Witzelsperger, Josef and Remmele, Edgar

Rapeseed oil fuel aftertreatment in decentralized oil mills in order to reduce element contents

The contents of phosphorus, calcium and magnesia in rapeseed oil fuel can be reduced with suitable added substances and citric acid. Depending on the original contents, the used amounts of added substances, citric acid and filter aids must be adjusted, whereas other quality parameters have to be regarded.

Keywords
Rapeseed oil for fuel, quality, element content

Abstract
Landtechnik 65 (2010), no. 1, pp. 54-57, 2 figures, 3 tables, 4 references

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 magnesia in rapeseed oil fuel is becoming more and more important [1]. If the requirements with regard to a lower content of these elements in rapeseed oil fuel are tightened, the current technical equipment of small-scaled oil mills will no longer enable fuel qualities to be produced, which are conform to the limits according to DIN V 51605. Therefore, suitable techniques for the aftertreatment of rapeseed oil would become necessary for this purpose [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 trial variants is given in **table 1**, **table 2** and **table 3.** 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 and coding

Codierung ***Code***	Bezeichnung ***Term***	Produktname ***Product name***	Hersteller ***Manufacturer***
NP *ZS*	Nullprobe *zero sample*	–	–
KG1/2 *DE1/2*	Kieselgur 1/2 *diatomaceous earth 1/2*	KG1/*DE1*: Celatom FW-14 KG2/*DE2:* Celatom FW-60	Eaglepicher Minerals
SG1/2 *SG1/2*	Silica Gel 1/2 *silica gel 1/2*	SG1/*SG1*: Trisyl SG2/*SG2:* Trisyl 300	Grace Davison
SG3 *SG3*	Silica Gel 3 *silica gel 3*	SG3/*SG3:* BFX	PQ Europe
CE1/2 *CE1/2*	Cellulose 1/2 *cellulose 1/2*	CE1/*CE1*: EFC 250 C CE2/*CE2:* EFC 250 C-PLUS	J. Rettenmaier & Söhne
BE1/2 *BE1/2*	Bleicherde 1/2 *bleaching earth 1/2*	BE1/*BE1*: Tonsil 919 FF BE2/*BE2*: Tonsil 9191 FF	Süd-Chemie
BEM *BEM*	Bleicherde-mischung *bleaching earth mixture*	BEM/*BEM:* 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.

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.

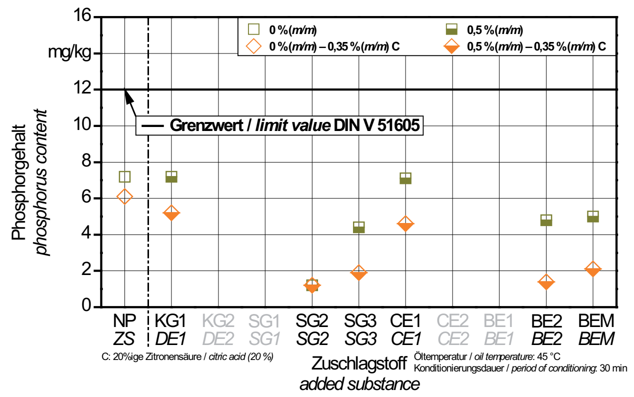
By adding silica gel SG3, bleaching earth BE2 and the bleaching earth mixture BEM, a reduction of the sum of contents of calcium and magnesia was also observed, though to a lesser extent. The addition of 0.35 weight-% of citric acid (20 %)

Table 2

Experimental variants (pilot plant experiments I) depending on concentration of added substances, oil temperature while conditioning, period of conditioning, concentration of added citric acid (20 %)

		Probencodierung Technikumsversuche I ***Coding of samples at pilot plant scale I***			
	Einheit ***Unit***	**0 % (m/m)**	**0 % (m/m) – 0.35 % (m/m) C**	**0.5 % (m/m)**	**0.5 % (m/m) – 0.35 % (m/m) C**
Konzentration Zuschlagstoff *Concentration of added substance*	% (m/m)	0.0	0.0	0.5	0.5
Öltemperatur *Oil temperature while conditioning*	° C	45	45	45	45
Konditionierungsdauer *Period of conditioning*	min	30	30	30	30
Konzentration 20%ige Zitronensäure *Concentration of added citric acid (20 %)*	% (m/m)	0.0	0.35	0.0	0.35

Fig. 1



Phosphorus content (DIN EN 14107) of rapeseed oil samples after treatment without and with added substances, without and with citric acid (20 %) (trials at pilot plant scale I)

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.

During the investigations, an increasing acid number with a rising storage time of the turbid oil was noticed, which was not caused by the aftertreatment of the rapeseed oil fuel.

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. 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.

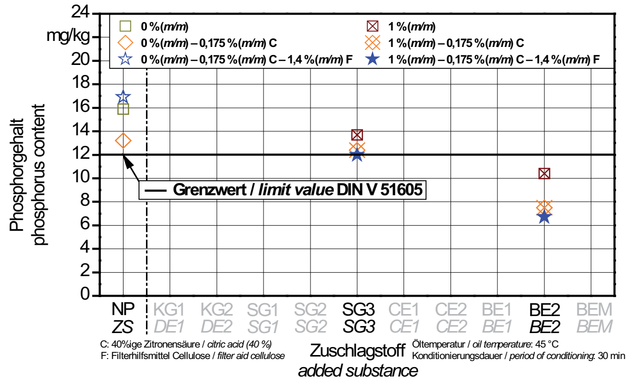
The noticed reduction of the sum of contents of calcium and magnesia by using added substances, citric acid (40 %) and the filter aid cellulose was analogous to the parameter phosphorus

Table 3

Experimental variants (pilot plant experiments II) depending on concentration of added substances, oil temperature while conditioning, period of conditioning, concentration of added citric acid (40 %) and concentration of added filter aid

		Probencodierung Technikumsversuche II *coding of samples at pilot plant scale II*					
	Einheit *Unit*	**0 % (m/m)**	**0 % (m/m) – 0.175 % (m/m) C**	**0 % (m/m) – 0.175 % (m/m) C – 1.4 % (m/m) F**	**1 % (m/m)**	**1 % (m/m) – 0.175 % (m/m) C**	**1 % (m/m) – 0.175 % (m/m) C – 1.4 % (m/m) F**
Konzentration Zuschlagstoff *Concentration of added substance*	% (m/m)	0.0	0.0	0.0	1.0	1.0	1.0
Öltemperatur *Oil temperature while conditioning*	° C	45	45	45	45	45	45
Konditionierungsdauer *Period of conditioning*	min	30	30	30	30	30	30
Konzentration 40%ige Zitronensäure *Concentration of added citric acid (40 %)*	% (m/m)	0.0	0.175	0.175	0.0	0.175	0.175
Konzentration Filterhilfsmittel *Concentration of added filter aid*	% (m/m)	0.0	0.0	1.4	0.0	0.0	1.4

Fig. 2



Phosphorus content (DIN EN 14107) of rapeseed oil samples after treatment without and with added substances, without and with citric acid (40 %), without and with filter aid (trials at pilot plant scale II)

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.

With a rising storage time of the turbid oil the acid number increased, independent from the treatments carried out.

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 is 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

At laboratory scale, the use of added substances allowed the contents of phosphorus, calcium and magnesia in rapeseed oil fuel to be reduced. The use of citric acid (20 %) provides a relatively more noticeable reduction of these element contents. In the laboratory, the combination of citric acid with bleaching earths BE1 and BE2 and also with the bleaching earth mixture BEM provided the best results.

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 rapeseed 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.

In the case of tightened limit values of phosphorus, calcium and magnesia in rapeseed oil fuel according to DIN V 51605, which is discussed presently, small-scaled oil mills are still able to produce standard conform rapeseed oil fuel by using the described aftertreatment techniques.

Literatur Books are signed with ●

[1] Deutsches Institut für Normung e.V.: (Vornorm) DIN V 51605. Kraftstoffe für pflanzenöltaugliche Motoren - Rapsölkraftstoff – Anforderungen und Prüfverfahren. Beuth Verlag GmbH, Berlin, 2006

[2] ● Remmele, E.: Handbuch Herstellung von Rapsölkraftstoff in dezentralen Ölgewinnungsanlagen. 2., neu bearbeitete und erweiterte Auflage. Fachagentur Nachwachsende Rohstoffe e.V., Gülzow, 2009

[3] Witzelsperger, J. und Remmele, E.: Nachbehandlung von Rapsölkraftstoff dezentraler Ölmühlen zur Minderung von Elementgehalten. Landtechnik 63 (2008), H. 4, S. 205-207

[4] ● Witzelsperger, J. und Remmele, E.: Prüfung der Eignung von Verfahren zur Reduktion ablagerungs- und aschebildender Elemente in Rapsölkraftstoff bei der dezentralen Erzeugung. Reihe Berichte aus dem TFZ, Nr. 20. Technologie- und Förderzentrum im Kompetenzzentrum für Nachwachsende Rohstoffe (TFZ), Straubing, 2009

Authors

M.Sc. (Univ.), Dipl.-Ing. (FH) Josef Witzelsperger is scientist at the Department “Biogenous Fuels, Lubricants and Process Substances” of the Technologie- und Förderzentrum (TFZ/Technology and Support Centre) at the Kompetenzzentrum für Nachwachsende Rohstoffe (Centre of Excellence for Renewable Resources), Schulgasse 18, 94315 Straubing, E-Mail: poststelle@tfz.bayern.de

Dr. Edgar Remmele is director of the Department “Biogenous Fuels, Lubricants and Process Substances” of the TFZ.

Notice

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

Acknowledgement

The authors would like to thank the Bavarian State Ministry for Food, Agriculture and Forestry, Munich, for financing the studies and the participating companies for their support.