Comparative assessment of the frying efficiency of standard and low linolenic rapeseed oils: Principal Component Analysis (PCA)

Ming-Ming Hu1, Chuan-Qi Zhang1, Xin-Yu Wu1

1National R&D Center for Freshwater Fish Processing, College of Life Science, Jiangxi Normal University, Nanchang 330022, China.

*Corresponding to: Ming-Ming Hu, National R&D Center for Freshwater Fish Processing, College of Life Science, Jiangxi Normal University, 99 Ziyang Avenue, Nanchang 330022, China. E-mail: 2006abc-hmm@163.com.

Author contributions
Mingming Hu wrote the manuscript and provided data on statistical analysis of results, with discussion of results; Chuanqi Zhang assisted in editing the work and Xinyu Wu assisted in the collection and processing of data. All authors critically revised the article.

Competing interests
The authors declare no conflicts of interest.

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Abbreviations
RSO, regular rapeseed oil; LLRO, low-linolenic rapeseed oil; PCA, principal component analysis; SFA, saturated fatty acids; UFA, unsaturated fatty acids; AV, acid value; IV, iodine value; PV, peroxide value; p-AV, p-anisidine value; TOTOX, total oxidation; CDV, carbonyl group value; FAC, fatty acids composition; OSI, oxidative stability index; TPC, total polar compounds; PCA, principal component analysis.

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Abstract
In this research, the performance of regular rapeseed oil (RSO) and modified low-linolenic rapeseed oil (LLRO) during frying was assessed using a frying procedure that commonly found in fast-food restaurants. Key physicochemical attributes of these oils were investigated. RSO and LLRO differed for initial linolenic acid (12.21% vs. 2.59%), linoleic acid (19.15% vs. 24.73%). After 6 successive days frying period of French fries, the ratio of linoleic acid to palmitic acid dropped by 54.49% in RSO, higher than that in LLRO (51.54%). The increment in total oxidation value for LLRO (40.46 unit) was observed to be significantly lower than those of RSO (42.58 unit). The changes in carbonyl group value and iodine value throughout the frying trial were also lower in LLRO compared to RSO. The formation rate in total polar compounds for LLRO was 1.08% per frying day, lower than that of RSO (1.31%). In addition, the formation in color component and degradation in tocopherols were proportional to the frying time for two frying oils. Besides, a longer induction period was also observed in LLRO (8.87 h) compared to RSO (7.68 h) after frying period. Overall, LLRO exhibited the better frying stability, which was confirmed by principal component analysis (PCA).

Keywords: frying, rapeseed oil, frying oil, frying stability, principal component analysis
Introduction

Deep-frying is a time-honored and extensively utilized method of food preparation around the world, as it lends foods a distinctive aroma, taste, visually pleasing color, and a crispiness that are unrivaled by alternative cooking techniques [1]. Essentially, deep-frying involves immersing food in a mass of hot oil, generally at temperatures ranging from 150 to 190 °C [2]. During the frying process, oil which is heated for long time in the presence of water and air, undergoes a series of physical and chemical reactions and results in the production of toxic or carcinogenic compounds [3]. These reactions mainly comprise oxidation, hydrolysis and polymerisation accompanied by lots of degradation products including various volatile and non-volatile compounds [4]. These generated products affect the quality of frying oil, as well as the sensory qualities of the food fried [5]. Consequently, the choice of frying oil, as a vital part of fried food during frying, is distinctly important for the product quality.

Oil stability denotes the ability of an oil to endure high temperatures during frying. As a result, saturation levels have emerged as a crucial criterion for choosing suitable frying oils. A multitude of research has indicated that oils rich in saturated fatty acids (SFA) and low in unsaturated fatty acids (UFA) exhibit improved stability when used for frying, independent of nutritional considerations [6]. Furthermore, the number of unsaturated bonds in fatty acids plays a crucial role in determining the oxidation rate of oil. Studies by Ahmad Tarmizi et al. [7] revealed that the relative oxidation rates of stearic acid (18:0), oleic acid (18:1), linoleic acid (18:2), and linolenic acid (18:3) follow the ratio of 1:10:100:150. Whereas, the stability of an oil is not exclusively dependent on its level of saturation. Other factors, such as the presence of minor components like phytosterols and tocopherols, can also affect oil stability [8, 9].

Nowadays, the array of vegetable oils utilized for deep-frying is largely contingent upon their accessibility, cultural customs, and thermal stability. Significantly, palm oil and soybean oil have become extensively used in domestic cooking and frying worldwide due to their economic viability. Concurrently, canola oil is often employed in Canada and many European countries, while peanut and sunflower oils are also favored in certain nations [10]. While hydrogenated fats are known for their adverse effects on human health and saturated ones are still under discussion, vegetable unsaturated fats have become focal topic, and among them, monounsaturated fats are progressively reported according to their functionality and health benefits with an inherent better stability to oxidation than polyunsaturated fats [11, 12]. Recently, utilization of modified vegetable oils such as high-oleic rapeseed oil, high linolenic flaxseed oil, and high-oleic sunflower oil, is progressively available in the market, especially in fast food restaurants.

Principal component analysis (PCA) is a multivariate statistical tool which is applied for identifying the predominant patterns in dataset and reducing the dimensionality with the purpose of highlighting the differences as well as similarities between samples [13]. PCA is also a rather prevailing chemometric technique among the multiple exploratory methodologies, which is widely used to evaluate food quality [14]. In recent years, the effective application of PCA has been reported by many studies [15, 16].

Therefore, this work aims to evaluate the frying performance of regular and low linoleic rapeseed oils during batch frying of French fries under simulated frying protocol in fast food restaurants in China. The influences of deep-frying on the quality changes of regular and modified rapeseed oils, including color, acid value (AV), iodine value (IV), peroxide value (PV), p-anisidine value (p-AV), total oxidation (TOTOX), carbonyl group value (CGV), fatty acids composition (FAC), oxidative stability index (OSI), total polar compounds (TPC) and tocopherols, as well as the correlation between physicochemical parameters and principal component analysis (PCA) were determined. This research is expected to provide beneficial information for the choice of suitable frying oil used in catering industry.

Materials and methods

Materials and reagents

Rapeseed oil (RSO) and low linolenic rapeseed oil (LLRO) were obtained from a local market in Shanghai, China. Pre-fried French fries were provided by the supplier, Inner Mongolia Lamb Weston Potato Co., Ltd. Chromatographic grade solvents such as benzene, n-hexane, n-heptane, and tetrahydrofuran were purchased from Sinopharm Chemical Reagent Co., Ltd., situated in Shanghai, China. The internal standards α-, β-, γ-, δ-tocopherols were purchased from Sigma-Aldrich Inc., based in St. Louis, MO, USA.

Sample preparation

The present research was done to emulate the frying process in restaurants, following the methodology outlined by Hu et al. [17] with slight modifications. The oils were subjected to heating for 12 hours daily, with frying intervals occurring every 12 minutes over a span of six consecutive days. This frying procedure took place in a stainless steel deep fryer, Model OFE-28 (Yixi, Shanghai, China), where the temperature was maintained at 170 ± 5°C. For the experimental procedure, 13 liters of each oil type (RSO and LLRO) were utilized. In every frying cycle, a batch of 200 grams of pre-fried French fries was fried for 3 minutes, and this process was repeated every 12 minutes throughout the daily 12-hour period for six uninterrupted days. Filtration crucial, employing filter powder from Dallas Special Adsorbent Co., Qingdao, China, and paper from Yixi, Shanghai, China, was performed every six hours during the frying sessions. Subsequent to filtration, additional fresh frying oil was introduced to replenish the oil to its initial level in the fryer. Upon completion of each day's frying session, 350 milliliters of oil were gathered, placed in dark amber bottles, and stored at -20°C for future analysis.

Determination of AV, PV, IV and p-AV

AV and PV were assayed according to the AOCS Official Methods Cd 3d-63 and Cd 8b-90, respectively. IV and p-AV were performed following ISO Methods 3961:2018 and 6885:2016, respectively.

Determination of OSI

The OSI value of oil was assayed by Rancimat 743 at 110°C (Metrohm, Switzerland) following the ISO Method 6886:2016.

Determination of TPC

Levels of TPC in oil samples were measured using a Testo 270 Deep-frying Oil Tester (Testo Inc., Germany) following the manufacturer’s instructions. The measurements are based on the dielectric constant of oil samples, which have high correlation with the concentration of TPC [18].

Determination of color

Measurement of color was carried out according to the ISO Method 27608:2010.

Analysis of FAC

Following the AOCS Official Method Ce 1f-96 (Reprinted 2009), the FAC was ascertained using gas chromatography (Agilent Technologies, Shanghai, China). This method was interfaced with a Flame Ionization Detector (FID) and utilized a polycapillary column, model varian cp 7489 (0.000 m × 250 μm × 0.20 μm, VARIAN, Shanghai, China). The injection port temperature was kept at 250°C. The initial oven temperature was set at 160°C for a duration of 5 minutes before ramping up to 210°C at a rate of 10°C per minute. Helium of ultra-high purity was employed as the carrier gas, with a flow rate adjusted to 1.3 mL/min, and the split ratio was configured to 50:1.

Determination of tocopherols in oils

The measurement of tocopherol concentrations in oils was carried out following the ISO Method 9936:2006. This procedure utilized a normal-phase High-Performance Liquid Chromatography (HPLC) instrument (Agilent Technologies, Shanghai, China) paired with a
fluorescence detector (Agilent Technologies, Shanghai, China). The settings for the detector’s excitation and emission wavelengths were adjusted to 292 nm and 394 nm, respectively. In terms of chromatographic separation, a LiChrospher 100 DIOL column (250 mm × 4 mm, internal diameter 5 μm) functioned as the stationary phase and was kept at a constant temperature of 30°C. The mobile phase was composed of a blend of n-hexane and tetrahydrofuran in a volumetric ratio of 96:13:8.5, which was pumped at a flow rate of 1 mL/min. The tocopherols (including α-, β-, γ- and δ-tocopherols) in oil samples were identified using external calibration for their individual isomer. The standard curves of α-, β-, γ- and δ-tocopherols were prepared by plotting the peak area against the standard concentration (mg/kg). The regression equations for α-, β-, γ- and δ-tocopherols were as follows: y = 12.81x – 3.31, y = 21.53x – 1.27, y = 24.3x – 4.77, and y = 16.33x – 4.57, respectively. The coefficients of determination (R²) were 0.9998, 0.9996, 0.9998 and 0.9998, respectively.

Statistical analyses

Each sample was analyzed three times, and the results are shown as means ± standard deviations (SD). The data were assessed using single-factor analysis of variance (ANOVA) with IMB SPSS Statistics (Version 20). Statistical significance was determined using Duncan’s multiple range tests, with a p value < 0.05 indicating significance. PCA was used to analyze the data obtained.

Results and discussion

Fatty acids profile of the fresh frying oils

The FAC can affect the appearance, flavor, shelf life, and processing behavior of vegetable oils, which are crucial for studying the properties of frying oils [19]. As shown in Table 1, the most prominent fatty acids in fresh RSO were oleic acid (62.60%), linoleic acid (19.15%) and linolenic acid (12.21%). Whereas, a relatively higher amount of oleic acid (65.66%) and linoleic acid (24.73%), and a lower contribution of linolenic acids (2.59%) were observed in fresh LLRO. The total monounsaturated fatty acids (MUFA) were the higher in LLRO (65.66%). A high content of MUFA in oils is desirable owing to the health benefits [20]. Irrespective of the minor antioxidative components, oils with high amounts of MUFA and low amounts of unstable polyunsaturated fatty acids (PUFA) showed better frying performance over regular oils [21].

Changes in FAC of frying oils during frying

As shown in Table 1, FAC changed over the frying time. In two kinds of frying oils, unsaturated fatty acids reduced while saturated fatty acids increased progressively over the frying time. At the end of frying procedure, it was observed that linoleic acid decreased by 0.47% and 10.75% in RSO and LLRO, respectively. In contrast, palmitic acid increased gradually over the increase of frying time in two kinds of frying oils (119.62% and 84.23%). Linoleic acid (C18:2) is more susceptible to oxidation than palmitic acid (C16:0). Thus, C18:2/C16:0 was reported to be a valid indicator for oxidative deterioration in used oils [22]. At the end of frying period, C18:2/C16:0 dropped by 54.49% and 51.54% in RSO and LLRO, respectively, indicating that LLRO had better oxidative stability than RSO.

Table 1 Fatty acid composition (%) of deep-fried oils during frying process

<table>
<thead>
<tr>
<th>FAC (%)</th>
<th>Day 0</th>
<th>Day 1</th>
<th>Day 2</th>
<th>Day 3</th>
<th>Day 4</th>
<th>Day 5</th>
<th>Day 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>RSO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C16:0</td>
<td>4.18 ± 0.01</td>
<td>5.75 ± 0.00</td>
<td>6.62 ± 0.01</td>
<td>7.54 ± 0.02</td>
<td>8.60 ± 0.01</td>
<td>8.96 ± 0.01</td>
<td>9.18 ± 0.04</td>
</tr>
<tr>
<td>C18:0</td>
<td>1.86 ± 0.01</td>
<td>1.47 ± 0.00</td>
<td>1.50 ± 0.01</td>
<td>1.58 ± 0.00</td>
<td>1.52 ± 0.01</td>
<td>1.55 ± 0.01</td>
<td>1.59 ± 0.00</td>
</tr>
<tr>
<td>C18:1</td>
<td>62.60 ± 0.44</td>
<td>62.24 ± 0.28</td>
<td>62.20 ± 0.57</td>
<td>59.41 ± 0.31</td>
<td>62.24 ± 0.29</td>
<td>60.75 ± 0.36</td>
<td>61.33 ± 0.41</td>
</tr>
<tr>
<td>C18:2</td>
<td>19.15 ± 0.13</td>
<td>19.53 ± 0.09</td>
<td>19.44 ± 0.22</td>
<td>20.34 ± 0.11</td>
<td>19.18 ± 0.17</td>
<td>19.90 ± 0.26</td>
<td>19.06 ± 0.07</td>
</tr>
<tr>
<td>C18:3</td>
<td>12.21 ± 0.06</td>
<td>11.01 ± 0.03</td>
<td>10.24 ± 0.01d</td>
<td>11.13 ± 0.04</td>
<td>8.46 ± 0.01</td>
<td>8.82 ± 0.01</td>
<td>8.83 ± 0.02</td>
</tr>
<tr>
<td>C20:0</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>C18:2/C16:0</td>
<td>4.57</td>
<td>3.40</td>
<td>2.94</td>
<td>2.70</td>
<td>2.23</td>
<td>2.22</td>
<td>2.08</td>
</tr>
<tr>
<td>ESFA</td>
<td>6.05</td>
<td>7.22</td>
<td>8.12</td>
<td>9.12</td>
<td>10.12</td>
<td>10.51</td>
<td>10.77</td>
</tr>
<tr>
<td>ΣUFA</td>
<td>93.96</td>
<td>92.78</td>
<td>91.88</td>
<td>90.88</td>
<td>89.88</td>
<td>89.47</td>
<td>89.22</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>LLRO</th>
<th></th>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C16:0</td>
<td>6.09 ± 0.71</td>
<td>6.11 ± 0.72</td>
<td>7.56 ± 0.40</td>
<td>8.76 ± 0.17</td>
<td>9.84 ± 0.41</td>
<td>10.24 ± 0.11</td>
<td>11.22 ± 0.16</td>
</tr>
<tr>
<td>C18:0</td>
<td>1.83 ± 0.71</td>
<td>1.86 ± 0.04</td>
<td>1.62 ± 0.09</td>
<td>1.80 ± 0.03</td>
<td>1.86 ± 0.35</td>
<td>1.91 ± 0.44</td>
<td>1.93 ± 0.18</td>
</tr>
<tr>
<td>C18:1</td>
<td>67.73 ± 0.00</td>
<td>64.35 ± 2.29</td>
<td>65.11 ± 1.09</td>
<td>63.97 ± 0.87</td>
<td>63.41 ± 0.97</td>
<td>63.2 ± 0.82</td>
<td>62.64 ± 1.07</td>
</tr>
<tr>
<td>C18:3</td>
<td>2.59 ± 0.00</td>
<td>5.59 ± 4.39</td>
<td>5.34 ± 3.91</td>
<td>5.20 ± 3.83</td>
<td>5.16 ± 3.61</td>
<td>5.23 ± 3.74</td>
<td>4.75 ± 3.21</td>
</tr>
<tr>
<td>C20:0</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>C18:2/C16:0</td>
<td>3.57</td>
<td>3.56</td>
<td>2.69</td>
<td>2.31</td>
<td>2.00</td>
<td>1.88</td>
<td>1.73</td>
</tr>
<tr>
<td>ESFA</td>
<td>7.92</td>
<td>7.97</td>
<td>9.19</td>
<td>10.56</td>
<td>11.71</td>
<td>12.16</td>
<td>13.16</td>
</tr>
<tr>
<td>ΣUFA</td>
<td>92.08</td>
<td>91.73</td>
<td>90.81</td>
<td>89.40</td>
<td>88.30</td>
<td>87.75</td>
<td>86.82</td>
</tr>
</tbody>
</table>

Note: RSO, rapeseed oil; LLRO, low linolenic rapeseed oil; SFA, saturated fatty acids; UFA, unsaturated fatty acids; N.D., not detected. Means within rows with different lowercase letters differ significantly (p < 0.05)
Changes in AV
During the oxidation of fried oil, hydroperoxides are generated. This process includes the formation, polymerization, and decomposition of hydroperoxides, all of which happen simultaneously. The initial stage is characterized by an accumulation of hydroperoxides that proceeds at a rate faster than both their polymerization and decomposition. As a certain concentration threshold is surpassed, the pace of polymerization and degradation quickens, resulting in a significant rise in free fatty acids that in turn elevates the AV [23]. As shown in Figure 1a, regardless of the type of oils, the accumulation of FFA increased over frying period. Generally, edible oil with AV over 3.00 mg KOH/g may result in human gastrointestinal discomfort, diarrhea and liver damage [24]. However, the AV of the four frying oils were lower than 3.0 mg KOH/g during the frying process. This may be due to filtering and replenishing fresh oil during frying. Throughout the entire frying period, the increase of AV was found to be the lower in RSO (2.44 mg KOH/g), with relatively higher increase in LLRO (2.70 mg KOH/g). This was partly because oils with higher level of oleic acid presented a higher FFA content in the heated oil [25]. In general, the FFA content produced by hydrolysis is too low, and have poor correlation with the quality of the food, thus, AV is not suitable to be used alone as quality indicator for frying oils [17]. Whereas, it may be an alternative parameter of the extent of oil adulteration if applied in combination with other indicators.

Changes in PV
As shown in Figure 1b, there was a tendency of fluctuating change in PV during the entire frying period. Generally, PV changes depend on the type of frying oil and the frying conditions. Waghmare et al. [24] found that PV increases significantly with the extension of frying time, which may be attribute to a shorter frying period and a lower frying temperature, while more studies have reported that PV fluctuated irregularly during frying [17], which are consistent with our findings. The PV is an indicator of the initial formation of peroxides or hydroperoxides during the oxidation of fried oil. Hydroperoxides are unstable and break down into secondary products or form carbonyl and aldehyde compounds as frying time continues. Therefore, using only the PV to assess the degradation of frying oil is not very reliable.

Changes in p-αV
During the oxidative degradation of frying oil, many secondary aldehyde products, mainly 2-alkenals and 2,4-alkadienals, may be produced. p-αV is an effective indicator of the relative levels of non-volatile unsaturated aldehyde compounds in the frying oil and can reflect changes in the amount of secondary oxidation products that arise from the breakdown of hydroperoxides. As shown in Figure 1c, both frying oils exhibited similar performance after frying, namely, the p-αV of both oils increasing rapidly during the first two days before leveling off. The p-αV of regular RSO rose from 4.24 unit to 46.88 unit after 4 days’ frying, while the p-αV of LLRO increased from 3.54 unit to 42.84 unit. Regular RSO had a higher p-αV compared to LLRO both before and after frying, indicating that regular RSO was more susceptible to producing volatile aldehydes. Previous research has associated the formation of volatile aldehydes with the content of ΣPUFA, which are the main targets of heat oxidation reactions. Since regular RSO is rich in ΣPUFA, it shows higher p-αV levels. These findings agree with the report by Przybylaksi et al. [26], where the modified canola oil and soybean oil with lower PUSA consistently exhibited lower p-αV than the regular ones.

Changes in TOTOX
Since PV is usually applied to evaluate the primary oxidation stage of oil, and the p-αV is suitable for assessing the secondary oxidation of oil [27]. Thus, p-αV is commonly used in conjunction with PV in the industry to determine the TOTOX given as follows [23]:

\[
\text{TOTOX} = 2\text{PV} + \text{p-αV},
\]

which provides sufficient information about the overall oxidative status of the frying oil. As in p-αV, the TOTOX value increased sharply for all frying oils in first two days’ frying (Figure 1d).

After the fourth day of frying, the TOTOX value for LLRO (40.46 units) increased significantly less (p < 0.05) compared to RSO (42.58 units), further confirming LLRO’s greater resistance to oxidation compared to RSO. Meanwhile, a lower TOTOX value was observed in modified LLRO compared to regular RSO, in line with their relative percentage of PUFAs. Regardless of the slightly different levels of saturated fatty acids for two frying oils, oils containing lower amount of PUFAs possess better oxidative stability and lower TOTOX value as the relative oxidation rate of PUFAs (linoleic and linolenic acids) is at least ten times higher than that of MUFA (oleic acid) [28].

Changes in color
Color is a visual but subjective indication of oil deterioration when subjected to excessive heat. Figure 2a displays changes in color for the frying oils (RSO and LLRO) during 6 days of frying. As shown in Figure 2a, RSO presented a higher initial red color units (1.03) compared to LLRO (0.37). Whereas, a linear increase in darkness with frying time was observed for both two frying oils during the frying procedure. Even though the initial colors of two frying oils were different, there was a slightly faster rate of darkening in RSO during the frying period. Generally, the darkening of oils is caused by the accumulation of nonvolatile decomposition products and α-, β-unsaturated carbonyl compounds [23]. In addition, it should be noted that oils darkening may also be affected by the usage of coloring agents in the food industry and the degradation of tocopherols in the frying oils.

Changes in IV
IV is used as a measure of the oil’s degree of unsaturation. A drop in IV may be owing to the oxidative and polymerized reactions occurred at the unsaturated bonds of the oil. As shown in Figure 2b. The IV decreased steadily for two frying oils used. The change in IV of LLRO (9.92) was found to be significantly lower (p < 0.05) than and RSO (10.29), suggesting that RSO was more prone to oxidation than LLRO. After the frying trial (6 days), the iodine values of LLRO and RSO were found to be 99.91 and 105.37, respectively. A similar steady decrease in the IV in soybean oil, canola oil and high oleic Moringa oleifera seed oil (HOMO) during frying was observed by Abdulkarim et al. [20], while HOMO displayed a more gradual decline in IV, mainly due to its higher MUFA content and lower PUFA levels.

Changes in GCV
GCV is a valuable tool for evaluating the quality of frying oils, as it quantifies the total carbonyl compounds resulting from thermal oxidation, hydrolysis, and polymerization during the frying process. These compounds often contribute to unpleasant and rancid flavors and reduce the nutritional value of fried foods [29]. Hence, GCV can be used as a good indicator of oil deterioration. As depicted in Figure 2c, both frying oils showed a similar fluctuating increase in GCV with extended frying time. Whereas, the GCV was kept at a low level (< 30 meq/kg), this also may be attributed to the addition of fresh oil during frying. Additionally, GCV was significantly lower (p < 0.05) in LLRO than in RSO, indicating that fewer carbonyl compounds were generated in LLRO. Similar to TOTOX, the modified LLRO displayed a significant lower total GCV compared to regular RSO.

Changes in OSI
Automatic oxidation of oil is the main factor leading to rancidity and deterioration, thus OSI measured by the Rancimat test can provide a dynamic determination and is a crucial metric for assessing frying oil quality. As shown in Figure 2d, RSO exhibited a lower initial induction period (8.01 h) compared to LLRO (10.54 h), and both the induction period of LLRO and RSO presented a gradual decrease during the frying trial. However, LLRO consistently exhibited a significantly longer induction period compared to RSO, regardless of the frying duration, demonstrating LLRO’s superior oxidation resistance. As expected, a significant (p < 0.05) longer induction period was observed in modified LLRO (8.87 h) compared to regular RSO (7.68 h) after frying. The longer induction period in LLRO could be attributed to the low percentages of PUFAs. Ramroudi et al. [30]
have also found that vegetable oil samples contained high amount of PUFA had lower OSI, which is in agreement with our results.

**Changes in TPC**

Measuring TPC is considered one of the most objective, accurate, and reliable methods for assessing frying oil deterioration, as the measured components are non-volatile and polar, representing the major reactions occurring during deep frying [22]. As presented in Figure 3, RSO presented a higher TPC (3.03%) compared to LLRO (2.06%) before frying, and increased levels of TPC with frying time were observed irrespective of the type of frying oil during the frying period, however, the levels of TPC for all frying oils were far below the maximum limit of 24-27% for frying oil to be edible in many European countries [24], which may be also due to filtering and replenishing fresh oil during frying. Both two frying oils displayed excellent frying stability, but there was statistically significant (p < 0.05) difference among the frying oils, with LLRO accumulating the lower TPC after 6 days of frying. Regression analysis showed that the formation rates in TPC were 1.08% and 1.31% per frying day for LLRO and RSO, respectively. These findings were consistent with the previous report that modified canola oil and soybean oil with lower levels of PUFA accumulated less polar components than the regular ones during frying [26].

**Changes in tocopherols**

Tocopherols act as natural antioxidants, and their concentration and isomeric forms are known to influence the stability of frying oils [31]. The amounts of tocopherols decreased rapidly at the first three frying days after which the rate slowed down for the all the frying oils during the increase of frying time (Figure 4). Although the initial tocopherols contents of four frying oils were different (SS5 and 662 ppm for RSO and LLRO, respectively), at the end of the frying trial (6 days), the reduction rates of tocopherols during the frying process were found to be slightly higher in LLRO (31.20%), with the lower percentage obtained in RSO (30.53%). This may be attributed to its lower level of PUFA; the rate of tocopherol oxidation increased with the decrease in the level of UFA, especially PUFA in the oil. Since more double bonds in PUFA compete with tocopherols as substrates for oxidation, suggesting a faster reduction of these antioxidants [32].

Analysis of relative degradation of different forms of tocopherols (data not shown) showed that γ-tocopherol displayed the fastest degradation rate, followed by δ-tocotrienol and α-tocopherol, while β-tocopherol showed the best stability. An opposite reduction rate of tocopherols to our current results was reported by Gordon and Kourimská [33]. However, the findings in order of degradation rate of tocopherols from our investigations agreed with the previous studies [26].

**Correlation between different parameters**

A Pearson correlation coefficients (PCC) analysis was performed to determine the relationships among all quality parameters in deep-fried oils. As shown in Table 2, AV, p-AV, TOTOX, CGV and TPC were positively and significantly correlated with the r values ranging from 0.749 to 0.984. In contrast, significantly negative correlations were found between tocopherols and TPC (r = −0.921), and between C18:2/C16:0 and TPC (r = −0.918). Several studies have also reported the correlation coefficient in the range of 0.842 to 0.960 between p-AV and TPC for various frying oils under deep-frying conditions [34]. Therefore, although TPC is considered as the most important indicator to assess the frying performance of frying oil, other assessment parameters that are highly correlated with TPC may be the alternative methods. However, it should be noted that TPC showed poor relationships with PV, IV and OSI (r = 0.227 to 0.603), although there was a clear correlation between IV and OSI. In addition, tocopherols content was positively correlated with C18:2/C16:0 (r = 0.829) due to the antioxidant activity of tocopherols, which was helpful to prevent linoleic acid (C18:2) from oxidation.

**Principal component analysis (PCA)**

In this study, PCA was accomplished to obtain a better understanding physicochemical changes and further evaluate the frying performance of regular and modified rapeseed oils during deep frying. As depicted in Figure 5, the first two principal components (namely, PC1 and PC2) represented 89.12% of the total variability (PC1: 72.82% and PC2: 16.30%). With regard to the loading plot (Figure 5a), the information on correlations among analyzed parameters can be provided. PC1 was primarily correlated to AV, p-AV, TOTOX, CGV, TPC and color on the positive side along with tocopherols and C18:2/C16:0 on the negative side. Interestingly, the loading plot revealed a negative correlation of OSI and tocopherols from the others, which was in good agreement with the correlation coefficient of negative values as presented in Table 2. PC2 was positively characterized by OSI and PV. Besides, a visible cluster involving TPC, CGV, TOTOX, color and p-AV was observed, suggesting their high correlation. This observation also agreed with previous PCC analysis shown in Table 2.

As regards the score plot displayed in Figure 5b, it is easy to visually discriminate the differences in frying performance between two frying oils. Indeed, during the whole frying period, PC1 separated the modified LLRO with a better frying stability (in the relatively negative side) from the regular RSO. Also, PC2 distinguished each frying session along with a linear correlation of PCA score points for two frying oils from the 1st to 6th frying day suggesting a decline in the quality for two frying oils during consecutive frying sessions. This result was similar to a previous report that the PCA score points of frying oils decreased proportionally with the increasing frying circles [24]. In addition, Zribi et al. [35] found that refined olive oil/palm oil blend among the various blended oils during deep frying showed better frying performance as evidenced by its higher PCA score point.

**Table 2 Correlation coefficients of the physicochemical parameters determined in frying oil samples**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>AV</th>
<th>PV</th>
<th>p-AV</th>
<th>TOTOX</th>
<th>IV</th>
<th>CGV</th>
<th>TPC</th>
<th>OSI</th>
<th>Color</th>
<th>Tocopherols</th>
<th>C18:2/C16:0</th>
</tr>
</thead>
<tbody>
<tr>
<td>AV</td>
<td>1</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>PV</td>
<td>0.407</td>
<td>1</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>p-AV</td>
<td>0.69&lt;sup&gt;−&lt;/sup&gt;</td>
<td>0.409</td>
<td>1</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>TOTOX</td>
<td>0.69&lt;sup&gt;−&lt;/sup&gt;</td>
<td>0.44</td>
<td>0.999&lt;sup&gt;−&lt;/sup&gt;</td>
<td>1</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>−0.77&lt;sup&gt;−&lt;/sup&gt;</td>
<td>−0.688&lt;sup&gt;−&lt;/sup&gt;</td>
<td>−0.719&lt;sup&gt;−&lt;/sup&gt;</td>
<td>−0.734&lt;sup&gt;−&lt;/sup&gt;</td>
<td>1</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td></td>
</tr>
<tr>
<td>CGV</td>
<td>0.732&lt;sup&gt;−&lt;/sup&gt;</td>
<td>0.168</td>
<td>0.922&lt;sup&gt;−&lt;/sup&gt;</td>
<td>0.911&lt;sup&gt;−&lt;/sup&gt;</td>
<td>−0.516&lt;sup&gt;−&lt;/sup&gt;</td>
<td>1</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td></td>
</tr>
<tr>
<td>TPC</td>
<td>0.749&lt;sup&gt;−&lt;/sup&gt;</td>
<td>0.227</td>
<td>0.943&lt;sup&gt;−&lt;/sup&gt;</td>
<td>0.935&lt;sup&gt;−&lt;/sup&gt;</td>
<td>−0.571&lt;sup&gt;−&lt;/sup&gt;</td>
<td>0.984&lt;sup&gt;−&lt;/sup&gt;</td>
<td>1</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td></td>
</tr>
<tr>
<td>OSI</td>
<td>−0.139</td>
<td>0.044</td>
<td>−0.492&lt;sup&gt;−&lt;/sup&gt;</td>
<td>−0.482&lt;sup&gt;−&lt;/sup&gt;</td>
<td>−0.134</td>
<td>−0.628&lt;sup&gt;−&lt;/sup&gt;</td>
<td>−0.603&lt;sup&gt;−&lt;/sup&gt;</td>
<td>1</td>
<td>−</td>
<td>−</td>
<td></td>
</tr>
<tr>
<td>Color</td>
<td>0.929&lt;sup&gt;−&lt;/sup&gt;</td>
<td>0.299</td>
<td>0.865&lt;sup&gt;−&lt;/sup&gt;</td>
<td>0.859&lt;sup&gt;−&lt;/sup&gt;</td>
<td>−0.704&lt;sup&gt;−&lt;/sup&gt;</td>
<td>0.918&lt;sup&gt;−&lt;/sup&gt;</td>
<td>0.922&lt;sup&gt;−&lt;/sup&gt;</td>
<td>−0.404&lt;sup&gt;−&lt;/sup&gt;</td>
<td>1</td>
<td>−</td>
<td></td>
</tr>
<tr>
<td>Tocopherols</td>
<td>−0.724&lt;sup&gt;−&lt;/sup&gt;</td>
<td>−0.02</td>
<td>−0.816&lt;sup&gt;−&lt;/sup&gt;</td>
<td>−0.801&lt;sup&gt;−&lt;/sup&gt;</td>
<td>0.4</td>
<td>−0.956&lt;sup&gt;−&lt;/sup&gt;</td>
<td>−0.921&lt;sup&gt;−&lt;/sup&gt;</td>
<td>0.676&lt;sup&gt;−&lt;/sup&gt;</td>
<td>−0.896&lt;sup&gt;−&lt;/sup&gt;</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>C18:2/C16:0</td>
<td>−0.841&lt;sup&gt;−&lt;/sup&gt;</td>
<td>−0.393</td>
<td>−0.952&lt;sup&gt;−&lt;/sup&gt;</td>
<td>−0.95&lt;sup&gt;−&lt;/sup&gt;</td>
<td>0.82</td>
<td>−0.892&lt;sup&gt;−&lt;/sup&gt;</td>
<td>−0.918&lt;sup&gt;−&lt;/sup&gt;</td>
<td>0.335</td>
<td>−0.935&lt;sup&gt;−&lt;/sup&gt;</td>
<td>0.829&lt;sup&gt;−&lt;/sup&gt;</td>
<td>1</td>
</tr>
</tbody>
</table>

Note: AV, acid value; PV, peroxide value; p-AV, p-anisidine value; TOTOX, total oxidation; IV, iodine value; CGV, carbonyl group value; TPC, total polar compounds; OSI, oxidative stability index; p < 0.05; **p < 0.01.

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Figure 1 Changes in acid value (a), peroxide value (b), p-anisidine value (c) and Totox value (d) during frying.

Figure 2 Changes in color (a), iodine value (b), carbonyl group value (c) and oxidative stability index (d) during frying.
Figure 3 Changes in total polar compounds during frying

Figure 4 Changes in tocopherols during frying

Figure 5 Principal component analysis applied to study the variation amongst the oil samples and their characteristics for the first two factors: (A) Loading plot (B) Score plot
Conclusions

In the present study, a comprehensive investigation for the physical and chemical characteristics of regular and low linolenic rapeseed oils was carried out under simulated frying practice of fast-food restaurants to evaluate the effect of the frying process on oil properties. The results indicated that LLRO had superior frying stability compared to RSO, evidenced by its significantly lower increases in p-AV, TOTOX, GGV, and TPC, as well as smaller decreases in C18:2/C16:0 and IV, and a longer induction period, though the degradation rate of tocopherols in LLRO was observed to be relatively faster than other frying oils due to lesser competition with PUFA as substrates for oxidation. PCA results indicated that total polar compounds were highly correlated with p-AV, TOTOX, GGV and color as supported by PCC analysis, which further demonstrated a better frying performance of LLRO. Therefore, it can be concluded that LLRO could be considered as a healthier alternative frying oil used in fast food restaurants due to its lower linolenic acid and better frying stability. However, the relationship between linolenic acid and the stability of frying oil remains unclear. Further research should be carried out to determine detailed mechanisms and factors influencing the stability of frying oil during frying.

References

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