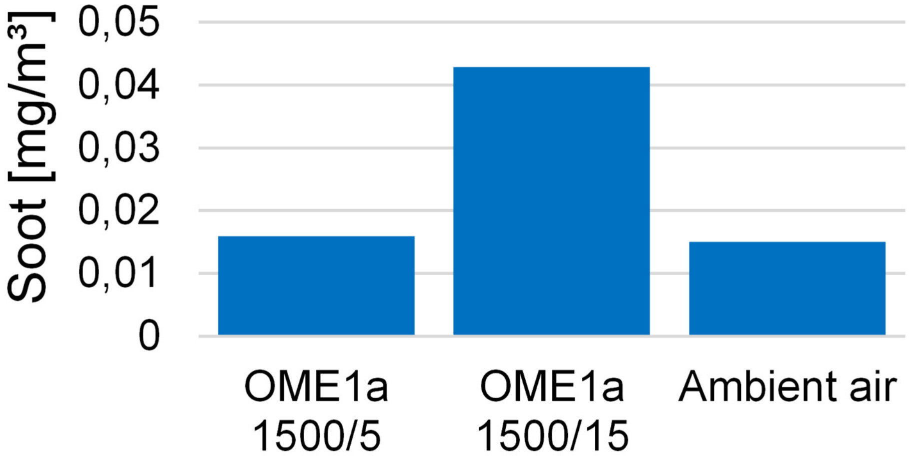

Fig. 5: Comparison of soot concentration in exhaust gas of OME1a operation and ambient air in Vienna (measured on 1. June 2017)

4.1.2 HC and CO emissions

Unburnt hydrocarbons and carbon monoxide are very efficiently converted in modern catalysts and don’t form a major challenge for exhaust aftertreatment. Still, these emissions may become a problem, if catalysts light-off temperature isn’t reached. Unburnt hydrocarbons are also evident for the combustion quality at different conditions and partly account for possible efficiency losses. In diesel engines HC and CO become relevant at low lambda values, because due to the combustion process some of the fuel is partly or not oxidised. The problem is especially observed at low engine loads, since cylinder temperature and pressure are relatively low and the combustion reactions are slowed down. Fig. 6 and Fig. 7 display the specific HC and CO emissions as a function of lambda at the low load point OP-1500/5. No difference is measured between diesel reference and the blend with 20 vol% OME1. The other fuel blend, 20 vol% OMEmix, is generally found to produce less unburnt hydrocarbons. Increasing the substitution rate to 100% reduces HC even further.

Regarding the CO emissions at low load, no particular differences are seen in Fig. 7. The emissions rise for all fuels at lambda values below 1.4. It has to be noticed, that neat OMEmix produces not only the least HC, but also the lowest CO emissions.

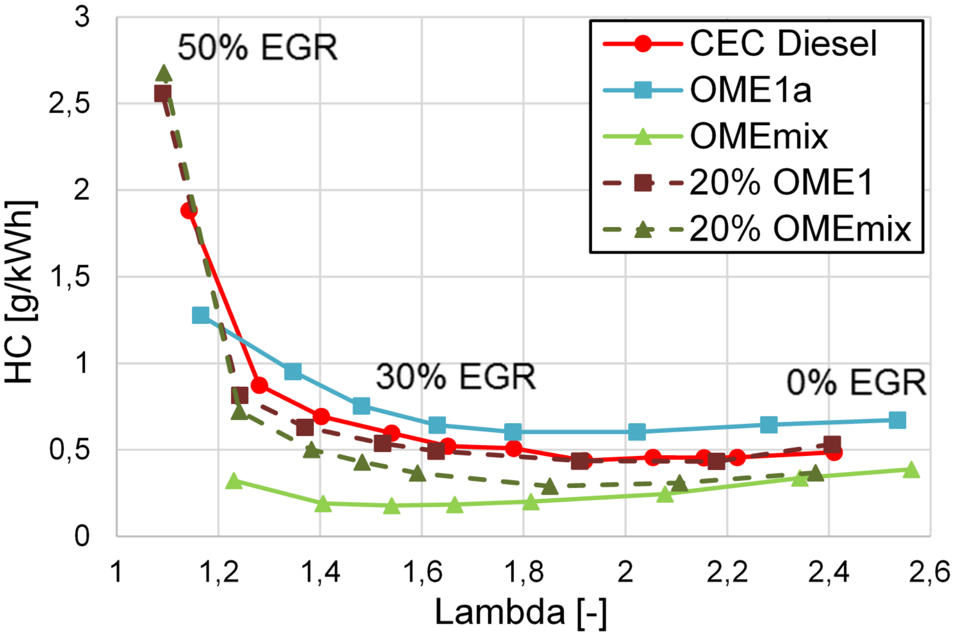

Fig. 6: Unburnt hydrocarbon emissions as a function of lambda at OP-1500/5; variation of EGR rate; charge pressure const. 130 mbar, MFB50% 7.5 °CAaTDC

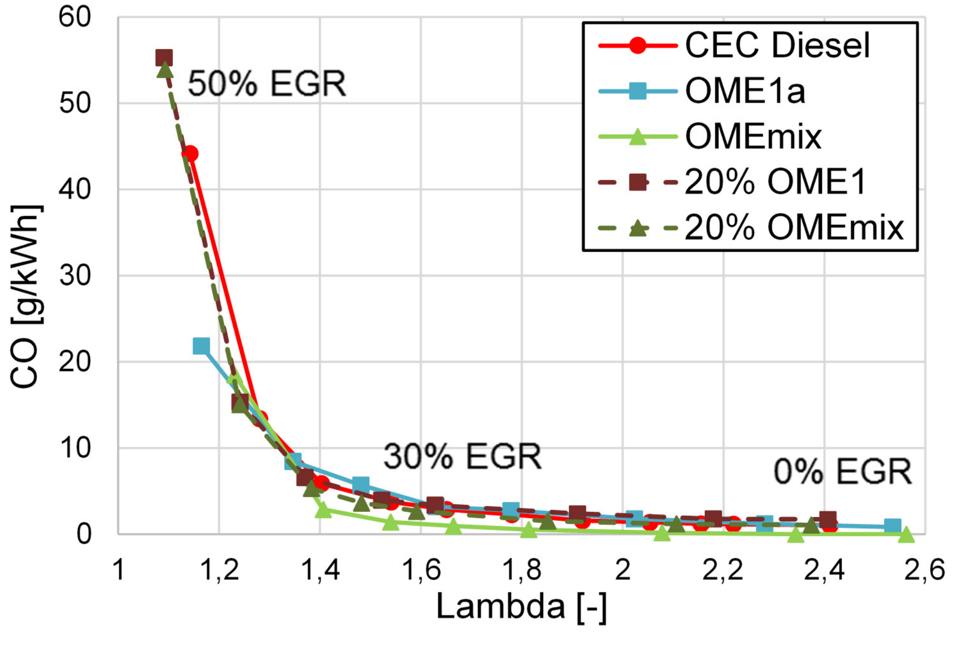

Fig. 7: Carbon monoxide emissions as a function of lambda at OP-1500/5; variation of EGR rate; charge pressure const. 130 mbar, MFB50% 7.5 °CAaTDC

Due to the higher prevailing temperatures at high load operation, the emissions of unburnt hydrocarbons in OP-1500/15 are noticeably reduced compared to the results at the lower load point, see Fig. 8. No significant difference is measured between the different fuels. It is found that OME1a and OMEmix produce slightly less CO emissions than the other fuels, but in general the curves displayed in Fig. 9 are very similar to the results at the lower load point.

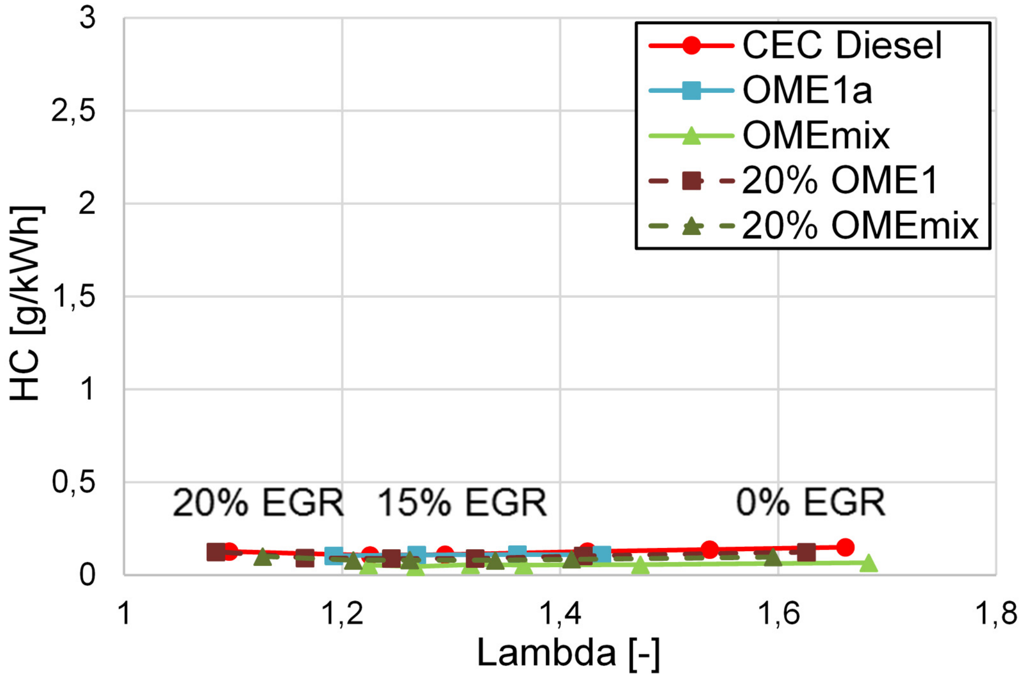

Fig. 8: Unburnt hydrocarbon emissions as a function of lambda at OP-1500/15; variation of EGR rate; charge pressure const. 1250 mbar, MFB50% 7.5 °CAaTDC

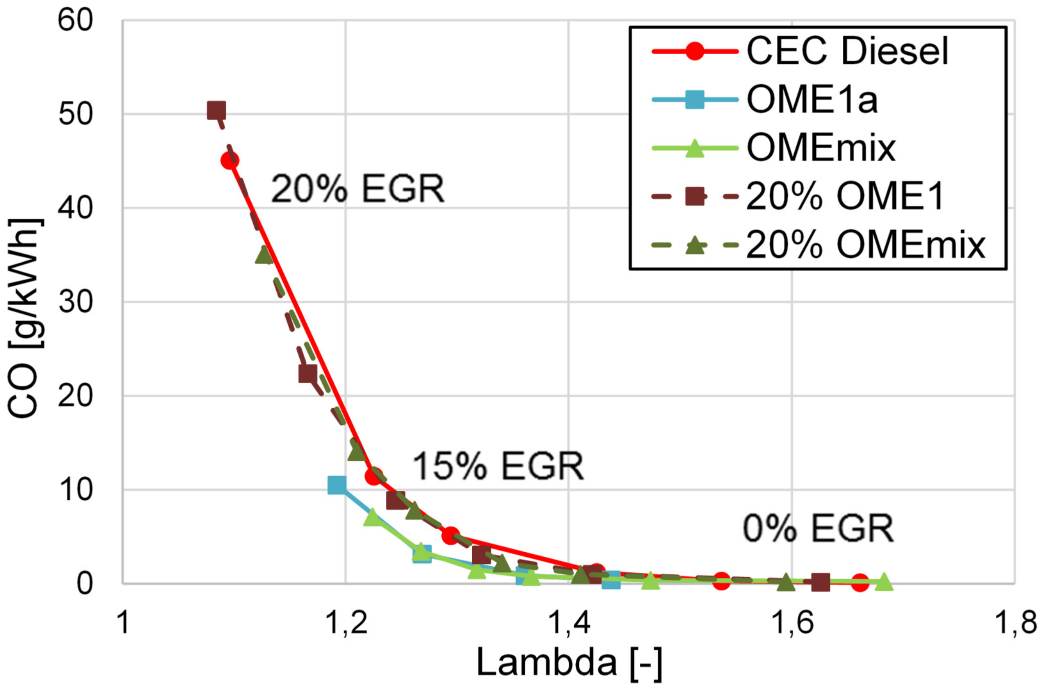

Fig. 9: Carbon monoxide emissions as a function of lambda at OP-1500/15; variation of EGR rate; charge pressure const. 1250 mbar, MFB50% 7.5 °CAaTDC

4.2 Efficiency and combustion analysis

The thermodynamic analysis of the low load point operation revealed no difference in combustion between diesel, diesel-OME blends or neat OMEs. The different fuels, however, required an adjustment of the injection timing, in order to achieve the same MFB50%. The indicated efficiency is measured to be 38.5% at an optimal MFB50% at 7.5 °CAaTDC (the resolution at the MFB50% variations is 2.5 °CAaTDC starting at 0 °CAaTDC). A variation of the EGR rate at constant MFB50% of 7.5 °CAaTDC doesn’t affect the combustion efficiency until reaching 45% EGR. At 50% EGR the lambda value is 1.2 and efficiency decreases.

At OP-1500/15 the limit set for nitrogen oxide emissions leads to efficiency values that are significantly lower than the theoretically possible combustion efficiency if NOx emissions weren’t taken into account. If the combustion position is to be held at optimum, 17.5% EGR is needed to achieve the limit of 2 g/kWh NOx, as depicted in Fig. 10. The dependence of the NOx emissions on the EGR rate shows a linear trend and it is very similar for all investigated fuels.

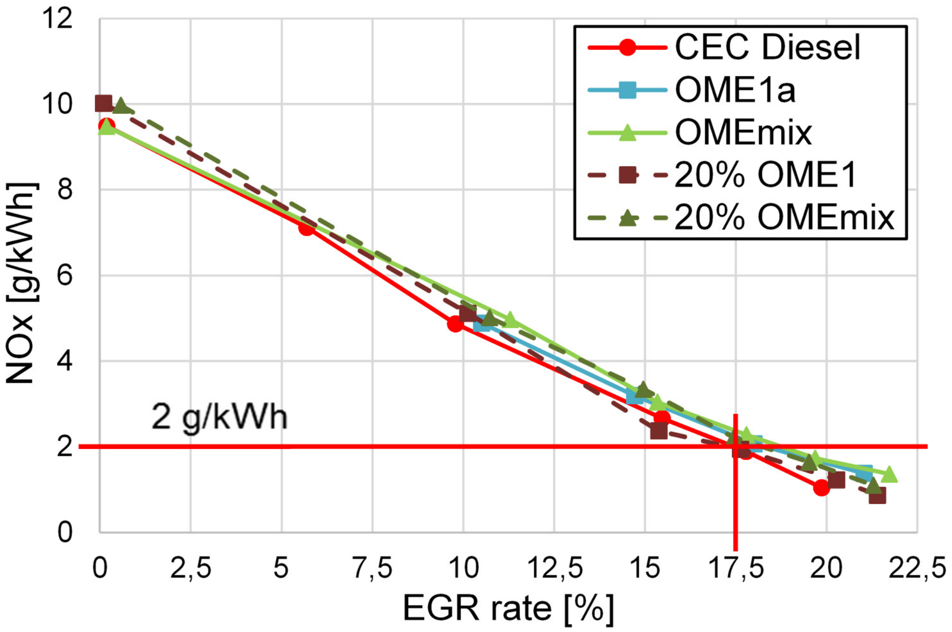

Fig. 10: NOx emissions as a function of EGR rate at OP-1500/15; charge pressure const. 1250 mbar, MFB50% 7.5 °CAaTDC

The way the indicated efficiency changes with increasing the EGR rate is shown in Fig. 11. Both OME blends show higher tolerance against high amounts of recirculated exhaust gas than diesel, however their efficiency is comparable to the efficiency of diesel reference operation. The efficiency of operation with neat OMEs is at a lower level until 20% EGR, but it doesn’t decrease the same way as with other fuels when raising the EGR rate. For this reason, the difference to the efficiency of diesel reference at 2 g/kWh NOx is noticeably reduced.

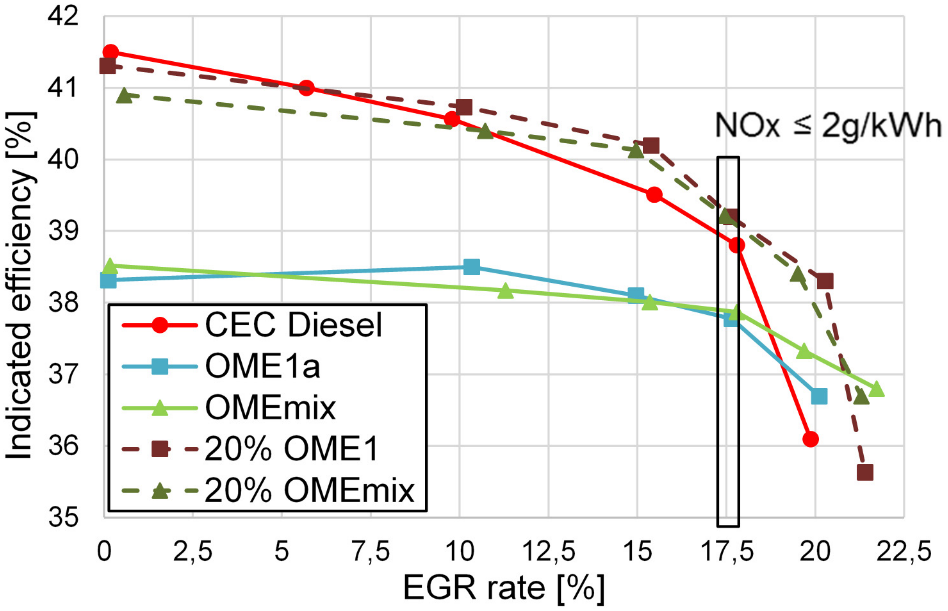

Fig. 11: Indicated efficiency as a function of EGR rate at OP-1500/15; charge pressure const. 1250 mbar, MFB50% 7.5 °CAaTDC

As seen in Fig. 3 and Fig. 4, operation with 17.5% EGR at high load produces much more soot and particle emissions than with 15% EGR. However, as displayed in Fig. 12, at operation with 15% EGR the injection timing has to be adjusted so that MFB50% takes place at 12.5 °CAaTDC, otherwise the NOx limit isn't met. The efficiency plots in Fig. 13 prove, that operation with 15% EGR and MFB50% 12.5 °CAaTDC is preferable to operation with 17.5% EGR and MFB50% 7.5 °CAaTDC (see correspondent indicated efficiency in Fig. 11).

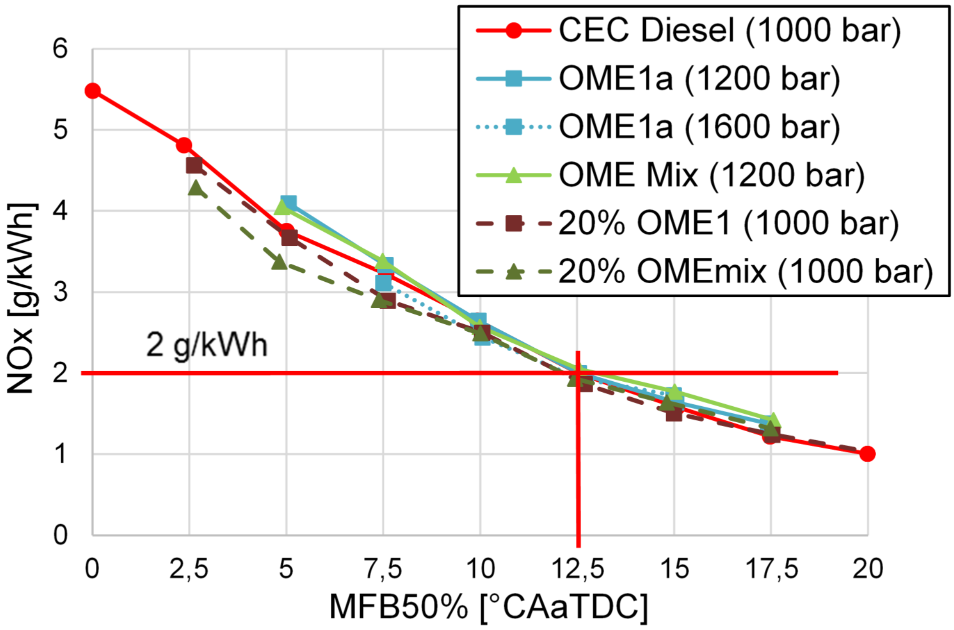

Fig. 12: NOx emissions as a function of MFB50% at OP-1500/15; charge pressure const. 1250 mbar, 15% EGR

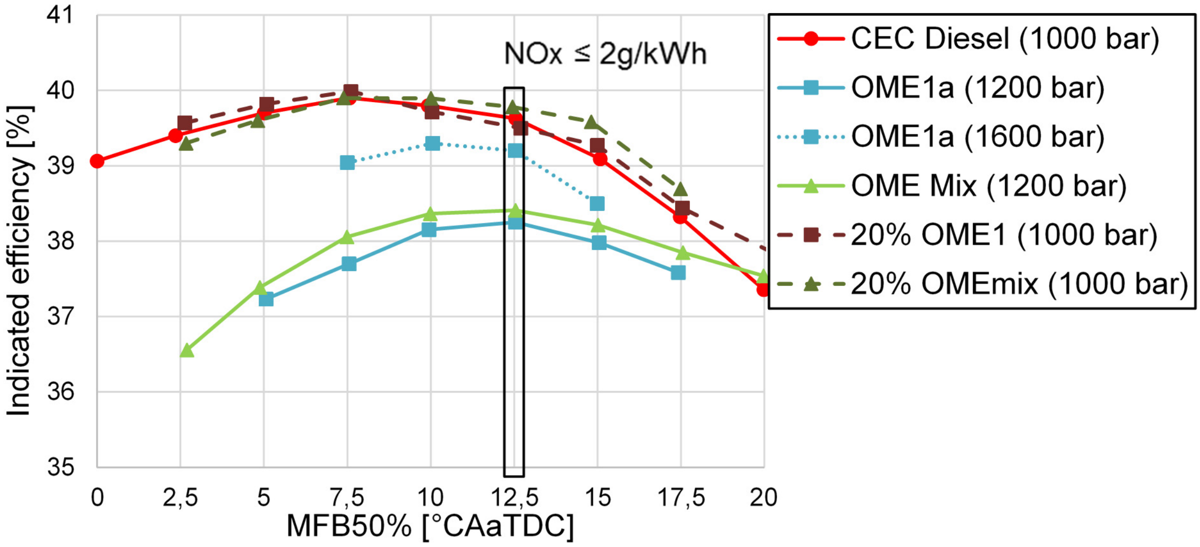

Fig. 13: Indicated efficiency as a function of MFB50% at OP-1500/15; charge pressure const. 1250 mbar, 15% EGR

Fig. 13 visualizes, that there is no efficiency difference between diesel and the diesel-OME blends. It is also shown, that the efficiency of neat OME operation lies almost 2% points below the reference values. Due to the much lower lower heating value of OME compared to diesel, the fuel injection takes more time and results in an extended duration of the main combustion, which decreases the thermodynamic efficiency. The injection pressure was chosen to be 1200 bar for the investigations with pure OMEs (for comparison diesel is injected with 1000 bar), in order to reduce the injection duration. This step, however, was not enough to achieve this. By further increasing of the injection pressure a part of this drawback can be compensated, as exemplarily shown for OME1a at 1600 bar injection pressure, but diesel efficiency can’t be completely matched.

In contradiction to the common case and to the diesel reference results, at neat OME operation with 1200 bar injection pressure the position of optimal efficiency MFB50% is not in the range of 7-10 °CAaTDC but is moved to later values. As can be seen from the indicated data below, Fig. 14, a bigger part of OME combustion takes places before the piston will reach TDC if injection pressure is not adjusted. This inevitably leads to higher thermodynamic losses, especially as a consequence of increased wall heat losses, which are the highest at TDC. For this reason moving MFB50% to a later position of approx. 12.5 °CAaTDC is favourable from efficiency point of view. It can be seen in Fig. 14, that the diesel reference has the more compact main combustion phase, followed by OME1a with increased injection pressure. OME1a at 1200 bar injection pressure shows a longer main combustion phase that also starts too early. However, the integrated heat release plot makes clear, that in general the neat OME fuels burn faster, as diesel has a longer post-combustion phase and needs more time until reaching MFB90%. The slower burn-off in diesel combustion is distinctive for the post-oxidation of the soot produced during the main combustion. This finding leads to the assumption, that if the flowrate of the injection system is adequately adapted, diesel efficiency could be beaten with OME without the need of increasing injection pressure. Latter also increases mechanical losses.

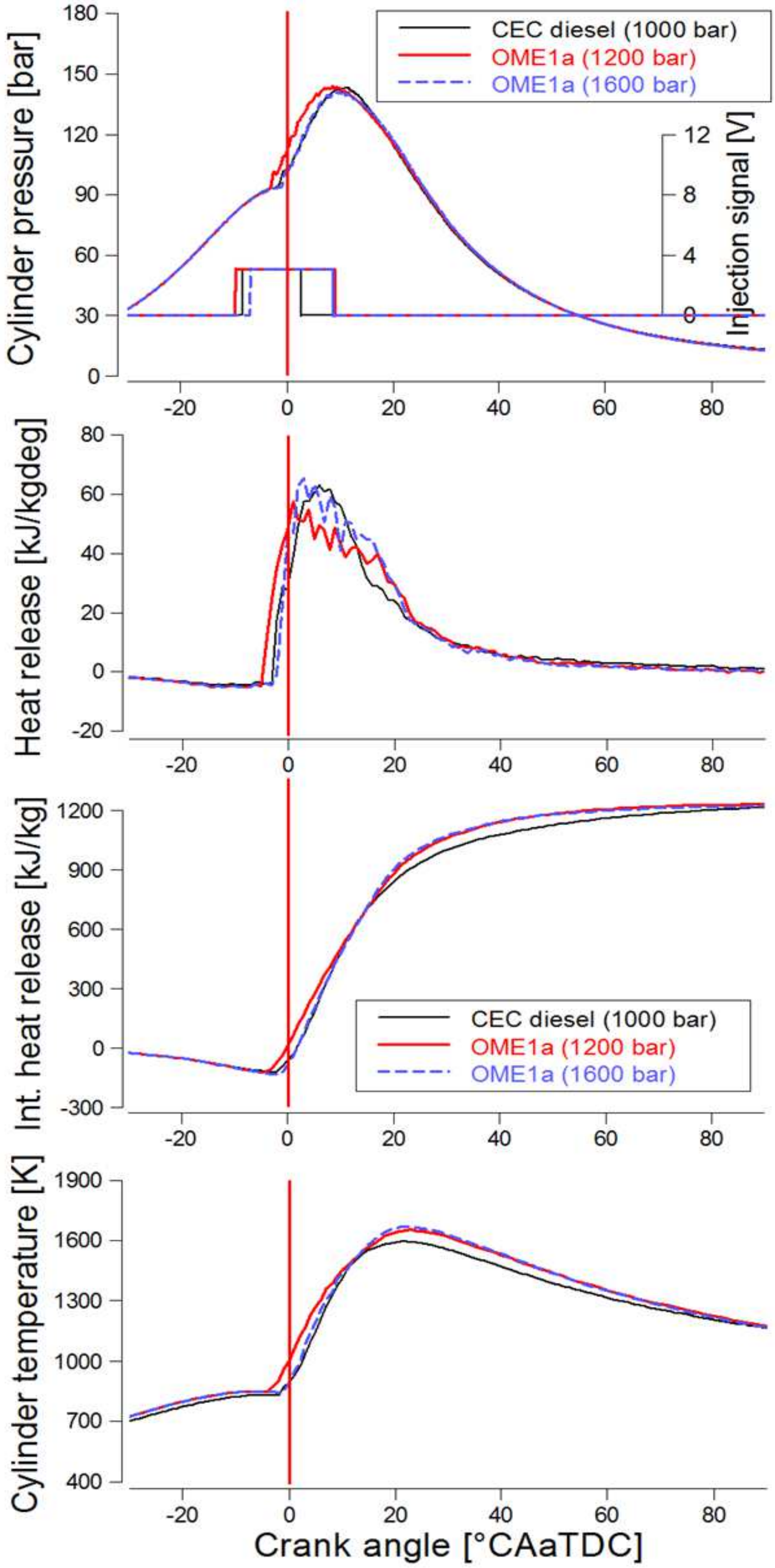

Fig. 14: Comparison of indicated data at OP-1500/15; 15% EGR; MFB50% 7.5 °CAaTDC

5 Analysis of POMDME production from lignocellulosic biomass

POMDME production is evaluated based on its industrial production needs and set up. Evaluation criteria are as follows:

Main categories:

- Energetic fuel efficiency: evaluation of the transfer rate of the chemical bound energy into the fuel fraction ($MJ_{Biomass}/MJ_{Fuel}$)
- Process effort: estimation of production costs of fuel production (€/MJ_{Fuel}) (includes biomass price, transport costs, production auxiliaries, energy costs as far as achievable)

Side categories:

- Greenhouse gas reduction: Calculations of greenhouse gas emissions of biofuels based on EU-Directive 2009/28/EG including cultivation and harvest, transport and production processes [2] and a comparison with standard diesel (% CO_2)
- Investment costs: Based on cost estimations and correlations of existing plants (Mio. €)

In a shortcut simulation POMDME production from lignocellulose is assessed. Basis is the production of 250.000 t/a of a POMDME mixture. Biomass gasification and subsequent methanol-synthesis is determined as reaction pathway. Fig. 15 shows a schematic overview of POMDME production from lignocellulosic feed.

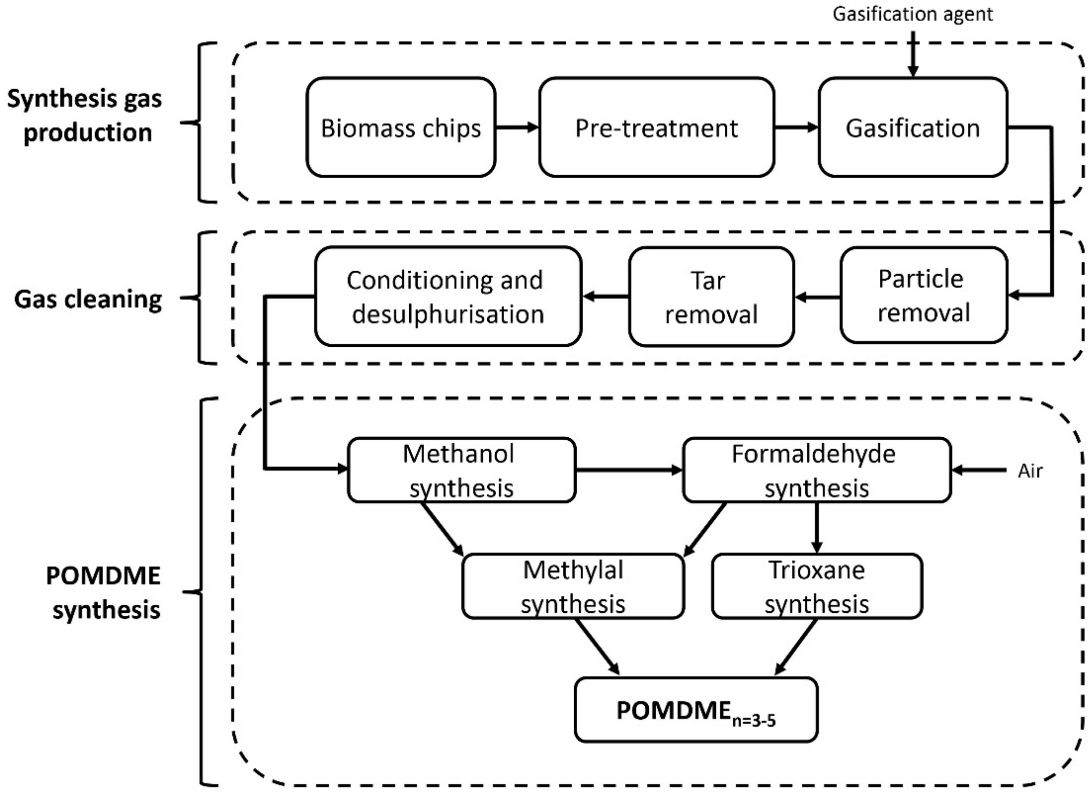

Fig. 15: OME production route based on lignocellulosic feed

Feed material in the calculations is spruce wood. Theoretical plant operating hours are 8000 h/a. Product composition is according to Burger et al. [20] 42,8% OME3, 33,8% OME4, 22,4% OME5 and 0,9% OME6. It is assumed that the whole biomass pre-treatment is part of the fuel production at a single biorefinery site. Biomass feed is 95 t/h spruce wood. After chipping with a drum chipper, this biomass amount corresponds to 368 m^3 of wood with a moisture content of 15% [28]. Selected gasification process is the Carbo-V process, operated by Linde [29].

Components	Gas composition [vol%]	Normalised gas composition for calculations [vol%]
CO	38 – 41	40,04
CO_2	24 – 27	25,85
H_2	31 – 33	32,43
CH_4	0,1 – 0,2	0,15
N_2	1 – 2	1,52
H_2S/COS	0,01	0,01

Tab. 3: Gas composition of Carbo-V process and normalised gas composition for calculations [29]

The Carbo-V process is a stepwise biomass gasification process. First step is a 450°C flash type pyrolysis, followed by an entrained flow gasifier for gaseous products and finally a fluidized bed gasifier for biochar gasification. [30] Gas composition after the gasification step is shown in Tab. 3. The Carbo-V process is limited to a scale of 160 MW_{th} fuel capacity, this corresponds to 720 t/d of bone dry biomass. Due to this fact a design of 3 parallel gasification units is performed. Gas cleaning is modelled with a selexol process. [31] To reach final sulphur concentration of less than 0.1 ppm in the feed gas, a metal absorber is applied. Methanol synthesis is simulated based on a slurry reactor of Air Products Liquid Phase Conversion company in a LPMeOH (low pressure methanol synthesis) process. [32] According to Fig. 15 the next building block in the OME process chain is formaldehyde. Formaldehyde production is simulated with the BASF process [33] to provide 22.000 kg/h for methylal and trioxane formation. Trioxane production is modelled based on the method of Grützner [34] and formaldehyde conversion is estimated with 100%, due to the application of a recycle stream. Additionally to trioxane, methylal is the second building block for OME production. A reactive distillation, with water as entrainer, according to Liu [35] is simulated and product purity of 98.7% is reached. Finally the production of OME mixture was calculated following the design of Burger et al. [20]. This design is based on a packed bed reactor with the acidic amberlyst 46 catalyst, with 3 subsequent distillation columns for product separation. Based on this model OME production is evaluated.

Evaluation results

Tab. 4 shows the results of the simulation. Based on these calculations the production of POMDME fuels is possible and feasible. To show a comparison with a 1st generation biofuel, a sodium methanol based biodiesel plant for rape seed oil conversion into biodiesel is simulated.

Fuel	Energetic fuel efficiency [$MJ_{biomass}/MJ_{Fuel}$]	Greenhouse gas reduction [% CO_2]	Process effort [€/MJ_{Fuel}]	Invest costs [Mio. €]
POMDME	2,77	70,9	0,025	532,2
FAME	1,01	38	0,026	16

Process effort: without taxes, biomass price 34,2 €/m3 without bark and at forest site, personnel costs: 2 persons per unit operation in 5 shift operation according to Austrian wage agreement chemical industry, excluding catalyst costs for: CO-Shift, formaldehyde synthesis, methylal synthesis, trioxane synthesis; maintenance costs: 2,5% of investment costs, transport of biomass and products of max. 200 km (average 93,7 km), 25% train and 75% truck transport, Investment costs: based on correlations [36] and chemical engineering plant cost index for 2014 with 579,8

Tab. 4: Results of biofuel production simulation

As Table 4 shows, investment cost of OME production are not competitive compared with biodiesel investment cost. Process effort is nearly similar, due to high fatty acid prices. Contrary to that, greenhouse gas savings of OME production are nearly double compared to biodiesel production. Moreover, availability of fatty acids is limited, whereas lignocellulose is highly available. To conclude, based on this model climate protection with OME as biofuel is possible, but high invest costs and high fuel prices are a hindrance for market introduction.

6 Comparative analysis

The insights gained from the engine studies clearly show the trends that can be expected with the use of the investigated fuels. In order to be able to compare their advantages and disadvantages for the diesel engine use in a quantitative manner, a direct comparison of the best points in the different applications is useful.

The high load point OP-1500/15 is critical for compliance with NOx and soot emission requirements due to the high combustion chamber temperatures and the low air-fuel ratio. The rise of the EGR rate causes a strong increase of soot emissions and a simultaneous reduction in efficiency. However, the strength of the oxygenated biofuels lies precisely in defusing the soot-NOx problem. Additionally, it is expected that the operation of the internal combustion engine at low loads will diminish proportionately as a result of the increasing hybridization of the drive train. These two considerations make it logical to compare the tested special fuels and combustion processes predominantly in OP-1500/15. However, the analysis could also be carried out analogously for the lower load point.

The overall assessment of the biofuel use is based both on the consideration of the combustion engine suitability and on the fuel production criteria. The assessed categories are efficiency, well-to-wheel and tank-to-wheel CO_2 emissions, particle mass and count. For a clearer presentation of the evaluation, characteristic numbers are defined, which represent the percentage change towards the diesel reference values. The diesel reference is given the number 100, e.g. 3% improvement in efficiency when using a biofuel would get the number 103, a deterioration of the same value - 97.

The CO_2 savings potential for biofuel production is determined within the framework of the production analysis and is described as “CO_2/energy unit”. It is included in the "CO_2 (well-to-wheel)" criterion. Thus, the CO_2 advantage increases with the substitution rate. The CO_2 savings in the production of oxymethylenether from lignocellulosic biomass are assumed to be 71% (see chapter 5 "Analysis of POMDME Production from lignocellulosic biomass" or [27]). An emission characteristic number of 62, e.g., means, that the emissions sum up to only 62% of the CEC diesel reference emissions. The system costs, which increase with the increased complexity of the use of the alternative fuels, are assessed in the column "System complexity". This assessment criterion accounts for the main component costs of turbocharging, basic engine, fuel system, exhaust gas aftertreatment and exhaust gas recirculation. Tab. 5 summarizes the evaluation for the best operating points. The improvements against the conventional CEC operation are displayed in green colour. Significant potentials of the use of biogenic oxymethylenethers in the diesel engine are visible. For example, by operation with OME1a at an injection pressure of 1600 bar 71% well-to-wheel CO_2 is saved and the particle mass in the exhaust gas is reduced to approx. 0% of the particle mass emissions of the diesel reference operation, which makes a reduction of almost 100%.

Fuel(combination)	Efficiency	Fuel CO_{2eq}/energy unit	CO_2 (well-to-wheel)	CO_2 (tank-to-wheel)	PM	PM#	System-complexity
CEC Diesel	100	100	100	100	100	100	~
OME1a (1600 bar)	99	29	29	107	0	0	--
OMEmix (1600 bar)	97	29	30	114	0	0	-
20% OME1	100	91	91	101	62	145	-
20% OMEmix	100	91	91	101	63	141	-

Tab. 5: Comparison of the results via characteristic numbers

Tab. 5 represents a slight efficiency disadvantage when operating with neat OMEs due to the already discussed not adapted injection system. Remarkable CO_2 well-to wheel savings of up to 70% compared to fossil diesel are achieved with neat OMEs. Substituting 20 vol% of the conventional diesel with OME1 or OMEmix helps form 9% less CO_2 and about 40% less particulate mass at this optimal operation point, at low load the improvement is even higher. Unfortunately a rise of particle number of about 40% compared to diesel is measured with the blends. Emissions of soot and particle number can be reduced to ambient levels by using neat OME. This way soot emissions are no longer a constraint in engine application and the exhaust gas recirculation rate is only restricted by efficiency concerns and possible methane emissions at stoichiometric operation. Due to the high corrosiveness of the oxymethylenethers special materials are needed for seals and fuel lines in the fuel system. Additionally, the very low boiling point of OME1 requires advanced safety and tank emission control measures. Both considerations are assessed by increasing system complexity in the last column of Tab. 5.

7 Conclusions and outlook

The study shows no significant differences in combustion quality and emissions between OME1 and OME2-6. Operating a diesel engine with OME blends is possible and has several advantages, the OME properties, however, make hardware and engine application adaptations necessary, even if small OME amounts are to be mixed. If the engine systems are to be modified, the operation with neat OME is strongly favourable, since it offers an extreme potential to further improve efficiency and emission levels of the compression ignition engine, perhaps even to sub-zero levels. As part of future activities, a detailed thermodynamic process calculation is to be conducted, in order to better assess the influence of the physicochemical properties of OME on their combustion performance. As shown in the production simulations, OME production needs strong support of public funding for market introduction according to the high invest costs, but the greenhouse gas savings potential of 71% is outstanding.

8 Acknowledgement

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ORIGINAL PAPER

Biogenous ethers: production and operation in a diesel engine

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Abstract

Fuels from lignocellulosic biomass have the potential to contribute to sustainable future mobility targets by reducing the fossil CO_2 emissions of the transport sector. Of special interest for the diesel engine are oxygenated fuels, since they can help to solve traditional conflicts of objectives like the soot–NO*x* trade-off or the efficiency–NO*x* compromise. Dibutyl ether (DBE) and oxymethylene ethers (OME) are among the most promising fuel candidates. The suitability of these compounds for diesel engines is investigated in this study. The fuels are injected in pure form as well as a diesel–biofuel blend with 20% volumetric biogenic share. During the course of these investigations special attention is given to soot and particle emissions, and also to measured engine efficiency. The combustion tests are combined with an analysis of suitable production paths of the evaluated bio-ethers as second generation biofuels. Production simulation shows high greenhouse gas savings potential, but also high investment costs.

Keywords Diesel engine · Dibutyl ether · Biofuel · Polyoxymethylene dimethyl ether · OME · POMDME · Biomass pulping

Abbreviations

DBE	Dibutyl ether
OME	Oxymethylene ether
POMDME	Polyoxymethylene dimethyl ether
CEC	Certified test diesel fuel
MTHF	Methyltetrahydrofuran
HFRR	High-frequency reciprocating rig
FAME	Fatty acid methyl ester
PTFE	Polytetrafluoroethylene
MFB	Mass fraction burned
EGR	Exhaust gas recirculation
CAaTDC	Crank angle after top dead center
EOI	End of injection
SOI	Start of injection
PM	Particle matter (mass)
PM#	Particle number

1 Introduction

Climate change concerns and legislative regulations require adequate measures to reduce the human impact on global warming. Increasing production and usage of renewable energy are seemingly the key to a biocarbon-based future and an economic as well as energetic independence from fossil fuels on a global scale. The transport sector contributes to about 23% [1] of the total greenhouse gas emissions in the European Union. Therefore, reducing CO_2 from traffic is crucial to achieve the desired climate-stabilizing objectives. Along with improvements in the efficiency of the internal combustion engines, the focus should be extended to defossilization of the fuels used.

Diesel engines with their high efficiency are of great importance for the transport of passengers and goods. However, the typical exhaust gas emissions from the combustion

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of conventional diesel fuel make further development inevitable, if future air quality regulations are to be met. Second generation biofuels have the potential to reduce the CO_2 emissions of the transport sector, while simultaneously mitigating ethical questions surrounding the issue of food production. Furthermore, oxygenated fuels provide beneficial combustion properties and can help to solve traditional conflicts of objectives like the soot–NOx trade-off or the efficiency–NOx compromise. Among many candidates dibutyl ether (DBE) and oxymethylene ethers (OME) are discussed to be promising alternatives to fossil fuels for future diesel engine powering. They can completely substitute diesel or may be mixed with it. Polyoxymethylene dimethyl ethers (POMDME, also called oxymethylene ethers or OME), are known to provide almost soot-free combustion and their usage might wipe out major constraints of diesel engines by reducing emissions and improving efficiency. Dibutyl ether on the other hand, possesses very high ignitability and advantageous molecule structure.

Lignocellulosic biomass is a sustainable, renewable energy source and serves as a feed material for the production of the bio-ethers discussed in this study. Dibutyl ether may be produced through biomass pulping, whereas oxymethylene ethers are obtained through biomass gasification [2].

Dibutyl ether is a volatile, colourless liquid with a fruity smell. Due to its high reactivity DBE shows a very short ignition delay [3] and some researchers use it as an ignition booster in blended fuels [4–7]. Tests with neat DBE in [3, 6] indicate that HC, CO and noise emissions are significantly reduced compared to diesel in most of the investigated operating points. DBE usage results in almost soot-free combustion according to [3, 6]. The authors give an approximate cetane number of 115 for DBE and explain that DBE and diesel combustion occur in a similar way and produce many soot precursors, as a result of which high soot emissions are expected. However, the oxygen content in the molecule and a different soot-oxidizing mechanism overcome the negative influence of the high ignitability and minimize the particulate matter emissions [8] examines the soot-oxidizing mechanism in the process of DBE combustion and reports missing soot luminescence in the post-oxidation combustion phase, probably resulting from a mechanism unusual for pure hydrocarbons and different particle composition. Additionally, [9] points out the very good mixture formation properties of DBE, which are a consequence of low viscosity (dynamic viscosity 0.64 mPa.s at 25 °C [3]), low boiling temperature and low heat of vaporization. These aspects result in high Reynolds numbers and a proper spray break-up [9, 10]. As stated in [11], the spray structure of neat DBE and its blends with diesel fuel show a larger spray angle and shorter liquid penetration length than pure diesel, providing improvements to atomization behaviour.

The properties of oxymethylene ethers depend on the molecule size and therefore on the number of oxymethylene units ($-CH_2O-$). The resulting formula is $H_3C-O(-CH_2O-)_n-CH_3$, with $n=0$ for DME (the simplest ether) and $n=1$ for dimethoxymethane (OME1, the simplest oxymethylene ether and the full acetal of formaldehyde and methanol). Molecule size with $n \leq 6$ offers combustion properties for alternative fuels. Oxymethylene ethers may be simply specified as OME_n. They are colourless liquids, their specific mass, cetane number and kinematic viscosity rise with molecule length. The main factors, which are responsible for nearly sootless combustion, are the high oxygen content of over 45 wt% and the absence of C–C bonds (C1 oxygenates). The significantly lower calorific value of OMEs can be considered as a disadvantage compared to conventional diesel. Generally, OME3-6 are found to have the best suitability for diesel engine applications, since their properties (boiling point, lubricity, viscosity) are closest to diesel [12–15].

Most of the OME combustion investigations found in literature discuss OME1 or mixtures of diesel and OME1. Until now, higher grade OMEs have been extremely difficult to synthesize. Exhaust soot emissions are reduced by OME1 add-on to diesel [16], the real advantage of OME, however, is demonstrated by using it as a pure substance [14, 17, 18]. In this case, the soot–NOx trade-off is avoided. It is proven that higher methane emissions are produced, when the engine is operated with OME1 or OME2 at near-stoichiometric conditions. Soot and particle emission characteristics of both fuels are very similar [13]. The tests with a mixture of the higher OME3-6 and the comparison of combustion results with OME1 and paraffinic diesel fuel in [12, 19, 20] confirm the previous findings of extremely low soot and particle emissions from OME combustion.

2 Tested fuels

In this study, a certified diesel fuel is used as reference for comparison and is briefly referred to as CEC. Dibutyl ether (DBE) is the first representative of the investigated oxygenated fuels. It is characterized by a low ignition temperature and therefore a very high cetane number of approx. 100 [6]. 1000 ppm of monocarboxylic acid is added to DBE to ensure sufficient lubricity. The gravimetric oxygen share of 13.1% in the DBE molecule is relatively low compared to the 40.3% in the second investigated fuel OMEmix. OMEmix stands for a mixture of the higher OMEs $n=2$–6. Its main components are OME3 (78.7%) and OME4 (19.8%) (area percent gained in the gas chromatographic analysis, in this case approx. weight %). Figure 1 displays the structural formula of the ethers used.

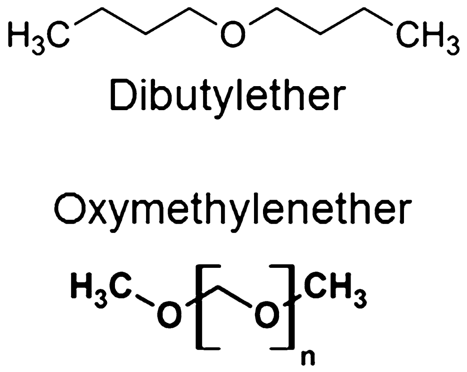

Fig. 1 Structural formula of the investigated fuels

The investigated compounds are injected into the combustion chamber both as a neat fuel and as a diesel–biofuel blend. The Renewable Energy Directive 2009/28/EC suggests a 10% renewable content in the fuel used for transport applications [21]. Most of it is assumed to be achieved by fuel blends with biogenous share. This value, however, is only applicable in regard to the mean value of the biocontent in transportation fuels. In order to further explore the potential of oxygenated biofuel add-on, the substitution rate for the engine tests in this study accounts for 20 vol%. The biogenic share of energy in the OMEmix/diesel blend is 12.6%, the corresponding biogenic energy share in the DBE/diesel blend is 16.8%. All fuels were analysed and the most important results are summarized in Table 1. The heat of vaporization of DBE is quoted in [3] and the viscosity of the OME blends in [22].

2.1 Production pathways of biogenous fuels

For DBE production, the pulping process of an ethanol organosolv process is simulated. The main components of lignocellulose (cellulose, hemicellulose and lignin) are separated. Afterwards, hemicellulose and cellulose are converted into fuels by fermentation and/or reactive processes and synthesis routes. Non-converted biomass fractions, such as lignin or hemicellulose may be combusted. A concept scheme of the biomass conversion is shown in Fig. 2 [23]. In this study, two different cases of side stream treatments are compared.

The first case (case 1) is an integrated conversion of the hemicellulose fraction into 2-methyltetrahydrofuran (2-MTHF) and the second case (case 2) is the thermal conversion of hemicellulose for steam and power generation.

Plant size is set on an industrial scale with a biomass consumption of 101 t/h. This is the same order of magnitude as proposed in literature [24]. Biomass source is the energy plant *Miscanthus sinensis* and process operation is based on the work of Alriols [25]. To increase production rates, initial production route is improved. The ethanol organosolv process is auto-catalysed by acetic acid, which is formed during the pulping process.

During ethanol organosolv pulping 40.7 t/h cellulose is gained. Cellulose is converted into glucose by enzymatic hydrolysation. Subsequent fermentation of glucose yields in acetone, butanol and ethanol. Product separation is performed by distillation. Product separation has to overcome one azeotrope of water and ethanol and additional one azeotrope of water and butanol. With this simulated process route 9.3 t/h butanol is produced and additional 2.9 t/h of acetone is gained. The ethanol formed is used for the pulping process to compensate ethanol losses. Additional need of energy is

Table 1 Properties of the tested fuels

	CEC diesel	DBE	20% DBE	OMEmix	20% OMEmix
Structural formula	$C_{12}H_{23}$[a]	$C_8H_{18}O$	$C_{11}H_{22}O_{0.2}$[a]	$C_{5.2}H_{12.4}O_{4.2}$[a]	$C_{10}H_{20}O$[a]
Cetane number (–)	54.5	~ 100	63.2	52.8	52.1
Density (15 °C) (kg/m^3)	833.5	773	820	1046	876
Lower calorific value (MJ/kg)	42.68	37.42	41.57	19.4	37.36
HFRR (µm)	413			409	
C-fraction (wt%)	85.4	72.2	83	43.3	74.8
H-fraction (wt%)	14.2	13,8	13.8	8.7	12.5
O-fraction (wt%)	–	13.1	2.4	47.9	11.8
H/C-ratio (atomic)	1.92	2.25	1.97	2.416	1.98
Boiling point (°C)	173–363	141	141–363	105–197	
Stoichiometric ratio (kg/kg)	14.5	12.8	14.2	5.9	12.44
Air demand for stoichiometric combustion (kg/MJ)	0.340	0.342	0.341	0.304	0.333
Heat of vaporization (kJ/kg)	358	286.8			
Kin. viscosity (40 °C) (mm^2/s)	2.4			0.96	~ 2

[a] Approximative assumption for calculation purposes

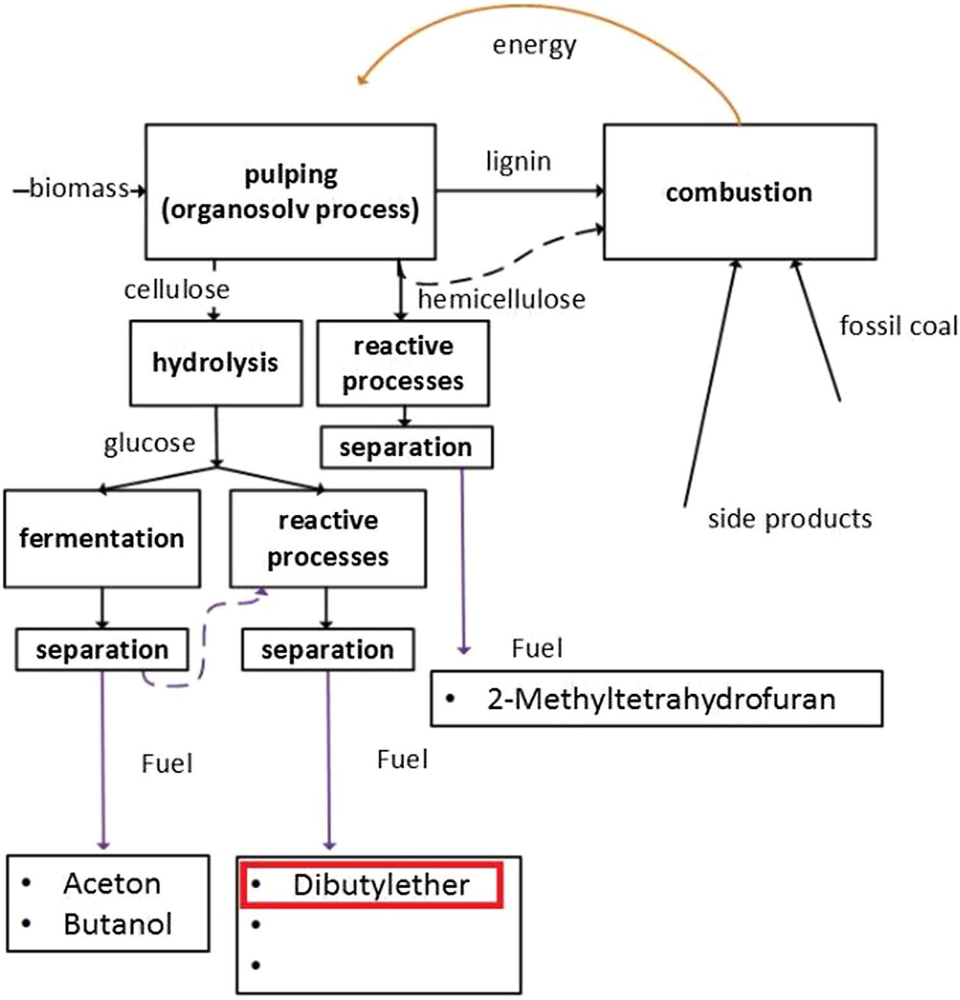

Fig. 2 Concept scheme for biomass conversion into fuels using organosolv pulping [23]

provided by coal combustion with a calculated CO_2 output of 111.3 g_{CO2}/MJ [26].

DBE can be produced by dehydration of butanol. The reaction may be carried out with different catalysts. Butene and water are the main byproducts; see Eqs. 1 and 2:

$$\text{DBE formation}: \; 2\, C_4H_{10}O \rightarrow C_8H_{18}O + H_2O, \tag{1}$$

$$\text{Butene formation}: \; C_4H_{10}O \rightarrow C_4H_8 + H_2O. \tag{2}$$

The selectivity of the reaction products is strongly dependent on the reaction conversion. For the DBE production a conversion of 50% is assumed, whereas reaction temperature is 237 °C [27]. In this case a particularly high selectivity for DBE is evident when using an Al_2O_3/SO_4 catalyst. Thus, 71.1 mol% of the butanol is converted to DBE and 27.9 mol% to butene [28]. Not converted butanol is recirculated and butene is used for energy generation. Eventually DBE is being purified through methods of extraction and distillation [27].

The production technology is an essential aspect also in the OME discussion. Based on preliminary OME production path analysis [29–34], [35] continues the investigations and makes an assessment of OME production costs and concludes that the production is competitive to conventional diesel fuel production. The feed stock for OME production in the cited study is, however, market available methanol and it has to be assumed that it is of fossil origin. OME production routes are also discussed in [36, 37], but an economic review is not made in these studies.

In the present study, bio-OME production from lignocellulose is assessed and evaluated in a shortcut simulation. Basis is the production of 250.000 t/a of an OMEmix. Biomass gasification and subsequent methanol synthesis is determined as reaction pathway. Figure 3 shows a schematic overview of OMEmix production from lignocellulosic feed.

Feed material in the calculations is spruce wood. Theoretical plant operating hours are 8000 h/a. It is assumed that the whole biomass pre-treatment is part of the fuel production at a single biorefinery site. Biomass feed is 95 t/h spruce wood. After chipping with a drum chipper, this biomass amount corresponds to 368 m^3 of wood with a moisture content of 15% [38]. Selected gasification

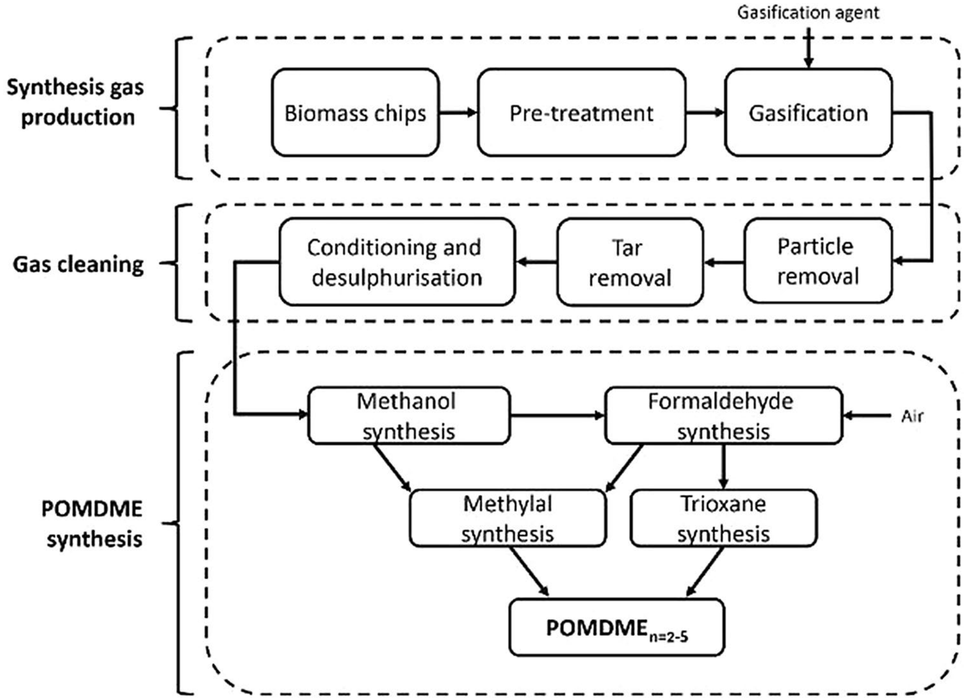

Fig. 3 OMEmix production based on lignocellulosic feed [20]

process is the Carbo-V process, operated by Linde [39]. The Carbo-V process is a stepwise biomass gasification process. First step is a 450 °C flash-type pyrolysis, followed by an entrained flow gasifier for gaseous products and finally a fluidized bed gasifier for biochar gasification [40]. The Carbo-V process is limited to a scale of 160 MWth fuel capacity, this corresponds to 720 t/day of bone dry biomass. Due to this fact a design of three parallel gasification units is performed. Gas cleaning is modelled with a Selexol process [41]. To reach final sulphur concentration of less than 0.1 ppm in the feed gas, a metal absorber is applied. Methanol synthesis is simulated based on a slurry reactor of Air Products Liquid Phase Conversion Company in an LPMeOH (low-pressure methanol synthesis) process [42]. According to Fig. 3, the next building block in the OME process chain is formaldehyde. Formaldehyde production is simulated with the BASF process [43] to provide 22.000 kg/h formaldehyde for methylal and trioxane formation. Trioxane production is modelled based on the method of Grützner [44] and formaldehyde conversion is estimated with 100%, due to the application of a recycle stream. Additionally to trioxane, methylal is the second building block for OME production. A reactive distillation, with water as entrainer, according to Liu [45] is simulated and product purity of 98.7% is reached. Finally, the production of OME mixture was calculated following the design of Burger et al. [34, 46]. This design is based on a packed bed reactor with the acidic Amberlyst 46 catalyst, with three subsequent distillation columns for product separation. Based on this model OME production is evaluated.

2.2 Production evaluation

Biofuel production is evaluated based on its industrial production needs and setup. Evaluation criteria are as follows:

- *Energetic fuel efficiency* Evaluation of the transfer rate of the chemical bound energy into the fuel fraction ($MJ_{Biomass}/MJ_{Fuel}$).
- *Process effort* Estimation of production costs of fuel production (€/MJ_{Fuel}) (includes biomass price, transport costs, production auxiliaries, energy costs as far as achievable).
- *Greenhouse gas reduction* Calculations of greenhouse gas emissions of biofuels based on EU-Directive 2009/28/EG including cultivation and harvest, transport and production processes [21] and a comparison with standard diesel (% CO_2).
- *Investment costs* Based on cost estimations and correlations of existing plants (€/L_{Fuel}).

Table 2 shows the results of the simulation. Based on these calculations the production of the investigated bioethers is possible and feasible. To show a comparison with a first generation biofuel, a sodium methanol-based biodiesel plant for rape seed oil conversion into biodiesel is simulated.

Table 2 Results of biofuel production simulation [20, 27, 47]

Fuel	Energetic fuel efficiency ($MJ_{biomass}/MJ_{Fuel}$)	Greenhouse gas reduction (% CO_2)	Process effort (€/MJ_{Fuel})	Invest costs (€/L_{Fuel})
FAME	1.01	38	0.026	0.006
DBE (case 1)	3.5	− 57.5	0.023–0.035	0.390
DBE (case 2)	5.5	67.1	0.017–0.039	0.627
POMDME	2.77	70.9	0.025	0.224

Process effort: without taxes, biomass price 34.2 €/m^3 without bark and at forest site (for POMDME) and 8–80 €/t (for miscanthus), personnel costs: 2 persons per unit operation in 5 shift operation according to Austrian wage agreement chemical industry, excluding catalyst costs for DBE production and CO-Shift, formaldehyde synthesis, methylal synthesis, trioxane synthesis; maintenance costs: 2.5% of investment costs; transport of biomass and products of max. 200 km (average 93.7 km), 25% train and 75% truck transport; investment costs: based on correlations [48] and chemical engineering plant cost index for 2014 with 579.8

Based on the process simulation, mass and energy balances of the two cases for DBE production are compared. Organosolv process fuels result from complex interconnections in a biorefinery with a production of several fuels at the same time. In many cases total processes based on the ethanol-organosolv-pulping with separate conversion of cellulose and hemicellulose have no positive CO_2 savings. If the fraction of hemicellulose is thermally utilized, positive CO_2 savings are achieved. As can be seen in Table 2 only the second case for DBE production, where hemicellulose is used to cover energy needs, results in a greenhouse gas reduction.

It turns out that the plant costs of the established production of biodiesel are much lower than the investment costs needed for innovative manufacturing processes. At the same time FAME shows a significantly better energetic fuel efficiency, since the production of DBE or OMEmix with the same energy content requires much more biomass feed. However, the process effort for the manufacturing of the bio-ethers is comparable to biodiesel, and is caused by the high rape seed oil price. The great advantage of these innovative fuels lies in their very high potential for CO_2 reduction of 67% (DBE) and 71% (OMEmix) towards fossil diesel, whereas biodiesel achieves only about 38% in this aspect. Furthermore, rape seed does not belong to the second generation biofuels and its availability is limited, whereas feed stock for DBE and OMEmix is highly available.

3 Test engine and test methodology

A modern in-line four-cylinder diesel engine is used as a test engine. The low availability and the high purchase costs of the fuels make single cylinder operation reasonable. Only the first cylinder is fired, the other three are deactivated and their gas exchange is separated from the gas exchange of the fired cylinder. The cylinder has a displacement of 537 cm^3 and a compression ratio of 17.5. Bore and stroke are 88 and 88.34 mm, respectively. The original high-pressure common rail injection system is equipped with seven-holes nozzles solenoid injectors. Charging is performed with an external electrically driven supercharger. An electrically adjustable flap valve is used to adjust the necessary exhaust gas back pressure. Cooled high-pressure exhaust gas recirculation is applied. The standard exhaust gas aftertreatment system has been removed. Emissions sampling takes place in the raw exhaust gas. The temperatures of the charge air and the fuel are conditioned. The standard sealing materials in the fuel system are inappropriate for the tested fuels and are replaced with PTFE seals. Figure 4 shows a schematic overview of the test bench.

The test engine is equipped with high- and low-pressure indication and standard exhaust gas measurement, as well as AVL Micro Soot Sensor 483 and AVL Particle Counter 489. Additionally an AVL Smoke Meter 415S is used.

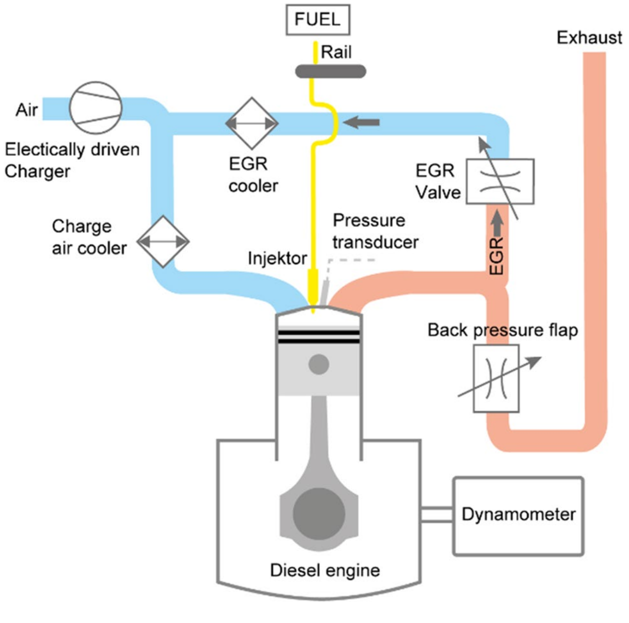

Fig. 4 Schematic layout of the test bench

The investigations are carried out at two operating points at the Institute for Powertrains and Automotive Technology at the Vienna University of Technology. The first point is defined by an engine load of 5 bar indicated mean effective pressure at 1500 rpm, the second – 15 bar indicated mean effective pressure also at 1500 rpm; see Table 3. Variations of the air–fuel ratio, the EGR rate and the MFB50% (by adjusting the start of injection) are carried out. The difference between intake and exhaust pressure (negative scavenging pressure) is held constant through the variations, however, depending on the load point. This way the effect of the gas exchange on the indicated efficiency is being isolated and the influence of other combustion parameters can be better observed. The results of the variations are analysed and the optimum operating parameters for the respective fuel are determined. The pure diesel operation is the reference for the comparison. In order to create boundary conditions for the fuel comparison, an upper limit for NO*x* emissions of 2 g/kWh is set. The maximum intake manifold pressure is limited to 2250 mbar (abs.). The first tests with pure OMEmix imposed the necessity of increasing the injection pressure at the higher load point, since operating at the same pressure as with diesel resulted in very long injection durations due to the significantly lower lower heating value of OMEmix. All specific emission values in this study are with respect to indicated engine work.

4 Results of the combustion investigations

4.1 Dibutyl ether

4.1.1 Soot and particle emissions (DBE)

The most effective measure for the in-cylinder reduction of the nitrogen oxide emissions is the increase of the EGR rate. In case of conventional diesel fuel, this leads to an increase of soot emissions, so that a compromise must be made when designing the operating parameters. According to literature, DBE is expected to show advantageous properties for reducing soot and particle number in the combustion process of the diesel engine due to its oxygen content, absence of double bonds between the carbon atoms and enhanced spray formation. Starting with the lower load point, the specific soot emissions of DBE and a blend of diesel and 20% DBE are compared to the results of diesel reference operation by means of a variation of the exhaust gas recirculation rate (EGR rate). Figure 5 displays the findings.

Table 3 Investigated operating points with engine parameters

Load point notation	OP-1500/5	OP-1500/15
Speed (rpm)	1500	1500
p_{mi} (bar)	5	15
Rail pressure (bar)	~670	~1000 (1200+for pure OMEmix)
Injection pattern	Single injection	Single injection
Intake manifold pressure (mbar)	variable	2250
Δpressure exhaust-intake (mbar)	270	500

For each of the three fuels about 20% EGR is needed in order to lower the NO*x* emissions under the set limit of 2 g/kWh. However, no significant soot production occurs before 30% EGR. It is visible that the soot mass emissions of neat DBE operation remain lower in comparison to diesel and at 50% EGR the reduction is more than 40%. Nevertheless, the effect is not as strong as expected. Furthermore, the exhaust gas in blend operation shows a remarkably higher soot mass content than reference operation. The behaviour of

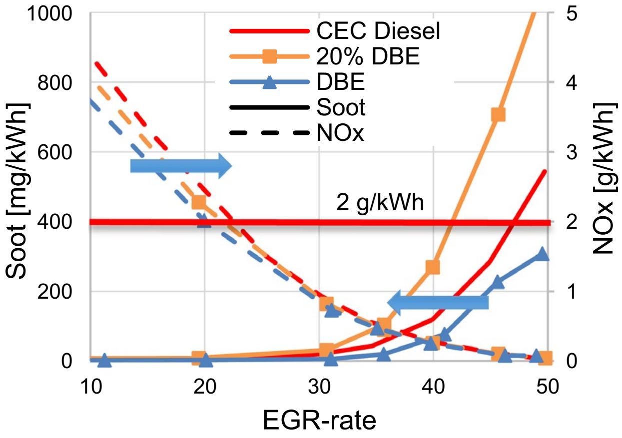

Fig. 5 Soot mass and nitrogen oxides at OP-1500/5; variation of EGR rate, intake manifold pressure const. 1130 mbar; MFB50% 7.5 °CAaTDC

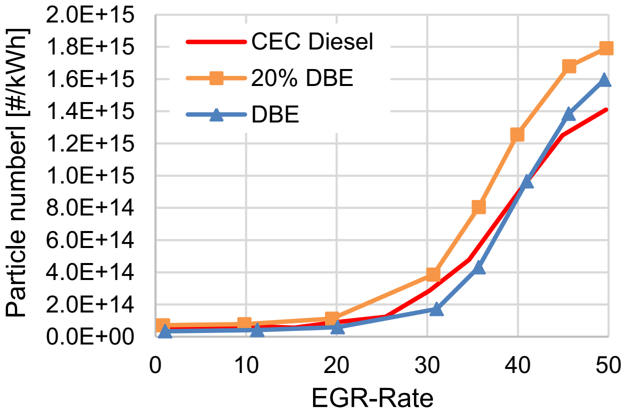

Fig. 6 Particle number at OP-1500/5; variation of EGR rate, intake manifold pressure const. 1130 mbar; MFB50% 7.5 °CAaTDC

the particle number over a variation of EGR rate is shown in Fig. 6. In this case the particle count of neat DBE and diesel are almost equal (within a repeatability tolerance) and the blend produces slightly more particles.

Both figures lead to the assumption that since particle number in blend operation does not exceed the diesel reference value with the same factor as soot mass emissions do, the particles must be bigger and heavier than in diesel reference operation. At first these results look surprising, however, the influence of the very high ignitability of DBE should not be underestimated. The add-on of 20% DBE to diesel shortens the duration between the start of injection and the start of combustion, also called ignition delay, as Fig. 7 proves. This effect is very pronounced for neat DBE. Interesting in this matter is also the duration between the end of injection and the start of combustion. It is the longest in the case of diesel and the shortest for DBE. Figure 8 displays these relations in a quantitative manner.

The reaction zone of a diesel fuel jet stabilizes at a location downstream of the fuel injector once the initial autoignition phase is over. This distance is referred to as flame lift-off length [46]. The short ignition delay of neat DBE reduces the lift-off length and leaves less time for spray evaporation, thus more locally fuel rich zones and more diffusive combustion occur. Due to the advantageous properties of the DBE molecule, the negative effect of the high cetane number on soot production is compensated, as can be seen in Fig. 6 for the lower load point. Adding only 20% DBE to the diesel fuel on the other hand has a very negative impact on soot and particle production, because the DBE fraction of the fuel autoignites earlier and consequently ignites the diesel portion. The ignition delay is shortened compared to pure diesel and less premixed combustion takes place (see Fig. 7), therefore the emissions rise.

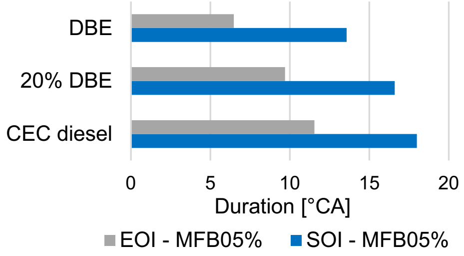

Fig. 8 Duration from start/end of injection to combustion beginning MFB05%; intake manifold pressure const. 1130 mbar; MFB50% 7.5 °CAaTDC, 45% EGR

For the observations of the higher load point (OP-1500/15), the NO*x* limit of 2 g/kWh represents a real constraint. In order to fulfil this requirement, a high EGR rate or a delayed centre of combustion is needed. The investigations proved that the second measure is preferable, since increasing the EGR rate effects a stronger emission rise and efficiency deterioration than retarding the ignition timing. Figure 9 shows the development of soot mass and particle number emissions for diesel, 20% DBE and neat DBE over a variation of the centre of combustion at higher load. To reach the target of highest possible efficiency under the mentioned boundary conditions, 15% EGR and a MFB50% of 12.5 °CAaTDC are needed here. Lambda value is 1.25–1.3 and soot and particle production are enhanced in comparison to the lower load point OP-1500/5.

At higher load the fuel injection duration is longer and ignition and combustion begin before the end of injection. Therefore, the flame front is much closer to the injector nozzle. Due to high fuel and burnt gas amount the locally rich combustion zones are more and the high combustion temperatures also lead to pyrolysis of fuel droplets. All these aspects account for increased soot emission levels. Because

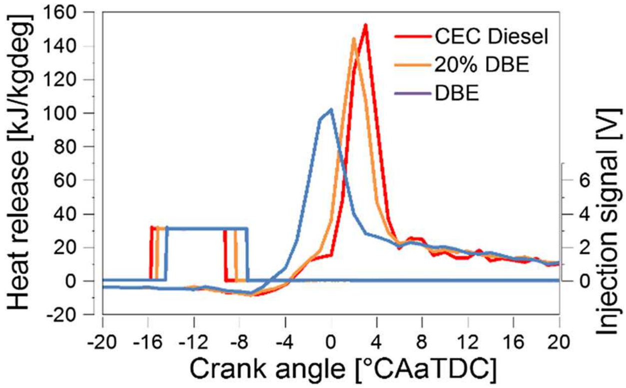

Fig. 7 Injection timing and heat release rate at OP-1500/5; intake manifold pressure const. 1130 mbar; MFB50% 7.5 °CAaTDC, 45% EGR

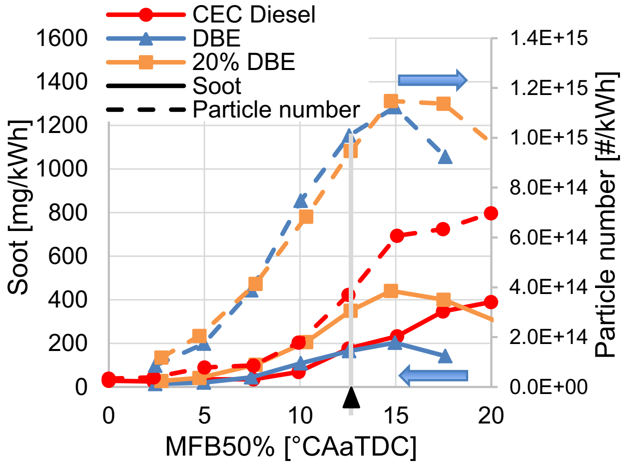

Fig. 9 Soot mass and particle number at OP-1500/15; variation of combustion center MFB50%, 15% EGR; NO*x* emissions ≤ 2 g/kWh at MFB50% 12.5 °CAaTDC

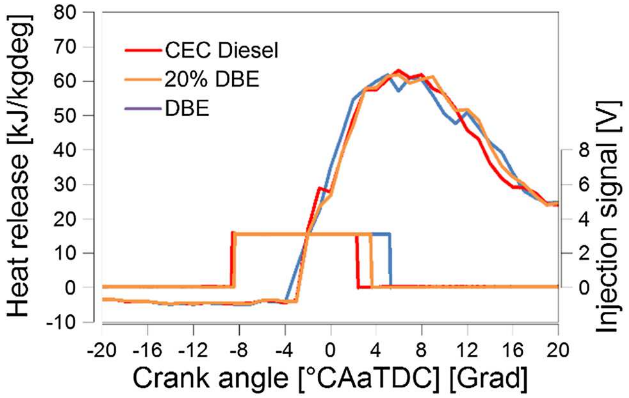

Fig. 10 Injection timing and heat release rate at OP-1500/15; MFB50% 12.5 °CAaTDC, 15% EGR

of the reduced lower heating value of DBE in regard to diesel, the injection of the highly ignitable ether takes even longer, which means that a larger amount of the fuel is injected into a burning flame zone; see Fig. 10.

As a result DBE does not improve the soot emissions of the diesel engine at the tested load point. According to the explanations of the behaviour at OP-1500/5, 20% DBE increases the soot mass output also at OP-1500/15.

Particle number emissions of DBE and 20% DBE are similar and more than twice higher than at neat diesel operation. To properly explain this enormous increase in particle count a detailed analysis of the spray and droplet formation is needed. However, it can be concluded from Fig. 9 that in contrast to the lower load point the particles at DBE and 20% DBE operation must be smaller and/or lighter than the particles originating from diesel.

4.1.2 Efficiency (DBE)

In terms of efficiency no significant differences are measured between the three fuels. At higher load the percentage share of wall heat loss is less, which adds to the higher efficiency value of 1% point, as displayed in Fig. 11.

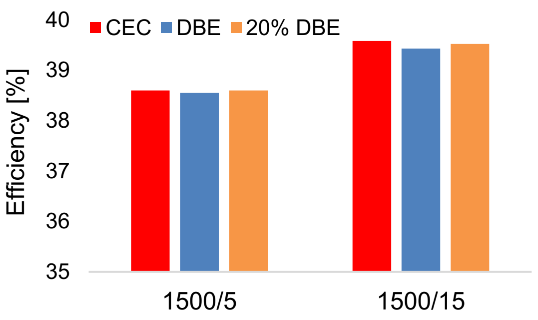

Fig. 11 Maximum engine efficiency for both load points under a limit consideration of NO$x \leq 2$ g/kWh

4.2 Oxymethylene ether

4.2.1 Soot and particle emissions (OMEmix)

Figure 12 shows the soot–NOx trade-off for the CEC diesel reference in BP-1500/5 and compares it with the behaviour of the diesel–OMEmix fuel blend and the operation with OMEmix.

The rise in soot mass emissions is profound in the case of diesel for EGR rates higher than 35%. Blending the fuel with 20 vol% OMEmix proves a soot reduction effect of about 50% at a NOx emission value of 0.25 g/kWh. The advantage is obvious even at higher EGR rates and allows using higher amounts of recirculated exhaust gases in order to achieve further reduction of nitrogen oxides, without exceeding given soot limits. It is also to be mentioned that at the same EGR rates operation with 20% OMEmix emits less nitrogen oxides. As expected, the soot–NOx trade-off is completely eliminated when using neat OMEmix. For this fuel the soot emissions remain below 0.1 mg/kWh even at 50% EGR, which results in an approximate λ value of 1.2.

The dependence of the particle number on the EGR rate reveals that the addition of 20 vol% OMEmix to diesel does not provide the same emission reduction effect as on soot mass. The particle number is almost unchanged by blending with OMEmix [20] (not shown here), which correlates with the results with the other ether DBE (Fig. 6). In the diesel–OMEmix blend diesel still accounts for about 87% of the energy content in the fuel. Since OMEmix burns "soot free" and additionally provides oxygen in the flame that can quickly react with the diesel molecules, the soot mass is reduced. However, the measurements suggest that

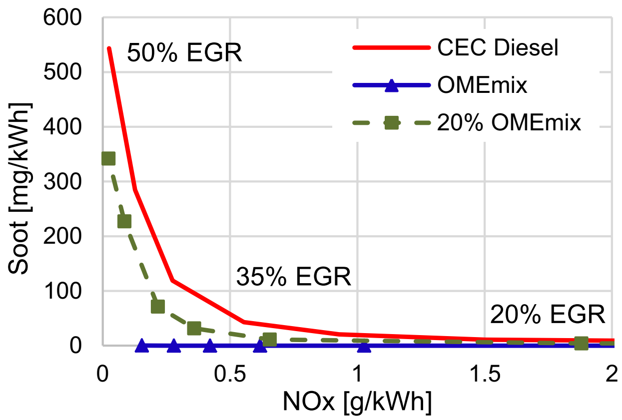

Fig. 12 Soot–NOx trade-off at OP-1500/5; variation of EGR rate; intake manifold pressure const. 1130 mbar, MFB50% 7.5 °CAaTDC [20]

blend operation emits finer particles, since their number is not noticeably reduced. The origin of these particles must lie in the diesel fuel, as the neat oxymethylene ether substances do not produce any significant particle emissions. The same trend of reducing soot emissions while having no significant influence on particle count is reported in literature with a blend of diesel and 25% OME1 [14].

Pure OMEmix on the other hand shows extremely low particle number—even at 50% EGR the value is in the range of 2×10^{11} particles per kWh or 5×10^{4} particles per cm^3 [20]. For comparison, at this point diesel is measured to produce 1.4×10^{15} particles per kWh or 2.7×10^{8} particles per cm^3.

At the higher load point OP-1500/15 no soot mass reduction is measured when operating with the 20 vol% oxymethylene blend; see Fig. 13. Particle number is very similar for both diesel reference and blend fuel (not shown here, [20]). Nevertheless, the superior qualities of neat OMEmix are present at higher loads as well. Soot mass and particle number are even further reduced with increasing EGR rate. The reason for this phenomenon is assumed to be the 70 °C drop of combustion temperature (from 0% EGR to 20% EGR, calculated in a separate combustion analysis) and an associated reduction of soot formation. At neat OMEmix operation with 20% EGR lambda is 1.2, soot mass is below 1 mg/kWh and particle number is measured to be 1×10^{12} particles per kWh or 1×10^{5} particles per cm^3 [20]. These values are still in the range of pollution concentration of ambient air in big cities [15, 49] and are achieved without any exhaust gas aftertreatment.

The results displayed in Fig. 13 show that the emissions of nitrogen oxides at OME operation are not reduced in the same way as in reference or blend operation. The analysis of the indicated data of the operation point with 20% EGR revealed that despite equal maximum cylinder temperature, in the case of OMEmix high temperatures are longer present on a time scale than with pure diesel. Therefore, more time is available for NO to form. Additionally, combustion of the OMEmix presented here requires less air and more air remains unreacted at constant intake manifold pressure. As a consequence, the lambda value is higher for OMEmix (1.2 at 20% EGR and 2250 mbar intake manifold pressure) than for diesel or the blend (1.1 at 20% EGR and 2250 mbar intake manifold pressure) and more oxygen can react to NO. For both reasons NO*x* emissions are higher for OMEmix operation than for diesel at the same EGR rate. It is logical to further increase the EGR rate in OMEmix operation; however, combustion quality downgrades.

Figure 14 compares the soot concentration and particle number in the exhaust gas of engine operation with OMEmix with the according concentrations in the laboratory ambient air. Compared to OP-1500/5, the values of OP-1500/15 are higher, but it should also be mentioned that the effect of the motor oil cannot be separated, since the oil used is not ash-free.

4.2.2 Efficiency and combustion analysis (OMEmix)

The thermodynamic analysis of the low load point operation OP-1500/5 revealed no difference in combustion between diesel, diesel–OMEmix blend or neat OMEmix. The different fuels, however, required an adjustment of the injection timing, in order to achieve the same MFB50%. The indicated efficiency is measured to be 38.5% and is barely affected by an increase in the EGR rate until reaching 45% EGR. At 50% EGR the lambda value is 1.2 and efficiency decreases.

At OP-1500/15 the limit set for nitrogen oxide emissions leads to efficiency values that are significantly lower than the theoretically possible combustion efficiency if NO*x* emissions were not taken into account. The way the indicated efficiency changes with increasing the EGR rate is shown in

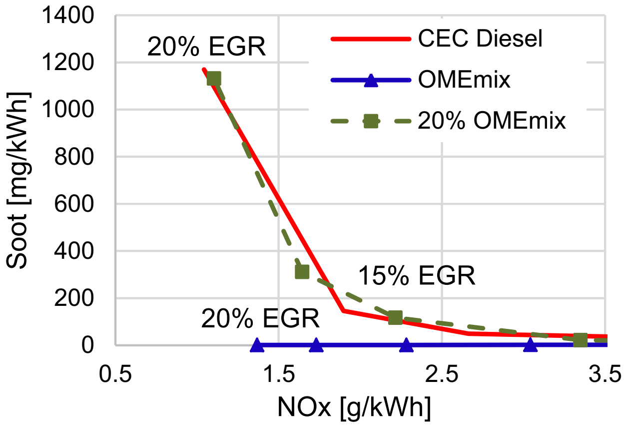

Fig. 13 Soot–NO*x* trade-off at OP-1500/15; variation of EGR rate; intake manifold pressure const. 2250 mbar, MFB50% 7.5 °CAaTDC [20]

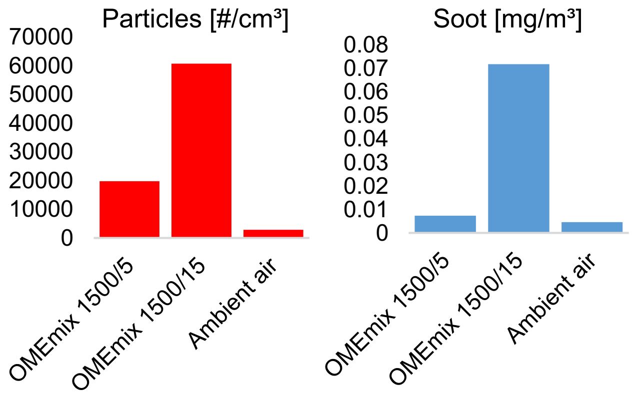

Fig. 14 Comparison of soot mass and particle number concentrations in OMEmix operation at both load points with laboratory ambient air concentration values

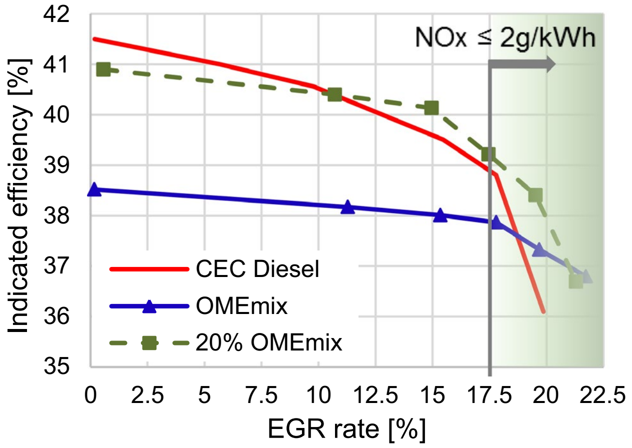

Fig. 15 Indicated efficiency as a function of EGR rate at OP-1500/15; intake manifold pressure const. 2250 mbar, MFB50% 7.5 °CAaTDC [20]

Fig. 15. The OMEmix blend shows higher tolerance against high amounts of recirculated exhaust gas than diesel; however, its efficiency is comparable to the efficiency of diesel reference operation. The efficiency of operation with neat OMEmix is at a lower level until 20% EGR, but it does not decrease the same way as with other fuels when raising the EGR rate. For this reason, the difference to the efficiency of diesel reference at 2 g/kWh NO*x* is noticeably reduced.

As seen in Fig. 13, operation with 17.5% EGR at high load produces much more soot emissions than with 15% EGR.

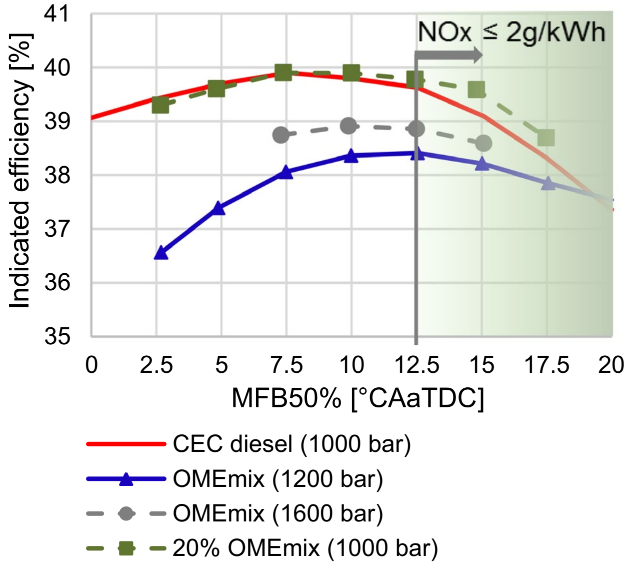

Fig. 16 Indicated efficiency as a function of combustion centre MFB50% at OP-1500/15; intake manifold pressure const. 2250 mbar, 15% EGR [20]

The efficiency plots in Fig. 16 prove that operation with 15% EGR and MFB50% 12.5 °CAaTDC is preferable to operation with 17.5% EGR and MFB50% 7.5 °CAaTDC (see correspondent indicated efficiency in Fig. 15).

Figure 16 visualizes that there is no efficiency difference between diesel and the diesel–OMEmix blend. It is also shown that the efficiency of neat OMEmix operation lies almost 2% points below the reference values. Due to the much lower lower heating value of OME compared to diesel, the fuel injection takes more time and results in an extended duration of the main combustion, which decreases the thermodynamic efficiency. The injection pressure was chosen to be 1200 bar for the investigations with neat OMEmix (for comparison diesel is injected with 1000 bar), in order to reduce the injection duration. This step, however, was not sufficient to achieve the desired result. By further increasing the injection pressure a part of this drawback can be compensated, as exemplarily shown for OMEmix at 1600 bar injection pressure, but diesel efficiency cannot be completely matched.

In contradiction to the common case and to the diesel reference results, at neat OMEmix operation with 1200 bar injection pressure the position of maximum efficiency MFB50% is not in the range of 7–10 °CAaTDC but is moved to later values. As can be seen from the indicated data in Fig. 17, a bigger part of OMEmix combustion takes places before the piston reaches TDC if injection pressure

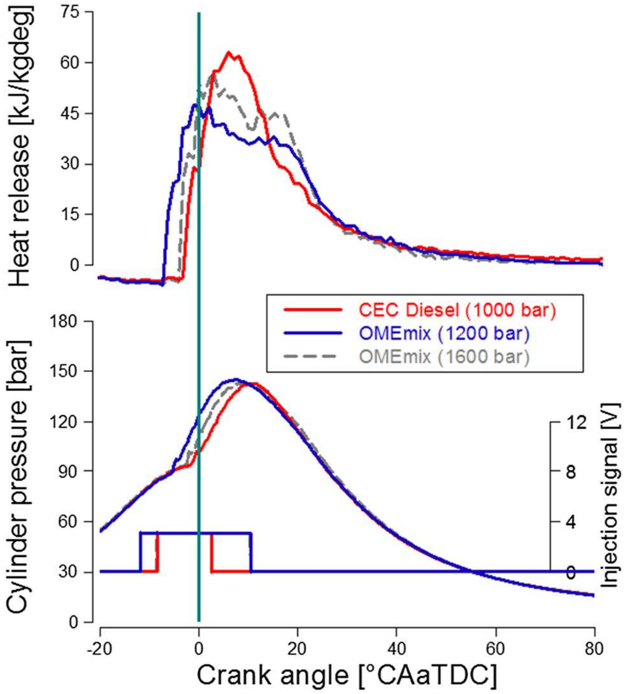

Fig. 17 Comparison of indicated data at OP-1500/15; 15% EGR; MFB50% 12.5 °CAaTDC

Table 4 Comparison of the results via characteristic numbers at OP-1500/15, maximal efficiency under the limit considerations of NOx ≤ 2 g/kWh and intake manifold pressure of 2250 mbar

Fuel (combination)	Engine efficiency	Fuel CO_2eq/ energy unit	CO_2 (well-to-wheel)	CO_2 (tank-to-wheel)	PM	PM#
CEC diesel	100	100	100	100	100	100
DBE	99	33	34	101	93	273
20% DBE	100	90	90	101	198	256
OMEmix	97	29	30	114	0	0
20% OMEmix	100	91	91	101	63	141

is not adjusted. This inevitably leads to higher thermodynamic losses, especially as a consequence of blowby and increased wall heat losses, which are the highest at TDC. For this reason moving MFB50% to a later position of approx. 12.5 °CAaTDC is favourable from an efficiency point of view. It can be seen in Fig. 17, the diesel reference has a more compact main combustion phase, followed by OMEmix with 1600 bar injection pressure. OMEmix at 1200 bar injection pressure shows a longer main combustion phase that also starts too early. These findings lead to the assumption that if the flowrate of the injection system is adequately adapted, the same efficiency as in operation with CEC diesel could be reached with OMEmix without the need of increasing injection pressure, which also increases mechanical losses. This expectation has recently been proven in [50].

5 Comparative analysis

The insights gained from the engine studies clearly show the trends that can be expected when using the investigated fuels. In order to be able to compare their advantages and disadvantages for diesel engine use in a quantitative manner, a direct comparison of the results is useful. For this purpose, the optimal operation parameter settings for all fuels at 1500/15 are depicted.

The overall assessment of the biofuel use is based both on the consideration of the combustion engine suitability and on the fuel production criteria. The assessed categories are engine efficiency, well-to-wheel and tank-to-wheel CO_2 emissions, particle mass and count. For a clearer presentation of the evaluation, characteristic numbers are defined, which represent the percentage change towards the diesel reference values. The diesel reference is given the number 100, e.g. a 3% improvement in engine efficiency when using a biofuel would get the number 103, a deterioration of the same value 97.

The CO_2 savings potential for biofuel production is determined within the framework of the production analysis and is described as "CO_2/energy unit". It is included in the "CO_2 (well-to-wheel)" criterion. Thus, the CO_2 advantage increases with the substitution rate. The CO_2 savings in the production of oxymethylene ether from lignocellulosic biomass are assumed to be 71%, and for DBE 67% (as can be seen in Table 2). An emission characteristic number of 34, e.g. means that the emissions add up to only 34% of the CEC diesel reference emissions.

Table 4 summarizes the evaluation of the best adapted parameter settings for each of the fuels. Significant potentials of the use of biogenic oxymethylene ethers and dibutyl ether in the diesel engine are visible. For example, by operation with DBE 66% well-to-wheel CO_2 is saved. The greenhouse gas savings with OMEmix are 70% and the particle mass in the exhaust gas is reduced to approx. 0% of the particle mass emissions of the diesel reference operation, which makes a reduction of almost 100%. Substituting 20 vol% of the conventional diesel with OMEmix helps emit 9% less CO_2 and 37% less soot, at low load the improvement is even higher. Unfortunately, a rise in particle number compared to diesel is measured with the blends. Emissions of soot mass and particle number can be reduced to ambient air levels by using neat OME. This way soot emissions are no longer a constraint in engine application and the exhaust gas recirculation rate is only restricted by efficiency concerns and possible methane emissions at stoichiometric operation. The 14% rise in tank-to-wheel CO_2 emissions at OMEmix operation is a result of the ratio of the fuel carbon content to its heating value and gets higher with a higher OME fraction in the fuel blend. However, it must be noticed that for future biofuel applications and related greenhouse gas assessment not solely the tank-to-wheel balance, but the holistic well-to-wheel calculation of the carbon footprint must be observed.

6 Conclusion and outlook

This study investigates the diesel engine suitability of two alternative diesel fuels—dibutyl ether and oxymethylene ether—and describes pathways for their production. The results of the production simulation are evaluated and combined with the engine tests findings. Manufacturing of both fuels requires high amounts of biomass and high investment costs, the process costs, however, are acceptable. An important advantage of the tested fuels is the potential to produce them as second generation biofuels, which considerably mitigates the ethical dispute on the competition between fuel and food production. Both dibutyl ether and oxymethylene ether show good performance in the used diesel engine. By optimizing the injection system for fuels with low lower heating value, possible efficiency drawbacks can be compensated. Soot and particle emissions can be reduced to an extreme extent by using neat oxymethylene ethers and in this case the classical soot–NO*x* trade-off is being eliminated. Dibutyl ether usage on the other hand could not effectively decrease soot emissions. Nevertheless, both fuels offer significant greenhouse gas reduction potentials by up to 70%.

Detailed research is needed to explain the discrepancy between the soot and particle emissions of dibutyl ether in this work and the findings reported in the quoted literature. The impact of the additivation with the lubricant monocarboxylic acid on the soot emissions is to be checked. Additionally, it is interesting to understand the rise in particle number when using both investigated blends. Comprehensive examination of spray formation and break-up will be helpful on this issue.

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6

Damyanov, A.; Hofmann, P.; Pichler, T. M.; Schwaiger, N.: **Biogenous Ethers – Production and Operation in a Diesel Engine**; MTZ worldwide, Vol. 80, Issue 1, p. 66-71; Jan 2019; https://doi.org/10.1007/s38313-018-0126-1

Biogenous Ethers –
Production and Operation in a Diesel Engine

Biofuels from lignocellulose can significantly contribute to the greenhouse gas emissions reduction of the transport sector. Oxygenated fuels like Di-n-butyl ether and oxymethylene ethers are among the most promising alternatives for diesel engines. The suitability of these compounds is investigated in a research project conducted at the Institute for Powertrains and Automotive Technology at Vienna University of Technology and the Institute of Chemical Engineering and Environmental Technology at Graz University of Technology. The fuels show CO_2 saving potential by up to 70 % and remarkable soot reduction properties.

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–	CEC	DBE	20 % DBE	OMEmix	20 % OMEmix
Cetane number [-]	54.5	~100	63.2	52.8	52.1
Density (15 °C) [kg/m³]	833.5	773	820	1046	876
Lower calorific value [MJ/kg]	42.68	37.42	41.57	19.4	37.36
C-fraction [wt%]	85.4	72.2	83	43.3	74.8
H-fraction [wt%]	14.2	13,8	13.8	8.7	12.5
O-fraction [wt%]	–	13.1	2.4	47.9	11.8
Boiling point [°C]	173–363	141	141–363	105–197	–

TABLE 1 Properties of the tested fuels (© IFA)

1 DI-N-BUTYL ETHER AND OXYMETHYLENE ETHERS AS DIESEL SUBSTITUTE FUELS

Fuels from lignocellulosic biomass have the potential to contribute to sustainable future mobility targets by reducing the fossil CO_2 emissions of the transport sector. Of special interest for the diesel engine are oxygenated fuels, since they can help to solve traditional conflicts of objectives like the soot-NO_x trade-off. Di-n-butyl Ether (DBE) and Oxymethylene Ethers (OME) are among the most promising fuel candidates.

Due to its high reactivity, DBE ($C_8H_{18}O$) shows a very short ignition delay and is used by some researchers as an ignition booster in blended fuels [1, 2]. The properties of the other investigated fuel, OME, depend on the molecule size and therefore on the number of oxymethylene units ($-CH_2O-$). The resulting formula is $H_3C-O(-CH_2O-)_n-CH_3$. Generally, OME with molecule sizes n = 3 to 6 are found to have the best suitability for diesel engine applications, since their properties are closest to diesel [3-5].

In this study, a certified diesel fuel is used as reference for comparison and is briefly referred to as CEC. DBE is additivized with 1000 ppm of monocarboxylic acid to ensure sufficient lubricity. OMEmix, the second investigated fuel, consists mainly of OME3 (approximately 78.7 wt%) and OME4 (approximately 19.8 wt%). The investigated compounds are injected into the combustion chamber both as a neat fuel and as a diesel-biofuel-blend with 20 vol% biogenic share. The most important fuel properties are summarized in **TABLE 1**.

2 PRODUCTION PATHWAYS OF DBE AND OMEMIX AS SECOND-GENERATION BIOFUELS

For DBE production, the pulping process of an ethanol organosolv process is simulated. The main components of lignocellulose (cellulose, hemicellulose and lignin) are separated. Afterwards, hemicellulose and cellulose are converted into fuels by fermentation and/or reactive processes and synthesis routes. A concept scheme of the biomass conversion is shown in **FIGURE 1** (left). In this study

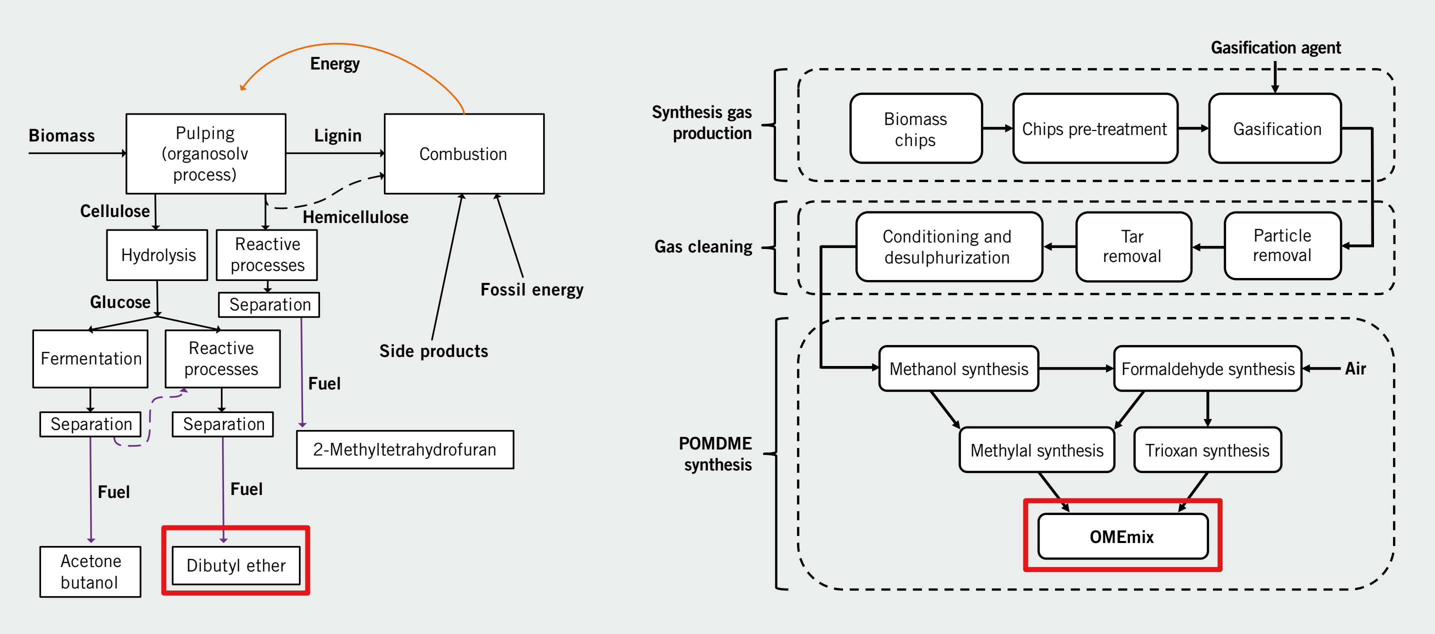

FIGURE 1 Concept scheme for biomass conversion into fuels using organosolv pulping and biomass gasification [4, 5] (© ICVT)

Fuel	Energetic fuel efficiency [$MJ_{biomass}/MJ_{fuel}$]	Greenhouse gas reduction [% CO_2]	Process effort [$€/MJ_{fuel}$]	Invest costs [$€/L_{fuel}$]	Process effort: without taxes, biomass price 34.2 €/m^3 for spruce wood without bark and 8 to 80 €/t for Miscanthus, personnel costs: two persons per unit operation in five shift operation according to Austrian wage agreement chemical industry, 8000 h/a operating h, excluding catalyst costs for DBE production, CO-Shift, formaldehyde synthesis, methylal synthesis, trioxane synthesis; maintenance costs: 2.5 % of investment costs; transport of biomass and products of maximum 200 km (average 93.7 km), 25 % train and 75 % truck transport; investment costs: based on correlations [10] and chemical engineering plant cost index for 2014 with 579.8
FAME	1.01	38	0.026	0.006	
DBE (scenario 1)	3.5	-57.5	0.023–0.035	0.390	
DBE (scenario 2)	5.5	67.1	0.017–0.039	0.627	
OMEmix	2.77	70.9	0.025	0.224	

TABLE 2 Results of biofuel production simulation [4, 5] (© IFA)

two different cases of side stream treatments are compared – case one is an integrated conversion of the hemicellulose fraction into 2-Methyltetrahydrofuran and case two is the thermal conversion of hemicellulose for steam and power generation.

Plant size is set on an industrial scale with a biomass consumption of 101 t/h. Biomass source is the energy plant Miscanthus Sinensis and process operation is based on the work of [6]. During ethanol organosolv pulping, 40.7 t/h cellulose are gained. Cellulose is then converted into glucose by enzymatic hydrolyzation. Subsequent fermentation of glucose yields in acetone, butanol and ethanol. Product separation is performed by distillation. Formed ethanol is used for the pulping process to compensate ethanol losses. Additional need of energy is provided by coal combustion with a calculated CO_2 output of 111.3 gCO_2/MJ. DBE can be produced by dehydration of butanol. Butene and water are the main byproducts from the reaction, which in this case is carried out with an Al_2O_3/SO_4 catalyst. Not converted butanol is recirculated and butene is used for energy generation. Eventually DBE is being purified through methods of extraction and distillation.

Basis for the OME production simulation is the manufacturing of 250.000 t/a of an OMEmix. Biomass gasification and subsequent methanol-synthesis is determined as reaction pathway, **FIGURE 1** (right). Biomass feed in the calculations is 95 t/h spruce wood. Selected gasification process is the stepwise biomass gasification Carbo-V process, operated by Linde. Gas cleaning is modelled with a selexol process and methanol synthesis is simulated based on a slurry reactor of Air Products in a low pressure methanol synthesis process. Formaldehyde production is simulated with the BASF process [7] to provide formaldehyde for methylal and trioxane formation. Trioxane production is modelled based on the method of Grützner [8]. Additionally to trioxane, methylal is the second building block for OME production. After a reactive distillation with water as entrainer, the production of OME mixture is calculated following the design of Burger [9].

Evaluation criteria and the results of the simulations are illustrated in **TABLE 2**. To show a comparison with a first generation biofuel, a sodium methanol based biodiesel plant for rape seed oil conversion into biodiesel is simulated. However, rape seed does not belong to the second-generation biofuels and its availability is limited, whereas feed stock for DBE and OMEmix is highly available.

3 COMBUSTION INVESTIGATIONS

A modified common-rail diesel engine is used as a test engine. The investigations are carried out at two operating points: OP-1500/5 and OP-1500/15 at 5 and 15 bar indicated mean effective pressure and 1500 rpm. In order to create boundary conditions for the fuel comparison, an upper limit for NO_x emissions of 2 g/kWh is set. The fuel is injected through a single injection event.

3.1 RESULTS FOR SOOT EMISSIONS AND EFFICIENCY AT DBE OPERATION

Starting with the lower load point, the specific soot and NO_x emissions of DBE and the 20-% DBE blend are compared to the results of diesel reference operation by means of a variation of the Exhaust Gas Recirculation rate (EGR rate), **FIGURE 2** (left). It is visible that

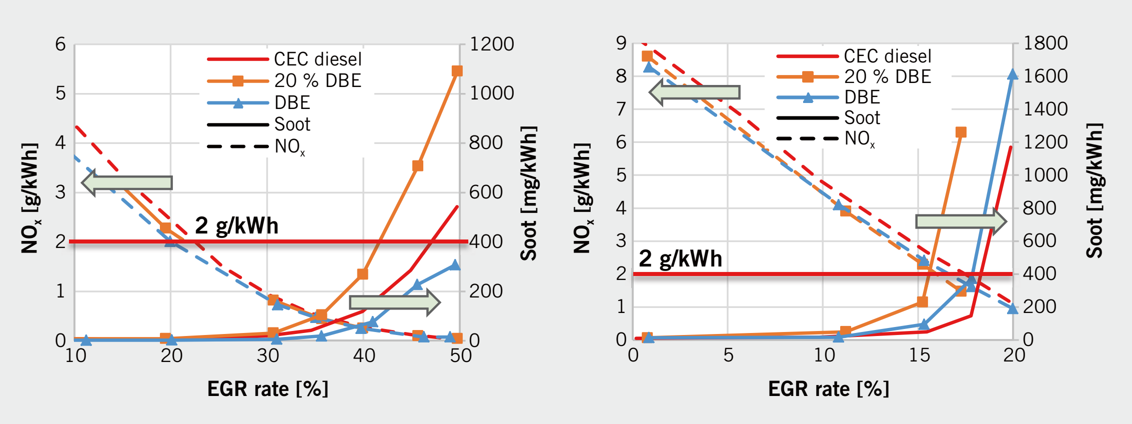

FIGURE 2 Soot mass and nitrogen oxides at OP-1500/5 (left) and OP-1500/15 (right) (variation of EGR rate, center of combustion MFB50% at 7.5 °CA after Top Dead Center (TDC) [5]) (© IFA)


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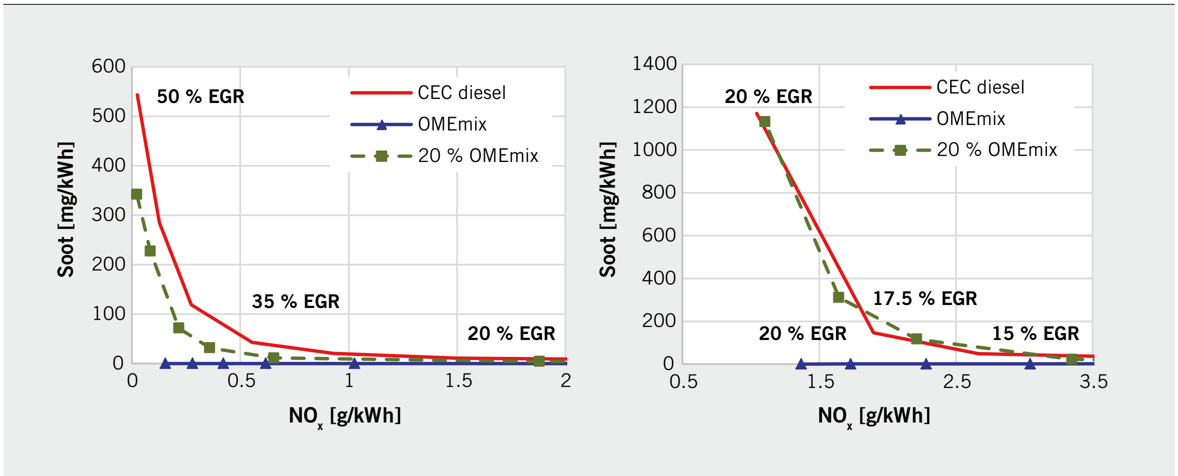

FIGURE 3 Soot-NO$_x$ trade-off at OP-1500/5 (left) and OP-1500/15 (right) (variation of EGR rate, center of combustion MFB50% at 7.5 °CA after TDC [4]) (© IFA)

the soot mass emissions of neat DBE operation remain lower in comparison to diesel and at 50 % EGR the reduction is more than 40 %. However, the exhaust gas in blend operation shows a remarkably higher soot mass content than diesel reference operation.

The short ignition delay of neat DBE reduces the lift-off length of the injected fuel jet and leaves less time for spray evaporation, thus more locally fuel rich zones and more diffusive combustion occur. Due to the advantageous properties of the DBE molecule (oxygen content, no C=C double bonds), the negative effect of the high cetane number on soot production is compensated, **FIGURE 2** (left). On the other hand, adding only 20 vol% DBE to the diesel fuel has a very negative impact on soot production, because the DBE fraction of the fuel autoignites earlier and consequently ignites the diesel portion [5].

In order to fulfill the requirement of maximal 2 g/kWh NO$_x$ at OP-1500/15, a high EGR rate and/or a delayed center of combustion (MFB50%) is needed. **FIGURE 2** (right) shows the development of the soot mass emissions for diesel, 20 % DBE and neat DBE over a variation of the EGR rate at OP-1500/15. At higher load the fuel injection duration is longer and ignition and combustion begin before the end of injection. Due to high fuel and burnt gas amount, the locally rich combustion zones are more than at the lower load point. Because of the reduced lower heating value of DBE in regard to diesel, the injection of the highly ignitable ether takes longer, which means that a larger amount of the fuel is injected into a burning flame zone. All these aspects account for increased soot emission levels [5]. In terms of efficiency no significant differences are measured between the three fuels.

3.2 RESULTS FOR SOOT EMISSIONS AND EFFICIENCY AT OMEMIX OPERATION

FIGURE 3 (left) displays the soot-NO$_x$ trade-off for the CEC diesel reference in BP-1500/5 and compares it to the behavior of 20 % OMEmix and neat OMEmix operation. Blending the fuel with 20 vol% OMEmix proves a soot reduction effect of about 50 % at an NO$_x$ emission value of 0.25 g/kWh. The soot-NO$_x$ trade-off is completely avoided when using neat OMEmix. For this fuel the soot emissions remain below 0.1 mg/kWh even at 50 % EGR. The exhaust gas of pure OMEmix combustion shows extremely low particle number – even at 50 % EGR the value is in the range of 2×10^{11} particles/kWh. For comparison, at this point diesel is measured to produce 1.4×10^{15} particles/kWh [4]. At the higher load point OP-1500/15, no soot mass reduction is measured when operating with 20 % OMEmix, **FIGURE 3** (right). Nevertheless, the superior qualities of neat OMEmix are present at higher loads as well. At neat OMEmix operation with 20 % EGR, soot mass is below 1 mg/kWh and particle number is measured to be 1×10^{12} particles/kWh [4].

The thermodynamic analysis of the low load point operation OP-1500/5 revealed no difference in combustion and efficiency between diesel, 20 % OMEmix and neat OMEmix. The way the indicated efficiency changes with increasing the EGR rate and changing the MFB50% at OP-1500/15 is shown in **FIGURE 4**. The OMEmix blend shows higher tolerance against high amounts of recirculated exhaust gas than diesel; the efficiencies are comparable.

Due to the much lower lower-heating value of OMEmix compared to diesel, the fuel injection takes more time and results in an extended duration of the main combustion, which decreases the thermodynamic efficiency. In order to reduce the injection duration, the injection pressure is chosen to be 1200 bar for the investigations with neat OMEmix (for comparison diesel is injected with 1000 bar). By further increasing the injection pressure, a part of the efficiency drawback can be compensated, as exemplarily shown for OMEmix at 1600 bar injection pressure.

4 SUMMARY

The production of DBE and OME as second-generation bio-fuels is feasible, but requires high amounts of biomass and high investment costs. The process costs, however, are acceptable. Both fuels prove good performance in the test engine. At higher load, OME combustion shows an efficiency disadvantage due to its low lower-heating value in combination with an unadapted injection system. Soot and particle emissions can be reduced to a very low level by using neat OMEs and in this case the classical soot-NO$_x$ trade-off is being avoided. DBE usage on the other hand cannot effectively decrease soot emissions in this study. Nevertheless, both fuels offer significant well-to-wheel CO$_2$ reduction potentials by up to 70 %.

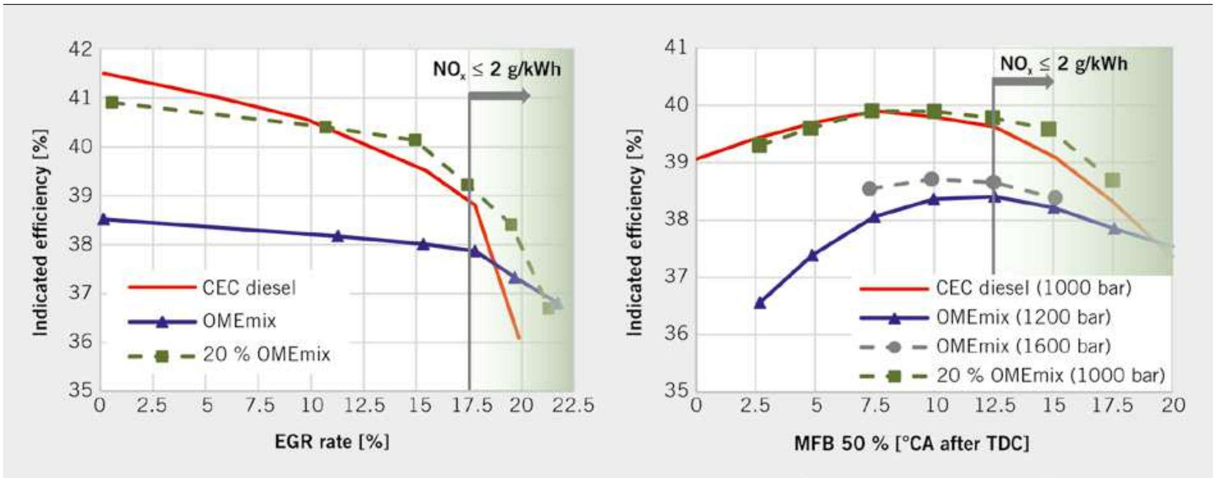

FIGURE 4 Indicated efficiency in OP-1500/15 as a function of the EGR rate at MFB50% 7.5 °CA after TDC (left) and as a function of the center of combustion with 15 % EGR (right) [4] (© IFA)

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7

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ORIGINAL PAPER

Operation of a diesel engine with intake manifold alcohol injection

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Abstract

The usage of ethanol and two different mixtures of ethanol and gasoline (E85 and E65) was investigated on a modified diesel engine designed to work in a dual-fuel combustion mode with intake manifold alcohol injection. The tests were conducted at five operating points covering low, medium and high load and different engine speeds. Additionally, an engine-process simulation model was built for the test engine and selected operating points from the engine test bed measurements were analysed with it. The discussion of the simulation results allows an efficiency analysis and therefore a better understanding of the findings of the engine test stand experiments. With rising alcohol amount, a significant reduction of soot mass and particle count was observed at all operating points. At some load conditions, substituting diesel with ethanol, E65 or E85 led to a reduction of the NOx emissions; however, the real benefit concerning the nitrogen oxides was introduced by the mitigation of the soot–NOx trade-off. The indicated engine efficiency in dual-fuel mode showed an extended tolerance against high EGR rates. It was significantly improved with enhanced substitution ratios at high loads, whereas it dropped at low loads. Substituting diesel with manifold injected alcoholic fuels impressively reduced the engine CO_2 emissions at medium and high load operating points. Degrading combustion quality, irregular combustion phenomena and poor process controllability at low load and knock as well as auto-ignition at high load limited the maximum ethanol energy share to approximately 70% and 30%, respectively.

Keywords Diesel engine · Dual fuel · Ethanol · Alcoholic fuel

Abbreviations

EtOH	Ethanol
E85	Mixture of 85 vol% ethanol and 15 vol% gasoline
E65	Mixture of 65 vol% ethanol and 35 vol% gasoline
CEC	Certified test diesel fuel
OP	Operating point
EGR	Exhaust gas recirculation
MFB	Mass fraction burned
CAaTDC	Crank angle after top dead center
c_p	Specific heat capacity at constant pressure
c_v	Specific heat capacity at constant volume

1 Introduction

The transport sector is a major contributor to the greenhouse gas emissions in the European Union with a share of about 24% in 2016 [1]. Reducing CO_2 from traffic is crucial for achieving the desired climate stabilizing objectives and lowering the dependence on fossil fuels. The efforts on this field should be supported by rational as well as technically and economically feasible sustainable solutions. Increasing the usage of biofuels is one of these solutions [2]. Ethanol, in particular, is a very well-known fuel produced from different sources and by various methods [2–4]. Currently, new production processes are being used and developed to obtain a so-called second-generation biofuel from wastes and residuals mitigating the issues surrounding the competition to food production [5, 6].

Despite the present alternative powertrain development, the diesel engine is predicted to remain crucial for mobility of people and goods in the long term due to its unmatched efficiency, robustness and operation cost and flexibility. Therefore, the search for diesel substitute fuels that are sustainable and of wide availability is of high priority. The

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usage of ethanol is normally assumed with spark ignition engines, but not with a compression ignition engine, because of the very low cetane number of this fuel. However, there are several different possibilities to utilize this alcohol in a diesel engine and it is expected to defuse the classical soot–NOx trade-off due to its high oxygen content, advantageous molecule structure and better mixture formation and combustion process. Ethanol can be used as a single fuel in a dedicated ethanol compression ignition engine with a higher compression ratio. Such engines are available in the market. To ensure ethanol ignition, however, fuel additives are necessary [7]. Adding the alcohol to the conventional diesel fuel in the form of a so-called "blend" is another way of using it in a diesel engine. Though it is the simplest method, the ethanol quantity is very limited due to separation issues, poor ignitibility and current diesel norm EN590 violation in terms of cetane number and flash point [8]. Perhaps, the most promising technique for ethanol usage in a diesel engine is the unconventional application in the form of a dual-fuel combustion process. In this case, the alcoholic fuel is fed into the engine as a separate fuel and diesel is directly injected into the combustion chamber. The ignition of the diesel fuel starts the combustion of the alcohol–air mixture. This approach provides high substitution ratios and flexible operation based on the fuel availability—diesel only or dual fuel.

The dual-fuel combustion process itself is not a novelty, it has been used in certain applications since the very early age of the internal combustion engine with different fuels, mostly natural gas [9, 10], but also liquefied petroleum gas [9], gasoline [11], hydrogen [9], reformed gases [12, 13] and other alternative fuels [14]. It was in 1901 that Rudolf Diesel obtained a US patent covering the concept of the dual-fuel engine [15]. Similarly to the other low reactivity fuels mentioned, alcohols like ethanol or methanol [8, 16, 17] can also be very successfully utilized in a dual-fuel-designed diesel engine. There are several possibilities to configure the dual-fuel system depending on the mixture formation method—external or internal. On the one hand, the alternative fuel can be added to the intake air upstream via manifold injection [18], carburettor or evaporator—a method widely known as "fumigation". On the other hand, the fuel may be directly injected into the combustion chamber through a dedicated injector [19] or a special dual-fuel injector for diesel and alternative fuel.

This study handles the operation of a diesel engine in a dual-fuel mode with an intake manifold ethanol injection. Several researchers have published articles on investigations of the dual-fuel combustion process with alcohols. The findings, however, are not always consistent and differ at some points, as can be concluded from a comprehensive review of many publications on this topic in [20]. It is believed that the discrepancies in the results found in literature have their origin in the differences of the used test engines, investigated load points, operating conditions and ethanol/diesel ratios. To obtain a wider perspective on the potentials and limits of the ethanol–diesel dual-fuel operation, in this study several important parameters were varied in wide ranges at five different operating points on a modern common rail diesel engine. Since the market availability of the gasoline–ethanol mixtures is higher, E85 and E65 were also tested parallel to pure ethanol. The literature review did not offer satisfactory explanations for the observed efficiency changes with rising amount of intake manifold alcohol injection; therefore, an engine-process model for the test engine was generated and selected operating points from the engine experiments were implemented. The conducted efficiency loss analysis supports the understanding of the measured results.

This article does not describe the potential CO_2 savings, which would result by the usage of renewable ethanol, but only deals with the engine-related aspects. If, however, bioethanol is used, the holistic CO_2 savings would be significantly higher. Bioethanol by the Austrian ethanol producer AGRANA, for instance, delivers certified GHG-savings of approximately 70% compared to fossil diesel fuel.

2 Investigated fuels

In this study, a certified CEC test diesel fuel was used as a reference for comparison. Technically pure ethanol was the first representative of the investigated oxygenated fuels. However, the intake manifold injected fuel does not necessarily have to be of high purity—a great advantage lies in the possibility of using lower-grade ethanol, since even higher water contents had no harmful impact on the engine. Additionally, E65 and E85 gasoline–ethanol mixtures were supplied, because their availability at filling stations is more presumable. E85 (RF-01-08) was delivered by a supplier and E65 was self-mixed (35 vol% winter quality gasoline RF-04-03). Table 1 gives an overview of some of the tested fuel properties.

3 Test engine and test methodology

3.1 Test engine and measurement equipment

A modern inline four-cylinder diesel engine was modified for single-cylinder operation and used as a test engine. Only the first cylinder was fired, while the other three were deactivated and their gas exchange was separated from the gas exchange of the fired cylinder. The cylinder had a displacement of 537 cm^3 and a compression ratio of 17.5. Bore and stroke were 88 and 88.34 mm, respectively. The original high-pressure common rail diesel injection system

Table 1 Properties of the investigated fuels

Fuel notation	Diesel	EtOH	E85	E65
Ethanol/gasoline ratio [vol%/vol%]	–	100/0	85/15	65/35
Density [kg/m^3]	831	789	782	773
Lower heating value [MJ/kg]	42.68	26.68	29	31.46
Cetane number [–]	54	8	–	–
Research octane number [–]	–	111	105	101
C-fraction [wt%]	85.4	51.5	56.5	62.8
H-fraction [wt%]	14.2	13.7	12.8	13.8
O-fraction [wt%]	0.4	34.1	29.8	23.3
H/C atomic ratio [–]	1.99	3.2	2.72	2.65
O/C atomic ratio [–]	0.004	0.5	0.4	0.28
gCO$_2$/MJ	73.3	71.22	72.02	73.12
gH$_2$O/MJ	29.94	46.54	40.08	39.69

Table 2 Investigated operating points with engine parameters

Operating point OP-	1500/5	1500/15	2000/5[a]	2000/20	3000/20
Speed [rpm]	1500	1500	2000	2000	3000
IMEP [bar]	5	15	5	20	20
Power output [kW]	3.3	10	4.5	17.9	26.8
Rail pressure [bar]	~670	~1040	~800	~1240	~1400
Intake manifold pressure (abs.) [mbar]	1130	2250	1230	2500	2600
Δp exhaust-intake [mbar]	270	500	330	300	300

[a] Will not be discussed in further detail due to similarity to OP-1500/5

was equipped with seven-hole nozzle solenoid injectors and could handle a pressure of up to 2000 bar. Charging was performed with an external electrically driven supercharger. An electrically adjustable flap valve was used to adjust a turbocharger comparable exhaust gas back pressure. Cooled high-pressure exhaust gas recirculation was applied. The standard exhaust gas aftertreatment system was removed and emission sampling took place in the raw exhaust gas. The temperatures of the charge air and the fuel were conditioned.

The alcoholic fuel was injected with a pressure of 4.5 bar (abs.) into the intake air through a conventional gasoline injector, which was installed in a specially designed intake manifold.

The test engine was equipped with high- and low-pressure indication and standard exhaust gas measurement, as well as AVL Micro Soot Sensor 483 and AVL Particle Counter 489. Additionally, an AVL Smoke Meter 415S was used.

3.2 Test methodology

The investigations were conducted at five operating points, which cover a typical commercial vehicle engine operating map. The engine load varied between 5 and 20 bar indicated mean effective pressure (IMEP) and the speed was between 1500 and 3000 rpm. The most important engine operating parameters are depicted in Table 2.

Variations of the exhaust gas recirculation (EGR) rate, of the combustion centre position MFB50% (by adjusting the start of injection) and of the proportion of diesel fuel to alcoholic fuel (as percent energy share of the alcoholic fuel in relation to the total fuel energy, [%e.]) were carried out. The pure diesel operation was the reference for the comparison. All specific emission values in this article are with respect to the indicated engine work. The results at OP-1500/5 may be seen as representative for OP-2000/5, therefore OP-2000/5 will not be discussed in further detail in the following sections.

3.3 Simulation model

Besides the experimental investigations at the engine test bed, a 0D/1D-simulation model of the combustion process was additionally built and selected operating points were analysed with it. The software used was GT-POWER (v2016). An important feature of the simulation is the optional efficiency loss calculation, which contributes to the understanding of eventual efficiency differences between the discussed operating modes. The approach used for burn rate calculation was three pressure analysis (TPA) and required three measured pressure curves: intake, cylinder and exhaust. The test bed measurements delivered the input and calibration data for the simulation.

4 Results of the combustion investigations

At first, the effect of substituting diesel by an intake manifold injected alcoholic fuel is best demonstrated by increasing the substitution ratio. On the one hand, ethanol is characterized by a high octane number and low ignitability, therefore combustion may be retarded or incomplete, if pressure and temperature in the combustion chamber and/or ignition energy are not sufficient. On the other hand, since ethanol takes part at the combustion process in a premixed state and its ignition is externally induced, irregular combustion phenomena such as knock and pre-ignition are possible at high in-cylinder pressures and temperatures despite its high octane number. The high compression ratio of the diesel engine may promote knock within the alcoholic fuel charge due to higher compression peak temperature and pressure.

In the course of the investigations, at low load, degrading combustion quality, poor controllability and high cycle variation determined the maximum possible alternative fuel amount. In this project, a maximum substitution rate of

60–70% energy share was possible with the fuels used. At high loads it was the occurrence of knock and auto-ignition that prohibited further increase of the substitution ratio. Nevertheless, at OP-1500/15 still 50–60%e. (% energetic) substitution rate was achieved; the corresponding ranges for OP-2000/20 and OP-3000/20 were measured to be approximately 40%e. and 25%e., respectively. In accordance with its higher octane number, pure ethanol ensured slightly higher substitution rates at high load testing, whereas at OP-1500/5 it failed to provide stable combustion before E65 and E85 did.

4.1 HC and CO pollutant emissions

Compared to the diesel reference operation, the output of unburnt or partly burnt fuel was found to be considerable at dual-fuel mode, especially at low loads; Fig. 1. As can be seen in the graph for OP-1500/5, the amount of unburnt hydrocarbons (HC) and carbon monoxide (CO) steeply rose with the substitution rate. This severe disadvantage resulted in lower engine efficiency. The higher load points provided higher in-cylinder temperatures and pressures, hence ignition and combustion of the cylinder charge were much better supported and the incomplete combustion influence on engine efficiency diminished, Fig. 2. Experiments on a methanol fumigated diesel engine in [21] showed that the HC and CO emissions were also reduced with increase in intake air temperature.

4.2 Efficiency and CO_2 emissions

Increasing the substitution rate at OP-1500/5 resulted in a considerable drop of engine efficiency until approximately 30% energy share and affected no significant further changes up to the maximum possible alcoholic fuel amount; Fig. 3. In contradiction to this case, a very pronounced efficiency gain was measured at the medium and high load operating points, as can be seen in Figs. 3 and 4. Due to prolonged combustion duration and associated efficiency loss, the highest efficiency at "diesel only" operation was measured at an MFB50% of 17.5° CAaTDC for OP-2000/20 and at an MFB50% of 20° CAaTDC for OP-3000/20. Substituting diesel by an intake manifold injected alcoholic fuel at high load testing moved the highest efficiency combustion centre to more advanced MFB50%, but, as could be expected, cylinder peak pressure, pressure rise rate and nitrogen oxide emissions were very high. Operating the engine in dual-fuel mode with high alcoholic fuel energy share not only impressively increased the engine efficiency, but also introduced a much higher tolerance against high EGR rates; Figs. 5 and 6. This benefit allowed the application of higher EGR rates without degrading the efficiency the same way as in pure diesel operation mode. In other words, a strong mechanism for mitigating the efficiency–NOx trade-off was introduced. In Fig. 6, the already mentioned additional engine efficiency

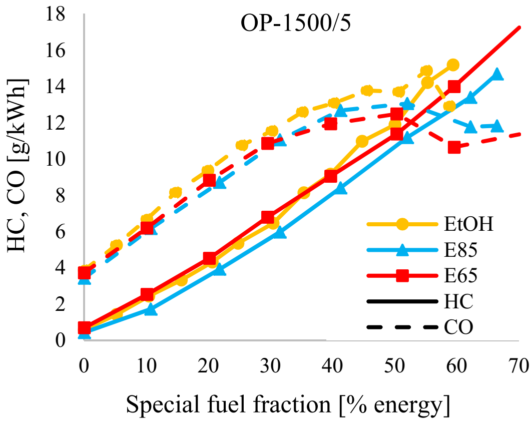


Fig. 1 HC and CO emissions at OP-1500/5, 30% EGR, MFB50% = 7.5° CAaTDC

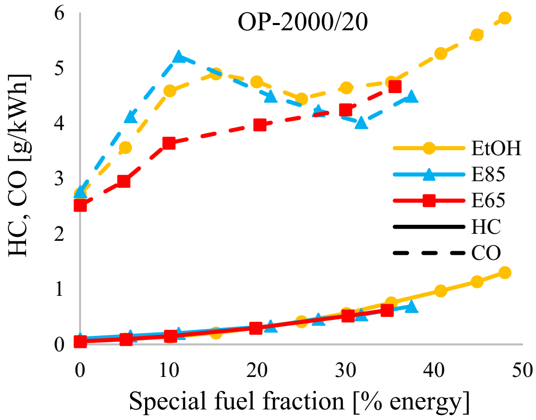


Fig. 2 HC and CO emissions at OP-2000/20, 0% EGR, MFB50% = 17.5° CAaTDC

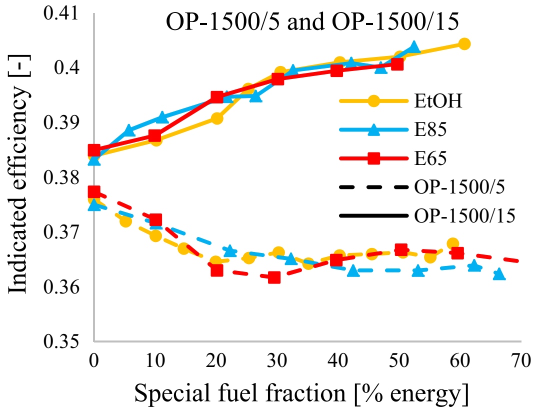


Fig. 3 Indicated efficiency at OP-1500/5 with 30% EGR and OP-1500/15 with 15% EGR; MFB50% = 7.5° CAaTDC

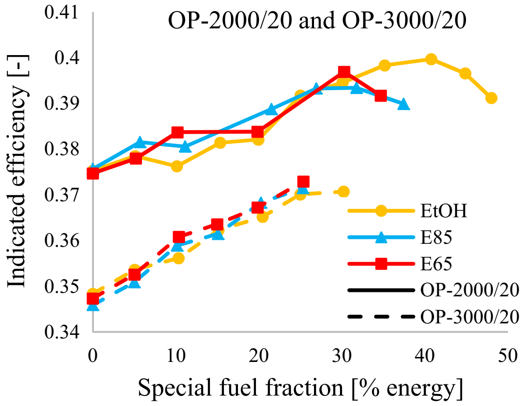


Fig. 4 Indicated efficiency at OP-2000/20 with MFB50% = 17.5° CAaTDC and OP-3000/20 with MFB50% = 20° CAaTDC; 0% EGR

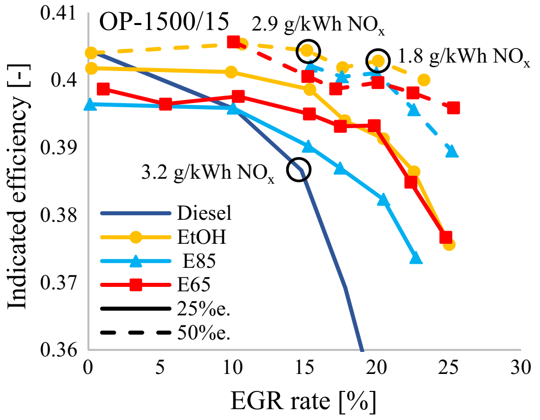


Fig. 5 Indicated efficiency at OP-1500/15, MFB50% = 7.5° CAaTDC

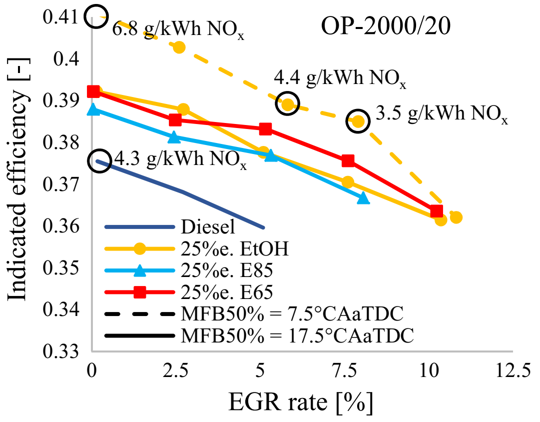


Fig. 6 Indicated efficiency at OP-2000/20

enhancement, which results from advancing MFB50% when operating in dual-fuel mode at high loads, is shown together with the measured NOx values for some interesting points.

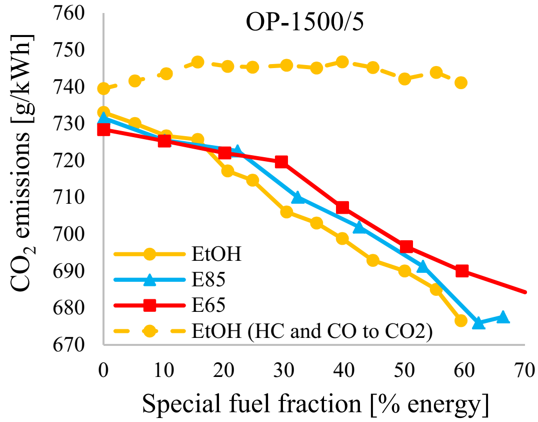


Fig. 7 CO_2 emissions at OP-1500/5, 30% EGR, MFB50% = 7.5° CAaTDC

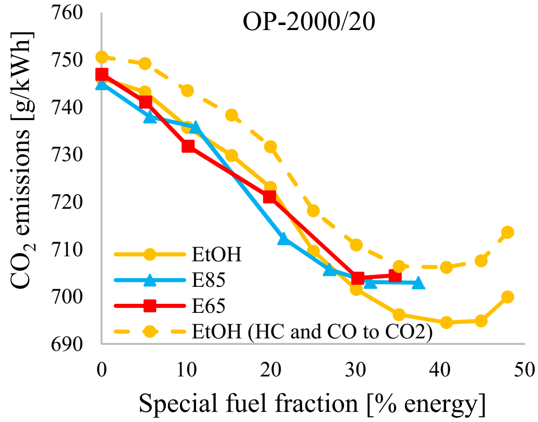


Fig. 8 CO_2 emissions at OP-2000/20, 0% EGR, MFB50% = 17.5° CAaTDC

A remarkable reduction of the raw exhaust gas carbon dioxide emissions was measured with increase in substitution rate at all operating points, e.g. Figs. 7 and 8. Apart from OP-1500/5 (and OP-2000/5), the CO_2 reduction reflects the efficiency increase at dual-fuel operation mode, which is illustrated by a comparison between Figs. 4 and 8. As will be proved later in this paper, the poor dual-fuel efficiency at OP-1500/5 is the consequence of high amounts of unburnt fuel, which do not react to CO_2. At dual-fuel operation mode, the part of the fuel that gets ignited combusts thermodynamically more efficiently than diesel at “diesel only” operation; therefore, less energy input (= less fuel that ignites and burns) is needed to deliver the same engine power output and less CO_2 is produced. The part of the fuel, which does not ignite and combust, is emitted as HC emissions and reduces the net engine efficiency. Additionally, the CO emissions increased with higher substitution rate. Unlike unburnt fuel (HC emissions), CO is a (incomplete) combustion product and its formation reduces the amount of the complete combustion product CO_2. However, knowing this, the operation at load points with high HC and CO emissions cannot be rated as CO_2 advantageous, since in a real-world application these pollutants would be converted to CO_2 in an oxidation catalyst. For this reason, within a simplified approach the full conversion of HC and CO to CO_2 was calculated for the case with pure ethanol operation following the presumption that all measured HC emissions in fact are unburnt ethanol molecules. The resulting CO_2 emissions are added to the measured CO_2 emissions in Figs. 7 and 8. As can be seen at low load operation with ethanol, the theoretical CO_2 emissions are even slightly higher than in "diesel only". Nevertheless, at medium and high load operation with significantly less HC and CO pollutants, the CO_2 savings are still considerable.

Summarizing these results, at high loads the indicated engine efficiency was significantly improved at dual-fuel operation mode with enhanced substitution ratios, whereas it dropped at low loads (similar results are also stated in [22]). The combustion process tolerance against high EGR rates allowed more exhaust gas to be recirculated without affecting engine efficiency the same way as at "diesel only" operation. Substituting diesel with manifold injected alcoholic fuels impressively reduced the engine CO_2 emissions at medium and high load operating points.

4.3 NOx, soot and particle emissions

The results of the NOx and soot emissions measurements over the substitution rate for the tested operating points are depicted in Figs. 9 and 10. The soot mass in the exhaust gas was very effectively reduced at all operating points even when a relatively small diesel amount was replaced by ethanol, E85 or E65. The reduction, however, was at its strongest for approximately the first 20–30% of substituted energy share. Afterwards, soot reduction continued only at a moderate rate or even stagnated.

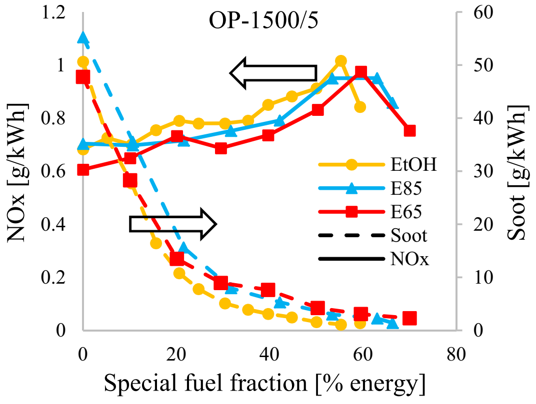


Fig. 9 NOx and soot emissions at OP-1500/5, 30% EGR, MFB50% = 7.5° CAaTDC

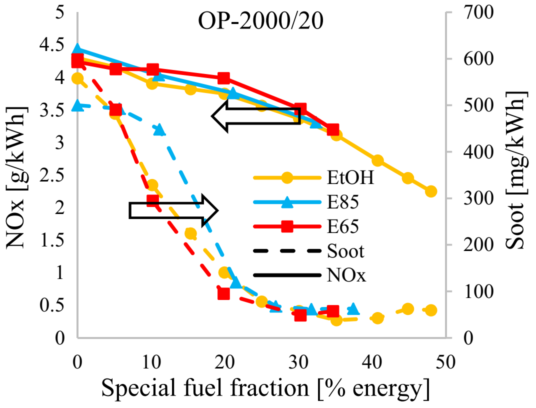


Fig. 10 NOx and soot emissions at OP-2000/20, 0% EGR, MFB50% = 17.5° CAaTDC

Several factors play an important role in minimizing the soot emissions at dual-fuel operation. Ethanol per se is a substance, known for its almost soot-free combustion. The molecule contains only two carbon atoms, which are single bonded, the H/C ratio is higher than for many other fuels and the oxygen atom is available for the combustion directly within the reaction zone. Furthermore, the low boiling point of 78 °C promotes faster homogenization. Distinctive for the dual-fuel combustion process with external alcohol supply is the fact that enough time is available for the air–fuel mixture to be premixed and homogenized before the diesel jet induces the ignition. Thus, the locally fuel-rich zones are less and the formation of soot is limited. The lower aromatics amount also reduces the tendency to form soot precursors [23]. By replacing diesel, the appearance of diffusive diesel combustion is reduced and therefore less soot is produced. Ethanol has also a very high enthalpy of evaporation, which causes a strong cooling effect. With the cylinder charge temperature sinking, the injected diesel fuel needs more time to auto-ignite, its ignition delay is prolonged and more time remains available for diesel spray homogenization.

The behaviour of the NOx emissions over the substitution rate depends on the load conditions: at OP-1500/5 an increase was measured, while a strong reduction occurred at the tests with 20 bar IMEP. The most important factors for NOx formation are temperature, reactant availability and time. The extended ignition delay results in a faster and more compact combustion with higher heat release and higher peak temperatures. This aspect and the higher oxygen availability, which ethanol provides, increase the NOx production. The charge cooling effect of the ethanol evaporation decelerates the pollutant onset [22]. The combustion of the premixed mixture reduces the local peak temperatures, because the heat is released in the whole combustion chamber and not only in a small area around the diesel jet. Higher thermodynamic combustion efficiency means that less fuel is burnt and therefore less heat is released, which also may lower the NOx output. Additionally, ethanol burns with a lower flame temperature than diesel due to the composition of the combustion products [7, 24]. Whether the NOx emissions rise or sink when substituting diesel through manifold injected alcoholic fuel depends on the weight and occurrence of the factors listed above.

As can be seen in an earlier publication on this topic [8], with higher substitution rate the ratio NO_2/NO got higher, because less NO and more NO_2 were produced compared to "diesel only" operation. The sinking in-cylinder charge temperature due to the alcohol's higher heat of evaporation surely may contribute to this phenomenon [21], the main reason, however, is believed to be the presence of free hydroperoxyl radicals HO_2, which are delivered within alcohol combustion [16, 21, 25].

Together with the soot mass, the particle number also dropped, as diesel was replaced by the alternative fuel. By mitigating the smoke problem of the diesel engine, more EGR could be used as an in-cylinder measure for further NOx emission reduction—the diesel typical soot–NOx trade-off was weakened. Figures 11 and 12 illustrate the particle–NOx trade-off for low and medium load and different substitution rates. An outstanding advantage is visible for dual-fuel operation mode, in particular for OP-1500/5.

In [16, 23, 26], the chemicophysical features of the soot emitted from a dual-fuel ethanol–diesel system are investigated and it is reported that the results indicate a significant effect of ethanol on the particle number, but not on the average size. Furthermore, the impact of the ethanol-premixed charge on the soot nanostructural features is found to be negligible.

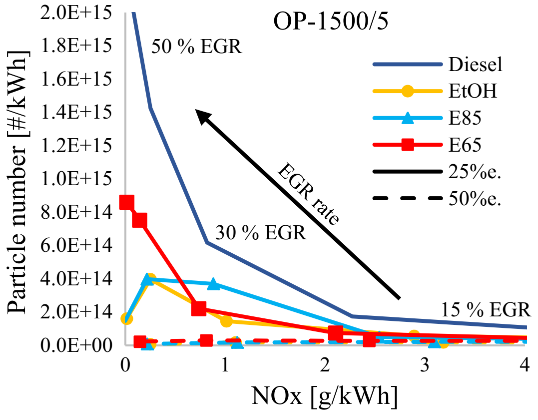


Fig. 11 Particle number–NOx trade-off at OP-1500/5, MFB50% = 7.5° CAaTDC

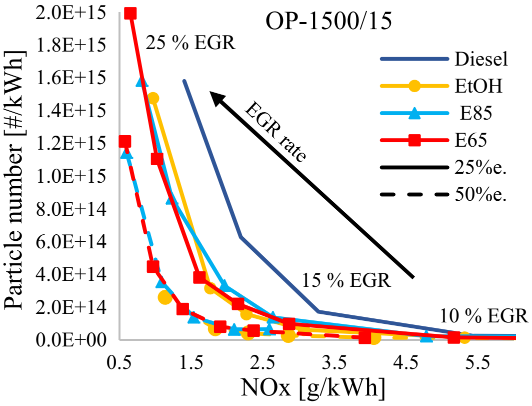


Fig. 12 Particle number–NOx trade-off at OP-1500/15, MFB50% = 7.5° CAaTDC

4.4 Combustion analysis

The analysis of the indicated data generally showed that at dual-fuel mode, the combustion process is characterized by a shorter burning duration; Figs. 13 and Fig. 14. At low load in dual-fuel mode, more time was needed for combustion to start and the diesel injection had to be advanced. Compared to diesel reference operation, at medium and higher load, the ignition delay in dual-fuel mode was shortened and the same MFB50% was set by a retarded injection timing. After ignition occurred, the main combustion phase was completed faster than at "diesel only" operation. The post-combustion phase, which is distinctive for the oxidation of the soot formed during the diesel main combustion phase, was in most cases shorter and with a lower heat release. From an efficiency point of view, all this aspects lead to a thermodynamic beneficial cylinder pressure curve shaping. Their precise value is tightly dependent on load point, EGR,

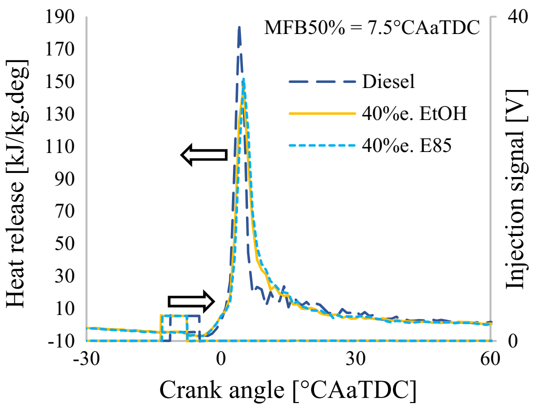


Fig. 13 Indicated heat release rate at OP-1500/5, 30% EGR, MFB50% = 7.5° CAaTDC

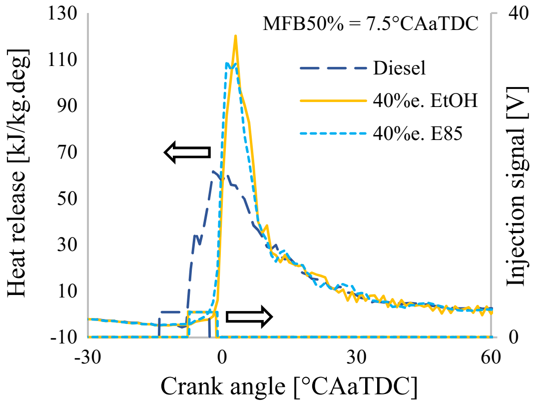


Fig. 14 Indicated heat release rate at OP-1500/15, 15% EGR, MFB50% = 7.5° CAaTDC

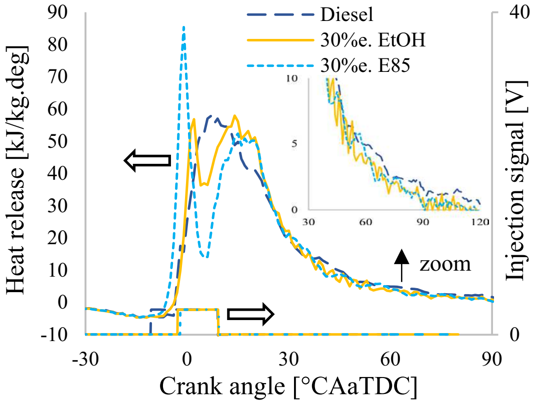


Fig. 15 Indicated heat release rate at OP-2000/20, 0% EGR, MFB50% = 17.5° CAaTDC

manifold pressure, MFB50%, engine speed and, of course, fuel.

Besides the above-mentioned, at some conditions a very important combustion phenomenon was detected—a cyclic reproducible auto-ignition of the premixed homogenous charge. For internal combustion engines, there are three major combustion processes [27]: (1) spark ignition (SI) with premixed flame propagation, (2) compression ignition (CI) with non-premixed (diffusion) flame and (3) homogeneous charge compression ignition (HCCI) with bulk auto-ignition of a premixed charge. If the diesel amount in dual-fuel mode was only as much as it is needed to initiate mixture ignition, the process could be seen as similar to (1).

With the fuel fractions used in the current project, however, the process was somewhere between (1) and (2): a compression ignition of the diesel fuel and a subsequent ignition and a flame propagation of the premixed (air/ethanol) charge. With pre-ignition occurring, the process becomes a mix of (3) and (2). If all of the ethanol does not auto-ignite, a part of it has to burn deflagratively, so the whole combustion process represents a combination of (1), (2) and (3).

Figure 15 shows the heat release in diesel reference operation and dual-fuel operation mode with 30% energy share of ethanol or E85 at OP-2000/20, MFB50% was at 17.5° CAaTDC. As can be seen, the combustion in the case of ethanol clearly begins before the start of the diesel injection. After a rapid and intensive heat release, the main combustion of the injected diesel continues at a moderate rate. With E85 (and E65), the combustion starts even earlier and the heat release of the premixed stage is remarkably higher. According to the octane number of the fuels, E85 is more reactive and ignites easier than ethanol. The described auto-ignition of the premixed charge was not accidental, but permanent and stable in every cycle. It appeared with late MFB50% at medium and high load and was more distinct at low speeds. As could be expected, it emitted more noise, but the cylinder peak pressure was only inconsiderably higher than in the diesel reference operation (approx. 150 bar). The experiments proved that the auto-ignition was existent even after the diesel supply had been completely turned off. Figure 16 shows the same operating point, but with an advanced MFB50% of 7.5° CAaTDC. This combustion centre position was much too early for diesel reference operation and resulted in an efficiency decrease due to a disadvantageous heat release timing. As can be seen in the graph, in the case of “diesel only”, a lot of energy is released long before the piston reaches the top dead centre, thus high blow-by and wall heat losses occur.

Since dual-fuel operation provided a much faster combustion, engine efficiency was even impressively increased at an MFB50% of 7.5° CAaTDC; see Fig. 6. Cylinder peak pressure was, however, in the range of 200 bar and the energy fraction of the alcoholic fuel had to be lowered to 25%e. to prevent mechanical damage. The maximum

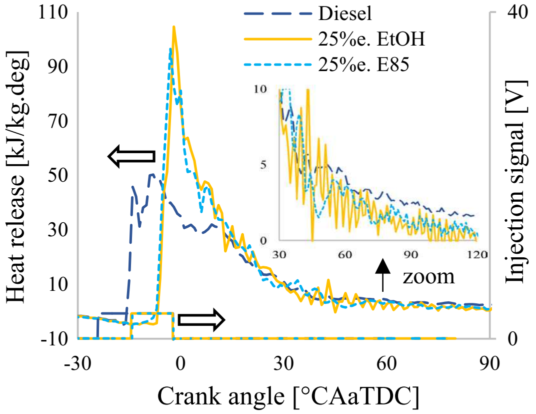


Fig. 16 Indicated heat release at OP-2000/20, 0% EGR, MFB50% = 7.5° CAaTDC

pressure rise rate with 25%e. ethanol was 8.5 bar/°C A at an MFB50% of 17.5° CAaTDC and 18 bar/°CA at an MFB50% of 7.5° CAaTDC. For demonstration purpose, tests with 40%e. were also conducted and the maximum pressure rise rate reached 26 bar/°CA at an MFB50% of 7.5° CAaTDC (these results are not illustrated here). Compared to Fig. 15, advancing MFB50% in Fig. 16 demands a much earlier start of injection and the diesel combustion starts before the theoretical start of the ethanol auto-ignition, so no pre-ignition is detected. In both cases shown above, the pure diesel operation features a higher heat release in the post-oxidation phase than dual-fuel operation.

According to the findings of the literature survey, the combustion process in dual-fuel mode may be designed to fit different concepts, e.g. [17, 18]. The occurrence of knock and auto-ignition as well as the feasibility of different combustion concepts depend mainly on the properties of the fuel. Auto-ignition and knock can be supressed or controlled by optimizing the ethanol energy fraction, the EGR rate, the global air/fuel equivalence ratio, the intake air temperature and the compression ratio. The correct adjustment of these parameters can extend the engine's operating region and diesel substitution rates [28].

5 Simulation results and efficiency loss analysis

5.1 Simulation results

The quality of the 0D/1D single-cylinder simulation model was verified by a comparison with the experimental data, both indicated and conventional. Calculated power output, airflow, fuel consumption and engine efficiency closely matched the test values at all operating points. The original purpose of the simulation was to explain the engine efficiency differences visible in Figs. 3, 4, 5 and 6 in a quantitative manner. Some important simulation results are selected and discussed here. The findings are based on OP-2000/20.

The attempt to simply determine the cylinder temperature as a result of the indicated pressure and cylinder geometry by using a common post-processing software tool was found to be inappropriate, since the presence of a second fuel changes the composition and consequently the thermodynamic properties of the cylinder charge. The chosen simulation package considers these factors, and the calculated O_2, CO_2 and H_2O mass fractions are shown in Fig. 17.

It can be seen that "diesel only" combustion requires more oxygen, mainly due to the lower process efficiency at this setting. In dual-fuel mode, the CO_2 fraction is lower and that of water is higher. This distribution suggests less charge-related efficiency losses, because the heat capacity ratio of water is higher than of CO_2—at 1273 K the values are as follows: O_2 1.302; CO_2 1.172; H_2O 1.23. Figure 18 confirms this assumption for the working cycle. Engine efficiency gains as a result of reduced losses due to real charge composition and real fluid properties are expected according to this finding. During the compression stroke, c_p/c_v is lower in dual-fuel mode because a mixture of ethanol and air has a lower heat capacity ratio than pure air.

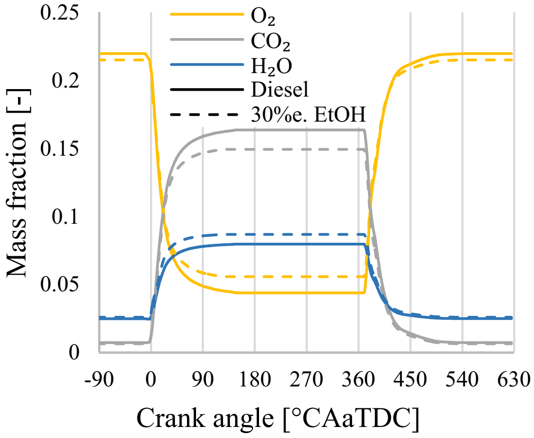


Fig. 17 Simulated combustion cycle O_2, CO_2 and H_2O mass fractions at OP-2000/20, 0% EGR, MFB50% = 17.5° CAaTDC. Comparison between "diesel only" operation and dual-fuel operation with 30% ethanol energy share

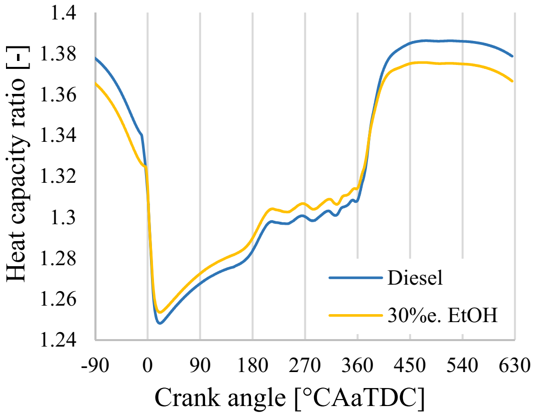


Fig. 18 Simulated heat capacity ratio c_p/c_v at OP-2000/20, 0% EGR, MFB50% = 17.5° CAaTDC. Comparison between "diesel only" operation and dual-fuel operation with 30% ethanol energy share

With the known variables cylinder pressure and charge composition, the cylinder average temperature can be calculated. As can be seen in Fig. 19, the cylinder temperature in dual-fuel operation with 30% ethanol energy share is lower than in "diesel only" operation throughout the whole cycle (except for the short range after TDC). The simulated heat flux from the fluid to the walls is shown in Fig. 20. In the range of 0 to 7° CAaTDC, a marginally higher heat transfer occurs when operating with 30%e.

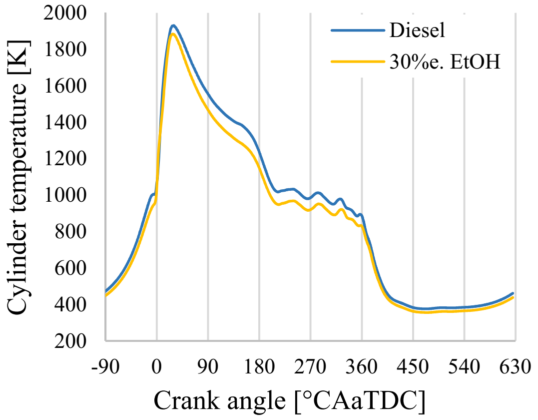


Fig. 19 Simulated cylinder temperature at OP-2000/20, 0% EGR, MFB50% = 17.5° CAaTDC. Comparison between "diesel only" operation and dual-fuel operation with 30% ethanol energy share

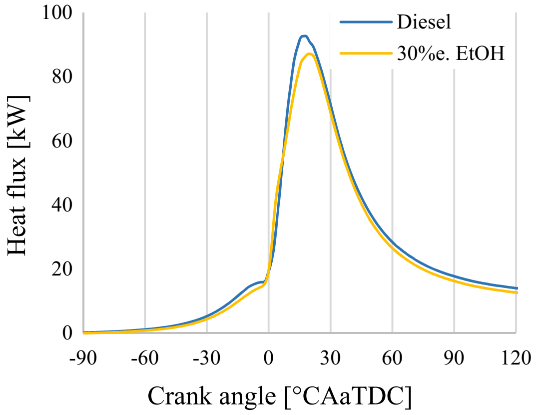


Fig. 20 Simulated heat flux from fluid to wall at OP-2000/20, 0% EGR, MFB50% = 17.5° CAaTDC. Comparison between "diesel only" operation and dual-fuel operation with 30% ethanol energy share

ethanol, apart from that the heat flux in dual-fuel mode is lower.

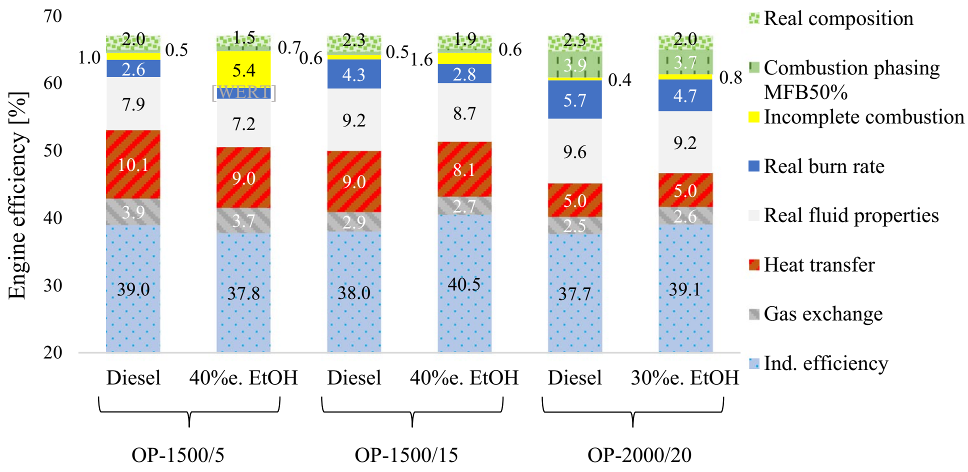
5.2 Efficiency loss analysis

An efficiency loss analysis is shown in Fig. 21 for low, medium and high load operation. In agreement with the engine test bed findings, compared to the diesel reference operation, the indicated efficiency in dual-fuel mode is reduced only at the 5 bar indicated mean effective pressure load point. The bar chart clearly visualizes the source of the major efficiency loss—a high percentage of incomplete combustion, as it was presumed in Fig. 1. At the other investigated load points, a higher share of incomplete combustion is also encountered in dual-fuel mode, it is however significantly lower than at OP-1500/5 and is being overcompensated by a series of efficiency gains.

Due to the changed fluid composition, the real charge and real fluid properties losses sink at all dual-fuel operating points. Since MFB50% was held approximately equal for each pair "diesel only—dual-fuel", the loss due to combustion phasing is also basically identical. In a similar way, the constant pressure difference "exhaust – manifold" was set to exclude the gas exchange influence on the combustion process efficiency. The "real burn rate" shares in the diagram prove the accelerated combustion at dual-fuel mode to be one of the main reasons for higher efficiency.

Another loss that is generally reduced when operating with intake manifold alcoholic fuel injection is the wall heat transfer. Surprisingly, despite the evidence in Fig. 20, the calculated heat transfer loss at OP-2000/20 is equal for both combustion processes. The efficiency loss is calculated by relating the specific particular work loss to the work that would result from the brought-in fuel energy with no losses at all (100% efficiency). The software calculated 2.6 bar mean effective pressure loss due to heat transfer for the "diesel only" case and 2.5 bar for the dual-fuel case with 30%

Fig. 21 Results of the efficiency loss analysis for three operation points. Comparison between "diesel only" operation mode and dual-fuel operation



ethanol energy share, so both cases differ by only 0.1 bar. However, dual-fuel mode operation also requires less fuel energy than diesel reference operation (2.73 vs 2.85 kJ/cycle), so the percentage heat loss share in this case is barely changed. At OP-1500/15 for example, the mean effective pressure lost due to wall heat losses in "diesel only" operation is 3.58 bar and 3 bar in dual-fuel mode, whereas the fuel energy in the first case is 2.13 and 2 kJ/cycle in the second. These values lead to a significantly reduced heat transfer loss in dual-fuel mode.

It should be noted that the calculated values for wall heat transfer have to be interpreted with care when comparing stratified operation (as in pure diesel mode) and partially premixed operation (as in dual-fuel mode), as the used wall heat transfer model in the 0-dimensional approach (Woschni Classic) does not account for stratification effects. Therefore, wall heat loss for stratified operation tends to be overestimated in comparison to homogenous (or partly homogenous) operation.

6 Conclusions

The usage of ethanol and two different mixtures of ethanol and gasoline (E85 and E65) was investigated on a modified diesel engine designed to work in a dual-fuel combustion mode with intake manifold alcohol injection. The maximum ratio of alcohol to diesel fuel was limited by irregular combustion phenomena like degrading combustion quality and poor process controllability at low load and knock as well as auto-ignition at high load. At low load testing, up to 70% of the diesel energy could be substituted by the alcoholic fuels, whereas at high loads the maximum substitution rate declined to 30%e. With rising alcohol amount, a significant reduction of soot mass and particle number of up to 99% (depending on load point and substitution ratio) was observed. At some testing points, substituting diesel with ethanol, E65 or E85 led to a reduction of NOx emissions; however, the real benefit concerning the nitrogen oxides was introduced by the mitigation of the soot–NOx trade-off. The low soot emissions in dual-fuel operation mode allowed a further increase of the EGR rate, which helped lower the NOx emissions far below the diesel reference operation values. The indicated engine efficiency was significantly improved with enhanced substitution ratios at medium and high loads (by up to 6%), whereas it dropped at low loads (by approx. 3%). The combustion process tolerance against high EGR rates in dual-fuel mode allowed more exhaust gas to be recirculated without affecting engine efficiency the same way as in "diesel only" operation. Substituting diesel with manifold injected alcoholic fuels impressively reduced the engine CO_2 emissions at medium and high load operating points. The catalytic conversion of the high HC and CO emissions measured at low load operation would eventually lead to higher tailpipe CO_2 emissions.

The analysis of the indicated data generally showed that at dual-fuel mode, the combustion process is characterized by a shorter burning duration. At low load, more time was needed for combustion to start at dual-fuel mode. Compared to diesel reference operation, at medium and higher load, the ignition delay was shortened. At some conditions and higher loads, a cyclic reproducible auto-ignition of the premixed homogenous charge occurred.

A simulation model was built for the test engine and selected operating points from the engine test bed measurements were implemented into the model to generate an efficiency loss analysis. The calculations showed that the high amounts of unburnt fuel at dual-fuel operation were the main reason for efficiency degradation, whereas the reduced losses due to real charge composition, real fluid properties, real burn rate and heat transfer enhanced the efficiency of the engine at dual-fuel mode.

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Biogenous Ethanol: CO_2 Savings and Operation in a Dual-Fuel Designed Diesel Engine

Bioethanol: CO_2-Einsparungen und Einsatz im Dual-Fuel Dieselmotor

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Abstract

The usage of ethanol and two different mixtures of ethanol and gasoline (E85 and E65) were investigated on a modified diesel engine designed to work in a dual-fuel combustion mode with intake manifold alcohol injection. The maximum ratio of alcohol to diesel fuel was limited by irregular combustion phenomena like degrading combustion quality and poor process controllability at low load and knock as well as auto-ignition at high load. With rising alcohol amount, a significant reduction of soot mass and particle number was observed. At some testing points, substituting diesel with ethanol, E65 or E85 led to a reduction of NOx emissions, however, the real benefit concerning the nitrogen oxides was introduced by the mitigation of the soot-NOx trade-off. The indicated engine efficiency in dual-fuel mode showed an extended tolerance against high EGR rates. It was significantly improved with enhanced substitution ratios at high loads, whereas it dropped at low loads. An efficiency loss analysis was conducted for better understanding of the measured efficiency values. Substituting diesel with intake manifold injected alcoholic fuels impressively lowered the engine CO_2 emissions. A case study of the bioethanol production by AGRANA demonstrated the high ability of bioethanol to reduce the holistic well-to-wheel CO_2 emissions of the dual-fuel powered diesel engine.

1. Introduction

The transport sector is a major contributor to the greenhouse gas emissions in the European Union with a share of about 24 % in 2016 [1]. Reducing CO_2 from traffic is crucial for achieving the desired climate stabilizing objectives and lowering the dependence on fossil fuels. The efforts on this field should be supported by rational as well as technically and economically feasible sustainable solutions. Increasing the usage of biofuels is one of these solutions. Ethanol, in particular, is a very well known fuel produced from different sources and by various methods.

Despite the present alternative powertrains development, the diesel engine is predicted to remain crucial for mobility of people and goods in the long term due to its unmatched efficiency, robustness and operation cost and flexibility. Therefore, the search for diesel substitute fuels that are sustainable and of wide availability is of high priority. The usage of ethanol is normally assumed with spark ignition engines but not with a compression ignition engine, because of the very low cetane number of this fuel. However, there are several different possibilities to utilize this alcohol in a diesel engine and it is expected to defuse the classical soot-NOx trade-off due to its high oxygen content, advantageous molecule structure and better mixture formation and combustion process. Ethanol can be used as a single fuel in a dedicated ethanol compression ignition engine with a higher compression ratio. In order to ensure the ethanol ignition, however, fuel additives are necessary [2]. Adding the alcohol to the conventional diesel fuel in the form of a so-called "blend" is another way to use it in a diesel engine. Though it is the simplest method, the ethanol quantity is very limited due to separation issues, poor ignitibility and current diesel norm EN590 violation in terms of cetane number and flash point. Perhaps the most promising technique for ethanol usage in a diesel engine is the unconventional application in the form of a dual-fuel combustion process. In this case, the alcoholic fuel is fed into the engine as a separate fuel and the ignition of the directly injected diesel fuel starts the combustion of the alcohol-air mixture. This approach provides high substitution ratios and flexible operation based on the fuel availability – diesel only or dual-fuel.

This study handles of the operation of a diesel engine in a dual-fuel mode with an intake manifold ethanol injection. Several researchers have published articles on investigations of the dual-fuel combustion process with alcohols. The findings, however, are not always consistent and differ at some points, as can be concluded from a comprehensive review of many publications on this topic in [3]. The literature review did not offer satisfactory explanations for the observed efficiency changes with rising amount of intake manifold alcohol injection, therefore an engine-process model for the test engine was generated and selected operating points from the engine experiments are analysed with it. The conducted efficiency loss analysis supports the understanding of the measured results.
Furthermore, the role of bioethanol as a biogenic energy carrier is introduced. Special attention is given to the production of bioethanol and the greenhouse gas saving potentials of this fuel. A case study of AGRANA's bioethanol plant in Austria is presented.

2. Bioethanol-fuel from socio-economic perspective

Currently, bioethanol is mainly obtained as a so-called first generation biofuel. That includes every conventional fermentation procedure for agricultural raw materials containing sugar and starch in which the fruit of the respective raw material plant is exploited.
A major discussion topic about first generation biofuels is the frequently raised ethical question concerning the competitiveness between foodstuffs and biofuels. However, increased grain prices, as happened it the near past, are driven by two main factors – poor yield in key producing countries and activity in the international finance sector. According to the World Bank [4], more than 50 % of food price increases derive from crude oil prices, not the production of biofuels. In 2008, just 4 % of the world's grain was used for bioethanol production, taking the combined production of animal feed into consideration. Since 2008 EU Biofuels production increased by 68 % [5], while global food prices dropped by 20 % [6]. Moreover, the Food and Agriculture Organization of the United Nations (FAO) and the International Food Policy Research Institute (IFPRI) recognize the chances sustainable and ethically maintainable biofuel production could offer for both food security and modern bioenergy development [7] [8]. EU ethanol production uses less than 1 % of EU agricultural land, while 6 % of agricultural land in the EU is unused. Only 2 % of EU grain supply and only 6 % of EU sugar substrate are utilised for bioethanol. For each tonne of ethanol, one tonne of a high protein animal feed is produced and the soya imports from abroad are reduced, meaning that soya-growing areas in export countries can be used to grow foodstuffs.
Regarding nature aspects, it is up to every country to implement strictest policies to guarantee wildlife preservation and nature conservation. In Europe, but especially in Austria, a stringent set of rules and environmental regulations apply.
Despite a perceptible trend towards drive train electrification, liquid fuels are expected to retain their crucial role in mobility also in the next decades, especially in hard-to-electrify

sectors. Organizations like the International Renewable Energy Agency (IRENA) and the International Energy Agency (IEA) often call for more biofuels in EU's policy on energy and climate and stress on the importance of bioethanol [9] [10]. The United Nations Framework Convention on Climate Change (UNFCCC) also addresses the strengths of bioethanol in reducing CO_2 emissions from transport.

The newly approved Renewable Energy Directive (known as RED II) confirms the importance of sustainably produced crop-based biofuels such as European ethanol to achieving EU climate goals. However, it still caps the contribution these low-carbon fuels can make at each Member State's 2020 levels, up to 7 % energy share.

2.1 Bioethanol by AGRANA

In Pischelsdorf (Lower Austria), AGRANA BETEILIGUNGS-AG operates a bioethanol fuel plant and a starch factory, collectively referred to as "biorefinery". The residual starch slurry produced in the starch factory is processed into bioethanol and animal feed DDGS (Distiller's Dried Grain with Solubles) at the bioethanol plant. Up to 620 000 tons of grain per year can be converted to 240 000 m^3 or 190 000 tons of bioethanol. In addition to the fuel, up to 190 000 tons of DDGS can be produced each year. This high-quality, certified GMO-free protein-rich animal feed helps to make the production of bioethanol commercially viable, with the quantities produced replacing up to a quarter of Austria's soya imports from countries that can no longer guarantee GMO-free production. As a by-product of bioethanol production, up to 135 000 tons of biogenic carbon dioxide are produced for the food industry and various technical applications.

The raw material sources for the bioethanol production are surplus cereals such as wheat, rye, triticale, barley and maize, all in animal feed quality. Food quality crops are not used. Today, the starch-containing residuals from the wheat starch processing at the starch factory (second flour, small grains and residual starch slurry) make ca. 25 % of the bioethanol raw material. An additional facility is planned to start operation in 2019, material streams from wheat starch production will then account for ca. 45 % of the raw material for bioethanol production. Especially the residual slurry from wheat starch production will be converted into ca. 80 000 m^3 of bioethanol with this compound plant.

The delivered raw material is fed via a silo intermediate storage to the grinding, suspended by addition of water, then enzymatically and thermally liquefied and introduced into a simultaneous saccharification and fermentation. In the course of the saccharification, the dextrins contained are decomposed by enzymes into monosaccharides. This raw material is then converted by yeast fermentation into an alcoholic mash, which is subsequently processed in a multi-stage distillation to raw alcohol. Via molecular sieves, a further dehydration of the raw alcohol to fuel alcohol is carried out.

The protein-rich distillation residuum (distiller's wash) is centrifuged. The thin slurry (centrate) is concentrated in the evaporation to syrup or occasionally recirculated to the liquefaction process. The thick slurry (wetcake), which are the centrifugalized fibre residuals, is mixed with the syrup and then carefully dried and pelletised to storable DDGS.

The bioethanol plant is equipped with two energy supply systems: a calorific power plant located nearby and a thermal waste incineration plant owned by the EVN group supplying high-pressure steam. The total efficiency of the industrial compound (electricity and steam) is hence higher than for a stand-alone facility. The energy sources for steam generation are 25 % coal and 75 % waste. For power generation 35 % hydropower, 52 % natural gas, 3 % solid or liquid biomass, 2 % other renewable energy and 8 % wind energy are used.

In 2018, the average price of European domestic ethanol (T2) free on board Rotterdam barge was 473 €/m³ (average Jan-Nov 2018). Currently, approx. 50-60 % of the bioethanol produced in Pischelsdorf is exported.

In order to assess the sustainability of bioethanol production at the AGRANA facilities, life-cycle analyses (as defined by ISO 14.040) are carried out. They include every process related to emissions and energy, both domestically and abroad, which is necessary to run vehicles on petrol or bioethanol.
As a biofuel producer, AGRANA has to provide the results of the greenhouse gas savings through external certifications in accordance to the International Sustainability and Carbon Certification (ISCC), Figure 1. Some EU countries, like England, accept that no cultivation emissions are to be accounted for the raw material residual starch slurry (calculation method ISCC EU). The greenhouse gas savings from bioethanol produced by AGRANA are between 68 and 72 % and are certified by SGS.

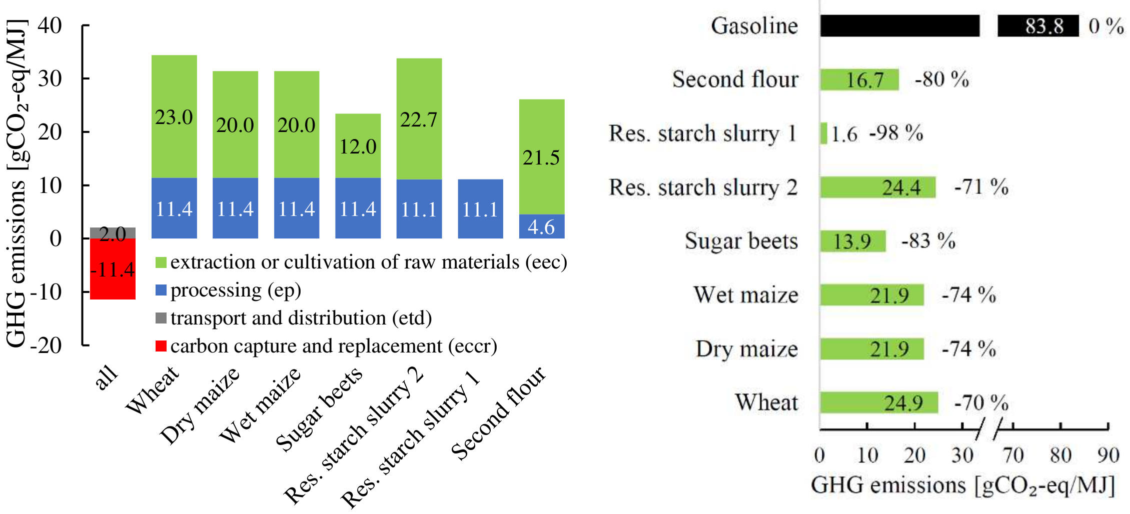

Figure 1: GHG shares (left) and GHG emissions and reductions (right), calculated in accordance to EU Directive 2009/28/EC for bioethanol from different raw materials; starch slurry 1 calculation method ISCC EU, starch slurry 2 – ISCC DE (AGRANA 2017)

3. Investigated Fuels

Table 1 shows some of the properties of the investigated fuels. In this study, a certified CEC test diesel fuel was used as a reference for comparison.

Table 1: Properties of the investigated fuels

Fuel notation	Diesel	EtOH	E85	E65
Density [kg/m^3]	831	789	782	773
Lower heating value [MJ/kg]	42,68	26,32	29	31,46
Cetane number [-]	54	8	-	-
Octane number [-]	-	111	98	101
C-fraction [wt %]	85,4	52,7	56,5	63,2
H-fraction [wt %]	14,2	12,8	12,8	13,2
O-fraction [wt %]	0,4	33,8	29,8	23,1
H/C atomic ratio [-]	1,99	2,92	2,72	2,51
O/C atomic ratio [-]	0,004	0,48	0,4	0,27
gCO_2/MJ	73,3	73,87	72,02	73,96
gH_2O/MJ	29,94	44,08	40,08	37,94

Technically pure ethanol was the first representative of the investigated oxygenated fuels. However, the intake manifold injected fuel does not necessarily have to be of high purity – a great advantage lies within the possibility to use lower grade ethanol, since even higher water contents had no harmful impact on the engine. Additionally, E65 and E85 gasoline-ethanol mixtures were supplied, because their availability at filling stations is more presumable. E85 (RF-01-08) was delivered by a supplier and E65 was self-mixed (35 vol% winter quality gasoline RF-04-03), which is the reason for the higher octane number compared to E85. The last two rows make it visible that the alcoholic fuels do not necessarily produce less CO_2 than diesel. The calculation results are strongly dependent on the lower heating value and the C/H/O-ratio from the fuel analysis.

4. Test engine, test methodology and measurement equipment

A modern in-line four-cylinder diesel engine was modified for single cylinder operation and used as a test engine. Only the first cylinder was fired, the other three were deactivated and their gas exchange was separated from the gas exchange of the fired cylinder. The cylinder had a displacement of 537 cm^3 and a compression ratio of 17.5. Bore and stroke are 88 and 88.34 mm, respectively. The original high pressure common rail diesel injection system was equipped with seven-holes nozzles solenoid injectors and could handle a pressure of up to 2000 bar. Charging was performed with an external electrically driven supercharger. An electrically adjustable flap valve was used to adjust a turbocharger comparable exhaust gas back pressure. Cooled high-pressure exhaust gas recirculation (EGR) was applied. The standard exhaust gas aftertreatment system has been removed and emissions sampling took place in the raw exhaust gas. The temperatures of the charge air and the fuel were conditioned.

The alcoholic fuel was injected with a pressure of 4.5 bar (abs.) into the intake air through a conventional gasoline injector, which was installed in a specially designed intake manifold.

The test engine was equipped with high and low pressure indication and standard exhaust gas measurement, as well as AVL Micro Soot Sensor 483 and AVL Particle Counter 489. The investigations were conducted at five operating points, which cover a typical commercial vehicle engine operating map. The most important engine operating parameters are depicted in Table 2. Variations of the exhaust gas recirculation rate, of the combustion centre position MFB50% (by adjusting the start of injection) and of the proportion of diesel fuel to alcoholic fuel were carried out. All specific emission values in this article are with respect to indicated engine work.

Table 2: Investigated operating points with engine parameters

Operating point OP-	1500/5	1500/15	2000/5	2000/20	3000/20
Speed [rpm]	1500	1500	2000	2000	3000
p_{mi} [bar]	5	15	5	20	20
Power output [kW]	3,3	10	4,5	17,9	26,8
Rail pressure [bar]	~670	~1040	~800	~1240	~1400
Intake manifold pressure (abs.) [mbar]	1130	2250	1230	2500	2600
Δp exhaust-intake [mbar]	270	500	330	300	300

5. Results of the combustion investigations

In the course of the investigations, at low load, degrading combustion quality, poor controllability and high cycle variation determined the maximum possible alternative fuel amount. In this project, a maximum substitution rate of 60-70 % energy share was possible with the fuels used. At high loads it was the occurrence of knock and auto-ignition that prohibit further increase of the substitution ratio. Nevertheless, at OP-1500/15 still 50-60 %e. substitution rate was achieved; the corresponding ranges for OP-2000/20 and OP-3000/20 were measured to be approx. 40 %e. and 25 %e., respectively. In accordance to its higher octane number, pure ethanol ensured slightly higher substitution rates at high load testing, whereas at OP-1500/5 it failed to provide stable combustion before E65 and E85 did.

5.1 Efficiency and CO$_2$ emissions

Increasing the substitution rate at OP-1500/5 resulted in a considerable drop of engine efficiency until ca. 30 % energy share and affected no significant further changes up to the maximum possible alcoholic fuel amount, Figure 2 a). In contradiction to this case, a very pronounced efficiency gain was measured at the middle and high load operating points, as can be seen in Figure 2 a) and b). Due to prolonged combustion duration and associated efficiency loss, the highest efficiency at “diesel only” operation was measured at a MFB50% of 17.5°CAaTDC for OP-2000/20 and at a MFB50% of 20°CAaTDC for OP-3000/20. Substituting diesel by an intake manifold injected alcoholic fuel moved the highest efficiency combustion centre to more advanced MFB50%, but, as could be expected, cylinder peak pressure, pressure rise rate and nitrogen oxide emissions were very high.

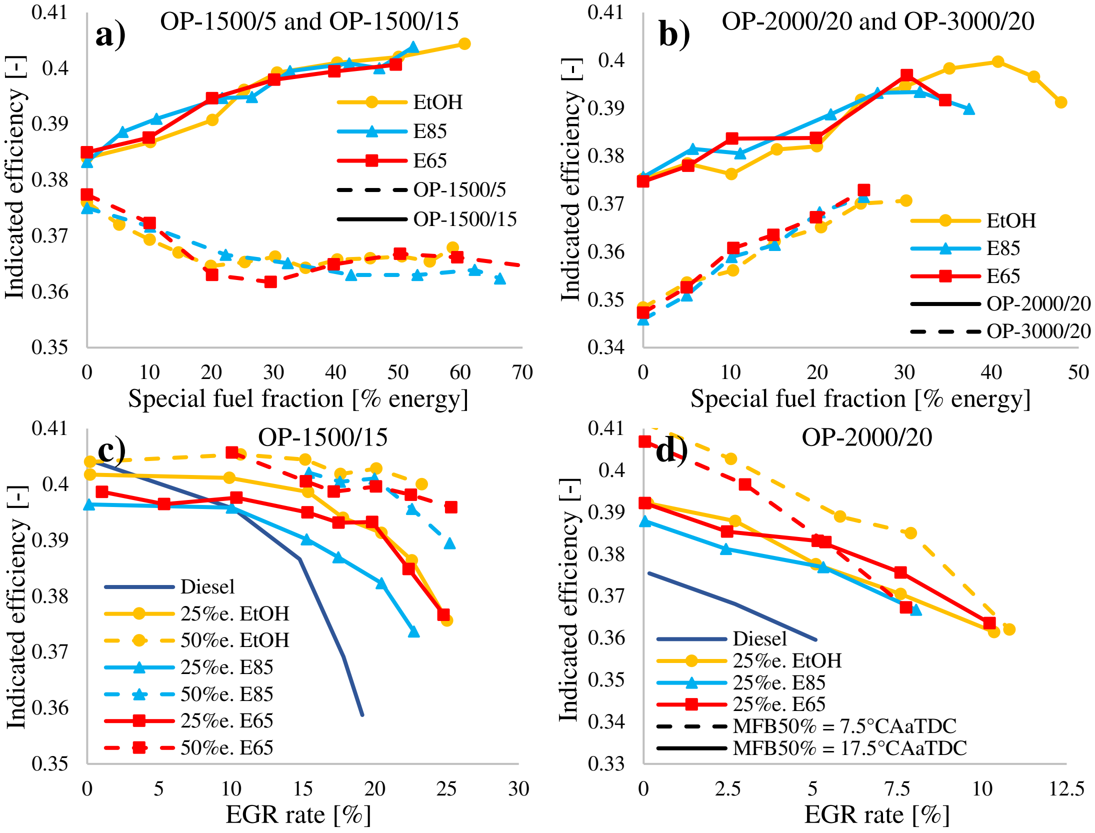

Figure 2: Indicated efficiency. ***a)*** *OP-1500/5 with 30 % EGR and OP-1500/15 with 15 % EGR; MFB50% = 7.5°CAaTDC;* ***b)*** *OP-2000/20 with MFB50% = 17.5°CAaTDC and OP-3000/20 with MFB50% = 20°CAaTDC;0 % EGR;* ***c)*** *at OP-1500/15, MFB50% = 7.5°CAaTDC;* ***d)*** *OP-2000/20*

Operating the engine in dual-fuel mode with high alcoholic fuel energy share also introduced a much higher tolerance against high EGR rates, Figure 2 c) and d). This benefit allowed the application of higher EGR rates without degrading the efficiency the same way as in pure diesel operation mode.

A significant reduction of the exhaust gas carbon dioxide emissions (tank-to-wheel) was measured with increasing substitution rate at all operating points, e.g. Figure 3 and Figure 4. Apart from OP-1500/5 (and OP-2000/5), the CO_2 reduction reflects the efficiency increase at dual-fuel operation mode, which is illustrated by a comparisson between Figure 4 and Figure 2 b). As will be proved later, the poor dual-fuel efficiency at OP-1500/5 is the consequence of high amounts of unburnt fuel, which do not react to CO_2. At dual-fuel operation mode, the part of the fuel that gets ignited combusts thermodynamically more efficient than diesel at “diesel only” operation, therefore less energy input (= less fuel that ignites and burns) is needed to deliver the same engine power output and less CO_2 is produced. The part of the fuel, which does not ignite and combust, is emitted as HC emissions and reduces the net engine efficiency. Additionally, the CO emissions increased with higher substitution rate. Unlike unburnt fuel (HC emisions), CO is an (incomplete) combustion product and its formation reduces the amount of the complete combustion product CO_2.
As can be seen in the diagramms, the regenerative nature of the biofuel allowed remerkable well-to-wheel CO_2 savings. For these calculations the 70 % GHG saving potential of AGRANA’s bioethanol was used.

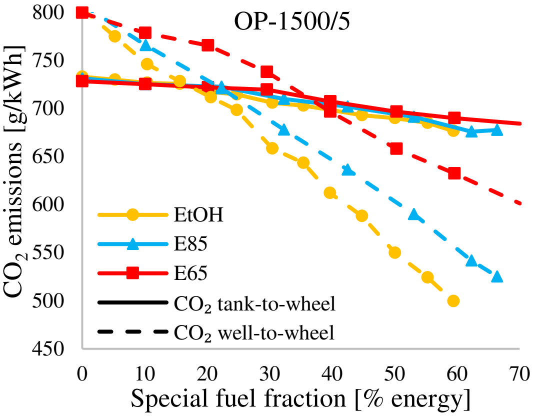

Figure 3: CO_2 emissions at OP-1500/5, 30 % EGR, MFB50% = 7.5°CAaTDC

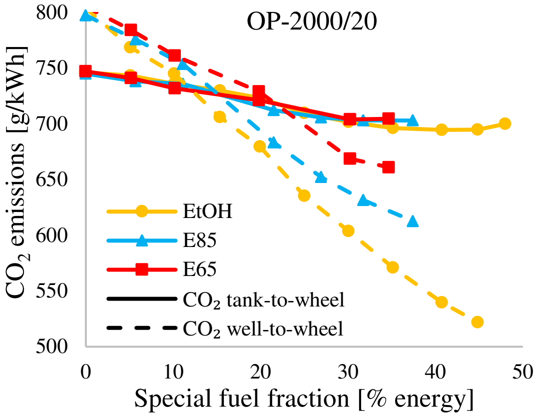

Figure 4: CO_2 emissions at OP-2000/20, 0 % EGR, MFB50% = 17.5°CAaTDC

5.2 Polluting emissions

5.2.1 NO_x, soot and particle emissions

The results of the NO_x and soot emissions measurements over the substitution rate for the tested operating points are depicted in Figure 5 and Figure 6. The soot mass in the exhaust gas was very effectively reduced at all operating points even when a relatively small diesel amount was replaced by ethanol, E85 or E65. Several factors play an important role for minimizing the soot emissions at dual-fuel operation. Ethanol per se is a substance, known for its almost soot free combustion. The molecule contains only two carbon atoms, which are single bonded, the H/C ratio is higher than for many other fuels and the oxygen atom is available for the combustion directly within the reaction zone. Furthermore, the low boiling point of 78°C promotes faster homogenisation. Distinctive for the dual-fuel combustion process with external alcohol supply is the fact that enough time is available for the air-fuel mixture to be premixed and homogenised before the diesel jet induces the ignition. Thus, the locally fuel rich zones are less and the formation of soot is limited. The lower aromatics amount also reduces the tendency to form soot precursors [11]. By replacing diesel, the appearance of diffusive diesel combustion is reduced and therefore less soot is produced. Ethanol has also a very high enthalpy of evaporation, which causes a strong cooling effect. With the cylinder charge temperature sinking, the injected diesel fuel needs more time to auto-ignite, its ignition delay is prolonged and more time remains available for diesel spray homogenisation.

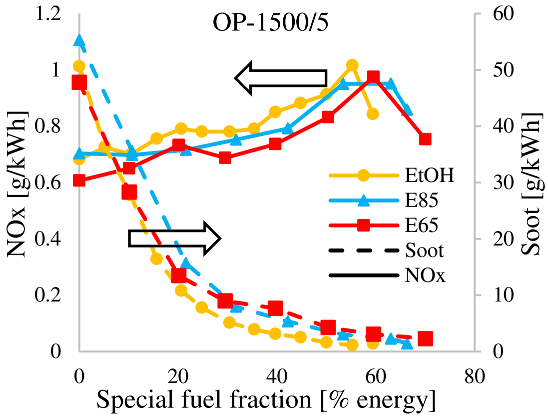

Figure 5: NOx and soot emissions at OP-1500/5, 30 % EGR, MFB50% = 7.5°CAaTDC

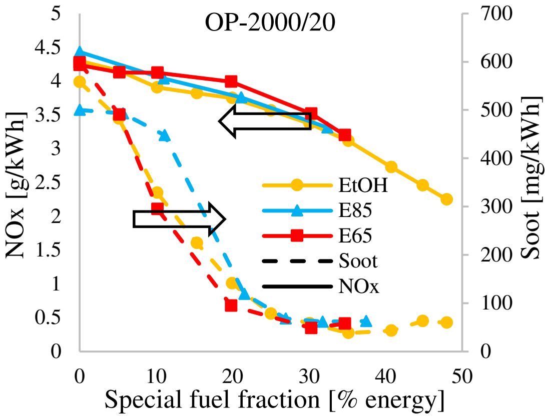

Figure 6: NOx and soot emissions at OP-2000/20, 0 % EGR, MFB50% = 17.5°CAaTDC

The behaviour of the NO_x emissions over the substitution rate depends on the load conditions: at OP-1500/5 an increase was measured, while a strong reduction occurred at the tests with 20 bar p_{mi}. The most important factors for NO_x formation are temperature, reactant availability and time. On the one hand, the extended ignition delay results in a faster and more compact combustion with higher heat release and higher peak temperatures. This aspect and the higher oxygen availability, which ethanol provides, increase the NO_x production. On the other hand, the faster combustion means that less time is available for NO_x formation. The charge cooling effect of the ethanol evaporation also decelerates the pollutant onset. The combustion of the premixed mixture reduces the local peak temperatures, because the heat is released in the whole combustion chamber and not only in a small area around the diesel jet.

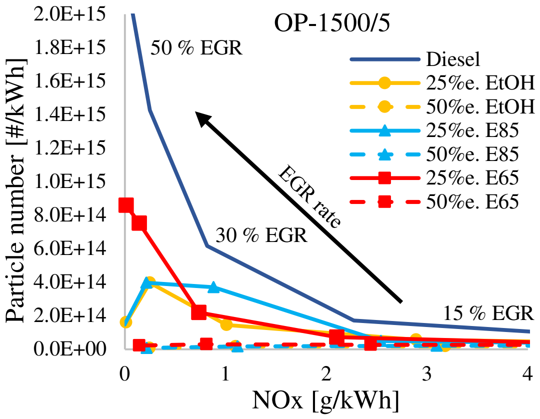

Figure 7: Particle number-NOx trade-off at OP-1500/5, MFB50% = 7.5°CAaTDC

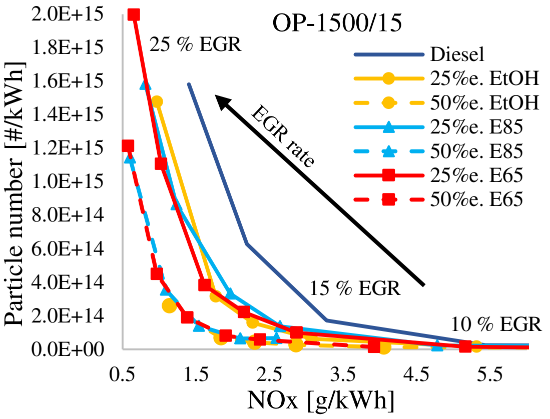

Figure 8: Particle number-NOx trade-off at OP-1500/15, MFB50%= 7.5°CAaTDC

Higher thermodynamic combustion efficiency means that less fuel is burnt and therefore less heat is released, which also may lower the NO_x output. Additionally, ethanol burns with lower flame temperature than diesel due to the composition of the combustion products [2] [12].Whether the NO_x emissions rise or sink when substituting diesel through manifold injected alcoholic fuel, depends on the weight and occurrence of the factors listed above.

Together with the soot mass, the particle number also dropped, as diesel was replaced by the alternative fuel. By mitigating the smoke problem of the diesel engine, more EGR could be used as an in-cylinder measure for further NO_x emissions reduction – the diesel typical soot-NO_x trade-off was weakened, Figure 7 and Figure 8. An outstanding advantage is visible for dual-fuel operation mode, in particular for OP-1500/5.

5.2.2 HC and CO emissions

Compared to the diesel reference operation, the output of unburnt or partly burnt fuel was found to be considerable at duel-fuel mode, especially at low loads. The amount of unburnt hydrocarbons (HC) and carbon monoxide (CO) steeply rised with the substitution rate. At OP-1500/5 the HC emissions rose by ca. 2 g/kWh per additional 10 %e. alcoholic fuel. This severe disadvantage resulted in lower engine efficiency, Figure 2 a). The higher load points provided higher in-cylinder temperatures and pressures, hence ignition and combustion of the cylinder charge were much better supported and the incomplete combustion influence on engine efficiency diminished.

5.3 Combustion analysis

The analysis of the indicated data generally showed that at dual-fuel mode the combustion process was characterised by a shorter burning duration, Figure 9. At low load in dual-fuel mode, more time was needed for combustion to start and the diesel injection had to be advanced. Compared to diesel reference operation, at middle and higher load, the ignition delay in dual-fuel mode was shortened and same MFB50% was set by a retarded injection timing. After ignition occurred, the main combustion phase was completed faster than at “diesel only” operation. The post combustion phase, which is distinctive for the oxidation of the soot formed during the diesel main combustion phase, was in most cases shorter and with a lower heat release. From an efficiency point of view, all this aspects lead to a thermodynamic beneficial cylinder pressure curve shaping.

Besides the above-mentioned, at some conditions a very important combustion phenomenon was detected – a cyclic reproducible auto-ignition of the premixed homogenous charge. Figure 9 c) shows the heat release in diesel reference operation and dual-fuel operation mode with 30 % energy share of ethanol or E85 at OP-2000/20, MFB50% was at 17.5°CAaTDC. As can be seen, the combustion in the case of ethanol clearly begins before the start of the diesel injection. After a rapid and intensive heat release the main combustion of the injected diesel continues at a moderate rate. With E85 (and E65) the combustion starts even earlier and the heat release of the premixed stage is remarkably higher. According to the octane number of the fuels, E85 is more reactive and ignites easier than ethanol. The described auto-ignition of the premixed charge was not accidental, but permanent and stable in every cycle. It appeared with late MFB50% at middle and high load and was more distinct at low speeds. As could be expected, it emitted more noise, but the cylinder peak pressure was only inconsequentially higher than in diesel reference operation (ca. 150 bar). The experiments proved that the auto-ignition was existent even after the diesel supply has been completely turned off. Figure 9 d) shows the same operating point but with an advanced MFB50% of 7.5°CAaTDC. This combustion centre position was much too advanced for diesel reference operation and resulted in an efficiency decrease due to a disadvantageous heat release timing. As can be seen in the graph, in the case of “diesel only” a lot of energy is released long before the piston reaches the top dead centre, thus high blow-by and wall heat losses occur.

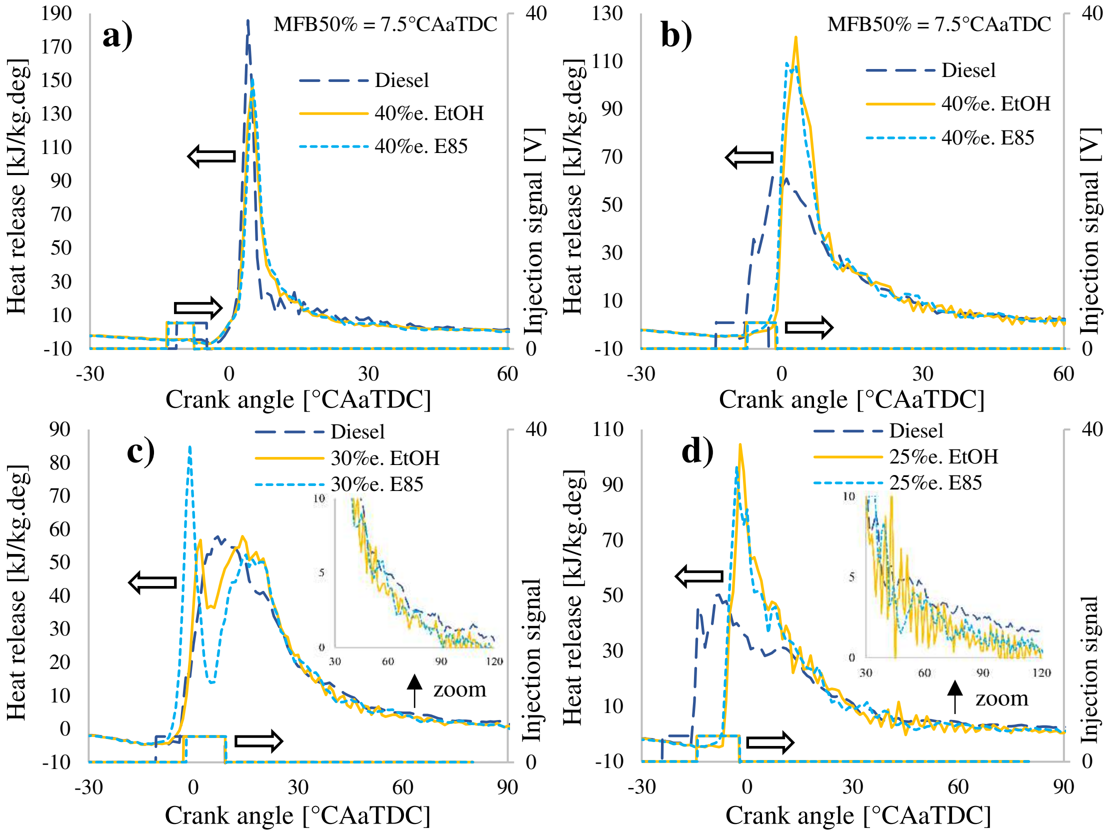

*Figure 9: Indicated heat release rates **a**) OP-1500/5, 30 % EGR, MFB50% = 7.5°CAaTDC; **b)** OP-1500/15, 15 % EGR, MFB50% = 7.5°CAaTDC; **c)** OP-2000/20, 0 % EGR, MFB50% = 17.5°CAaTDC; **d)** OP-2000/20, 0 % EGR, MFB50% = 7.5°CAaTDC*

Since dual-fuel operation provided a much faster combustion, engine efficiency was even impressively increased at a MFB50% of 7.5°CAaTDC, see Figure 2 d). Cylinder peak pressure was, however, in the range of 200 bar and the energy fraction of the alcoholic fuel had to be lowered to 25 % in order to prevent mechanical damage. The maximum pressure rise rate with 25 % ethanol was 8,5 bar/°CA at a MFB50% of 17.5°CAaTDC and 18 bar/°CA at a MFB50% of 7,5°CAaTDC. Compared to Figure 9 c), advancing MFB50% in Figure 9 d) demands a much earlier start of injection and the diesel combustion starts before the theoretical start of the ethanol auto-ignition, so no pre-ignition is detected.

5.4 Efficiency loss analysis

An efficiency loss analysis is shown in Figure 10 for low, middle and high load operation. In agreement to the engine test bed findings, compared to the diesel reference operation, the indicated efficiency in dual-fuel mode is reduced only at the 5 bar p_{mi} load point. The bar chart clearly visualises the source of the major efficiency loss – a high percentage of incomplete combustion. At the other investigated load points a higher share of incomplete combustion is also encountered in dual-fuel mode, it is however significantly lower than at OP-1500/5 and is being overcompensated by series of efficiency gains.

Due to the changed fluid composition, the real charge and real fluid properties losses sink at all dual-fuel operating points. Since MFB50% and the pressure difference “exhaust – manifold” are held approximately equal for each pair “diesel only – dual-fuel”, the losses due to combustion phasing and gas exchange are also basically identical. The “real burn rate” shares in the diagram prove the accelerated combustion at dual-fuel mode to be one of the main reasons for higher efficiency.

Another loss that is generally reduced when operating with intake manifold alcoholic fuel injection is the wall heat transfer. Surprisingly, the calculated heat transfer loss at OP-2000/20 is equal for both combustion processes. The efficiency loss is calculated by relating the specific particular work loss to the work that would result from the brought-in fuel energy with no losses at all (100 % efficiency). The software calculates 2.6 bar mean effective pressure loss due to heat transfer for the “diesel only” case and 2.5 bar for the dual-fuel case with 30 %e. ethanol, so both cases differ by only 0.1 bar. However, dual-fuel mode operation also requires less fuel energy than diesel reference operation (2.73 vs 2.85 kJ/cycle), so the percentual heat loss share in this case is barely changed.

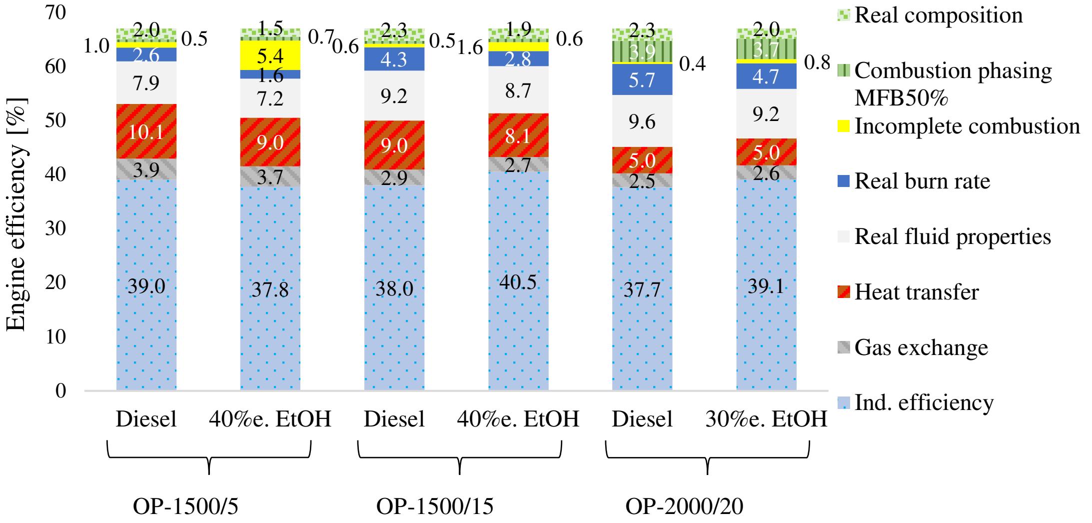

Figure 10: Results of the efficiency loss analysis for three operation points. Comparison between “diesel only” operation mode and dual-fuel operation

6. Summary

The usage of ethanol and two different mixtures of ethanol and gasoline (E85 and E65) were investigated on a modified diesel engine designed to work in a dual-fuel combustion mode with intake manifold alcohol injection. The maximum ratio of alcohol to diesel fuel was limited by irregular combustion phenomena like degrading combustion quality and poor process controllability at low load and knock as well as auto-ignition at high load. At low load testing, up to 70 % of the diesel energy could be substituted by the alcoholic fuels, whereas at high loads the maximum substitution rate declined to 30 %e. With rising alcohol amount, a significant reduction of soot mass and particle number was observed. At some testing points, substituting diesel with ethanol, E65 or E85 led to a reduction of NO_x emissions, however, the real benefit concerning the nitrogen oxides was introduced by the mitigation of the soot-NO_x trade-off. The indicated engine efficiency was significantly improved with enhanced substitution ratios at high loads (by up to 6 %), whereas it dropped at low loads (by ca. 3 %). The combustion process tolerance against high EGR rates in dual-fuel mode allowed more exhaust gas to be recirculated without affecting engine efficiency the same negative way as at “diesel only” operation. An engine-process simulation model showed that the high amounts of unburnt fuel at duel fuel operation were the main reason for efficiency degradation, whereas the reduced losses due to real charge composition, real fluid properties, real burn rate and heat transfer enhanced the efficiency of the engine at duel-fuel mode. Substituting diesel with manifold injected alcoholic fuels impressively reduced the engine CO_2 emissions at all investigated operating points. A case study of the bioethanol production by AGRANA demonstrated fuel related GHG saving potentials of up to 72 %. By using this bioethanol as a second fuel in the dual-fuel designed engine, the well-to-wheel CO_2 emissions could be cut down by almost 40 %.

7. Acknowledgements

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