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学位論文題目	Studies on the frying stability and quick quality evaluation method of local rapeseed Kizakinonatane oil (秋田産菜種油のフライ特性およびその迅速的品質評価法に関する研究)
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論文内容要旨

※ページ数は 3 頁以上 (図表を含む) とする。

Kizakinonatane, which was developed by the Tohoku National Agricultural Experimental Station, is one of the major domestic rapeseed cultivars in the Tohoku region. It was released as the first zero-erucic Japanese domestic rapeseed variety in 1989. Recently, the expeller-pressed Kizakinonatane oil (EPKO) has been receiving favorable consumer reviews because it is produced under low heat and without additional chemicals. EPKO has a characteristic taste, specific aroma, and enchanting color. Additionally, EPKO was selected as it is locally available and preferred in the Tohoku region. However, there is minimal literature on the constituents of the EPKO, and its frying stability has yet to be reported. This has raised concern among consumers and begets questions about how efficient and rapid quality control of this oil is currently possible.

The research described in this thesis sought to: a) analyze the characteristics and composition of the fresh EPKO, b) determine the frying stability of EPKO and, c) develop a practical technique for quick quality evaluation of frying oils using near-infrared (NIR) spectroscopy.

In Chapter 1, the research background and a general literature review that is related to the current study are presented.

In Chapter 2, the characteristics and composition of the fresh EPKO is analyzed for fatty acid composition, minor components, and physicochemical properties. Commercial refined, bleached, and deodorized canola oil (CO) was used for comparison. Results showed that EPKO contains unsaturated fatty acids, especially polyunsaturated fatty acids (PUFA) such as linoleic acid and linolenic acid, which are different from that of the CO. The EPKO had higher levels of minor compounds such as tocopherol, total phenolic, β -carotene, and chlorophylls as compared to that of the CO. As a result of the large amount of β -carotene in the EPKO, the EPKO was deeper yellow than the CO. Furthermore, the EPKO had a good oxidative stability index

(OSI), viscosity, low acid value and peroxide value that are within the limits allowed by the regulations.

In Chapter 3, a comprehensive study was conducted to compare the frying stability of EPKO and CO during the intermittent frying of frozen French fries at 180, 200, and 220°C for 7 h daily over 4 consecutive days, with or without fresh oil replenishment. Results obtained from both frying experiments clearly showed significantly slower rates of total polar compounds (TPC) and carbonyl value (CV) formation in the EPKO samples as compared to that of the CO samples during frying sessions. In other words, the EPKO exhibited a much better oxidative stability than that of the CO. The EPKO also displayed lower levels of viscosity and comparable color (optical density) values than that of the CO during the frying process. The EPKO showed a significantly higher acid value (AV) level than that of the CO in both frying experiments. The AV in every EPKO sample exceeded the discard level of 4 mg/g after 14 hours of frying, however, no CO oil sample exceeded that discard level. The high AV level of EPKO could be attributed to the fact that components which impair the quality of the oil, such as free fatty acids and chlorophyll, were not removed as they did not undergo the refining process. As more free fatty acids were released in the oil, it became more susceptible to thermal oxidation under elevated frying temperatures. The changes in the peroxide value (PV) were irregular during frying in both oils, which could be attributed to the fact that peroxides are unstable compounds and apt to break down to a variety of nonvolatile and volatile products under high temperatures. Replenishment with fresh oil had significant effects on all chemical and physical parameters, except the PV of the frying oils.

Results showed an obvious difference in fatty acid changes between both oils during deep frying. There was a significant decrease in linoleic acid contributions in the EPKO. In the CO, however, the linoleic acid decreased much more significantly than that of the EPKO in the frying experiments with and without replenishment. A deterioration of the linolenic acid was observed in the EPKO, and the CO samples also showed a greater change in the deterioration of the linolenic acid during the frying sessions. The PUFA/SFA (saturated fatty acid) ratios in the EPKO significantly decreased at the end of the frying sessions. In the case of the CO, the PUFA/SFA ratios were much more pronounced than that of the EPKO after 28 h of frying in both frying experiments (Table 4). The EPKO showed a significantly slower rate of antioxidants decomposition (tocopherols) than that of the CO during frying at 180 and 200°C. A rapid decrease in total polyphenols content was observed before 14 h of frying in both frying experiments. After 21 h of frying, the total polyphenols could only be quantified in the oil that was fried at 180°C, and had disappeared in all the oil samples after 28 h of frying without replenishment. A similar fast decrease in the polyphenols was also observed in the frying experiment with replenishment. Results show a rapid decrease in chlorophylls content in all EPKO samples when they were subjected to heating at different temperatures in both frying experiments, indicating that the chlorophyll pigments were sensitive to high temperature and that replenishment had little effects in preventing its loss under high temperatures.

Based on the results obtained from this study, the following conclusions were made: 1) EPKO appeared to be more stable during prolonged heating treatments in terms of CV, TPC, fatty acids, and minor components; 2) variations in antioxidants levels (mainly caused by different processing procedure) and degradation rates in oils appeared to explain, in part, some of the differences in frying stability. 3) fatty acid composition also has an effect on frying stability; 4) oil deterioration increases with increase in frying temperature and time; 5) frequent replenishment with fresh oil significantly improves the frying stability and prolongs the useful life of oils.

In Chapter 4, an investigation into the potential of the NIR spectroscopy as a

simple technique for the rapid determination of the degradation of frying oils was conducted using partial least-squares (PLS) regression. All spectroscopic data from the frying oil samples (156) were collected using a Foss NIRSystems model 6500 with disposable glass test tubes as oil sample containers. The transmission spectra were set from 700 to 2500 nm at a resolution of 2 nm. Oil samples were scanned 32 times for each spectrum. All samples were heated to 25°C in a water bath prior to the spectra collection. There was a strong correlation between the NIR predicted data and reference data in AV results, with coefficient of determination (R^2) values ranging from 0.96 to 0.99 and standard error of prediction (SEP) values from 0.17 to 0.48 mg/g. The most accurate model was the model that involves the first-derivative spectra in the wavelength range of 1800-2200 nm. It used five partial least-squares factors and produced a high coefficient of determination and low values of standard error of calibration (SEC), standard errors of cross-validation (SECV), and SEP. The high RPD (ratio of standard deviation of reference data in the validation set to SEP) value of 12.8 indicates that the model used in this study was useful.

Similar to the AV results, there were strong correlations between the NIR predicted data and the reference data in TPC results with R^2 values of 0.98 and SEP values from 1.04 to 1.4%. The most accurate model was the model that involves the first-derivative spectra in the wavelength range of 1100-1800 nm. It used six PLS factors and generated a high R^2 value and low values for SEC, SECV, and SEP. The RPD value was found to be 7.8. The current results demonstrate that frying oils can be successfully monitored to a very high accuracy using NIR spectroscopy. Furthermore, NIR spectroscopy has significant advantages over other measurement techniques; it is a fast and simple method that requires no sample preparation so it is a very practical method for measuring chemical changes such as AV and TPC values in edible oils during the frying process.

In Chapter 5, a general conclusion, limitations, and a suggestion for future research to this study are included. On the whole, the results presented in chapters 2, 3, and 4 comprising this work can serve as a guide to current literature for those who wish to use domestic rapeseed oil safely, and also indicate that NIR spectroscopy can be used as a rapid and accurate quality control tool for frying oils.

論文審査結果要旨

※単独ページとする。

安全に品質を管理された地域産菜種油の利用拡大は、地域経済活性化にとって重要である。その利用拡大には、地域産菜種油の品質特性およびフライ特性を把握する必要だけでなく、現場でも利用可能な品質評価技術も必要である。本研究はこれらのニーズに応えたもので、地域産菜種油のフライ特性の解明およびその迅速的品質評価技術の開発を行ったものである。

本研究では、まず、一般に使われている市販キャノーラ油を比較対象にし、地域産菜種油の脂肪酸組成および微量成分を厳密に分析・検討してその品質特性を明確にした。そして、地域産菜種油のフライ特性を調べるために、180℃、200℃及び220℃の加熱温度条件のもとでポテトのフライ試験を行い、同様に市販キャノーラ油と比較しながらフライ油の酸価（AV）、カルボニル価（CV）および総極性物質（TPC）などの劣化指標項目を分析し、フライ油の経時劣化特性を明らかにした。地域産菜種油は、対象キャノーラ油より高い熱安定性を有していることを見だし、健康上および安全上において市販キャノーラ油よりその優位性を明らかにした。さらにフライ油の脂肪酸組成およびトコフェロールやカロテノイドなどの微量成分とフライ油の熱安定性との関係を調べた結果、多価不飽和脂肪酸組成の差異が要因の1つであるだけでなく、トコフェロールやカロテノイド等の微量成分の抗熱酸化作用も明確にした。

次に近赤外分光法の迅速的性質や多成分同時分析などの特徴を利用して現場でも使える簡便なフライ油の品質評価技術の開発を試みた。フライ油の性状を考慮して油の取扱いしやすい試験管をセルにした近赤外スペクトル計測システムを考案した上で、フライ油の近赤外スペクトルとフライ油の酸価（AV）、および総極性物質（TPC）などの品質評価項目値との関係を明らかにした。その上に測定された近赤外スペクトルに対し微分処理を施した上で、さらに波長領域の最適化を行いながらフライ油劣化指標のAV値やTPC値等を高精度に予測するモデルの開発に成功した。

これらの結果より、本研究では、これまで分かっていない秋田県産菜種油の品質特性やフライ特性を初めて明らかにしたもので、地域産菜種油の利用拡大に有意に貢献する結果が得られている。さらに近赤外分光法を用いた現場でも使える簡便なフライ油の品質評価技術を開発したことで、菜種食用油の流通および使用上、健全性や安全性の確保において重要に貢献する結果も得られている。以上の審査結果から、審査員一同は本研究論文の学術的な新規性と実用的な有用性を評価し、博士学位を授与するに値すると判断した。