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# Rapeseed Oil Fuel Aftertreatment in Decentralized Oil Mills to Reduce Element Contents

*High contents of sedimenting and ash-forming elements like phosphorus (P), calcium (Ca) and magnesium (Mg) in cold-pressed locally produced rapeseed oil fuel can be reduced to under the limit set by DIN V 51605 by aftertreatment with added substances like bleached earth (hydrous aluminium silicate) or silica gel and citric acid. In laboratory experiments rapeseed oil with atypically high phosphorus, calcium and magnesium contents was treated with ten different additives, which are available on the market, as well as with citric acid, at different oil temperatures, purified and analyzed for relevant parameters according to DIN V 51605.*

The use of rapeseed oil fuel for the reliable operation of engines suitable for vegetable oil requires high-quality fuel according to DIN V 51605 [1]. As engine development progresses and more exhaust gas aftertreatment systems are used, the reduction of deposit and ash-forming elements, such as phosphorus, calcium, and magnesium in rapeseed oil fuel is becoming more and more important. If the requirements with regard to a lower content of these elements in rapeseed oil fuel are tightened, the current technical equipment of decentralized oil mills will no longer enable fuel qualities to be produced which conform to the standards. Therefore, suitable techniques for the aftertreatment of rapeseed oil would become necessary for this purpose [1].

In small plants, vegetable oil is gained in two process steps: oil pressing and multiple-stage solid/liquid separation by means of sedimentation and/or filtration. In general, the oil does not undergo additional treatment [14].

From the literature, it is known that bleaching earths [2, 8, 13, 15] and other added substances, such as diatomaceous earth [9, 10], cellulose [9, 10, 17], and synthetic silica gels [3, 4, 5, 6, 7, 8, 11, 12, 13, 15, 16] are suitable for the elimination of phosphorus, calcium and magnesium from vegetable oils.

The addition of acid (citric acid or phosphoric acid) and water to vegetable oil [14] allows phospholipids and the metal ions associated with them, such as calcium, magnesium, iron, and copper, to be removed from the oil.

It is the goal of this study to research different methods which could be suitable for the reduction of the phosphorus, calcium and

magnesium content of rapeseed oil fuel in decentralized vegetable oil production and to examine selected techniques with regard to their suitability for application in decentralized plants and their reduction potential at the laboratory scale. Other quality parameters of rapeseed oil fuel should not be affected by this treatment.

## Procedure

In batch trials, ten different adsorptive or absorptive substances which are available on the market as well as citric acid (C) (20%) were added to cold-pressed rapeseed oil with untypically high contents of phosphorus, calcium, and magnesium. Afterwards, the oil was treated at different temperatures and cleaned.

The turbid oil was stored at a constant temperature of 18° and under the conditions of permanent homogenization. For the batch trials, the oil batches, including the turbid matter contained in the oil, were homogenized to the highest possible degree. With the aid of an electric contact thermometer, the turbid oil was kept at a constant temperature and homogenized by a heating magnetic agitator. When the predetermined temperature was reached, the turbid oil was conditioned at this temperature for the determined period with or without an added substance and with or without citric acid. An overview of the trial variants is given in *Table 1* and *Table 2*.

In those variants where citric acid was added, the acid was first stirred into the oil for two minutes as soon as the turbid oil had reached the desired temperature. Only afterwards the prepared substance quantity was added to the turbid oil-citric acid mixture, which was subsequently conditioned at the

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## Keywords

Rapeseed oil for fuel, quality, element content

*Table 1: Description of experimental variants depending on concentration of added substances, oil temperature during conditioning, duration of condotioning and adding of citric acid*

	Unit	coding of samples							
		0-1-2-0	0-3-2-0	0-3-2-C	1-1-2-0	1-3-2-0	3-1-2-0	3-3-2-0	3-3-2-C
concentration of added substance	weight-%	0.0	0.0	0.0	0.2	0.2	1.0	1.0	1.0
oil temperature	°C	25	45	45	25	45	25	45	45
period of conditioning	min	30	30	30	30	30	30	30	30
concentration of added citric acid	weight-%	0.0	0.0	1.0	0.0	0.0	0.0	0.0	1.0

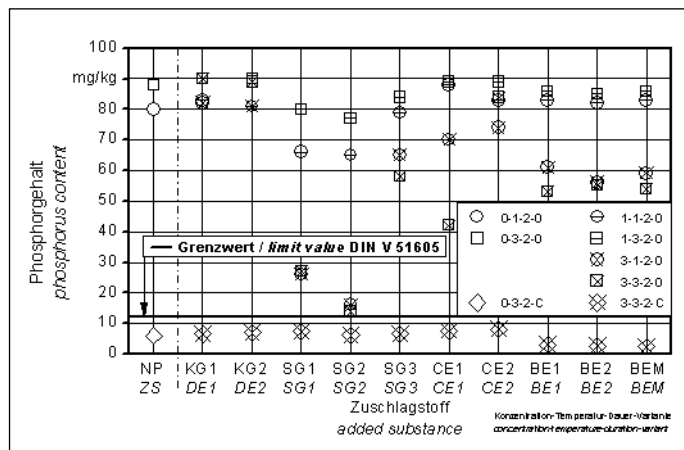


Fig. 1: Phosphorus content (DIN EN 14107) of rapeseed oil samples after treatment without/with citric acid (20 %) with variation of oil temperature during conditioning

set temperature for the determined period.

The oil was cleaned by means of centrifugation (20 min., 5,000 min<sup>-1</sup>) and subsequent vacuum filtration (at about 20°C) using a filter membrane (cellulose nitrate, mean pore width 1.2 µm). The goal was the most precise observation of the predetermined conditioning period possible and, hence, the contact duration of turbid oil, added substances, and citric acid. If possible, longer contact times of individual added substances in the treated oil due to a longer cleaning process should be excluded. At 3 to 12 mg/kg, the total contamination of the cleaned oils was always kept below the limit of 24 mg/kg according to DIN V 51605.

In order to guarantee constant oil quality over the entire trial period, turbid oil samples were taken from the storage tank at intervals of two weeks. Later, this period was extended to four weeks. These samples were cleaned, and the pure oil produced was analyzed based on parameters according to DIN V 51605.

The treated and cleaned oils were examined for the parameters phosphorus (DIN EN 14107), calcium and magnesium (DIN EN 14538), total contamination (DIN EN 12662), acid number (DIN EN 14104, oxidation stability (DIN EN 14112), ash content (DIN EN ISO 6245), and water content (DIN EN ISO 12937). In addition, an ICP element screening was carried out for all samples in order to detect potential contamination of the pure oil due to the treatment with added substances.

Table 2: Added substances applied and coding of experimental variants

Abbreviation	Term
ZS	Zero Sample
DE	Diatomaceous Earth
SG	Silicagel
CE	Cellulose
BE	Bleaching Earth
BEM	Bleaching Earth Mixture

**Influence on the phosphorus content**

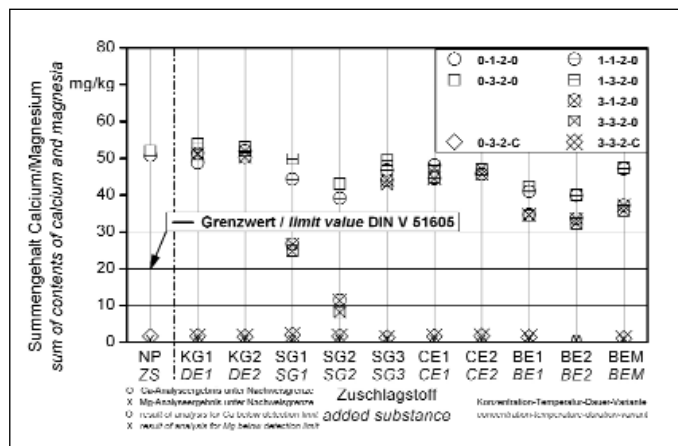
Given the high initial content, the addition of silica gels SG1 and SG2 (1 weight-% each) allowed the phosphorus content of the oil to be reduced significantly as compared with the reference sample, though not below the limit of 12 mg/kg according to DIN V 51605. The results are summarized in Figure 1. By adding cellulose C1 at a concentration of 1.0 weight-% and an oil temperature of 45°C, the phosphorus content is reduced by approximately 50%. Given an added quantity of 1.0 weight-% and an oil temperature of 45°C, silica gel SG3, bleaching earths BE1 and BE2, and the bleaching earth mixture BEM also reduce the phosphorus content, though to a lesser extent. In this trial series, diatomaceous earths KG1 and KG2 had no or virtually no influence on the phosphorus content. The noticeably positive effect of higher added substance concentration at a higher temperature (SG2, C1, BE1, BE2, SG3, BEM) does not apply to diatomaceous earths. The addition of 1.0 weight-% of citric acid at an oil temperature of 45°C allows the phosphorus content to be reduced significantly below the limit of 12 mg/kg according to DIN V 51605. The additional combination of citric acid and added substance seems useful only for bleaching earths BE1 and BE2 as well as the bleaching

earth mixture BEM in order to reduce the phosphorus content even more.

**Influence on the sum of calcium and magnesium contents**

In the present series of trials, only the addition of 1.0 weight-% of silica gel SG2 enables the sum of calcium and magnesium contents to be reduced below the limit of 20 mg/kg according to DIN V 51605. The results of the trial series with regard to the sum of calcium and magnesium contents are shown in Figure 2. In this trial series, diatomaceous earths KG1 and KG2, celluloses C1 and C2, and silica gel SG3 exerted no or virtually no influence on the sum of calcium and magnesium contents. At a concentration of 1.0 weight-%, silica gel SG1 reduces the sum of calcium and magnesium contents by about 50%, though not below the limit of 20 mg/kg according to DIN V 51605. At a concentration of 1.0 weight-%, bleaching earths BE1 and BE2 as well as the bleaching earth mixture BEM enable the sum of calcium and magnesium contents to be reduced only slightly. The noticeably positive effect of higher added substance concentration at higher temperatures on the reduction of the element content, which was determined for phosphorus, is less pronounced in the case of calcium and magnesium. Such an effect can only be detected if silica gels SG1, SG2, and SG3, bleaching earth BE2, and the bleaching earth mixture BEM are used. The addition of 1.0 weight-% of citric acid at an oil temperature of 45°C allows the sum of calcium and magnesium contents to be reduced from an initial 52 mg/kg to 1.6 mg/kg. The combination of citric acid and another added substance has virtually no additionally reducing effect on the sum of calcium and magnesium contents. In all analyses of the oils treated with citric acid, the magnesium content was below the detection limit.

Fig. 2: Sum of contents of calcium and magnesium (E DIN EN 14538) of rapeseed oil samples after Treatment without/with added substances, without/with citric acid (20 %) with variation of oil temperature during conditioning



### Influence on other quality parameters

The acid number as another quality parameter of rapeseed oil fuel according to DIN V 51605 is virtually not influenced by the treatments carried out. The limit of 2.0 mg KOH/g according to DIN V 51605 is not exceeded in any case. Oxidation stability is reduced by treatments with added substances except for cellulose C1 at a concentration of 1.0 weight-%. In some cases, a slight reduction can already be measured at a concentration of 0.2 weight-% (SG2, SG3, BEM). The added substances exert a wide variety of influences on the water content in the oil. The addition of silica gels SG1 and SG2 to the oil leads to a considerable increase in the water content, which may even exceed the limit of 750 mg/kg according to DIN V 51605. The addition of citric acid also causes an increase in water content. A combination of citric acid and dialomaceous earth KG1, silica gels SG1 and SG2, bleaching earths BE1 and BE2 and the bleaching earth mixture BEM as added substances causes the water content to increase even more, even though it remains below the limit according to DIN V 51605. In the reference samples, 3.6 and 4.0 mg/kg of potassium were measured. The treatment of the oil with dialomaceous earths KG1 and KG2 does not influence the potassium content. Silica gels SG1, SG2, and SG3, celluloses C1 and C2, and bleaching earths BE1 and BE2 slightly reduced the potassium content. The bleaching earth mixture BEM (concentration: 0.2 weight-%) increased the potassium content considerably from 3.6 to 16 mg/kg and from 4.0 to 14 mg/kg. If a combination of citric acid and added substances was used, no case occurred where potassium was detected in the oil.

The addition of silica gels SG1 and SG2, bleaching earths BE1 and BE2, and the bleaching earth mixture BEM leads to sodium input into the oil, though at a very low level. If the bleaching earth mixture BEM (concentration: 0.2 weight-%) was added, measured sodium contents were 11 mg/kg at an oil temperature of 25°C and 5.2 mg/kg at 45°C. If a combination of citric acid and added substances was used, no case was found where potassium was detected in the oil.

Other elements, such as iron, copper and zinc, were either not detected at all in the oil, or they were found at concentrations near the detection limit of the measuring technique in the reference sample or after treatment.

### Conclusions and future prospects

At the laboratory scale, the use of added substances allowed the contents of phosphorus, calcium, and magnesium in rapeseed oil fuel to be reduced. Silica gel SG2 proved to be particularly suitable for this purpose. However, treatment with added substances can also lead to an undesired enrichment with elements such as iron, potassium, copper, sodium, and zinc in the oil. The use of citric acid provides a relatively more noticeable reduction of the phosphorus, calcium, and magnesium contents in rapeseed oil fuel. If a combination of added substances and citric acid is used, the observed input of the mentioned elements by added substances can be avoided. In the laboratory, the combination of citric acid with BE1, BE2, and BEM provided the best results.

The effect of the added substance concentration with regard to the reduction of the element contents of phosphorus, calcium, and magnesium is often not linear, if interaction with other quality-determining characteristics is considered. Conditioning (concentration, oil temperature, duration) must be optimized specifically. Other studies are planned in order to examine the practical applicability of such methods for the aftertreatment of rapeseed oil fuel in decentralized oil mills first at the laboratory scale and then in field trials.

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