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INFLUENCE OF ACID NUMBER AND PEROXIDE NUMBER CONTENT ON THE QUALITY OF RAPE SEEDS FOR CONSUMPTION AND BIOFUEL INDUSTRY

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Summary. The present paper aimed at an evaluation of the acid number (TAN) and peroxide number contents in rape seeds from industrial processing, subjected to drying under natural conditions as well as in driers. The achieved results have indicated that regardless of the drying temperature and initial values of the studied parameters, the observed changes in TAN and LOO values were within permissible limits accepted by fat and fuel industry.

Key words: rapeseed, drying, acid number, seed properties, biofuels.

INTRODUCTION

The fat and biofuel industry has to maintain the possibly highest quality of its products, to meet the continually growing consumer's needs as well as the market's requirements in the conditions of EU members competition. Thus it is forced to make very scrupulous and detailed assessments of the purchased raw materials [Rybacki et al. 2001]. Their value is mainly determined by the drying and storing technology. Improper drying temperature is reflected in the seed's technological quality, namely in oxidation changes of fatty acids [Fornal et al. 1995, Krasucki et al. 2002; Tys et al. 2001].

Studies performed by numerous authors [Nellist et al. 1992, Niewiadomski 1992, Pathak et al. 1991, Sadowska et al. 1995, Tys et al. 2002] have indicated that the drying temperature significantly affects the technological value of rape seeds and rape seed oil. The values of acid number exceeded the permissible norms for raw oil in the case of wet seeds dried above 140^0C. Similar values of peroxide number for oil extracted from all the dried seeds were higher as compared with not dried seeds, furthermore, a sudden increase of that value exceeding permissible limits was observed for rape seeds dried above 140^0C. Such situation is explained by the authors, among others, by high initial water content in seeds. Drying using air at 75ºC to 82ºC did not affect the seed's viability unless their humidity exceeds 11.5%. When moisture content in rape seeds exceeds 12.5% or when it is planned to be stored for a longer time, lower temperatures should be applied [Weres J., Tys 2001]. Therefore, improper drying temperature has a direct impact on seed's technological quality, namely TAN and LOO [Krasucki et al. 2001, Krygier et al. 1995a, b], which are the cold-extruded oil quality indicators [Ratusz et al. 1997]. According to Colliver [1983], the process of seed drying is, beyond doubt, the production element that requires the highest inputs, thus low-temperature drying and conserving methods are a widely preferred way to store wet raw material [Crisp et al. 1994, Davison 1979, Ryniecki et al. 1991]. A comparison of various drying methods, made by Cenkowski [1989], Niewiadomski [1983], and Gawrysiak-Witulska et al. [2007], with reference to their influence on rape seed quality revealed that cool air was the most efficient one. It did not make the acid number increase, leaving it unchanged during further storage. However, drying at low temperatures is a long-time process occurring for several weeks. It should also be kept in mind that safe seed storage in that case can be realized only for a given period of time, which is determined by the seed's initial condition, i.e. its maturity and water content. Additional procedures such as aeration or pouring deteriorates seed's quality.

METHODS AND ASSUMPTIONS

The studied material consisted of rape seed samples from a large lot delivered by Fat Processing Company "Kruszwica" S.A. Each seed lot was represented by two samples: one dried in a drier at a given temperature, and another one dried under natural conditions. Samples were marked with labels stating their origin and supplier, and in the case of samples dried in a drier, also on the drier type and drying temperature.

Studies involved rape seeds dried in a drier at a given temperature as well as dried under natural conditions.

In the first case, it can be accepted that values of particular seed quality parameters after drying depended on the initial temperature and drying time as well as the type and age of the drier.

Based on the achieved information, it was assumed that natural drying conditions were the same for all cases. Hence, particular seed quality parameters after drying depended only on their initial values. In consequence, comparison of the examined parameters of seeds dried in driers and in the natural way, allows for concluding on the influence of the drier type and its technical parameters as well as on the raw material's qualitative traits.

The acid number's (TAN) determination was based on the method of neutralizing the free fatty acids present in a sample with KOH, which was in accordance with the norm PN-60/A-86918. Arithmetic mean from three determinations was taken for calculations.

The result was calculated from the following formula:

$$TAN = \frac{a \cdot 5,611}{m}, \tag{1}$$

a - volume of closely 0.1 N KOH solution used in titration [cm^3],

m - weight of oil \ fat [g],

5.61 - the amount of KOH 1cm^3 strictly contained in 0.1 N KOH solution [mg].

The peroxide number value (LOO) was assessed according to PN – 84/A 86918, which consisted in quantitative determination of iodine released from the potassium iodide due to peroxides present in a fat sample. Arithmetic mean from the three determinations was taken for calculations.

Study results were subjected to statistical analysis: among *post-hoc* tests available in Statistica software, the Tukey's test was selected. In order to illustrate the contribution of particular factors as the variability sources of dependent variables (seed quality parameters), besides classical variance analysis, also analysis of variance components was performed with the help of Statistica software and its mode for "planned comparisons".

RESULTS

The amount of free fatty acids expressed as the acid number (TAN) is one of the principle factors describing the oil stability. The raw material for oil production was characterized by acid number ranging from 0.20 to 5.80 mgKOH/g. Distribution of acid number values in the examined material is presented in Figure 1.

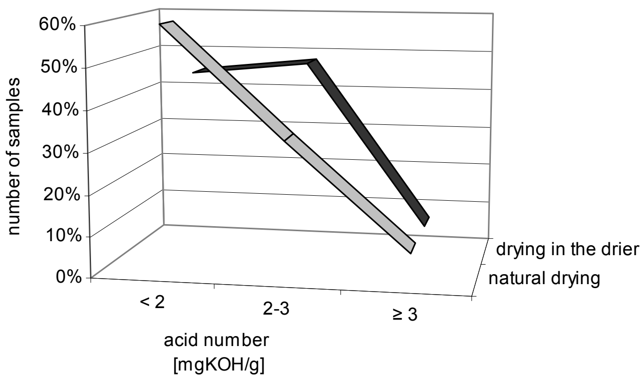

Fig. 1. Percentage distribution of acid number values in rape seeds after drying under natural conditions and in a drier

Figure 1 indicates that acid number for seeds dried in a drier was slightly higher than that for rape seeds naturally dried; however, in both cases, number of samples with TAN ≥ 3 mgKOH/g was low (7%). Because obligatory norm PN-90 R-66151 permits TAN values below 3 mgKOH/g, it can be concluded that, with reference to acid number, the quality of the examined seeds was good and even very good.

Figures 2 and 3 illustrate the dependence of acid number on drying temperature and moisture content of the determined material.

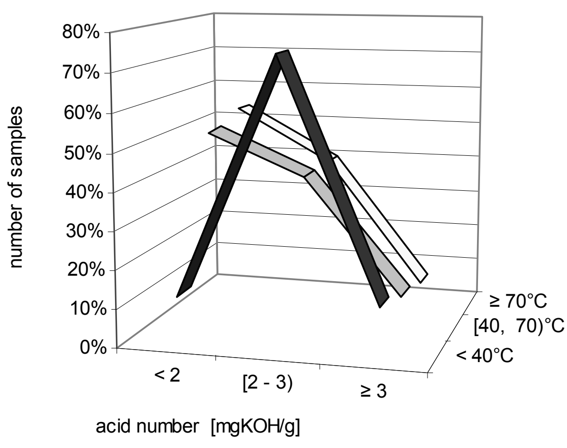

Fig. 2. Percentage distribution of acid number in the dried material at various temperatures

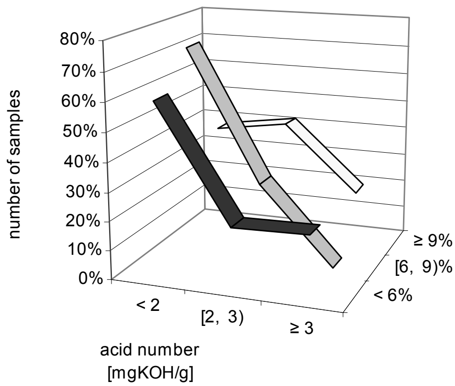

Fig. 3. Percentage distribution of acid number after drying depending on seed moisture content

In seeds dried at temperatures 40÷70^{o}C and above 70^{o}C, there was the largest number of samples with TAN < 2 mgKOH/g and slightly smaller with TAN ranging to 2÷3 mgKOH/g. For drying at temperatures below 40^{o}C, the majority of samples were characterized by acid number values 2÷3 mgKOH/g, while seeds with TAN < 2mgKOH/g comprised the smallest part. Number of samples with TAN higher than 3 mgKOH/g was low (13%, 9%, and 6%), regardless of the drying temperature. In practice, all seeds that contained the optimum moisture content of 6÷9% after the natural drying, were characterized by TAN < 3 mgKOH/g. Higher values of acid number could be found only after drying the drier or the wettest seeds.

The results from statistical analysis of the influence of moisture content and temperature on acid number changes are presented in Figure 4.

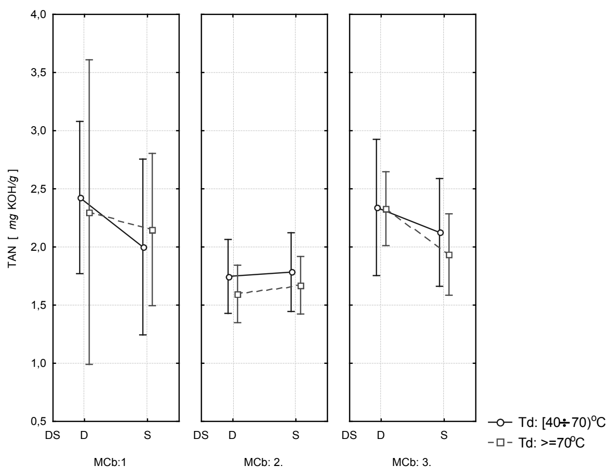

Fig. 4. Influence of drying on acid number values depending on seed moisture content (MC_b) and drying temperature (T_d)

The contrast significance tests for all combinations of the moisture content level MC_b and drying temperature indicated that the differences between TAN values after natural drying and drying in the drier were not statistically significant. Therefore, it can be said that the drying temperatures applied in the driers are safe from the point of view of acid number levels.

However, some characteristic features and tendencies for changing the acid number are apparent in Figure 4. Seeds that had 6÷9% of moisture content after natural drying, were characterized by the lowest mean acid number value and this number practically did not changed during the drying process. In less wet and the most wet seeds, average values of acid number decreased after drying.

Values of peroxide number in the studied material ranged from 0.20 to 5.90 mmolO/kg. Distribution of peroxide number in rape seeds naturally dried and in the drier is presented in Figure 5.

Figure 5 illustrates that LOO values in samples dried in the drier were slightly higher than those in seeds dried under natural conditions; however the differences of LOO values distributions were small.

Distribution of peroxide number values for the material dried at various temperatures is presented in Figure 6.

Distributions of LOO values for seeds dried at various temperatures were very similar. The largest number of samples were characterized by LOO < 2 mmolO/kg, whilst the smallest by LOO ≥ 3 mmolO/kg, although the differences between materials within particular LN ranges were small.

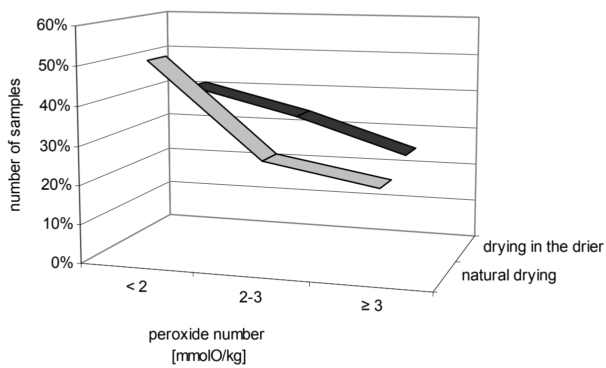

Figure 5. Percentage distribution of peroxide number in rape seeds after natural drying and drying in the drier

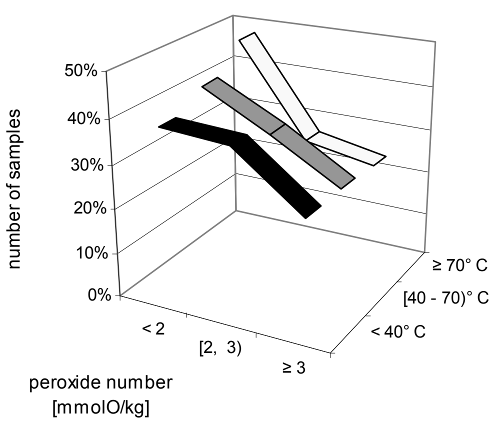

Figure 6. Distribution of peroxide number after drying depending on drying temperature

The contrast tests did not reveal statistically significant changes in mean LOO values during the drying process for all the range of material's moisture content and drying temperatures. Hence, it can be concluded that, similarly as in the case of acid number, drying temperatures applied in the driers were safe. It could be seen that at a higher moisture content, an increase of peroxide number during the drying was apparent, although it was higher at 40÷70)°C than at higher temperatures. The following hypothesis can thus be drawn: an increase of the observed LOO value would be higher and higher at higher moisture contents and longer drying time, and it would considerably worsen the rape seed quality. However, verification of this hypothesis requires further experiments within broader range of parameters.

CONCLUSIONS

Determinations of acid number and peroxide number as a major indicator of seed quality revealed that:

- Acid number appeared to be resistant to drying process. Regardless of the drying temperature and initial values of the studied parameters, the observed changes in TAN values were within the statistical error range. It can be concluded that fat is not hydrolyzed in fat during the drying and fat still remains "raw".
- Although within the studied range of drying parameters, no statistically significant TAN changes were found, the decrease of mean TAN values during drying the material with low moisture content (MC_b = 1) as well as very wet material (MC_b = 3) was recorded. It can be explained with the loss of fatty acids due to the leakage through injuries on a seed surface. Moreover, it was found that material with a larger number of injuries, was characterized with higher TAN value even before the drying process. The hypothesis is as follows: in damaged seeds, regardless of the type of injury, fat is less "protected" against decomposition and its destruction (hydrolysis) begins before drying.
- An increase of peroxide number (LOO) can be counted as a negative change resulting from the drying process. Despite of the LOO increase, the parameter level remained within permissible limits set by norms; hence, taking it into account, no worsening of raw material's quality occurred.
- The existing standards for biofuels in Poland and Europe specify the requirements for the final processing of oil products and fats, and therefore the methyl esters of higher fatty acids (FAME), but do not put any requirements as to oil from which the esters are produced, much less as to the raw materials to produce the oil. We can say that the oil produced from the seeds of oilseed rape is a good raw material for the production of biofuels.

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WPŁYW ZAWARTOŚCI LICZBY KWASOWEJ ORAZ LICZBY NADTLENKOWEJ NA JAKOŚĆ NASION RZEPAKU PRZEZNACZONYCH NA CELE SPOŻYWCZE I BIOPALIWOWE.

Streszczenie. Celem niniejszej pracy było określenie zawartości liczby kwasowej (LK) oraz nadtlenkowej (LN) w nasionach rzepaku pochodzenia przemysłowego przeznaczonych na cele spożywcze oraz biopaliwowe, poddanych procesowi dosuszenia w warunkach naturalnych oraz w suszarniach. Uzyskane wyniki wskazują iż niezależnie od temperatury suszenia i wartości początkowych badanych parametrów obserwowane zmiany LK jak i LN mieściły się w granicach dopuszczalnych przez przemysł tłuszczowy jak i paliwowy.

Słowa kluczowe: nasiona rzepaku, suszenie, liczba kwasowa, właściwości nasion, biopaliwa.