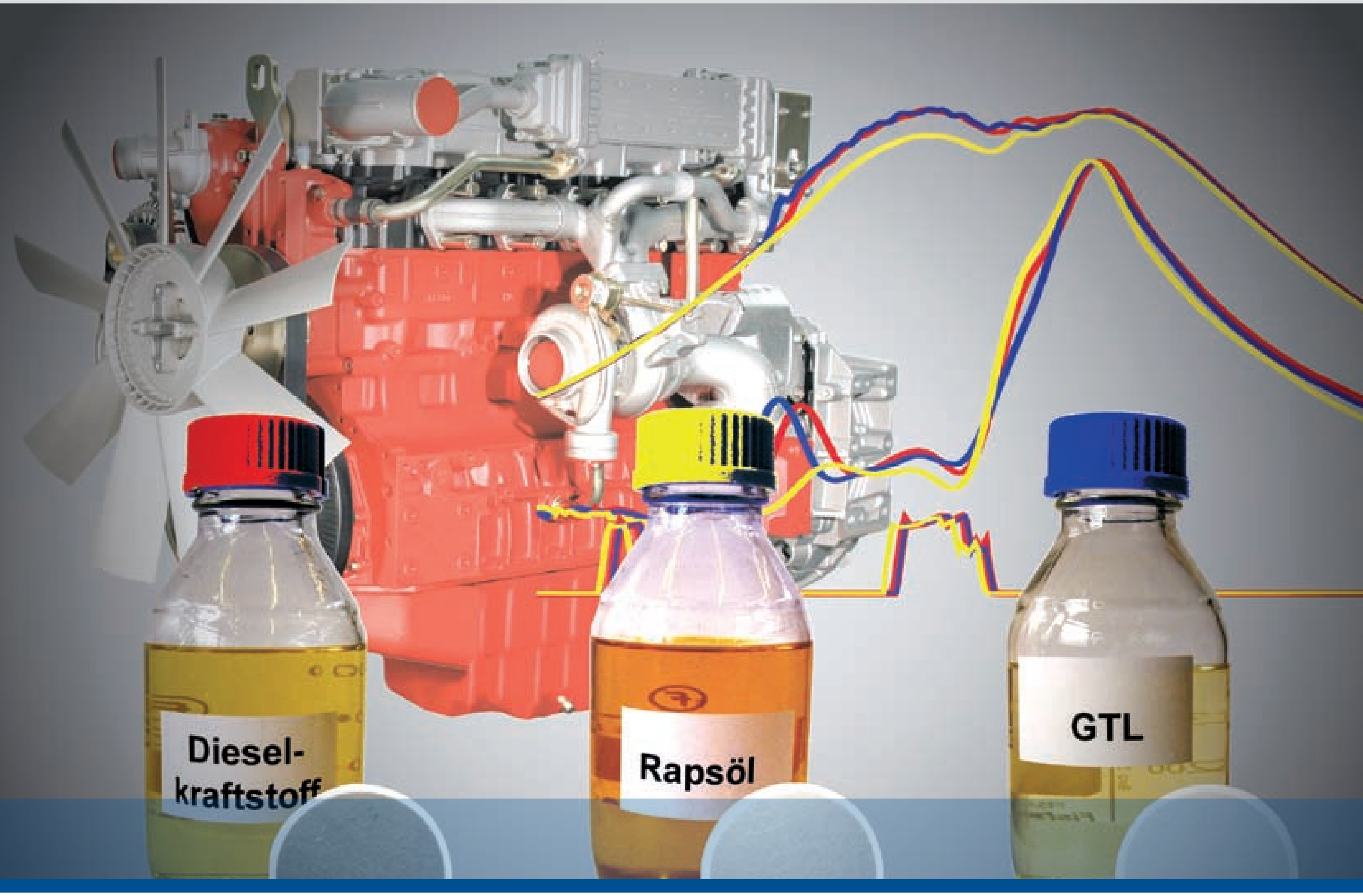

Engine Process Behaviour and Exhaust Emissions Alternative Fuels Compared with Diesel Fuel

Against the background of increasing discussions about the emission of greenhouse gases and limited fossil energy resources this contribution describes the potential of modern direct-injection diesel engines operated on 1st and 2nd generation alternative fuels. Focussing on demanding emission goals, the exhaust emissions and especially comparative mutagenicity research of the soluble organic particulate fraction are at the centre of this paper prepared by the University of Rostock.

1 Introduction

Increased discussions on carbon dioxide emissions and finite fossil energy resources result in the use of alternative fuels in vehicle engines. Discussing alternative fuels, the subdivision of these fuels into 1st and 2nd generation alternative fuels needs to be taken into account. Alternative fuels of the 1st generation are won without radical changes of their chemical structure. Typical examples are biogas and rape seed oil.

Alternative or synthetic fuels of the 2nd generation are tailor-made products from Fischer-Tropsch synthesis, such as GTL (Gas to Liquid) or BTL (Biomass to Liquid) fuels, **Figure 1**. Because of its origin BTL offers a high CO_2 reduction potential. These fuels are almost free of sulphur and aromatic compounds. They show high cetane numbers and fit well into the existing infrastructure. The quality of synthetic diesel fuel is independent from its origin from fossil or regenerative sources. However, because of its low density pure synthetic diesel fuel does not comply with the European Norm EN 590 for diesel fuel.

The **Table** shows the most important properties of the fuels used in the test runs, i. e. conventional diesel fuel, pure synthetic diesel fuel (GTL) and rape seed oil according to DIN V 51605.

Significant differences in the emission behaviour have to be expected especially due to the differences in the distillation characteristics, **Figure 2**, and an oxygen content of about 10 % in rape seed oil.

2 Description of the Experimental Conditions

First, the fuel properties essential for mixture formation and combustion are compared and evaluated in the present analyses. These properties are especially boiling behaviour and oxygen content.

The research work focuses mainly on a comparison of relevant engine process parameters such as ignition delay, rate of heat release and centre of energy conversion. The three fuels applied in the direct-injection test engines of modern design, e. g. conventional diesel fuel according to DIN EN 590:2004-03, GTL and rape seed oil according to DIN V 51605:2006-07, are compared at selected operating points in the BMEP-engine speed map. Generally, no alterations to the ECU application were made to adapt the test engines to the alternative fuels (apart from the engine test runs for the mutagenicity analyses). This was done to allow a comparative assessment of the specific properties of the fuels including their combustion properties. Thus, the difference in the lower calorific value of rape seed oil compared with the other fuels (GTL, diesel fuel) leads, for instance, to significantly prolonged injection durations.

The off-road engine used for the mutagenicity examination of the soluble organic particulate fraction had been modified for rape seed oil operation prior to the rape seed oil tests (adaptation of the low-pressure fuel system

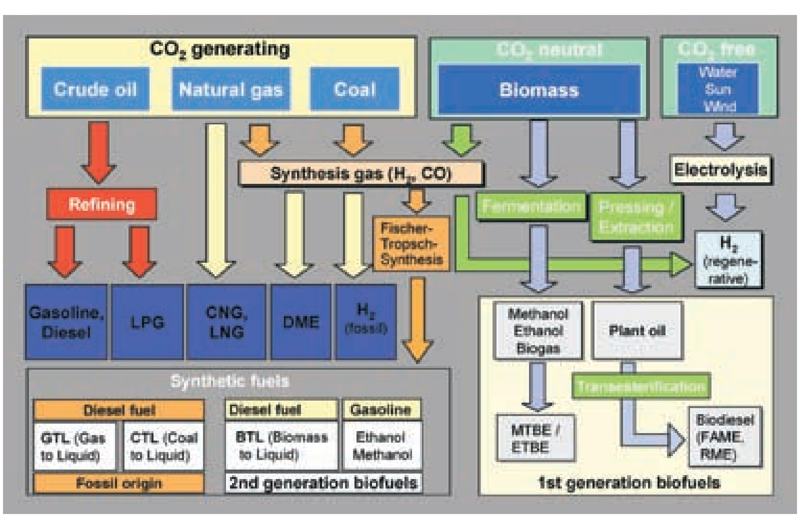

Figure 1: Conversion pathways of fossil and regenerative primary energy carriers to fuel

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MTZ Peer Review
The Seal of Approval for scientific articles in MTZ.
Reviewed by experts from research and industry.

Received .... 13th December, 2007
Reviewed .... 9th January, 2008
Accepted .... 21st January, 2008

Table: Comparison of fuel properties of diesel, GTL and rape seed oil

Fuel properties	reference fuel	test fuel	
	diesel fuel EN 590	GTL	Rape seed oil raffinate DIN V 51605
density at 15°C [kg/m³]	837	778	920
kinematic viscosity at 40°C [mm²/s]	2,74	2,58	34,7
cetane number [-]	52	78	38 – 42*
specific net calorific value [MJ/kg]	42,8	43,5	36,9
volumetric net calorific value [MJ/l]	35,8	33,8	33,9
sulphur content [mg/kg]	7	<5	6
hydrogen content [% m/m]	13,1	14,8	12,3
carbon content [% m/m]	86,3	84,8	78,2
H/C-ratio	1,8	2,1	1,9
total aromatic hydrocarbon content [% m/m]	26,9	<0,1	<0,1
IBP [°C]	174	204	167
FBP [°C]	354	317	crackpoint at 60 % (V/V)
oxygen content [%]	<0,5	–	10

*literature value [12]

and of the fuel injection map). This was done mainly because of the high relevance of the results.

2.1 Engine Test Results

To compare the alternative fuels (GTL and rape seed oil) with the conventional fuel thereby evaluating their potentials, stationary engine tests were carried out at a modern 2.2 l, 4 cylinder, direct injection diesel engine. The engine was equipped with a wastegate turbocharger and a serial-production common rail injection system. The cross comparisons were focussed especially on the engine operation at 2000 rpm and different BMEPs.

The thermodynamic analysis results, **Figure 3** and **Figure 4**, show that the energy release with GTL fuel (highest cetane number) starts earliest but is significantly delayed for rape seed oil especially at lower engine loads. This is mainly caused by the very different boiling properties of the fuels and is clearly visible in the rate of heat release (ROHR) during the pilot injection phase. Of additional influence is the reduced and strongly fluctuating fuel mass of the pilot injection at rape seed oil operation which is caused by the higher viscosity of this fuel type. This effect is not compensated by the standard engine application data for diesel fuel [5].

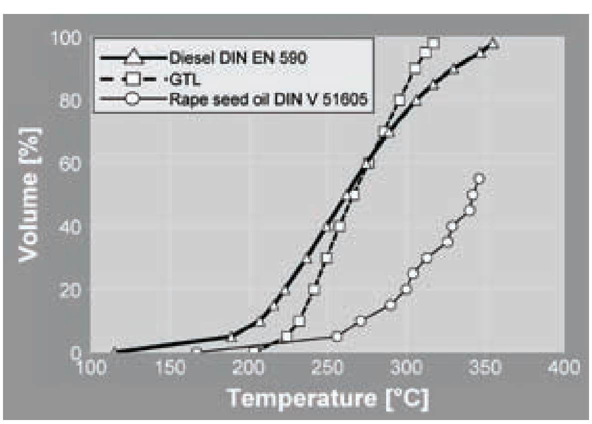

Figure 2: Comparison of distillation characteristics of diesel with GTL and rape seed oil

While only marginal differences in injection timing and EGR rates were found for diesel fuel and GTL operation, there were some deviations at identical BMEP for rape seed oil. Because of the lower calorific value of rape seed oil compared with diesel fuel and its higher viscosity an increased fuel injection duration is required which leads to a shift of the operation points in several ECU maps. Apart from a small advance of the start of injection this leads, above all, to reduced EGR rates in the case of rape seed oil operation. At 4 bar BMEP especially, higher charge air and compression pressures are generated.

A significant prolongation of the ignition delay (up to about 5 ° crsh.) combined with a clear retardation of the combustion appears for the lower loads because the distillation characteristics for rape seed oil are significantly shifted towards higher temperatures. The differences in the rates of heat release for the different fuels become considerably lower with increasing process temperatures (engine operation at higher loads).

The normalised fuel consumption (related to the calorific value of diesel fuel) shows that only in the lower load range an increased consumption in rape seed oil operation occurs. For all other load points the fuel consumption differences are within the measurement accuracy. The oxygen content in the rape seed oil causes a significant reduction of the particulate emission combined with a small increase in the engine-out NO_x emissions, Figure 4.

When using GTL fuel, a reduction of the particulate and HC emissions is to be seen. On the other hand, the NO_x emissions are at almost similar level compared to diesel fuel. Due to their higher EGR compatibility, the two alternative fuels have a favourable NO_x-PM trade-off which can be utilised in future applications.

2.2 AMES Test

Rape seed oil especially has met with criticism based on individual findings [6, 7] concerning the mutagenicity of its particulate emissions. For this reason, comparative toxicological analyses of particulate emissions from diesel fuel and vegetable oil operations were carried out to evaluate the hazardous potential of the combustion emissions. GTL combustion

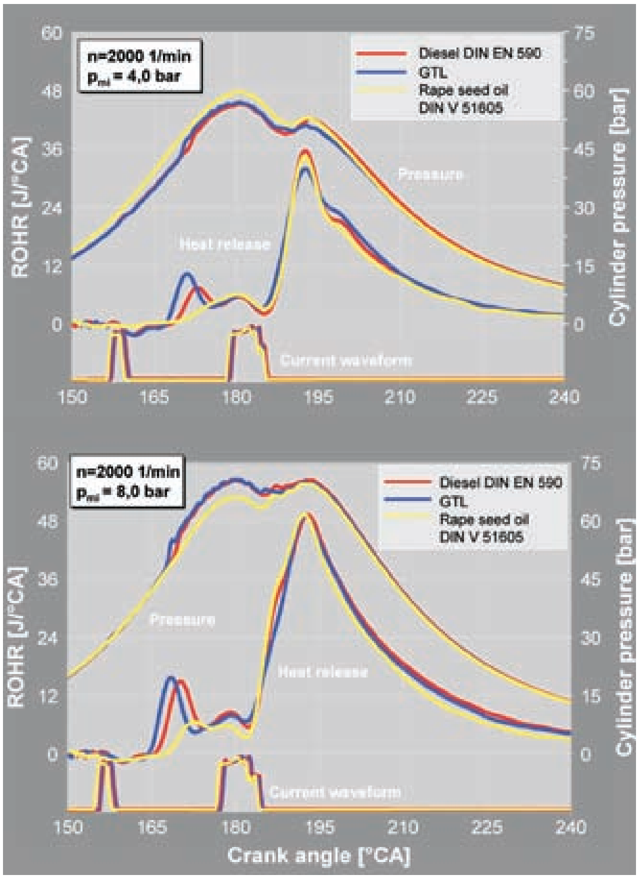

Figure 3: Thermodynamic comparison of diesel with GTL and rape seed oil

emissions show lower mutagenicity than diesel fuel emissions and are therefore not examined in this paper [7].

The AMES test [13] is a usual procedure to assess the mutagenicity of chemical compounds. This test brings the extractable components of the particulate emission (soot) into contact with specific bacteria strains. It consists of three phases:

- particle sampling
- sample processing (extraction)
- bacteriological test.

The test series is based on eight separately analysed load points as, in practice, engines are used at most different operation loads and are subject to strongly varying combustion and exhaust emission conditions. By this approach it was possible to compare the mutagenicities depending on the fuel type and on the engine operation point.

2.2.1 Particle Sampling

The mutagenic effect of engine exhaust gases is mainly attributed to the particulates in the exhaust gas. Therefore, the mutagenicity analyses presented here are based on exhaust gas particle mass sampled from the exhaust gas by means of filters. This filtering was done at an engine test bed. The test material was sampled at a modern, off-road TIER 3 engine with a common rail injection system, a VTG turbocharger and a cooled external EGR. Samples were taken at 8 different operation points which were determined on the basis of the exhaust gas test cycle C1 of the preliminary ISO standard 8178-4. An AVL „Smart Sampler“, i. e. a partial flow dilution tunnel working on the Constant-Volume-Sampling (CVS) principle, was used to sample the particulate material. The filter temperature was controlled at 52 °C.

The particulate material samples were filtered from a constant exhaust gas mass of 450 g at all load points. This procedure allowed a direct comparison of the two fuels at the individual load points.

2.2.2 Sample Processing

During the sample processing the loaded fibre glass filters were extracted using 150 ml of dichloromethane in the soxhlet over a period of 12 hours. Then, the extract was reduced to about 5 ml in a rotation evaporator and the dichloromethane was let-off using high-purity nitrogen. The viscous, oily residual was solved in 1.5 ml dimethylsulfoxide and in this form used for the AMES test.

2.2.3 Bacteriological Test

In the AMES test the filter extracts were tested for their mutagenic effect by means of the bacteria strains Salmonella typhimurium LT2(His-). The bacteria strains are modified in such a way that they can no

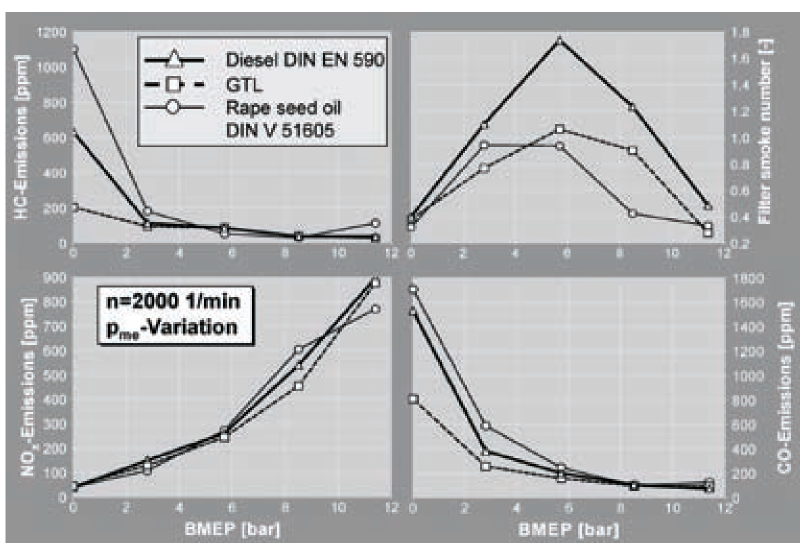

Figure 4: Comparison of engine-out emissions of diesel with GTL and rape seed oil

longer produce the vital amino acid histidine. In a histidine-free environment they can therefore only multiply if they can regain the histidine-production ability by back-mutation, i. e. under the influence of mutagenic substances.

The bacteria strains are used to record raster phase mutations (TA98) and base pair substitutions (TA100). The number of back-mutations (revertants) is taken as a measure for the mutagenicity. By adding rat liver extracts (S9-mix) enzymatically induced changes in mutagenicity in higher organisms are taken into account (metabolic activation).

The AMES test does not show a good correlation between carcinogenicity and mutagenicity for all classes of chemical compounds. However, a carcinogenic potential is identified with a reliability of about 83 % [10]. The AMES test was conducted according to OECD guideline 471 based on the protocol by Maron and Ames (1983) [13].

After an incubation period of 48 hours at 37 °C those bacteria colonies were counted that were able to back-mutate to the wild type and grow on the plates (number of revertants). For positive checks, the mutagenic materials 2-nitrofluorene and sodium-azide were used in the tests without a metabolic activation, whereas benzo[a]pyrene was used in the tests with S9-mix. Comparing the results with the negative checks, the share of revertants that did not appear spontaneously but was caused by test substances could be determined.

Especially with low numbers of spontaneous revertants it is difficult to determine the beginning of the linear dose-effect relation region. For this reason, the revertant numbers were counted as significantly increased only when they were twice as high as the number of spontaneous revertants [see 11, 14]. The next chapter uses the so-called mutagenicity factor to assess the mutagenicity of the soluble organic particulate fraction:

2.2.4 Results of the Analyses

The results of the mutagenicity tests using the bacteria strains TA98 and TA100 with and without metabolic activation are expressed in **Figure 5**, **Figure 6**, **Figure 7** and **Figure 8**. The diagrams show the mean values of the mutagenicity factors of the undiluted extracts.

Considering the results of the mutagenicity tests, it becomes obvious that the test results with the TA98 strain with and without S9-mix, under the aforementioned conditions, show a significant increase in the number of revertants compared with the negative checks for the reference diesel fuel, which is summarised by the increased mutagenicity factor. For rape seed oil and the same analysis conditions, this could only be observed at individual measuring points, Figure 5 and Figure 6.

The mutagenicity strongly depends on the engine load and is highest for diesel fuel operation at the measuring points 2, 3, 4, 6 and 8. It is remarkable that rape seed oil fuel shows considerably better results. Especially for the critical operation point 8 (idle running) a significantly lower mutagenicity was found for rape seed oil fuel compared to diesel fuel despite higher particle emissions for rape seed oil operation. A comparison of the direct mutagenicity (without S9-mix) with the indirect mutagenicity after metabolic activation of the extracts using rat liver enzymes (with S9-mix) does not allow explicit conclusions regarding the type of mutagens.

The test results using the TA100 bacteria strain with and without S9-mix lead to a remarkably lower increase in the numbers of revertants already at diesel fuel operation. This bacteria strain reacts less sensitive on the mutagens in the fuel-originated soot, Figure 7 and Figure 8)

Summarising, it can be stated that an higher mutagenic effect of rape seed oil soot compared to diesel fuel soot, as claimed in [6, 7, 15], is not confirmed by the results presented here. Apart from measuring point 7, the mutagenicity of rape seed oil soot has even been found to be significantly lower which coincides with the results of [9].

The results of the mutagenicity analyses need to be statistically supported by further tests and to be founded on a broader experimental basis. In the course of this further research, the emission reduction potential of modern exhaust gas treatment systems is to be taken into account especially.

3 Conclusions and Outlook

Liquid mineral fuels from crude oil are expected to play a dominant role in the transport sector for the next 20 years. Supplementary, alternative fuels will, however, gain in importance. This is induced by the increasing shortage of fossil fuels, ecologic

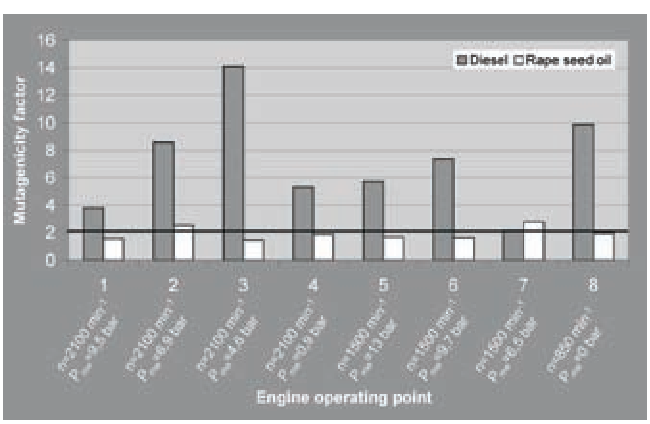

Figure 5: Mutagenicity of bacteria strain TA 98 without S9-mix

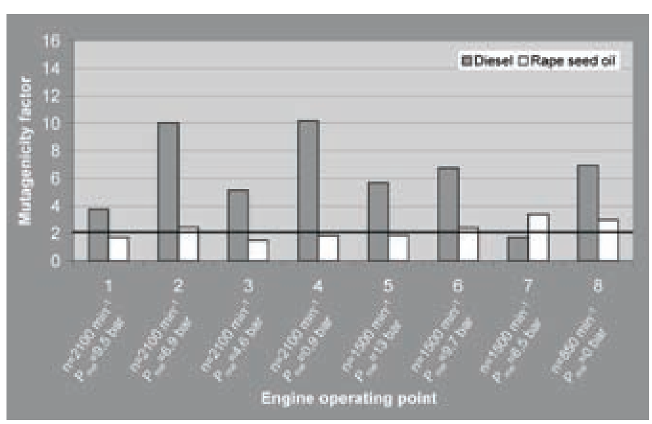

Figure 6: Mutagenicity of bacteria strain TA 98 with S9-mix

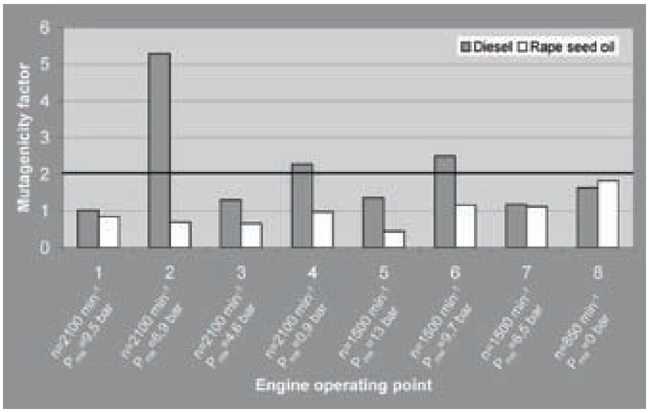

Figure 7: Mutagenicity of bacteria strain TA 100 without S9-mix

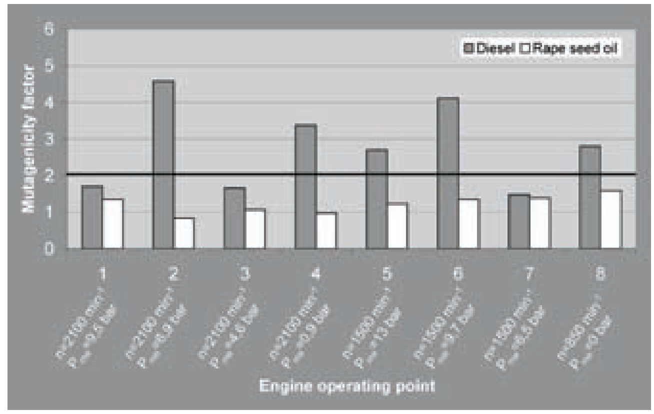

Figure 8: Mutagenicity of bacteria strain TA 100 with S9-mix

issues including the emissions of greenhouse gases, the global trend towards increasing mobility and last but not least the implementation of the EC guideline 2003/30/EG which requires a market share of 5.75 % for alternative fuels in 2010 [4].

The use of alternative fuels in combustion engines can replace a certain part of the fossil fuels within a short time and can thus reduce CO_2-emissions. The knowledge about combustion processes and heat release functions of future fuels is a prerequisite for the broad market introduction of biogenic fuels. The analyses of engine process functions showed that favourable NO_X-PM trade offs can be obtained for alternative fuels of both the first and the second generation. The engine control system has to be adapted fuel-selectively to exploit the emission reduction potentials of both alternative fuel categories. The necessary adaptation of an engine for second generation alternative fuels can be achieved simply by modification of the software functions in the ECU. Besides comprehensive changes to the ECU software, adaptations to the engine hardware are required for engine operation on first generation alternative fuels, which are available on the market today. This is especially the case for the components of state-of-the-art high pressure injection systems. Furthermore, a limitation of ash-producing components in the alternative fuels is mandatory to allow conflict-free operation of exhaust gas treatment systems in general and particle filters in particular when the engine is running on vegetable oils.

Comprehensive analyses of the soluble organic particle fraction by means of the AMES test showed no increased mutagenicity of the engine emissions during rape seed oil operation compared with diesel oil operation.

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The authors would like to thank the Shell Globus Solutions GmbH, Germany, for supplying the GTL fuel for the engine tests.