2nd VegOil

Demonstration of 2nd Generation Vegetable Oil Fuels in Advanced Engines

Work Package 3

Fuel Development

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Review on engine requirements

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1 Prolog

Engine experts are more and more concerned about the negative impact of phosphorus (P), calcium (Ca) and magnesium (Mg) on diesel engines. These elements are considered as poisonous for catalysts and can cause engine damages on soot filters, pistons, piston rings, injectors and valves[1].

In Work Package 3 - Fuel Development - of 2nd VegOil a new fuel quality standard with reduced values for P, Ca/Mg in rapeseed oil has to be established and produced.

In Task 3.1 therefore a survey on rapeseed oil fuel quality was given. Different fuel quality standards and known P, Ca/Mg reducing parameters to fulfil them have been analyzed.

In Task 3.2 the requirements of plant oil engines on fuel quality have been examined. From all characteristic and variable fuel properties, especially the ash building alkali and earth alkali have been of interest.

First, in a short historical review the interaction of engine technology and fuel quality standards with different P content till the valid DIN V 51605 is reported. Then, studies and papers are examined which indicate engine problems although rapeseed oil following the DIN V 51605 was used. Thus, many engine experts ask for an immediate improvement of the existing DIN V 51605 – especially for elements like P, Ca/Mg.

Many experts are also interested in experiences with other plant oils than rape seed oil and their impact on modified diesel engines and the possibility to reduce the content of P, Ca/Mg.
In literature there are many test experiences to be found with different plant oils already beginning in the 80ties. But due to a missing common plant oil fuel quality standard all this tests didn´t deliver systematic and verified results. Test runs based on the first plant oil quality norm DIN V 51605 have been done on rape seed oil because this is the only plant oil which the DIN V 51605 refers to.
For two years, in the DIN-subdivision UA 632.2, the DIN V 51605 commission works on establishing a general quality norm for other plant oils than rape seed oil. But results are not published yet. Because of lacking verified data material the 2nd VegOil project itsself focuses on gaining and reporting verified engine test results with different plant oils based on a DIN V 51605 analysis and a monitored demonstration program.

2 Phosphor, Calcium and Magnesium in Rapeseed Fuel – the Interaction between Engine Requirements and Fuel Quality Standards

Plant oil fuel standards in Germany always have been results of work sessions with differently interested group members. Owners of decentralized oil mills, plant oil traders, universities with agricultural background or public financed institutes like the Technologie- und Förderzentrum Straubing (TFZ) always have been interested in weaker than in stronger fuel quality limits. This reduced risks for farmers, oil millers or plant oil traders and gave more incentives to invest and expand into this new business.

On the opposite, engine producers or small plant oil technology companies have been interested in stronger property limits of fuel standard because they carry the risk of engine damages or higher emissions due to inadequate fuel standards. Because of the minority of the engine side in the work sessions, the requirements of plant oil engines usually have not been completely satisfied in the different fuel standards. Especially for P and later also for Ca/Mg, the different fuel standards never represented the value which had been asked for by engine experts.

2.1 Engine Requirements from the 30ths to the "Pre-Weihenstephan Standard" (8/1996)

In 1937, Gaupp did engine test runs on different plant oils and analysed combustion conditions, power, fuel consumption and lubrication oil quality. As result, technical rules like preheating the fuel, frequently cleaning of injection nozzles have been set up, but no comment on fuel quality or certain properties of this was given[2].

Also Ludwig Elsbett in 1983, the world-wide pioneer on plant oil technology, experimented with different plant oils and recommended no fuel specification in this time[3].

This changed completely after the so-called "Porsche Test" in 1991 which analysed the functionality of diesel engines with rapeseed oil as fuel[4]. At this time, Elsbett already knew about a negative impact of phosphorous on diesel engines and refused to deliver an Elsbett engine to the Porsche test bench which used a minor rapeseed oil quality with 94 ppm P[5].

In the following, there was no common sense on how much P could be in rapeseed oil as engine fuel. The East German engine producer Thüringer Motorenwerke (TMW) set a P limit of < 100 ppm for its special designed plant oil engines[6]. Elsbett at first mentioned a P limit of

30 ppm[7] and later of 15 ppm[8]. Dieselmotoren Schönebeck (DMS) (a license partner of Elsbett) had no requirement for P at all[9].

In 1993, the Vereinigte Werkstätten für Pflanzenöltechnologie (VWP) developed a technological system to adapt serial engines to rapeseed oil as fuel[10] and in 1994 VWP started the worldwide first test of 60 serial Mercedes passenger cars with this new technology. VWP from the beginning was aware of the engine risk due to a high content of P in rapeseed oil as fuel. For the two years' lasting fleet test, refined rapeseed oil with a P limit of 2 ppm and cold-pressed rapeseed oil with a P limit of 10 ppm was used[11]. Both fuel qualities showed good results in pre-chamber engines.

Work sessions organized from the Landtechnik Weihenstephan to set up a pre-quality standard for rapeseed oil in 1996 therefore had a wide-range of requirements for phosphorus from the engine companies. The pre-quality standard in 08/1996 was fixed to 25 ppm for phosphorus[12]. This value for P was too weak for VWP who pledged for 10 ppm and had to cancel orders and projects because of the gap between their engine requirements and weak P limits in fuel standards.

In 1997, the project "Pflanzenöl-Kleinst-BHKW's in Bayern (mini combined heat and power units for Bavaria)" organized by C.A.R.M.E.N. in charge of the Bavarian Ministry of Agriculture had to be stopped because of different opinions of the P content in the rapeseed fuel. While C.A.R.M.E.N. required a value of 25 ppm P but also an oxidation catalyst, VWP already had negative experience with the combination of oxidation catalysts and high P values in rapeseed fuel and set up a P limit of 10 ppm for its plant oil combined heat and power units (CHP) with oxidation catalyst. C.A.R.M.E.N. took reference to Widmann from the Technical University of Munich and chairman of the work sessions for the rapeseed oil quality standard who emphasized the unrealistic low P limit asked for by VWP and the expected problems of decentralized oil mills to fulfil this low P content in rapeseed oil[13].

Since C.A.R.M.E.N. required both - an oxidation catalyst with warranty and an insufficient P fuel standard - VWP had to step back from this project and an indirect subsidy of 500,000 DM.

In 1996 to 1998, the state of Baden-Württemberg via University of Stuttgart-Hohenheim subsidized a test fleet program which monitored more than 60 vehicles with swirl chamber and pre-chamber engines which had been modified from VWP to run on pure rapeseed oil[14].

To reduce the risk of bad fuel quality, the project was supplied by just one decentralized oil mill. Fuel analysis mostly reported a phosphor content < 10 mg/kg. With this fuel quality, engine analysis even after more than 150,000 km running distance detected no deposits in pre-chambers, on nozzles or pistons. Inside the combustion chamber even the honing structure looked like new[15].

After this positive results in Bavaria and Baden-Württemberg VWP decided to continuously insist on 10 mg/kg phosphor in rapeseed fuel. With the same Mercedes engines with oxidation catalysts in stationary or mobile use, VWP had good experiences with a P content of < 10 mg/kg and negative results with residues in pre-chambers, on pistons, glow plugs and nozzles with a P content of > 10 mg/kg in rapeseed fuel.

2.2 Engine Requirements for Phosphor in the Weihenstephan Standard 5/2000

In 2000, the pre-Weihenstephan standard for rapeseed oil as fuel was transformed to the final 5/2000 Weihenstephan standard. Two protocols of work sessions from 1999 and 2000 have been published[16]. In the 1999 and 2000 work sessions, VWP again asked for a reduced P content of 10 ppm. There would have been many reasons to follow this proposal:

- The chemical reaction of P as “poison” for catalysts have been acknowledged now from different sources.

- While the C.A.R.M.E.N. project for ten small plant oil pre-chamber CHP was stopped from VWP, a parallel CHP project with bigger D.I. engines had an almost 100 % damage quote. VWP thought that the insufficient fuel quality especially for the variable property phosphor had a good share for the high percentage of engine defects.

- VWP had a broken Mercedes engine with phosphor residues on piston, piston rings, glow-plugs and injector nozzles after two years and 7,000 km short distance operation and a monitored phosphor content of 26 mg/kg.

- A new testing method ASTMD 3231-94 allowed analysis of phosphor till a new detection limit of 0.2 mg/kg.

- From all fuel analysis done by the work session members, 90 % had a P content ≤ 10 mg/kg.

Following the discussion, the work session members decided to reduce the P content from 25 ppm to 15 mg/kg.

In choosing 15 mg/kg instead of 10 mg/kg as P limit for rapeseed oil as fuel, the work session members preferred a for decentralized oil mills comfortable standard but not a standard which is necessary for the engine technology. Additionally, a testing method for analyzing P was chosen which did not represent the best technical choice.

In this conflict, VWP decided to also support the new Weihenstephan standard 5/2000. But out of warranty reasons, VWP required a P content of 10 mg/kg and noted this at their official fuel standard documents. Already for the important 100 tractor program of the German Government with 56 from VWP modified tractors running from 2001 to 2005, VWP imposed its own P regulation of 10 mg/kg into the tractor user contract for farmers (table 1).

Features / Ingredients	Entity	Limit values max.	Limit values min.	Inspection Method
for rape seed oil characteristic features				
Density (15°C)	kg/m^3	900	930	DIN EN ISO 3675 DIN EN ISO 12185
Flash point by P.-M.	°C	220		DIN EN 22719
Heat value	kJ/kg	35000		DIN 51900-3
Kinematic viscosity (40 °C)	mm^2/s		38	DIN EN ISO 3104
Cold behaviour				Rotary viscosimetry (Test conditions will be elaborated)
Combustibility (Cetan figure)				Test procedure will be evalueted
Coke residue	Mass-%		0.40	DIN EN ISO 10370
Iodine figure	g/100 g	100	120	DIN 53241-1
Sulphur figure	mg/kg		20	ASTM D5453-93
variable features				
Total contamination	mg/kg		25	DIN EN 12662
Neutralisation number	mg KOH/g		2.0	DIN EN ISO 660
Oxidation stability (110 °C)	h	5.0		ISO 6886
Phosphorus content *	mg/kg		15	ASTM D3231-99
Ash content	Mass-%		0.01	DIN EN ISO 6245
Water content	Mass-%		0.075	Pr EN ISO 12937

*) Correction of the phosphorus content by VWP: 10 mg/kg

Table 1: Rapeseed oil quality standard Weihenstephan 5/2000[17] with correction of P content by VWP

2.3 Engine Requirements for P, Ca/Mg in the DIN V 51605

The Weihenstephan fuel standard 5/2000 was valid till 2006 and then transformed to the German quality norm for rapeseed oil as fuel, the DIN V 51605[18].

Parameter	Entity	Limit values		Inspection Method
		max.	min.	
Density at 15°C	kg/m^3	900.0	930.0	DIN EN ISO 3675 or. DIN EN ISO 12185
Flash point by Pensky-Martins	°C	220	-	DIN EN 2719
Kinematic viscosity at 40 °C	mm^2/s	-	36.0	DIN EN ISO 3104
Heat value	kJ/kg	36000	-	DIN 51900-1, -2, -3
Combustibility	-	39	-	
Coke residue	% (m/m)	-	0.40	DIN EN ISO 10370
Iodine figure	g Iod/ 100g	95	125	DIN EN 14111
Sulphur figure	mg/kg	-	10	DIN EN ISO 20884 DIN EN ISO 20846
Total contamination	mg/kg		24	DIN EN 12662
Acid figure	mg KOH / g		2.0	DIN EN 14104
Oxidation stability at 110 °C	h	6.0		DIN EN 14112
Phosphorus content	mg/kg		12	DIN EN 14107
Sum content of calcium and magnesium	mg/kg		20	DIN EN 14538
Ash content (oxid ash)	% (m/m)		0.01	DIN EN ISO 6245
Water content	% (m/m)		0.075	Pr EN ISO 12937

Table 2: DIN V 51605[19]

In case of the variable properties and especially for mineral elements important changes have been fixed. Due to numerous engine damages which were blamed for insufficient fuel quality, the P limit was lowered to 12 mg/kg.

Also a new property, calcium and magnesium, was implemented and fixed to a sum limit of 20 mg/kg. This happened because of many negative experiences of engine experts with deposits on pistons, nozzles, valves and blocked soot filters.

In 5.6.2 the DIN V 51605 explains the importance of a low content of ash producing elements. Basically as a limit for P, Ca/Mg the DIN 51605 says “the lesser the better”. For the expert group of the DIN V 51605 commission “the lesser the better” means 12 mg/kg for P and for 20 mg/kg for Ca/Mg.

VWP at this time already had test results with long-term test bench runs from the EC supported 100 % RENET with D.I. engines and a closed particulate/soot filter system from

Senertec. It was clearly impossible to sell and operate such rapeseed oil Senertec CHP with DIN V 51605 fuel quality at full warranty. VWP absolutely never agreed with the limits for P, Ca/Mg in the DIN V 51605 and asked clients of their plant oil fuelled CHPs to just use refined rapeseed oil or rapeseed oil from just one decentralized oil mill (Kramerbräuhof) to keep the 2 years' warranty.

Furthermore are other minerals as phosphorus (P), magnesium (Mg) and calcium (Ca) important for vegetable fuel quality, which are not mentioned at the DIN V 51605. The minerals potassium and sodium containing also in vegetable oils, but in a lower concentration than P, Ca and Mg, may also cause similarly effects on engines as P, Ca and Mg. So these minerals should be also tested and clarified out of vegetable oil to increase the risk of damages on engines and engine parts. In future also the minerals Na and K might also be admitted into the DIN V 51605.
Observations of Waldland at the 35-tractors program showed, that by reduction of phosphorus, calcium and magnesium in vegetable oil all parameters of the DIN V 51605 could been complied, accept the oxidation stability. By reduction of P, Ca and Mg the oxidation stablility of the vegetable oil has to be monitored and in case has to be stabilised.

3 Test Fleet and Test Bench Studies about the Negative Impact of a High P, Ca/Mg Content in Rapeseed Oil for Diesel Engines

In the following, the necessity of lowering the content of P, Ca/Mg in the DIN V 51605 was proven by practical test experiences with several engine types. The test results have been produced from the Austrian 35 tractors' program 2003 to 2008 and during a 1.000 hours' and 1.500 hours' test bench run from John Deere.

3.1 Engine Test Results on D.I. Engines (EURO I + II)

Target of the Austrian 35 tractors' program 2003 to 2008 was the assessment of applicability of conversion systems for rapeseed operation. In the course of the project 38 diesel engines (EURO I and EURO II) for operation with rapeseed oil have been converted. 18 tractors were equipped with one-tank-systems and 19 tractors and also a sprinkling-aggregate with a two-tank-system. Altogether all engines were operated approximately 59.000 operating hours.[20]

Requirement for the participating on the program with a tractor was a yearly minimum performance of the tractors of 350 hours as well as the condition that the tractors had to be younger than 5 years.[21]

At the beginning of the 35 tractors´ program all tractors were disassembled and equipped with conversion systems for rapeseed oil operation. Finally, at the end of the program the tractors again were disassembled check and analyse the engines.[22]

The tractors in the 35 tractors´ program were all operated with rape seed oil produced according to the Weihenstephan standard.[23]

It is important that all demonstration tractors were operated with rape seed fuel within a lower phosphorus content as foreseen in the Weihenstephan standard and also in the DIN V 51605 (see 2.2, table 1).

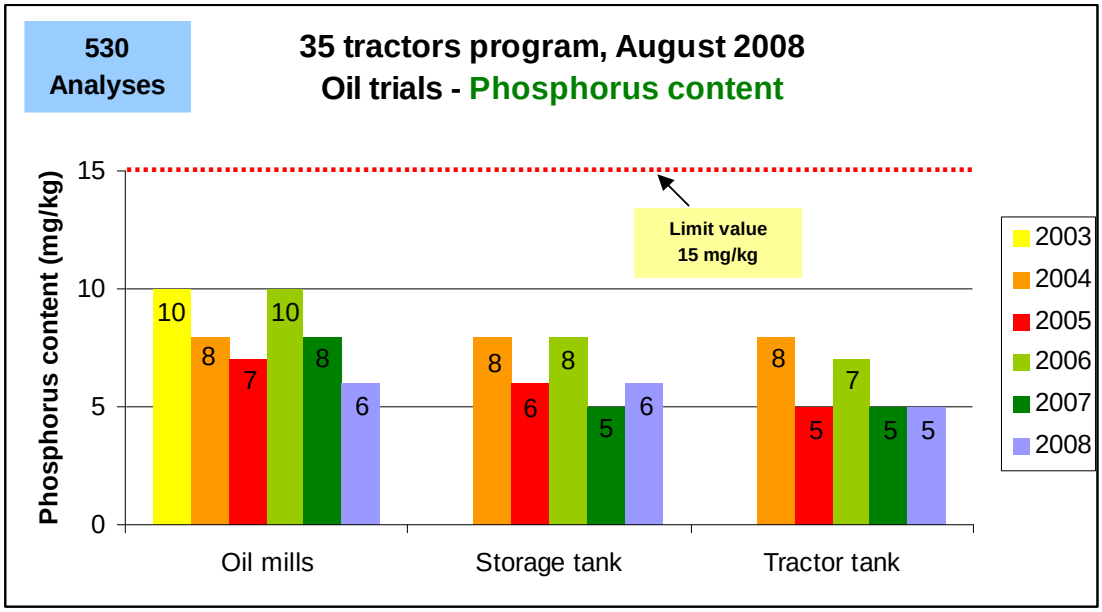


Table 3: Phosphorus content annual middle of rapes seed oil of 35 tractors´ program[24]

Table 3 shows the phosphorus content of rapes seed oil which was used for operating the tractors in the Austrian 35 tractors´ program from 2003 to 2008. At the Weihenstephan standard, the maximum content of phosphorus is defined by 15 mg/kg (see 2.2, table 1), the maximum content of phosphorus at the DIN V 51605 is defined by 12 mg/kg (see 2.3, table 2).

Right from the tractor tank, the average P content over five years was 6 mg/kg. Ca/Mg was not tracked over the years in the 35 tractors' program but rapeseed oil with 6 mg/kg P usually additionally measures from 6 to 10 mg/kg Ca/Mg.

The pictures which are discussed now in 3.1.1 to 3.1.3 were recorded from a Fendt Vario 714 tractor of Waldland which participated in the program. The Waldland tractor was operated 2.900 hours with rapeseed oil.[25]

Although the tractor was already operated for 2.900 hours, the following pictures show too much residues on pistons, nozzles and valves. The Fendt tractor fulfilled emission level EURO I and was used low, not more than 25 %. Since most of the tractors showed similar strong deposits on pistons, nozzles and valves, the 35 tractors' program gave a hint that maybe also a high content of P, Ca/Mg was responsible for the residues in plant oil fuelled engines. At this moment, a scientific correlation between residues on engine parts and content of P, Ca/Mg in the fuel was not scientifically proven.

The following pictures just show technical results of a long-term experimental and field study and an assumed negative impact of P, Ca/Mg on diesel engines. This was scientifically

proven later by the John Deere study on EURO II and III engines and from VWP within the 100 % RENET project.

3.1.1 P, Ca/Mg Tolerance of Pistons

As it can be seen on picture 1, on the piston of the participating tractor of Waldland at the 35 tractors' program are burning residues as well as irritation traces remarkable. The picture was recorded after 2.900 operating hours with rapeseed oil quality with a phosphorus content below DIN V 51605 (see 3.1, table 3).

High burning residues on pistons causes irritations on the cylinder-operation-box, as it can be seen in picture 2, in worst case a so called "piston seizure" happens, which is irreparable.

Picture 1: Piston, operated 2.900 h with rapeseed oil[26]

Picture 2: Cylinder-operation-box, operated 2.900 h with rapeseed oil[27]

3.1.2 P, Ca/Mg Tolerance of Injection Nozzles

At the 35 tractors' program it was seen, that on injection nozzles which are operated with rapeseed oil in quality with a phosphorus content below the DIN V 51605 happened unfavourable sediment residues which are referable to phosphorus.

Picture 3: Injection nozzle, operated 2.900 hours with rapeseed oil [28]

The injection nozzle in picture 3 was removed from the participating tractor of Waldland at the 35 tractors´ program operated 2.900 hours with rapeseed oil quality P < DIN V 51605 (see 3.1, table 3).[29] Remarkable in picture 3 are the fairly strong sediment residues on the

top of the injection nozzle. These sediment residues on injection nozzles are typically caused by elements like phosphorus.

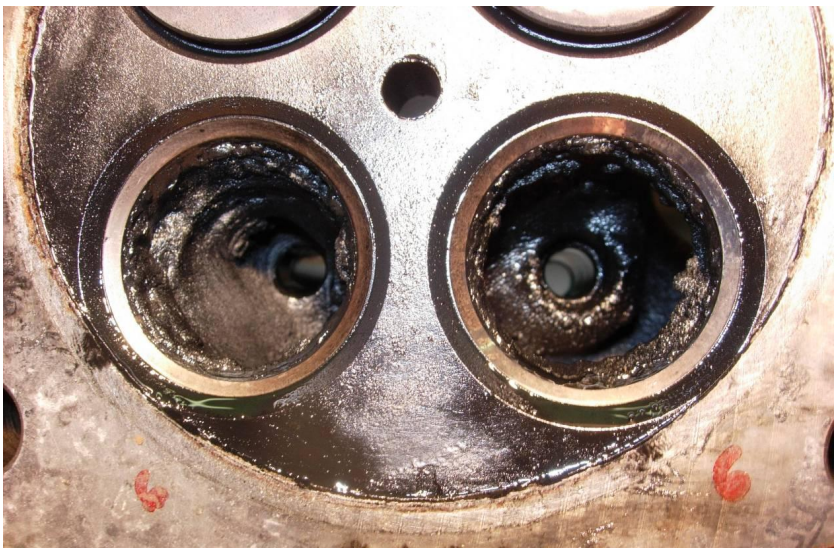
3.1.3 P, Ca/Mg Tolerance of Valves and Inlet Parts

Disassembling of tractor engines operated with higher rapeseed oil quality as DIN V 51605 showed that the oil quality maybe also caused unfavourable sediments on valves and inlet parts.

Picture 4: Inlet valves, operated 2.900 h on rapeseed oil [30]

After 2.900 operating hours on rapeseed oil (P < DIN V 51605) strong deposits could be seen on the inlet valves (see picture 4).

The operation of the Waldland tractor on higher rapeseed oil quality than DIN V 51605 caused typical residues on valves which arise from phosphorus These sediments endanger the engine by preventing unopposed air-flow which effect low exhaust gas values.



Picture 5: Air inlet port operated 2.900 h on rapeseed oil [31]

Picture 5 shows an air inlet port with heavy sediments of the Waldland tractor which participated on the 35 tractors' project, after 2.900 operating hours. As the sediments on the inlet valves the unopposed air flow is prevented of these residues which are typically referable to phosphorus.

3.2 Engine Test Results on Common Rail John Deere Engines (EURO II + III)

In January 2008 John Deere presented results of a research project with rapeseed fuelled tractors of John Deere and exhaust gas certified engines according to EURO II (TIER2) and EURO III (TIER3).

The engine development (hardware and software) was executed by VWP, the test bench runs inclusive analysis of fuel, lubrication oil and residues on engine parts have been made by the University of Rostock. The project lasted from 2005 till 2008 and was financed by the German Ministry for Agriculture (BMVEL), subsidy No 22014905.

The project results demonstrates the importance of improving the DIN V 51605, especially for the content of P, Ca/Mg.

At the project, test bench runs with certified engines operated with different rapeseed oil qualities according to DIN V 51605, however with lower element contents of P (phosphorus), Ca (calcium) and Mg (magnesium) as requested, have been done.

The following rapeseed oil qualities have been used in John Deere engines:[32]

- cold pressed rapeseed oil according to DIN V 51605, but with sum content of P, Ca and Mg of < 11 mg/kg
- fully refined rapeseed oil according to DIN V 51605, with zero P, Ca and Mg content (detection limit)
- cold pressed rapeseed oil according to DIN V 51605, with zero P, Ca and Mg content (detection limit).

The test bed results showed the negative impact of P, Ca and Mg according to DIN V 51605 in rapeseed oil on rapeseed fuelled tractors.

The actual required element content of P, Ca and Mg according to DIN V 51605 causes sediments on engine parts which cause damages. These unfavourable sediments do not occur if rapeseed oil according to DIN V 51605, but with a sum content of P, Ca and Mg to the detective limit is used. Based on the results, John Deere requires the removal of the elements P, Ca, Mg out of rapeseed oil to prevent damages on advanced engines.

3.2.1 P, Ca/Mg Tolerance of Pistons, Piston Rings

In pictures 6 and 7, pistons of John Deere tractors are shown operated 1.000 hours with rapeseed oil according to DIN V 51605, but with a sum content for P, Ca and Mg of < 11 mg/kg. As it is seen in pictures 6 and 7, heavy sediment residues are caused by the elements P, Ca and Mg. The sediment analysis was done by the University of Rostock.

Picture 6: Piston with sediments[33]

Picture 7: Piston and piston rings with sediments[34]

Pictures 8 and 9 and show pistons of John Deere tractors operated 1.500 hours with rapeseed oil according to DIN V 51605, but within a sum content of P, Ca and Mg < 1.5 mg/kg.

By operating the tractor with this rapeseed oil quality, preferably low burning residues on pistons occurred although the engine was operated 500 hours longer. The piston rings were free and moveable.

Picture 8: Pistons without sediments[35]

Picture 9: Piston without sediments and free piston rings[36]

By operating the tractor with this rapeseed oil quality, preferably low burning residues on pistons occurred although the engine was operated 500 hours longer. The piston rings were free and moveable.

3.2.2 P, Ca/Mg Tolerance of Turbocharger

The comparison of two turbochargers of John Deere tractors operated with different rape-seed oil qualities - according to DIN V 51605, but with a lower element content of P, C and Mg than required – showed significant differences.

Picture 10 shows a turbocharger operated 1.000 hours with rapeseed oil (DIN V 51605) with a sum content of P, Ca and Mg < 11 mg/kg. The turbocharger of picture 11 was operated 1.500 hours with rapeseed oil (DIN V 51605) within a sum content of P, Ca and Mg < 1.5 mg/kg.

Picture 10: Turbocharger covered with a grey phosphorus layer[37]

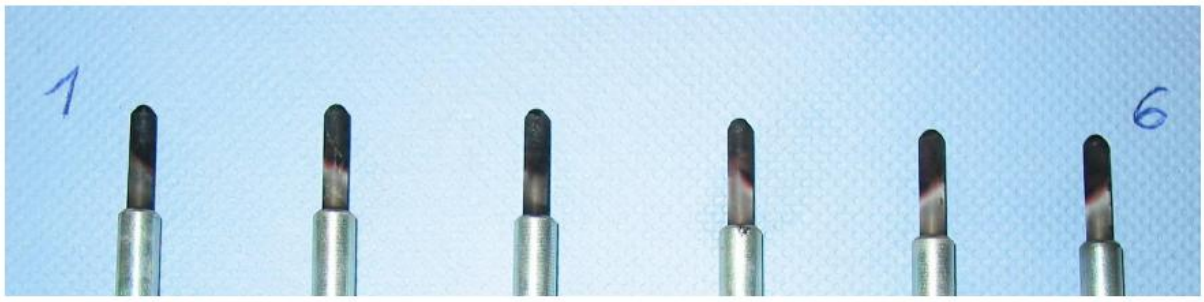
Picture 11: Turbocharger covered with typical black-coloured soot particles[38]

Like on the glow plugs discussed in 3.2.3, a relatively high content of P, Ca/Mg in the fuel leaves remarkable traces especially on hot engine parts. Pictures 10 and 11 show these parts of the turbochargers which are exposed to hot exhaust gas up to 750 °C. After 1.000 hours of test bench run with a P, Ca/Mg content of < 11 mg/kg, the turbocharger in picture 10 clearly shows the significantly light grey layer of P, Ca/Mg on the turbo shovels. Picture 11 instead records a dark, black layer of soot particles which is typical for P, Ca/Mg clear fuels.

3.2.3 P, Ca/Mg Tolerance of Glow Plugs

On glow plugs used on test bed engines fuelled with different rapeseed oil qualities (DIN V 51605) it can be seen on picture 12 that there are sediment residues on glow plugs which are operated 1,000 hours with rapeseed oil with an element sum content of P, Ca and Mg < 11 mg/kg.

Picture 12: Glow plugs with phosphorus sediments[39]



Picture 13: Glow plugs without phosphorus sediments[40]

In picture 13 instead, no traces of phosphorus can be spotted on the hot parts of the glow plugs because a fuel was used which had a P, Ca/Mg content below the analytical detection limit. The P, Ca/Mg content in the residues on the glow plugs was measured with an ICP analysis device by the University of Rostock.

3.2.4 P, Ca/Mg Tolerance of Fuel Filters

At the test bed of John Deere also the fuel filters were analysed for residues of the elements P, Ca and Mg.

Picture 14: Fuel filters after 1.000 hours' test bench run No. 1

The fuel filters which have been used in test bench run No. 1 with fuel containing < 11 mg/kg P, Ca/Mg showed a white, light grey substance on the surface of the filter material. After burning this filter material, the University of Rostock could prove by ICP analysis a significantly higher content of P, Ca/Mg in the ash in comparison to ash of burned new filter material with no traces of P, Ca/Mg in it.

Thus, John Deere claims that a fuel content of P, Ca/Mg which is higher than the detection limit is also responsible for reduced fuel filter changing periods < 200 hours.

4 Simulation of Optimal P, Ca/Mg Emissions of Modern Diesel Engines with Emission Stage 3b, 4 (Deutz Company)

While JDWM used test bench analysis to find out about the negative impact of P, Ca/Mg in rapeseed fuel to engines and maintenance intervals, the Deutz company chose a theoretical study to make a proposal for P, Ca/Mg limits in rapeseed oil as fuel[41].

For soot filters which are mandatory for emission stage 3b in 2012, Deutz announced all ash building elements like P, Ca/Mg potassium (K) and sodium (Na), zinc (Zn) as dangerous. Ash building elements can be washed out of the soot filter. During a 10.000 hours' lifetime of a soot filter the Deutz company proclaims not more than two or three washing units.

As ash building elements are also contained in lubrication oil, the industry developed new low SAP lubrication oils (S = sulphur, A = ash, P = phosphor) to minimize a loading of soot filters with ash building elements coming from the part of the lubrication oil which is burned through the combustion process[42].

For its simulation, the Deutz AG then counted the sum of ash building elements coming from the lubrication oil and the rapeseed oil which is used per hour from a 147 kW Deutz Natural Fuel Engine with a fuel consumption of 248.6 g/kWh at 50 % power rate.

The result of the calculation is visualized in the following tables 4 and 5.

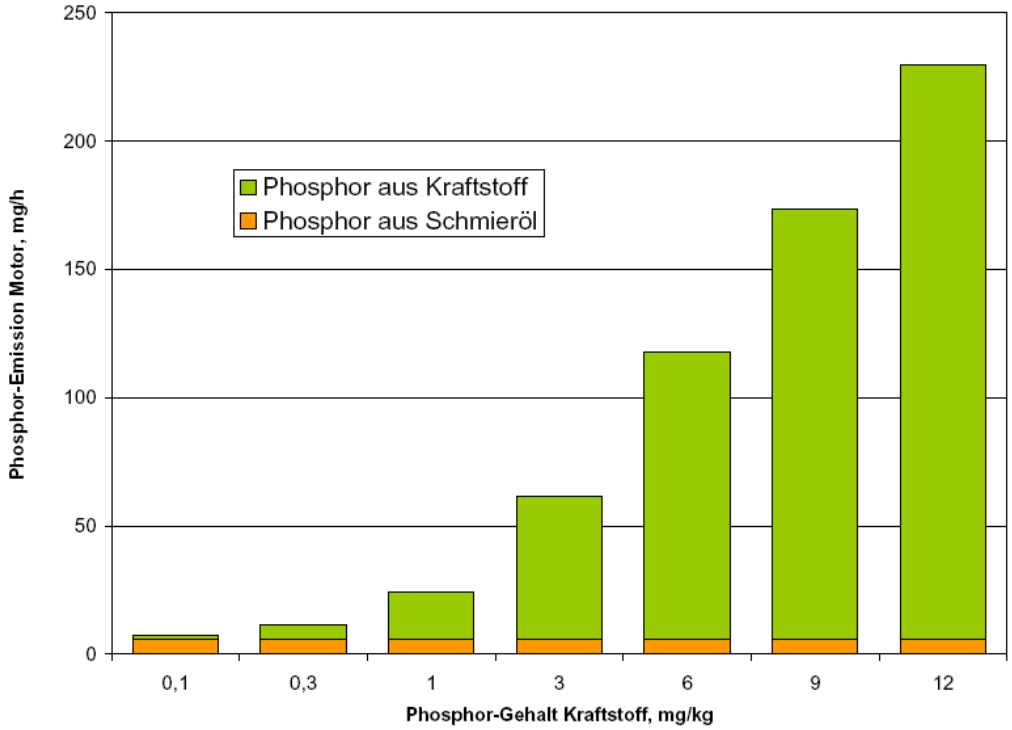


Table 4: Phosphorus emission in mg/h of lubricating oil (= orange) and fuel (= green) from engines[43]

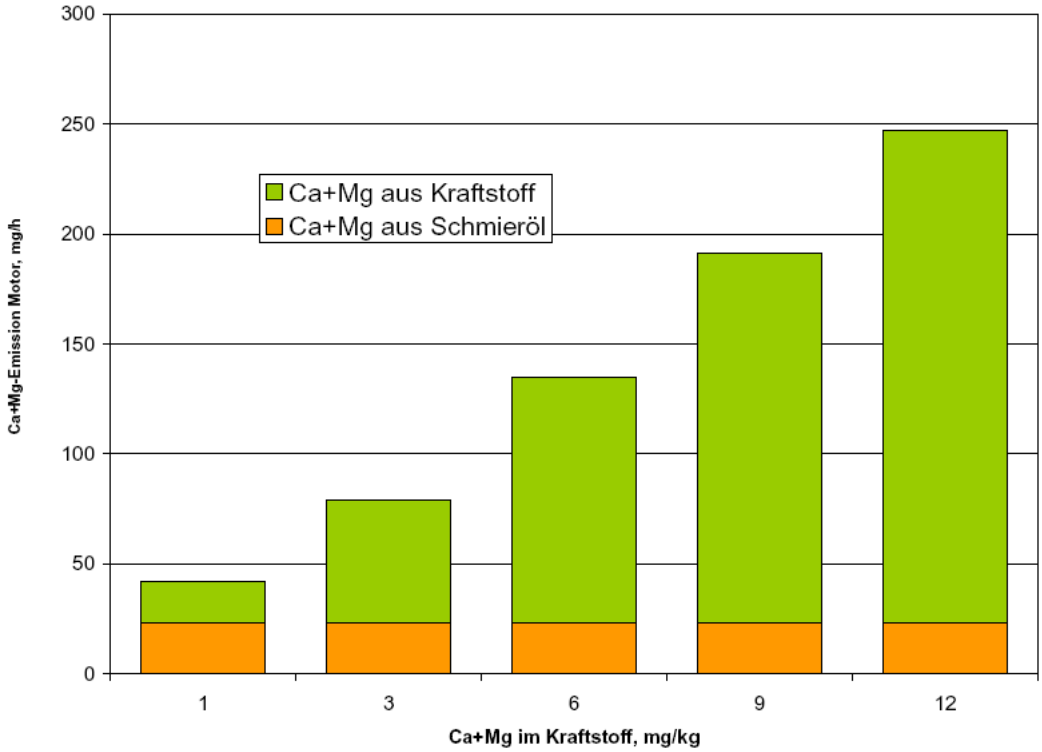


Table 5: Calcium and magnesium emission in mg/h of lubricating oil (= orange) and fuel (= green) from engines[44]

Table 4 and table 5 show the P and Ca/Mg emissions of the engine (y-axis) in mg/h coming from different fuel levels of P and Ca/Mg (green) in mg/kg (x-axis) and from the low SAP lubrication oil (orange) which always has the same level.

The Deutz company requires that the advantage of low SAP oils for soot filters may not be used up by unnecessary high P, Ca/Mg emissions from the fuel. Just the same P and Ca/Mg emissions from the lubrication oil and the fuel are tolerated.

For P emissions (table 4) the Deutz company sets up a limit of 0.2 to 0.3 mg/kg. With a P limit of 1 mg/kg the fuel would be already four times more poisonous to catalysts than the lubrication oil. This is not accepted by Deutz. The present P limit of 12 mg/kg in the DIN V 51605 would expand the poison danger for catalysts coming from rapeseed oil as fuel almost 50 times higher than accepted.

For Ca/Mg emissions (table 5) the Deutz company sets up a limit of 1 mg/kg. This is almost the same emission amount which also comes from the low SAP lubrication oil and means three washing units during the 10,000 hours' lifetime of the soot filter. For the present Ca/Mg limit of 20 mg/kg in the DIN V 51605 the Deutz company calculated 26 washing units.

A Ca/Mg limit of 3 mg/kg for Ca/Mg would need six washing units of the soot filter which is still not acceptable for Deutz.
As a result of the P, Ca/Mg emission simulation, Deutz demands a DIN V 51605 adaptation and new limits for P (0.2 to 0.3 mg/kg) and Ca/Mg (1.0 mg/kg).

5 Other Comments and Studies which Ask for a Reduction of P, Ca/Mg in the DIN V 51605

The experimental and field test results from the Austrian 35 tractors' program, the practical and scientific test bench runs from John Deere and the theoretical approach from Deutz showed the risk of engines fuelled with rapeseed oil following the DIN V 51605. The public learned about this by increasing engine damages due to rapeseed fuel with too much P, Ca/Mg in it.

As consequence there have been generally restrictions to use cold-pressed oil in tractors[45] and especially companies which adapted trucks to pure plant oil like Pflanzenöltechnik Nord (PTN) required refined rapeseed oil as fuel[46]. There have been additional comments[47] and studies from VWP, MAN and the Bundesverband Pflanzenöle e.V. which gave warnings about a too high value for P, Ca/Mg in the DIN V 51605.

5.1 100 % RENET: VWP Results of Analysis of Ash Producing Elements Blocking the Soot Filters

In the EC project 100 % RENET (Project No. NNES-2001-357) from 2001 till 2004, VWP worked on implementing several small SenerTec CHP in a German model region around Munich. The SenerTec CHP have been developed and modified from VWP to rapeseed oil as fuel[48].

In difference to serial SenerTec CHP running on diesel fuel, the new plant oil SenerTec co-generations modified by VWP very soon showed blocked soot filters. With a ICP spectrometer analysis, a very high up to then unknown weight percentage of calcium, phosphorus and magnesium was measured and detected by VWP. When investigating the crystal growth of these blocking elements in SenerTec soot filters, VWP found out that the phosphor, calcium and magnesium content of the used plant oil has got a strong linear impact on crystal growth in the soot filter.

So, test runs carried out by VWP showed that rapeseed oil having a phosphor content of 15 ppm (ppm = parts per million = mg/kg) enabled a vegetable oil SenerTec CHP to run 900 hours without changing the soot filter. After using a plant oil containing 10 ppm phosphor, the maximum loading weight of 25 grams of the soot filter was reached 450 hours later at 1,350 hours. The soot filter loading path in grams/hour of two CHP, one being fuelled with 15 ppm phosphor and the other being fuelled with 10 ppm phosphor, is shown in the following table.

Betreiber Name	Phosphor [ppm]	Testzyklen *)								
		150 Bh	300 Bh	450 Bh	600 Bh	750 Bh	900 Bh	1.050 Bh	1.200 Bh	1.350 Bh
BHKW 1 Institut f. E & U	10 ppm	2,7	5,5	8,3	11,0	13,8	16,5	19,3	21,8	24,6
BHKW 3 Herzog	15 ppm	3,9	8,2	12,3	16,1	20,0	24,1	---	---	---

*) Rußfilterrückstände in Gramm, in Abhängigkeit von verwendeter Rapsölqualität und Betriebsstunden

Table 6: Loading Path of Soot Filter in Grams/Hour with Two Different Qualities of Rapeseed Fuel[49]

The next table 7 shows a graphic of the soot filter loading cycle of the table 6 before. Depending on running hours of the CHP the graphic shows crystal growth in the soot filter (in grams) of two different fuel qualities of rapeseed oil with 10 ppm and 15 ppm P.

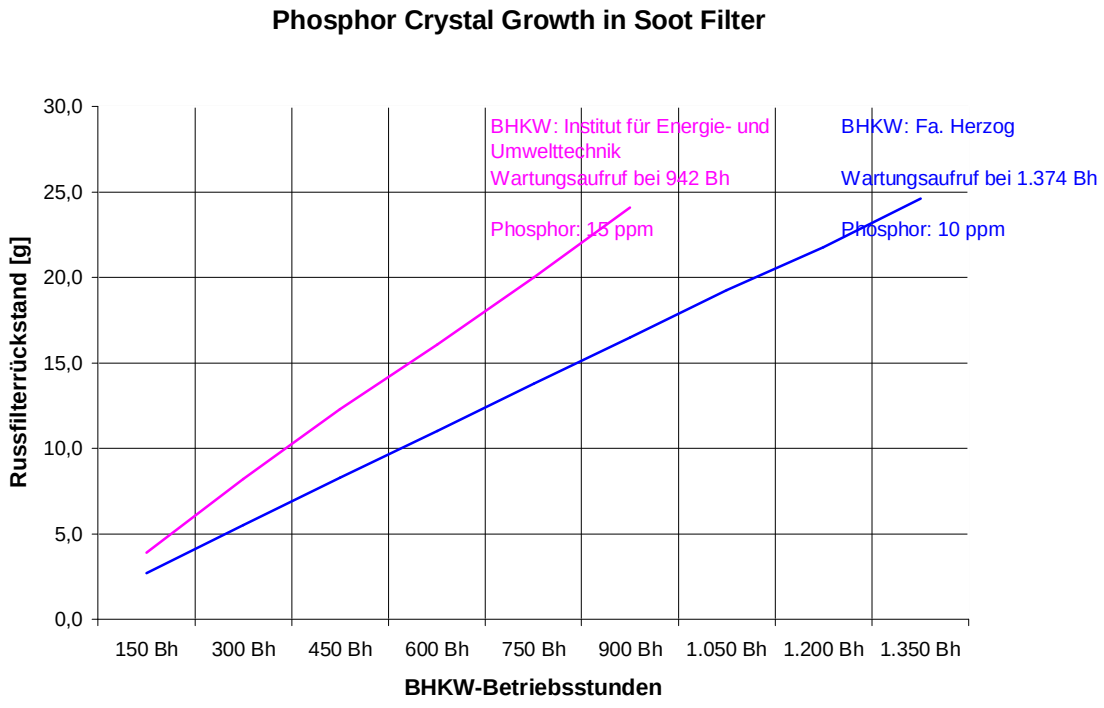


Table 7: Graphic Description of Soot Filter Loading in Gram Depending on Running Hours.[50]

As a side-effect of these analysis, two consequences occurred which have been important for the further success of vegetable oil as a fuel. VWP claimed for two changes in fuel standards at this time:

1. In the international accepted so-called “Weihenstephan standard 5/2000” for rapeseed oil as a fuel, not just phosphor but also calcium and magnesium may be analyzed in future.

2. The so far accepted phosphor benchmark of 15 ppm has to be reduced.

In these days the results from 100 % RENET in 2004 gave evidence to VWP that especially soot filters have a zero tolerance to P, Ca/Mg and presumably also to sodium (Na) and potassium (K) as substance not just in rapeseed fuel but in any fuel.

Today, VWP is convinced that rapeseed oil just can survive as pure 100 % bio-fuel strategy when P, Ca/Mg is limited to 1 mg/kg in sum. With values which are for example three to five times higher pure plant oil will end up as blend fuel to diesel. Therefore, the adaptation of the DIN V 51605 and the development of a new fuel quality is of highest importance for VWP[51]

5.2 MAN Comment on Phosphor as Catalyst Poison

With higher injection pressure, 2-stage turbocharging and high EGR (exhaust gas recirculation system) rates, the German company MAN will reach the existing and future emission standards together with a soot filter and a selective catalytic reduction (SCR). For this engine technology and emission after-treatment systems, MAN gives a warning for ash building elements in the fuel[52].

Phosphor is considered as highly poisonous for catalysts. Already the smallest dose is blamed for a not reversible deactivation of catalysts. Alkali and earth alkali like Calcium, magnesium and also sodium and potassium are considered as poisonous for catalysts as well. Every fuel should reduce the content of these elements to the limit of analytical detection[53]

5.3 Bundesverband Pflanzenöl e.V.: Position on P, Ca/Mg Content in Rapeseed Fuel

In a public hearing in the German parliament about the future biofuel strategy of the German Government, the Bundesverband Pflanzenöle e.V. was asked to attend the meeting as expert and give a written statement to questions of members of parliament[54].

In this statement, the zero tolerance of the companies MAN, Deutz, John Deere to P, Ca/Mg content in diesel/rapeseed fuel for modern diesel engines has been quoted. The Bundesver-

band Pflanzenöl e.V. gave a warning even for the governmental plan of a 7 % biodiesel blend to diesel. It stated a long-term risk for millions of cars with catalyst and soot filters because of the high limit for P, Ca/Mg in the biodiesel quality standard DIN 14214 in 2008.

For pure plant oil as fuel and pure plant oil as a raw material for the bio-diesel production, the Bundesverband Pflanzenöle made the proposal to reduce P, Ca/Mg in an adapted DIN 51605 to 1 mg/kg in sum.

6 Conclusion

Germany still is the leading country for using pure plant oil as fuel. As consequence, also the first world-wide fuel quality standard for rapeseed oil – the DIN V 51605 – was established in Germany. Especially for phosphor and later also for calcium and magnesium the development of the different rapeseed oil fuel standards always generated the same conflict between engine producers and rapeseed oil producers.

In work sessions for the Weihenstephan standard or the DIN V 51605, the commission members always decided not to implement challenging values neither for P, Ca/Mg in rapeseed oil nor for modern analysis methods to analyse the fuel quality in a higher definition.

For the engine producers, too much P, Ca, Mg, Na and K in rapeseed fuel increases the risk of engine damages followed by a common bad reputation for vegetable oil engines.

For the plant oil side, a high value for P, Ca, Mg Na and K means that all decentralized oil mills and analysis institutes can stay in the business; also maybe these 10 % or 20 % of oil mills and analysis institutes with the worst performance which would have to invest in machinery or capacity building to also be able to produce high quality fuel with challenging values for P, Ca/Mg.

What for decentralized oil mills means a comfortable situation, turns to the engine side into a deadly threat.

This example shows much about the principles how such work sessions with differently interested groups function. It is not the experience or knowledge which mainly influences the decisions, but the majority or minority principle. Engine and fuel quality are always two sides of the same coin and the variable elements phosphor, calcium and magnesium are a crucial factor for this partnership.

The history of the development of quality standards for rapeseed oil also is the history that engine experts never got the values for P, Ca/Mg which they actually required for their vegetable oil engines.

Today, the situation is the same. Deutz, John Deere Works Mannheim, MAN, VWP and others require max. 1.5 mg/kg for P, Ca, Mg, in rapeseed oil as fuel. The existing DIN V 51605 allows 32 mg/kg for P, Ca/Mg in rapeseed oil as fuel.

It is not sure whether the DIN V 51605 commission this time respects the engine requirements for P, Ca, Mg, and also for further parameters like Na and K. If not, it will favour the worldwide biofuel blend strategy and endanger the future of pure plant oil as 100 % bio-fuel and its production in decentralized oil mills.

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