Barbara ŁASKA,[1] Piotr PASYNIUK,[1] Florian ADAMCZYK,[2] Wojciech GOLIMOWSKI [1]
[1] Instytut Technologiczno-Przyrodniczy, Oddział w Poznaniu, Zakład Odnawialnych Źródeł Energii
ul. Biskupińska 67, 60-463 Poznań, Poland
e-mail: b.laska@itp.edu.pl
[2] Przemysłowy Instytut Maszyn Rolniczych
ul. Starołęcka 31, 61-369 Poznań, Poland

THE INFLUENCE OF PRESSING CONDITIONS AND COOLING DYNAMICS OF RAPESEED OIL AS BIOFUEL ON ITS OXIDATIVE STABILITY

Summary

Organic products undergo biodegradation processes in favourable conditions while being improperly stored. The production of vegetable oils by means of the pressing technology requires high electrical energy input which is converted by friction forces in screw extrusion presses into heat. The heat, in turn, is conducive to the organic mass degradation processes. The purpose of the study was to determine the impact of the pressing temperature and the dynamic oil cooling processes on the oxidative stability. The tests were carried out in the industrial environment in a production room of an oil and fat plant producing rapeseed oil. Based on the summarised test results, it can be concluded that the initial oil temperature and the cooling rate had a significant impact on the variable value. The higher the values of these parameters were, the longer the oxidative stability period was. The oxidative stability was more than 60 h for the hot-pressed oil and about 10 h for the cold-pressed oil. The oil free from solid impurities showed resistance at a level of 18 h.
***Key words**: oxidative stability, rapeseed oil, oil oxidation, oil pressing, biofuels*

WPŁYW WARUNKÓW TŁOCZENIA I DYNAMIKI SCHŁADZANIA OLEJU RZEPAKOWEGO JAKO BIOPALIWA NA JEGO STABILNOŚĆ OKSYDACYJNĄ

Streszczenie

Produkty organiczne ulegają procesom biodegradacyjnym w sprzyjających warunkach, podczas niewłaściwego ich przechowywania. Produkcja olejów roślinnych za pomocą technologii tłoczenia wymaga dużych nakładów energii elektrycznej, która na skutek sił tarcia w prasach ślimakowych jest przekształcana w ciepło. Ciepło natomiast sprzyja procesom degradacyjnym masy organicznej. Celem pracy było określenie wpływu temperatury tłoczenia oraz procesów dynamicznego schładzania oleju na stabilność oksydacyjną. Badania wykonywano w warunkach przemysłowych w hali produkcyjnej zakładu tłuszczowego, zajmującego się produkcją oleju rzepakowego. Na podstawie zebranych wyników badań można stwierdzić, że istotny wpływ na wartość zmiennej miała temperatura początkowa oleju i tempo schładzania. Im wyższe wartości tych parametrów, tym okres stabilności oksydacyjnej się zwiększał. Dla oleju tłoczonego na gorąco stabilność oksydacyjna wynosiła powyżej 60 h, dla tłoczonego na zimno około 10 h. Olej pozbawiony zanieczyszczeń stałych charakteryzował się odpornością na poziomie 18 h.
***Słowa kluczowe**: stabilność oksydacyjna, olej rzepakowy, utlenianie oleju, tłoczenie oleju, biopaliwa*

1. Introduction

Until recently, vegetable oil has been exclusively a food product. As the development of the automotive sector has been contributing to the increase of harmful gas emissions, the conventional fuels have been gradually replaced with biofuels. The current state of the art enables using biofuels in the form of pure vegetable oil (e.g. the Elsbett engine) as well as methyl esters in the ZS engine [1, 4, 9, 11, 19]. Renowned manufacturers of agricultural machines consider raw rapeseed oil complying with the DIN 51 605 to be stand-alone biofuel [18].

Vegetable oil is an organic matter which cannot be stored for a longer period of time in conditions conducive to degradation processes. Therefore, the essential problem to be resolved is the durability of raw materials used to produce biofuels. According to the mandatory standards on biofuels, both vegetable plants and methyl esters which are made of them must be resistant to oxidation. In both cases, the minimum stability period is a standardised value and amounts to 6 hours [10].

The oxidation changes in raw vegetable oils are determined by the composition of fatty acids, the content of natural anti-oxidants and pro-oxidants and the conditions in which oils are produced and stored [6]. The oxidation processes occurring during the storage period are free-radical reactions which result in the increase of viscosity and the acid value, change of odour and colour and the presence of deposits [23]. Vegetable oils are being oxidised when unsaturated fatty acids react with oxygen [2]. Oxidation is a chain reaction leading to fast qualitative changes. Under the impact of light, high temperature or access of air, polyunsaturated fatty acids may undergo polymerisation into insoluble particles, forming rubbers and deposits [5]. The vegetable oil oxidation degree depends mainly on the level of unsaturation of fatty acids, access to oxygen, sun beams, water as well as temperature, storage duration and the presence of anti-oxidants (e.g. tocopherols, carotenoids) and pro-oxidants (e.g. copper, iron, colourants) in the oil.

Proper storage limits the changes occurring in the oil; it is recommended to store fats in cold storage conditions with a limited access of oxygen and light [21]. Another way used to increase the resistance of oils to oxidative changes consists in the application of pro oxidants. To counteract the oxidation processes in vegetable oils, tocopherols, i.e.: δ- and γ-tocopherol and β-tocopherol [22], propyl gallate [3], tocotrienols, butylated hydroxy toluene (BHT), butylated hydroxyanisole (BHA), tertiary butyl hydroquinone (TBHQ), reduced sulphur and phosphorus compounds, aromatic and polymeric amine compounds [8, 13, 16, 20] are used. Research was also carried out on the impact of the oil production method on its durability [15, 20]. The research shows that the hot-pressed oils feature higher oxidative stability than the cold-pressed oils. This is caused by a higher process temperature, which makes it easier for such natural anti-oxidant compounds as carotenoids, tocopherols, sterols and phospholipids to pass from seeds to oil [12, 17, 21].

The purpose of the study was to increase the durability of rapeseed oil for the production of biofuels by extending the oil oxidative stability. The oil degradation processes are inhibited at a lowered temperature. It has been assumed that the shortening of the period of cooling down raw freshly extracted oil will cause the oxidative stability to be increased.

2. Research Test Methodology

To study the phenomenon of the rapeseed oil degradation rate change resulting from the shortening of its cooling period, samples were picked directly from several levels of its production. The oil was produced by means of a two-stage pressing technology. Rape seeds pressed on the first press (pre-pressing) showed a temperature of 19.5°C; the pomace was heated up to 120°C in an extruder and pressed again in another press. Oil samples of 200 g were picked directly from underneath the cold-pressing machines (of an average temperature amounting to 39.2°C) and hot-pressing machines (of an average temperature amounting to 51.3°C) and a filter (of an average temperature amounting to 37.2°C). Three samples of rapeseed oil were picked from each press and filter.

The research tests of the impact of the oil cooling dynamics on its oxidative stability were carried out in a production room of an oil and fat plant producing rapeseed oil at an experimental stations, which enabled to carry out the experiment on a laboratory scale (fig. 1).

The oil was being cooled down in two ways: freely (naturally) and dynamically (forcedly). The test station for dynamic cooling consisted of a Lauda RE 206 cryostat connected with two glass cylinders with a water jacket. A mechanical stirrer and a mercury thermometer of an indication accuracy of 0.1°C were placed in every cylinder.

The free cooling (SS) of the rapeseed oil samples was carried out in glass beakers of the same shape and volume. The samples were positioned on a table in a room where the air temperature was about 26°C. During the entire period of the temperature drop, the oil temperature was read by means of an ELMETRON CP-411 electronic measurement system every 5 minutes. The oil was being cooled down until it reached a temperature close to the ambient temperature.

The dynamic cooling (SD) of the rapeseed oil samples was carried out in cylinders with a water jacket, where they were intensely stirred and cooled down to a temperature not much higher than that of the cooling medium. The cooling medium showed a fixed temperature of 5°C. The oil temperature was being registered every 30 seconds until it reached about 7°C.

a) b)

Source: own study / Źródło: opracowanie własne

Fig. 1. Station for testing the free (a) and dynamic (b) cooling of oil

Rys. 1. Stanowisko do badań chłodzenia oleju w sposób swobodny (a) i dynamiczny (b)

The oxidative stability was determined by means of the accelerated oxidation test with the use of a Rancimat® instrument in accordance with the PN-EN ISO 6886:2009 standard.

The analysis was carried out in the following conditions:

- temperature of a reaction vessel: 110°C,
- volume of oxygen flowing through the sample: 10 $l \cdot h^{-1}$,
- sample weight: 3 g.

Determination of the oxidative stability by means of the Rancimat instrument consisted in accelerating the vegetable fat oxidation by heating up a sample in a reaction vessel and continuously passing a jet of air of a pre-set volume through the sample. This process was leading to the oxidation of fatty acids contained in the sample being analysed. In the first stage, peroxides (primary product of the reaction) were formed and then fatty acids underwent complete degradation, causing the formation of the secondary products of oxidation reaction containing volatile low molecular organic acids. The secondary products of the reaction were transported in an air jet to a measurement vessel filled with distilled water, where conductivity was being measured on a continuous basis. The increase of conductivity in the measurement vessel resulted from absorption of acids in the distilled water. The time which passed to the moment when the secondary products of the reaction occurred is referred to as the induction time or the oil stability index. The incubation time value demonstrates the anti-oxidation resistance of the sample. The longer the induction time was, the more stable the sample was.

The population of the collected results was subjected to the analysis of variance. Since the level of significance has been set at 5%, the inference is then encumbered with a 5% error risk.

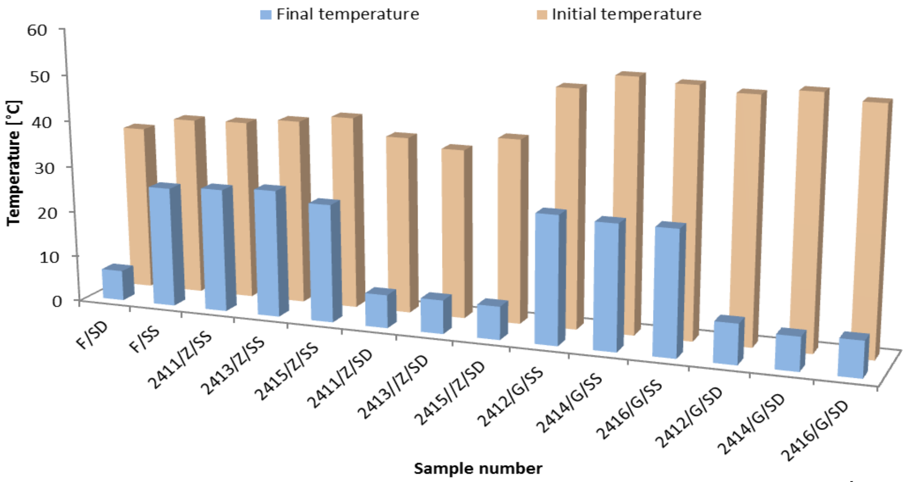
3. Review of Research Test Results

The average initial and final temperatures of the freely and dynamically cooled oil samples are presented on fig. 2. The hot-pressed oil reached an average initial temperature of 51.3°C at a variability coefficient of <10%, the cold-pressed oil: 39.2°C at a variability coefficient of <5%, the oil after filtration: 37.2°C at a variability coefficient of <10%.

The low initial temperature of the filtered oil resulted from the fact that it was the oil from the buffer tank, being a mixture of hot-pressed and cold-pressed oil. The oil was filtered an hour after the extraction (the period of time of filling up and emptying the oil buffer tank). Depending on the cooling method, the oil reached the final temperature of about 27°C when being freely cooled (variability coefficient of <5%), while the dynamically cooled oil reached the final temperature of about 7.5°C (variability coefficient of <10%). In this case, the large variations of the variability coefficient were caused by different oil cooling dynamics. The cause is suspected to be a non-uniform amount of foam in the collected samples which formed while the oil was being hot-pressed.

Within the entire examined time window, the average rate of the temperature change was 0.18°C·min^{-1} for the freely cooled cold-pressed oil, it was 0.25°C·min^{-1} for the hot-pressed oil and 0.17°C·min^{-1} for the oil from the filter. On the other hand, during the dynamic cooling, the average rate of the temperature change was 2.4°C·min^{-1} for the cold-pressed oil, it was 3.2°C·min^{-1} for the hot-pressed oil and 2.25°C·min^{-1} for the oil from the filter.

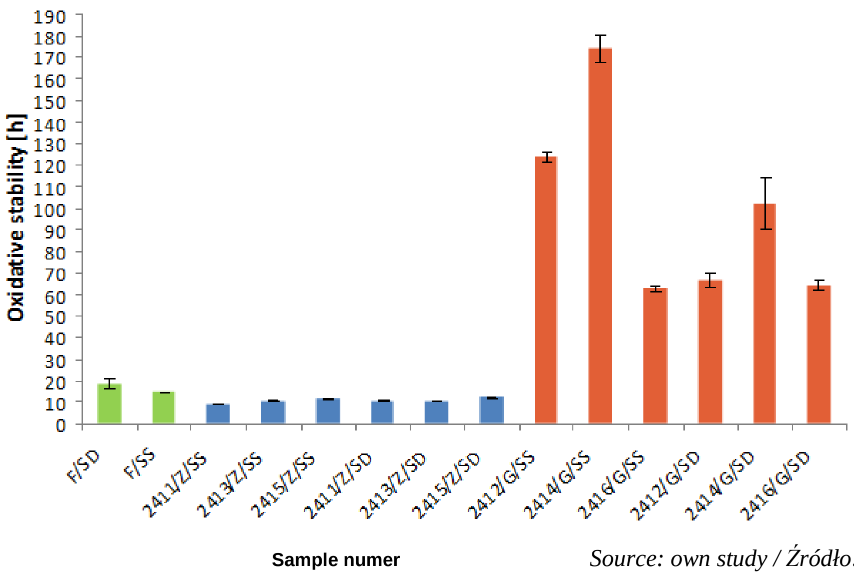
All the rapeseed oil samples collected from various stages of the production process featured oxidative stability longer than 6 h, which is assumed to be a minimum value in the quality standard for rapeseed oil as biofuel. The filtered oil oxidative stability was higher than that of the cold-pressed oil, which may result from the fact that the remains of seeds and colourants, which accelerate oil oxidation, had been removed in the course of the filtration process. The hot-pressed oil demonstrated the highest oxidative stability (fig. 3).



Source: own study / Źródło: opracowanie własne

Fig. 2. The initial and final temperatures of the freely and dynamically cooled oil samples: F - oil after filtration; Nom 2411 to 2416 - oil sourced straight from the pressing machine; Z - cold-pressed; G - hot pressed; SS - freely cooled; SD - dynamically cooled

Rys. 2. Temperatury początkowe i końcowe oleju schładzanego swobodnie i dynamicznie: F – olej po filtracji; nr 2411 do 2416 – olej prosto z prasy; Z – tłoczony na zimno; G – tłoczony na gorąco; SS – schładzany swobodnie; SD – schładzany dynamicznie



Source: own study / Źródło: opracowanie własne

Fig. 3. Rapeseed oil oxidative stability: F - oil after filtration; 241X - oil straight from the pressing machine; Z - cold-pressed; G - hot pressed; SS - freely cooled; SD - dynamically cooled

Rys. 3. Stabilność oksydacyjna oleju rzepakowego: F – olej po filtracji; 241X – olej prosto z prasy; Z – tłoczony na zimno; G – tłoczony na gorąco; SS – schładzany swobodnie; SD – schładzany dynamicznie

The oxidative stability amounted on average to 10.20 h ±2% for the cold-pressed, freely cooled oil and 10.95 h ±2% for the dynamically cooled oil; the differences in the oxidative stability values are not statistically significant. The freely cooled oil from the filter featured durability amounting on average to 14.68 h ±0,5%, while the dynamic cooling allowed to increase its durability on average to 18.38 h ±13%. However, the greater oxidative stability of the dynamically cooled oil from the filter did not significantly differ statistically from the value obtained for the freely cooled oil. The oxidative stability amounted to 120.30 h ±4% on average for the hot-pressed freely cooled oil and to 77.57 h ±12% on average for the dynamically cooled oil. The oxidative stability values for the hot-pressed oil significantly differed statistically from the values obtained for the cold-pressed oil and the oil from the filter. Moreover, statistically significant differences were found to exist between the oxidative stability of the hot-pressed freely and dynamically cooled oil, however, except for the freely cooled oil from the press 2416 for which the oxidative stability value did not vary to a statistically significant degree from the oxidative stability value for the dynamically cooled oil coming from the presses 2412 and 2416.

A correlation coefficient was calculated for the collected population of results. There was found to exist a strong relation between the initial temperature and the oxidative stability of the oil (0.85) as well as the rate of change of the temperature during the dynamic cooling of the oil and the oxidative stability which was 0.89 for the cold-pressed oil and 0.86 for the hot-pressed oil.

4. Summary and Conclusions

Samples of raw rapeseed oil sourced from various stages of the production process were characterised by the oxidative stability longer than 6 h, which is the minimum value according to the DIN 51 605 standard referring to the quality of rapeseed oil as biofuel. The dynamic cooling increased the oil oxidative stability after filtration. The filtered and dynamically cooled oil gained a higher value of the oxidative stability (above 18 h) than the freely cooled oil (above 14 h). However, these differences were not statistically significant. The oxidative stability of the filtered oil was higher than that of the cold-pressed oil, which may result from the fact that the remains of seeds and colourants, which accelerate oil oxidation, had been removed in course of the filtration process. A strong interdependence was found to exist between the oil production method and the oxidative stability. The average oxidative stability of the cold-pressed oil amounted to about 10 h whereas the hot-pressed oil showed, regardless of the applied cooling method, a very long durability time varying from 60 to 175 h. The high values of the oxidative stability of the hot-pressed oil, both freely and dynamically cooled, determined by the accelerated oxidation method, are highly doubtful. Such durability of oil has been unprecedented in the literature. The oil sampled immediately after hot-pressing showed visible impurities which could affect the correct performance of the Rancimat instrument. Despite that, multiple tests of the same samples gave similar results. To verify the performance of the Rancimat instrument, a cleaned sample was measured; however, such process interfered with its composition and gave different results that were close to the samples free from deposits. The extended duration of the oxidative stability may be caused by the fact that the hot-pressed oil includes tocopherols, carotenoids and sterols, which pass into oil under high temperature as these compounds have been identified as strong anti-oxidants. To increase the oxidative stability of raw vegetable oils, Isbell et al. [14] used an addition of oil from the plant *Limnanthes alba*, an oil which has a very high content of tocopherols being natural anti-oxidants and is therefore characterised by a very high level of oxidative stability reaching 247 h. According to Wroniak et al. [21], the period of oxidative stability of the hot-pressed rapeseed oil is longer by 50% than that of the cold-pressed oil. The authors reached the oxidative stability amounting to 5 h for the cold-pressed oil and about 6.7 h for the hot-pressed oil, determining this value for a filtered oil. Furthermore, according to Krygier and Płatek [15], the filtered hot-pressed rapeseed oil features oxidative stability amounting to about 8 h.

Based on the performed research tests, the authors came to a conclusion that the cooling of the oil after extracting would have a direct effect on its durability during storage. This is indicated by a strong positive correlation between the cooling rate and the oil anti-oxidation resistance duration.

5. References

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