Aftertreatment of rapeseed oil fuel to reduce element contents

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Introduction and Objective

The use of rapeseed oil fuel for the reliable operation of engines suitable for vegetable oil requires high-quality fuel. 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 magnesia in rapeseed oil fuel is becoming more and more important. By developing the pre-standard DIN V 51605 for rapeseed oil as fuel to the standard DIN 51605 [1], the requirements with regard to a lower content of these elements in rapeseed oil fuel were tightened. So, the current technical equipment of small-scaled oil mills will no longer enable fuel qualities to be produced, which are conform to the limits. Therefore, suitable techniques for aftertreatment to reduce the element content of rapeseed oil become necessary [2].
In trials at laboratory scale [3] it was shown, that the contents of the elements phosphorus, calcium and magnesia in cold-pressed rapeseed oil can be reduced significantly by the treatment with bleaching earth, silica gel or citric acid.
It was the aim of this study [4] to investigate promising techniques from the trials at laboratory scale to reduce the contents of phosphorus, calcium and magnesia in rapeseed oil fuel with regard to their suitability for application in small-scaled oil mills and their reduction potential. Other quality parameters of rapeseed oil fuel and the filterability were comprised for the analysis, because they should not be affected negatively by this treatment.

Approach

In trials at pilot plant scale I, cold-pressed, unstrained rapeseed oil (turbid oil) was treated with six different added substances (diatomaceous earth, 2 silica gels, cellulose, 2 bleaching earths) and citric acid (20 %), in batches of about 180 kg oil. The element contents of the oil (phosphorus 7,2 mg/kg, calcium and magnesia in sum 11,5 mg/kg) were already below the limits according to DIN V 51605. The turbid oil was heated up to 45 °C under the conditions of permanent homogenisation. At the predetermined temperature of 45 °C, the turbid oil was conditioned with added substances and citric acid in different combinations for 30 min. An overview of the added substances is given in Table 1. The purification process was organized like it is typical for small-scaled oil mills, using a chamber filter press. In trials at pilot plant scale II, rapeseed oil with contents of phosphorus (15,9 mg/kg), calcium and magnesia (in sum 30,9 mg/kg) above the limits according to DIN V 51605 was treated with the promising added substances SG3 and BE2 from the trials at pilot plant scale I. The rapeseed oil was also treated with citric acid (40 %) and cellulose as a filter aid in different combinations. Besides the capability for the reduction of element contents, there should be examined, whether it is possible to avoid an increasing water content in the oil by using higher concentrated citric acid and whether the filter aid cellulose has a beneficial impact to the oil volume flow rate during filtration. These trials were done analogous to the trials at pilot plant scale I. The treated and purified oil samples were examined for the parameters phosphorus, calcium and magnesia, acid number, oxidation stability and water content according to DIN V 51605. In addition, an ICP element screening was carried out for all samples in order to detect potential contaminations of the pure oil due to the treatment with added substances. The process of filtration was assessed by the taken oil volume flow rate during filtration and the fluid pressure at the chamber filter press.

Table 1: Added substances applied

abbreviation	term	product name	manufacturer
ZS	Zero Sample	--	--
DE1	Diatomaceous Earth 1	Celatom FW-14	Eaglepicher Minerals
DE2	Diatomaceous Earth 2	Celatom FW-60	Eaglepicher Minerals
SG1	Silica Gel 1	Trisyl	Grace Davison
SG2	Silica Gel 2	Trisyl 300	Grace Davison
SG3	Silica Gel 3	BFX	PQ Europe
CE1	Cellulose 1	EFC 250 C	J. Rettenmaier & Söhne
CE2	Cellulose 2	EFC 250 C-PLUS	J. Rettenmaier & Söhne
BE1	Bleaching Earth 1	Tonsil 919 FF	Süd-Chemie
BE2	Bleaching Earth 2	Tonsil 9191 FF	Süd-Chemie
BEM	Bleaching Earth Mixture	Obefil	Öl- u. Bioenergie GmbH

Results

Trials at pilot plant scale I

As compared with the reference sample, the single addition of silica gel SG2 at a concentration of 0,5 weight-% offered the best effect and allowed the phosphorus content of the oil to be reduced significantly from 7,2 to 1,2 mg/kg. The results are summarized in Figure 1. The addition of 0,35 weight-% of citric acid (20 %) allows the phosphorus content to be reduced only to 6,1 mg/kg. The combination of citric acid and added substances shows a more significant reduction of the phosphorus content of the oil. The combination of citric acid and silica gel SG3, bleaching earth BE2 and the bleaching earth mixture BEM enables the reduction of the phosphorus content of the oil nearly to the level when treated with silica gel SG2.

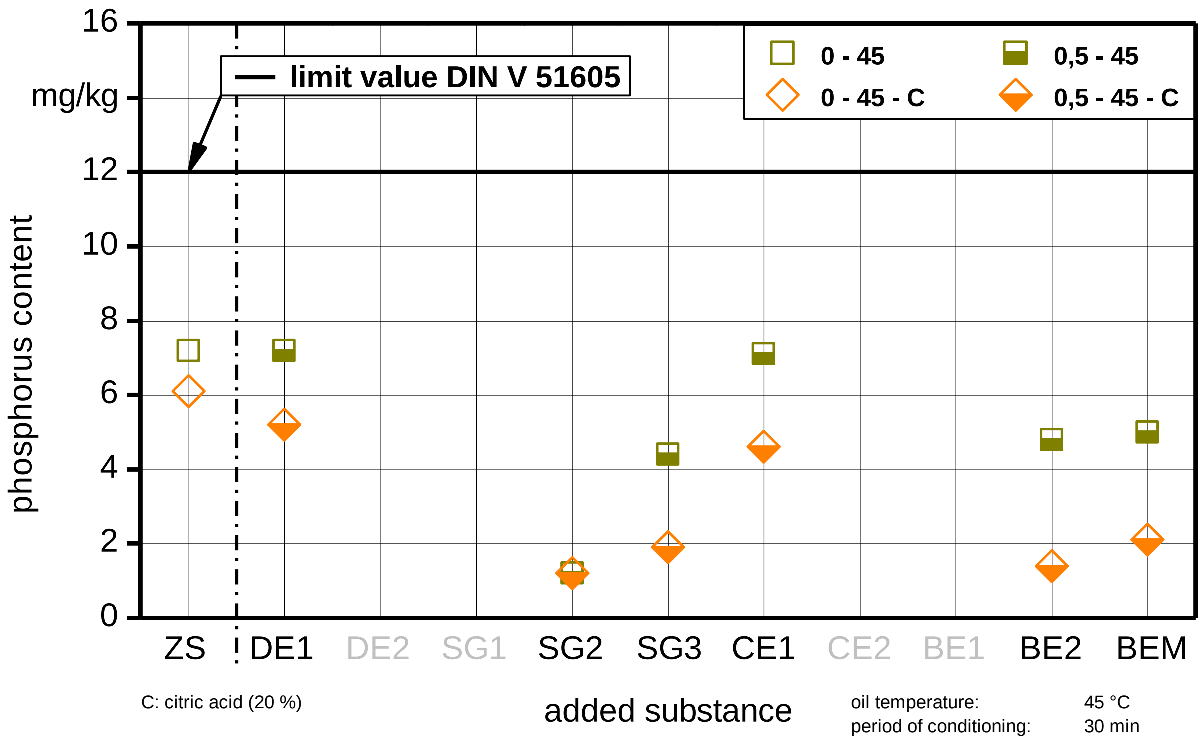

Figure 1: Phosphorus content (DIN EN 14107) of reference sample (ZS) and rapeseed oil samples after treatment (30 min at 45 °C) with added substances (0,5 weight-%), without/with citric acid (20 %)

Compared to the reference sample, the addition of silica gel SG2 at a concentration of 0,5 weight-% significantly reduced the sum of contents of calcium and magnesia from 11,5 to 1,7 mg/kg. By adding silica gel SG3, bleaching earth BE2 and the bleaching earth mixture BEM, a reduction of the sum of contents of calcium and magnesia was also observed, though to a lesser extent. The addition of 0,35 weight-% of citric acid (20 %) allows the sum of contents of calcium and magnesia to be reduced only to 9,4 mg/kg. On the other hand the combination of citric acid and added substances leads to a more significant reduction. The oxidation stability was not influenced by the treatments carried out,

although it could have been expected, that the contents of the natural antioxidant tocopherol in the oil would decrease due to the treatment with bleaching earths and therefore the oxidation stability as well. The addition of silica gel SG2 to the oil led to a considerable increase of the water content from 676 to 971 mg/kg and thus exceeded the limit of 750 mg/kg according to DIN V 51605. By treating the oil with all other added substances, the water content in the oil was reduced however. With a single addition of citric acid to the oil the water content was not influenced. The combination of citric acid and added substances led to an increase in the water content above the limit of 750 mg/kg according to DIN V 51605.
An enrichment with elements in rapeseed oil fuel from the added substances during the trials at laboratory scale [3] was not observed at the trials at pilot plant scale I. The contents of elements such as iron, potassium, copper, sodium, silicon and zinc were close to the detection limit. By using citric acid the oil volume flow rate during filtration was affected negatively.

Trials at pilot plant scale II
By adding bleaching earth BE2 the phosphorus content of the oil could be reduced more significantly from 15,9 to 10,4 mg/kg, compared with silica gel SG3 (13,7 mg/kg). The results of the trials at pilot plant scale II are shown in Figure 2. According to the results of these trial variants, it seems to be better to use citric acid (40 %) in combination with bleaching earth BE2, instead of using citric acid alone. By the additional use of the filter aid cellulose with a phosphorus content of 6,7 mg/kg the best result was achieved.

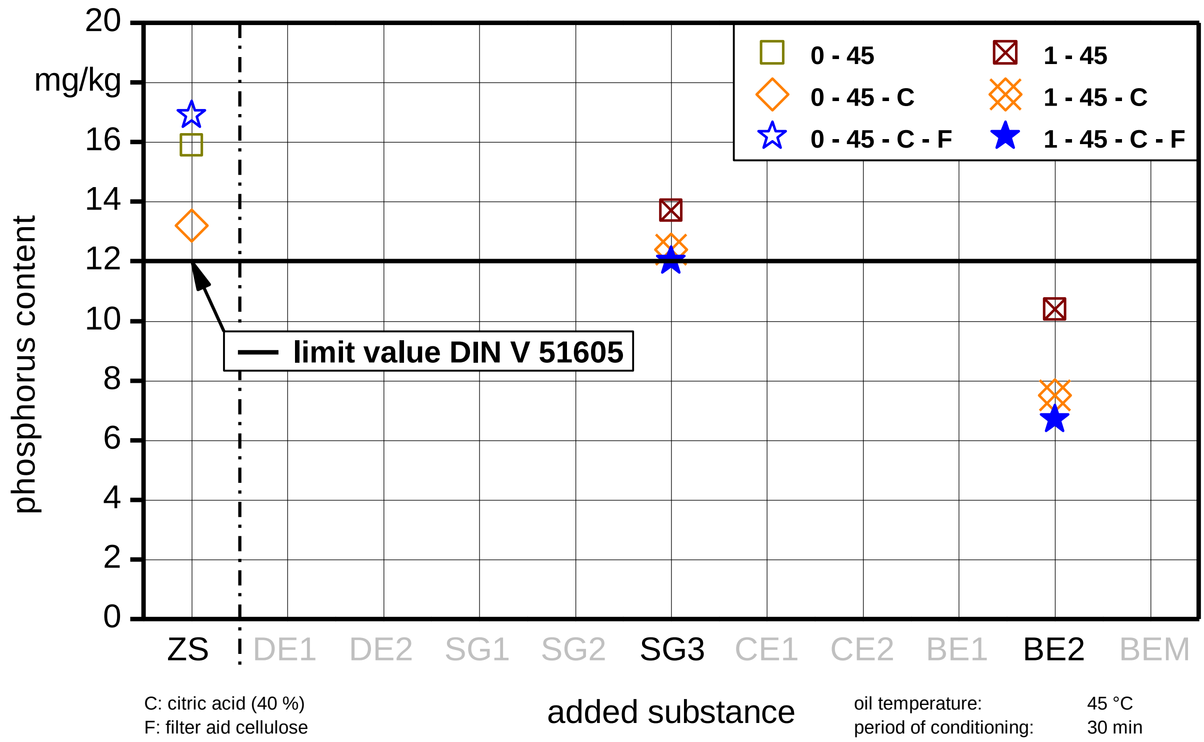

Figure 2: Phosphorus content (DIN EN 14107) of reference samples (ZS) and rapeseed oil samples after treatment (30 min at 45 °C) with added substances (0,5 weight-%), without/with citric acid (40 %), without/with filter aid (F)

Cellulose gave a more favourable structure to the filter cake in the chamber filter press. By this, the oil with the added bleaching earth BE2 and citric acid (40 %) was likely to pass through the filter cake easier (higher flow rate) and the phosphorus content could be reduced more effectively. The noticed reduction of the sum of contents of calcium and magnesia by using added substances, citric acid (40 %) and the filter aid cellulose was analogous to the parameter phosphorus content. Bleaching earth BE2, citric acid and the filter aid cellulose in combination showed a significant reduction of the element contents below the limit value of 20 mg/kg. The oxidation stability was not influenced by the treatments. By using citric acid (40 %) exclusively, the water content was not influenced. The combination of citric acid with an added substance or the filter aid cellulose led to a higher water content. Using higher concentrated citric acid (40 %) instead of citric acid (20 %), the water content in the oil was less increasing. An enrichment with elements in rapeseed oil fuel from the added substances, as seen in the laboratory trials, could not be verified. The oil volume flow rate during filtration was affected negatively by the exclusive use of citric acid (40 %). With additional use of the filter aid cellulose however, this negative effect of the treatment with citric acid (40 %) on the oil volume flow rate during filtration could be compensated.

Conclusions

During the trials at pilot plant scale I, the lowest element contents were analysed by using silica gel SG2. The combination of added substances (SG3, BE2 and BEM) and citric acid (20 %) provided a relatively more noticeable reduction of the element contents and therefore seems to be preferable. The chosen concentrations of 0,5 weight-% added substance and 0,35 weight-% citric acid (20 %) were suitable for the treated oil.

The treatment of the applied oil at the trials at pilot plant scale II with the combination of 1,0 weight-% bleaching earth BE2, 0,175 weight-% citric acid (40 %) and 1,4 weight-% filter aid cellulose showed the best results.

The carried out investigations for the aftertreatment of rapeseed oil fuel with adsorptive effective added substances, citric acid and the filter aid cellulose show, that the contents of the deposit and ash-forming elements phosphorus, calcium and magnesia in the oil can be reduced effectively.

According to the current state of knowledge the general suitability for the practical application at small-scaled oil mills is already given, but for a long-term and continuous application further investigations are necessary.

For a successful aftertreatment of rapeseed oil fuel, the definite knowledge about the quality of the untreated oil is decisive and regarding to this, the concentrations of added substances, citric acid and filter aids have to be adjusted specifically.

The results show, that even the tightened limit values of phosphorus, calcium and magnesia in rapeseed oil fuel according to DIN 51605, which was released in September 2010, can be achieved by small-scaled oil mills by using the described aftertreatment techniques.

Notice

The full research report "Berichte aus dem TFZ 20" is available at www.tfz.bayern.de.

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