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論文内容要旨

Deep frying is an old and most popular method of food processing, because it is not only easy and fast to operate, but also can give food crisp taste and attractive aroma, which is attributed to the chemical reactions in the process of frying. However, with the repeated frying for a long time, these chemical reactions will also produce undesirable products, leading to the deterioration of oil, and even with the intake of fried foods into the human body, which will have adverse effects on human health. Therefore, quality monitoring of frying oil is very important to ensure the safety of fried foods. At present, the quality evaluation indicators commonly used for frying oil are mainly divided into physical indicators and chemical indicators. However, the comparability and reproducibility of the results are not ideal for different frying oils and frying systems. With the increasing consumption of fried foods, it is urgent to develop new, fast, and widely applicable quality evaluation methods for frying oil.

In this research, frying oils were prepared from common edible oils and used as the research object. The composition, quality and flavor characteristics of frying oil were systematically studied by means of instrument analysis methods such as gas chromatography, liquid chromatography, gas chromatography-mass spectrometry and data processing methods such as regression analysis, correlation analysis and principal component analysis. After thoroughly understanding the deterioration characteristics of frying oil, three prediction models for the deterioration of frying oils were established. These models can be used to achieve the purpose of predicting the deterioration characteristics of edible oil during frying from the initial characteristics of the edible oil without going through complicated and time-consuming frying operations. The thesis consists of six chapters and is organized as follows:

In Chapter 1, the research background about deterioration mechanism of edible oil during frying and evaluation indicators of frying oil was described in detail. The chemical reactions that occur in edible oil during frying are mainly hydrolysis, oxidation and polymerization. Due to the occurrence of these reactions during frying, edible oil is gradually deteriorated. The indicators for evaluating the deterioration of edible oil are mainly physical indicators and chemical

indicators. Finally, the content, purpose and significance of this research were briefly introduced.

In Chapter 2, the initial composition characteristics, quality and flavor characteristics of 10 commercially available oils, namely olive, safflower, rapeseed, rice bran, natural sesame, sesame, corn, soybean, natural perilla, and perilla oils were analyzed. The results showed that initial total unsaturated fatty acid (TUFA) and total tocopherol (TToc) were in the range of 83.49%–95.28% and 16.40–236.05 mg/100 g by using gas chromatography and liquid chromatography, respectively. Olive, safflower, rapeseed, and rice bran oils contained much oleic acid and α -tocopherol contents; Natural sesame, sesame, corn, and soybean oils contained much linoleic acid and γ -tocopherol contents; Natural perilla and perilla oils contained much linolenic acid and δ -tocopherol contents (Fig.1). The initial carbonyl value (CV) and total polar compounds (TPC) in 10 oils were in the range of 2.36–6.30 $\mu\text{mol/g}$ and 0.0–6.0%, respectively. The initial CV and TPC of roasted oils were higher than natural pressed oils, and those of polyunsaturated fatty acids (PUFA)-rich oils (such as corn and soybean oils) were higher than monounsaturated fatty acids (MUFA)-rich oils (such as olive and safflower oils) (Fig.2). A total of 63 volatile compounds were detected by gas chromatography-mass spectrometry in the headspace of 10 oils, including 27 compounds produced during the roasting process that was only detected in roasted oils. It was their presence that caused the highest levels of volatile compounds to be detected in roasted oils. Except for roasted oils, olive oil was detected the highest content of volatile compounds. In addition to the special volatile compounds detected only in roasted oils, the proportion of alcohol detected was the largest among the volatile compounds detected, and the type of aldehydes was the most detected (Fig.3).

In Chapter 3, the changes in the essential composition of edible oils, namely fatty acids and tocopherols, were discussed during frying. Ten edible oils were intermittently fried with French fries at 180 °C and the frying oil sample was collected every 2.5 hours, a frying cycle. The results suggested that the content of TUFA and TToc decreased almost linearly with heating time (Fig.4 and Fig.5). Using the ratio of palmitic acid to oleic acid in the oils before deep frying ($C_{16:0}/C_{18:1}$) (Fig.6), a model, $Y_{TUFA} = \left[0.189 \left(\frac{C_{16:0}}{C_{18:1}} \right)^2 + 0.054 \left(\frac{C_{16:0}}{C_{18:1}} \right) + 0.185 \right] t$, was built that can be used to predict the decomposition rate of TUFA (Y_{TUFA}) during frying in a variety of unsaturated fatty acid-based oils. By establishing a dynamic decomposition index, TUFA and TToc in oils showed alternating dynamic decomposition in multiple frying cycles (Fig.7). With the decomposition of TUFA, the order of the decomposition rates of tocopherol homologues in 10 oils was γ -tocopherol > α -tocopherol > δ -tocopherol (Fig.8). Through multiple linear regression analysis, the order of the effects of the decomposition of the tocopherol homologues on the decomposition of TUFA in 10 oils during frying was also as follows: γ -tocopherol > α -tocopherol > δ -tocopherol.

In Chapter 4, the quality changes of 10 frying oils were measured by using the deterioration evaluation indexes, CV and TPC. Results showed that the CV and TPC of 10 oils increased linearly with heating time (Fig.9 and Fig.10). The effects of the changes in the composition (unsaturated fatty acids and tocopherols) of oils on the increase in CV and TPC with heating time were revealed by using multiple linear regression analysis. The results showed that among the changes of oil composition, the decrease of PUFA and γ -tocopherol had the greatest influence on the increase of CV and TPC. By correlating changes in degradation indicators with the initial composition of the oil (Fig.11 and Fig.12), the prediction models ($CV_t = \left[4.37 \left(\frac{PUFA}{TToc} \right)^2 - 5.64 \left(\frac{PUFA}{TToc} \right) + 3.36 \right] t + CV_0$ and $TPC_t = \left[0.024 \left(\frac{C_{18:2}}{C_{16:0}} \right)^2 -$

$0.065 \left(\frac{C_{18:2}}{C_{16:0}} \right) + 0.819 \left] t + TPC_0 \right)$ were established, respectively. Using these models, the CV and TPC of edible oil during frying at 180 °C can be predicted from the initial composition of the oil. At the same time, the frying life of edible oil can be inferred by using two models simultaneously according to the maximum allowable CV (50 µmol/g) and TPC (24%) stipulated by regulations.

In Chapter 5, the flavor changes in 10 oils during frying were evaluated. The change in volatile compounds level during frying was mainly related to the unsaturated fatty acid composition of the oil. The increase in the total peak area of volatile compounds was highest in oils with high oleic acid content, followed by linoleic acid rich oils (Fig.13). The aldehydes and alcohols detected in the oil accounted for a large proportion before and after heating. The effects of aldehydes, alcohols, and other volatile compounds detected on the flavor characteristics of oils during frying were explored by principal component analysis. The distribution of each oil on the score plot was mainly related to the fatty acid composition (Fig.14). The key volatile compounds affecting the changes during frying in oils with much MUFA were hexanal, (E)-2-hexenal, heptanal, (E)-2-heptenal, octanal, 2-octenal, nonanal, (E)-2-decenal, (E)-2-undecenal, 2-methyl-1-propanol, 1-pentanol, methylpyrazine, and butyl-cyclopentane. For oils rich in PUFA, the key volatile compounds were (Z)-2-penten-1-ol, acetic acid, and hexane. The correlation between the changes of volatile compounds detected and the decrease in TUFA and TToc, the increase in CV and TPC was analyzed, respectively. With the decrease of TUFA and TToc and increase of CV and TPC, most of the volatile compounds showed an increasing trend. The increase of pentanal showed a good correlation with the decrease of TUFA and TToc and increase of CV and TPC in most oils.

In Chapter 6, the main conclusions and limitations of this study and prospects for future work were presented. In general, this study can provide a deep understanding of the changes in composition, quality and flavor characteristics of edible oils during frying, accumulate scientific data for the research on the quality evaluation of frying oil. The establishment of three predictive models provides a reference and scientific basis for the establishment of a sound quality evaluating method for frying oil in the future.

Abbreviations used in figures:

OL: olive oil; SF: safflower oil; RS: rapeseed oil; RB: rice bran oil; CO: corn oil; SB: soybean oil; SS: sesame oil; NS: natural sesame oil; PL: perilla oil; NP: natural perilla oil;

C16:0, palmitic acid; C18:1, oleic acid; C18:2, linoleic acid; C18:3, linolenic acid; MUFA: monounsaturated fatty acid; PUFA: polyunsaturated fatty acid; TUFA: total unsaturated fatty acid; TToc: total tocopherol;

CV: carbonyl value; TPC: total polar compounds.

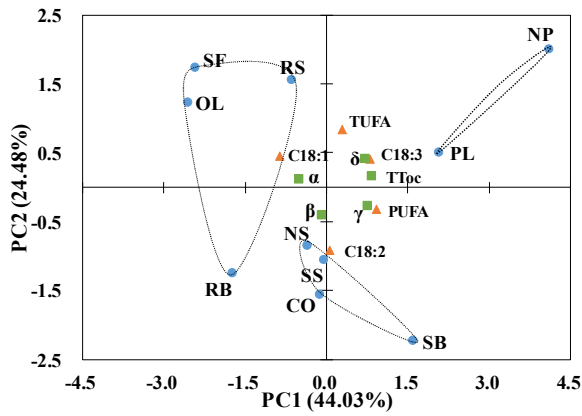


Fig.1 Principal component analysis of the initial composition of oils

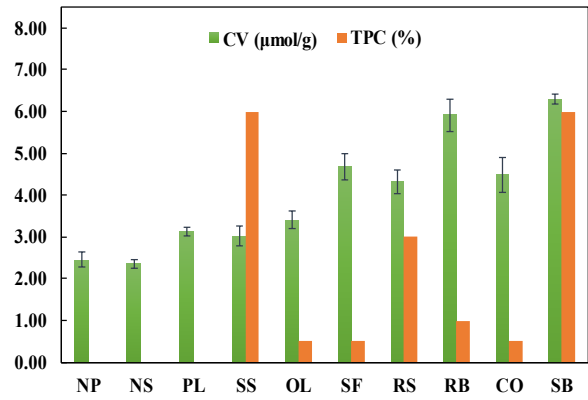


Fig.2 The initial CV and TPC content of oils

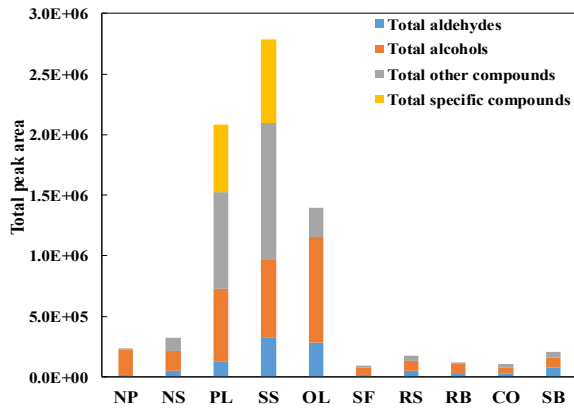


Fig.3 The initial content of volatile compounds detected in oils

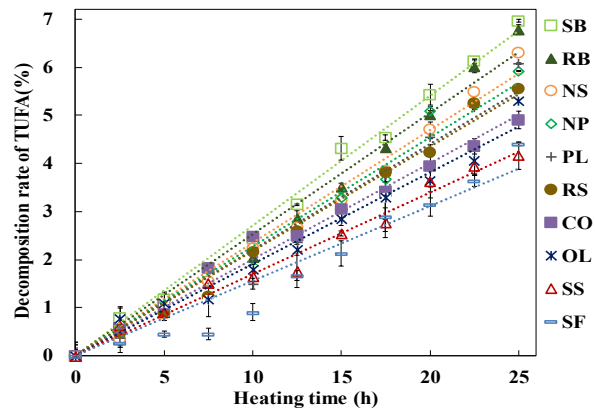


Fig.4 The decomposition rates of TUFA with heating time

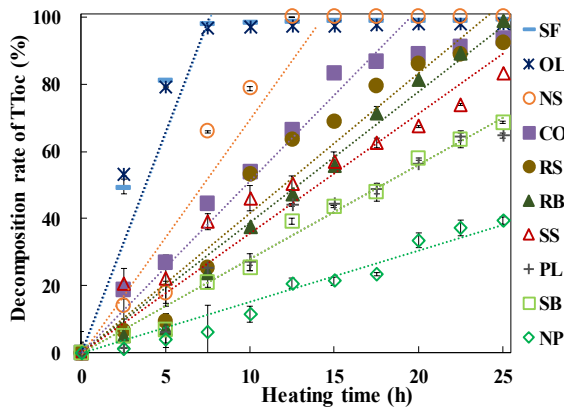


Fig.5 The decomposition rates of Ttoc with heating time

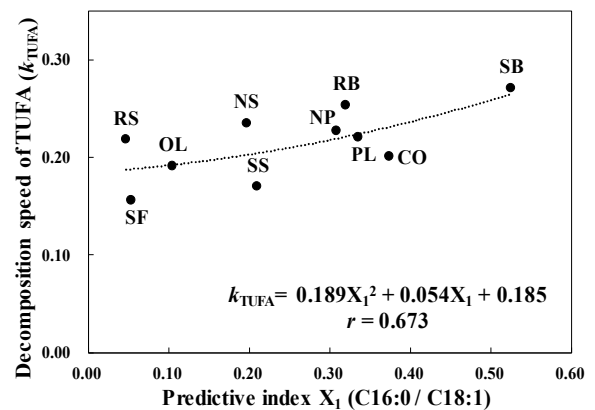


Fig.6 The relationship between the predictive index X_1 and the decomposition speed of TUFA

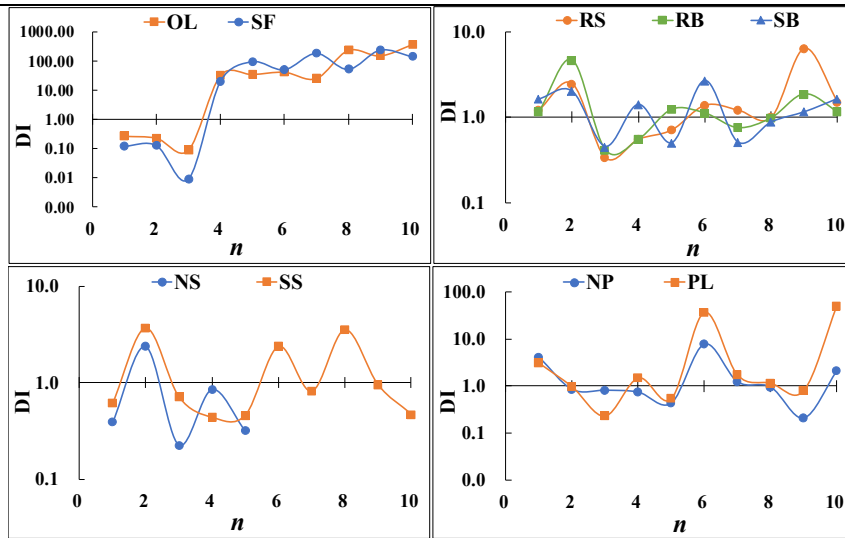


Fig.7 The dynamic index (DI) of oils during deep frying

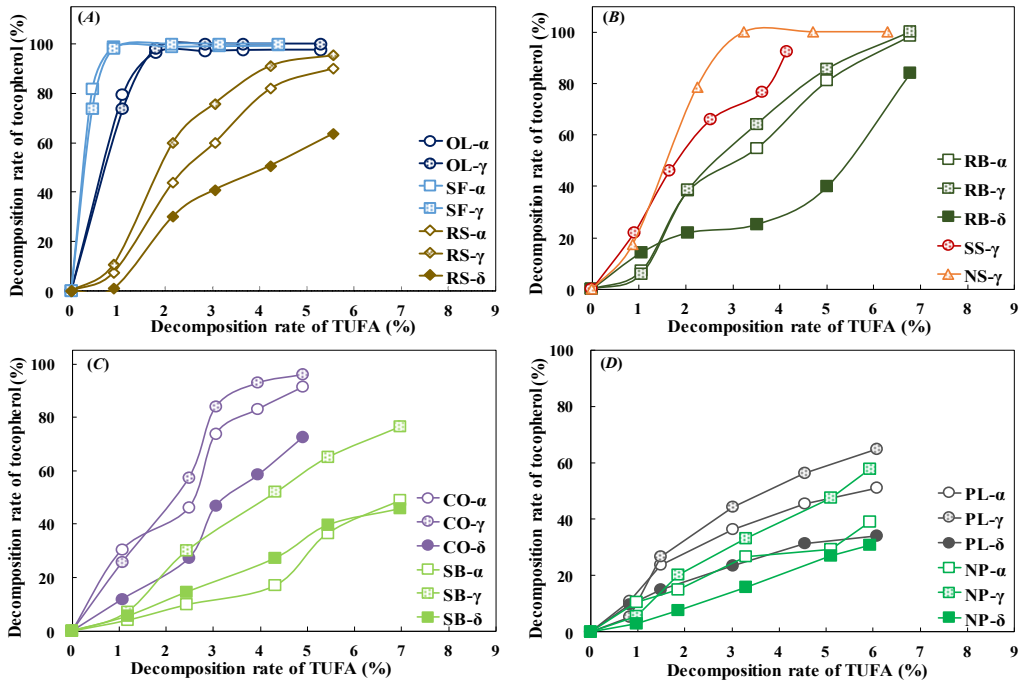


Fig.8 Relationship between decomposition rate of tocopherol homologues contents and that of TUFA contents during deep frying

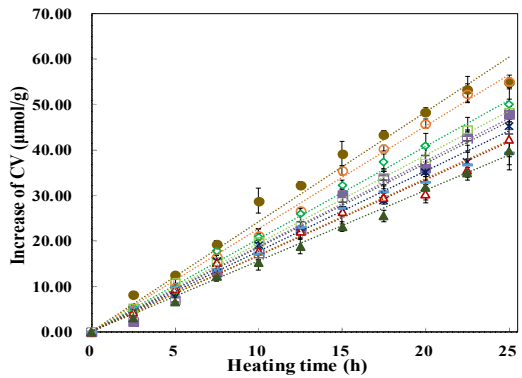


Fig.9 The increase of CV with heating time

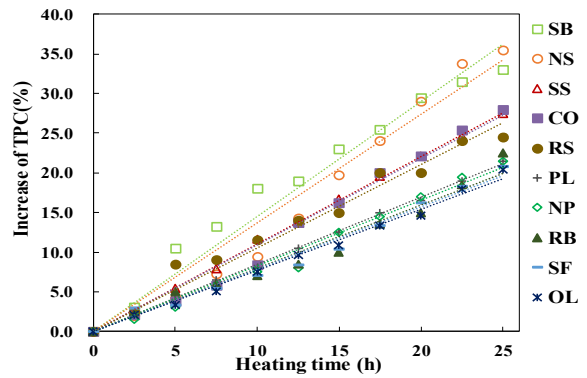


Fig.10 The increase of TPC with heating time

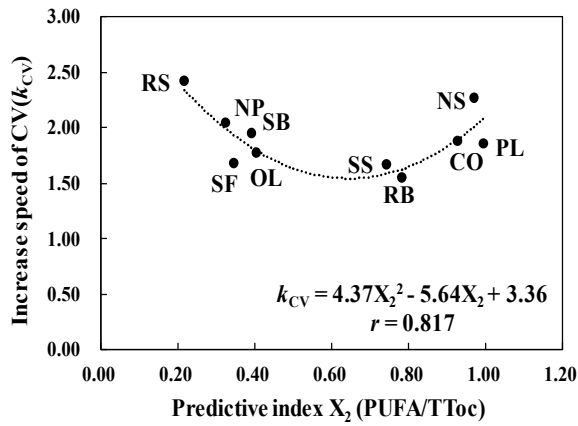


Fig.11 The relationship between the predictive index X_2 and the increase speed of CV

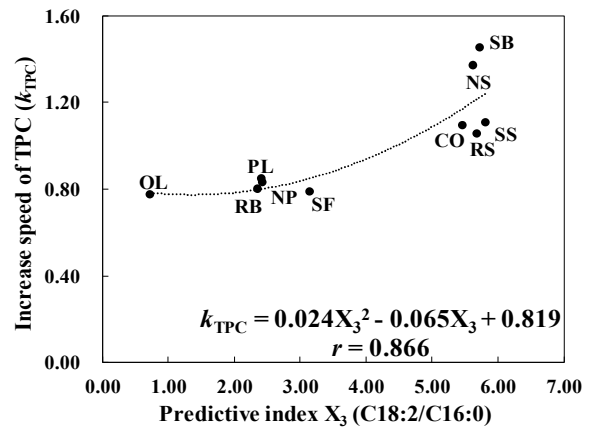


Fig.12 The relationship between the predictive index X_3 and the increase speed of TPC

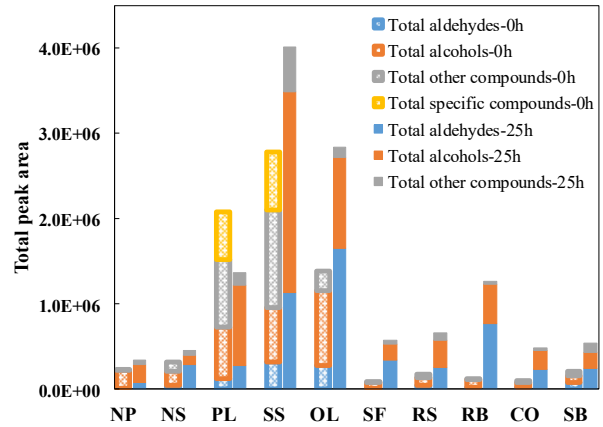
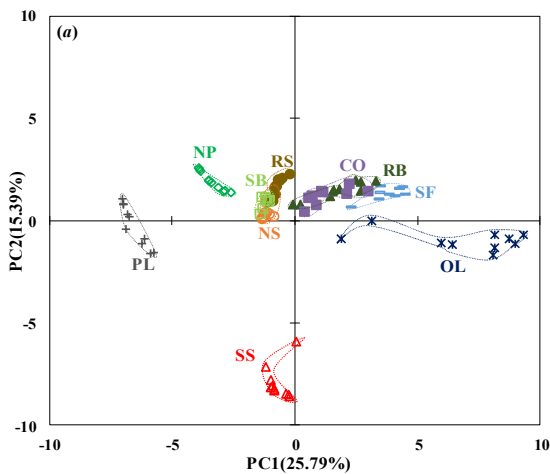
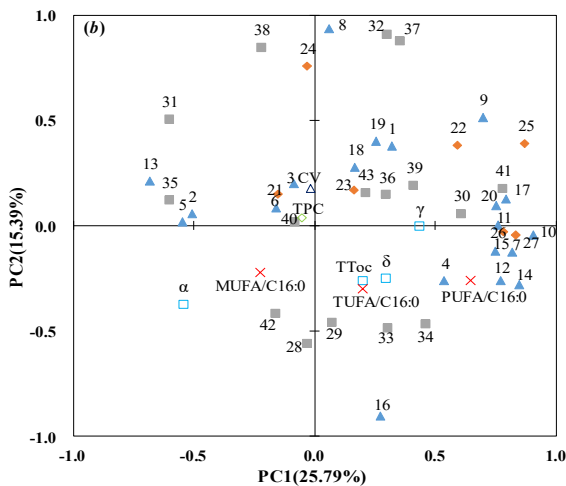


Fig.13 The content of volatile compounds detected in oils when heating for 0h and 25h



No.Volatile compound	No.Volatile compound	No.Volatile compound
1 Butanal	21 Ethanol	28 2-Hexanone
2 2-Butenal	22 2-methyl-1-Propanol	29 2-Octanone
3 2-methyl-Butanal	23 1-Penten-3-ol	30 methylpyrazine
4 Pentanal	24 (Z)-2-Penten-1-ol	31 2-Ethyl-6-methylpyrazine
5 (E)-2-Methyl-2-butenal	25 1-Pentanol	32 2,3,5-Trimethylpyrazine
6 (E)-2-Pentenal	26 1-Heptanol	33 Ethyl Acetate
7 Hexanal	27 1-Octanol	34 2-pentylfuran
8 Furfural		35 Toluene
9 (E)-2-Hexenal		36 1-Heptene
10 Heptanal		37 Acetic acid
11 (E)-2-Heptenal		38 Hexane
12 Octanal		39 methyl-Cyclopentane
13 (E,E)-2,4-Heptadienal		40 Heptane
14 2-Octenal		41 butyl-Cyclopentane
15 Nonanal		42 Decane
16 (E)-2-Nonenal		43 Decamethylcyclopentasiloxane
17 (E)-2-Decenal		
18 2,4-Undecadienal		
19 (E,E)-2,4-Decadienal		
20 (E)-2-undecenal		

Fig.14 Principal component analysis of changes in CV, TPC, tocopherols (TOC), unsaturated fatty acids (UFA), and all volatile compounds during frying: (a) Scores; (b) Loading.

▲ Aldehyde:1-20 ◆ Alcohol:21-27 ■ Others:28-43 △ CV ◇ TPC □ TOC × UFA

論文審査結果要旨

本論文は、フライ油の品質に影響を及ぼす食用油の内部組成特性と、品質劣化によって生成する代謝物との関連を、メタボロミクス手法によって多方面かつ総合的に解析した研究結果を纏めたものである。フライに使用する前の食用油の種類、脂肪酸の組成特性および抗酸化成分トコフェロールの組成特徴に基づき、フライ過程における食用油の品質劣化特性の多指標総合評価モデルを構築し、以下のような成果を得た。

1. 10種食用油の初期組成特性解析により、一価不飽和脂肪酸 (MUFA) の多い食用油は α -トコフェロールを多く含み、多価不飽和脂肪酸 (PUFA) と一価不飽和脂肪酸の組成量が類似の食用油は γ -トコフェロールの含量が高く、多価不飽和脂肪酸が主成分である食用油は δ -トコフェロールが多い特徴を見出した。内部組成特性から、食用油は3つのカテゴリーに分けられた。食用油の初期品質を示すカルボニル価 (COV)、総極性化合物 (TPC) および香気特性の解析結果から、初期品質としては生絞り油が最も高く、香気は焙煎油が最も強く、一価不飽和脂肪酸 (MUFA) の多い食用油は多価不飽和脂肪酸 (PUFA) の多い食用油より安定性が高い、などの特徴を解明した。

2. 10種食用油の不飽和脂肪酸 (TUFA) および総トコフェロール (TToC) の熱分解は加熱時間に線型的な変化 ($Y_{TUFA}=K_{TUFA} * t$ 、 $Y_{TToC}=K_{TToC} * t$) であること明らかにした。フライ前の各食用油のパルミチン酸 (C18:0) とオレイン酸 (C18:1) の比率は、フライ過程の食用油の不飽和脂肪酸分解速度 K_{TUFA} と高い相関関係にあることを見出し、**C16:0/C18:1** の値を指標として、不飽和脂肪酸分解の予測モデル①の構築に成功した。

$$Y_{TUFA} = \left[0.189 \left(\frac{C16:0}{C18:1} \right)^2 + 0.054 \left(\frac{C16:0}{C18:1} \right) + 0.185 \right] t \quad \dots \textcircled{1}$$

また、フライ過程でのトコフェロール同族体の分解速度は $\gamma > \alpha > \delta$ -TOCの順に速く、一価不飽和脂肪酸 (MUFA) の多い食用油ではトコフェロール (TToC) の分解が先行して食用油の安定性を高める特徴があり、多価不飽和脂肪酸 (PUFA) の多い食用油では、トコフェロールと不飽和脂肪酸の間に相互交替的な分解挙動を見出した。

3. フライ過程で生成されたカルボニル化合物 (CV) および総極性化合物 (TPC) の量は、フライ時間に線型的な関係 ($CV_t = K_{CV} * t + CV_0$ 、 $TPC_t = K_{TPC} * t + TPC_0$) で増加することを解明した。これまでに得られた多数のデータを用いて、重回帰分析法による食用油の品質劣化が主にその内部組成特性に依存する関係を精査した。フライ油の CV 生成速度 (K_{CV}) はフライ前の各食用油の **PUFA/TToC** 比值と、TPC の生成速度 (K_{TPC}) はフライ前の各食用油の **C18:2/C16:0** 比值と最も高い相関関係にあることを見出し、フライ油の二次酸化物生成量の予測モデル(式②)、および総極性化合物発生量の予測モデル(式③)の構築に成功した。また、予測モデルの変形式(④&⑤)によって、フライ油の安全使用限界値 (CV=50 $\mu\text{mol/g}$ 、TPC=24%) に達する最大のフライ時間 (t_{CV} 、 t_{TPC}) を導き出すことができた。

$$CV_t = \left[4.37 \left(\frac{PUFA}{TToc} \right)^2 - 5.64 \left(\frac{PUFA}{TToc} \right) + 3.36 \right] t + CV_0 \quad \dots \textcircled{2}$$

$$TPC_t = \left[0.024 \left(\frac{C18:2}{C16:0} \right)^2 - 0.065 \left(\frac{C18:2}{C16:0} \right) + 0.819 \right] t + TPC_0 \quad \dots \textcircled{3}$$

$$t_{CV} = \frac{CV_t - CV_0}{4.37 \left(\frac{PUFA}{TToc} \right)^2 - 5.64 \left(\frac{PUFA}{TToc} \right) + 3.36} \quad \dots \textcircled{4}$$

$$t_{TPC} = \frac{TPC_t - TPC_0}{0.024 \left(\frac{C18:2}{C16:0} \right)^2 - 0.065 \left(\frac{C18:2}{C16:0} \right) + 0.819} \quad \dots \textcircled{5}$$

4. フライによる食用油の品質と特徴に大きく影響する重要な要素の1つである揮発性成分の変化特性は、不飽和脂肪酸の組成特性との緊密な関係にあることを見出した。オレイン酸が多い食用油にはアルデヒド類化合物が中心とした14個揮発性成分が顕著に増加する特徴があり、リノール酸およびリノレン酸の多い食用油ではアルコール類など9つの化合物が重要な揮発性成分であることを明らかにした。10種のフライ油に共通している揮発性成分の濃度変化はカルボニル化合物 (CV) および総極性化合物 (TPC) 量の増加と高い相関関係にあることを見出し、食用油の品質評価パラメータとしてこれらの揮発性成分が利用できることを示した。

以上、本論文はフライ過程における食用油の劣化特性およびトコフェロールの抗酸化作用の役割を明らかにした。構築されたフライ油の品質予測指標および劣化評価モデルは新たな品質評価手法として有用である。したがって、本論文は博士の要件を十分満たすものであると評価される。

最終審査の結果の要旨

本論文の内容は、令和2年2月19日(水)午前10時50分より、生物資源科学部大学院棟 M216 教室において、公開の博士学位論文発表会で発表された。口頭発表後、質疑応答が行われた。質疑の内容は、メタボロミクス手法を用いて構築されたフライ油品質評価モデルのフライ油の温度変化における対応の可能性を問うもの、フライ油の品質評価モデル利用のさらなる有用性展開の可能性を問うもの、品質評価モデルの評価指標導入の、生産地の異なる同一品種油による評価モデルの精度への影響を問うものなど、多岐にわたる内容が質疑されたが、それぞれに適切かつ丁寧に回答した。

以上により審査委員会は博士学位を授与するに値すると判断した。