Malays. Appl. Biol. (2018) 47(2): 89–94

OXIDATIVE STABILITY OF PALM OLEIN ADDED WITH ETHANOL EXTRACT OF CURRY LEAVES AND SENSORY QUALITY OF THE FRIED PRODUCT

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Accepted 27 April 2018, Published online 25 May 2018

ABSTRACT

In this study, curry leaves extract was used to minimize the oxidation process upon deep-fat frying. Crude extract was isolated from dried and ground curry leaves using ethanol and excess solvent was evaporated off. Three systems of frying oil; I) palm olein without curry leaves extract, II) palm olein with 0.02% curry leaves extract and III) palm olein with 0.04% curry leaves extract were prepared and fried repeatedly to 6 consecutive batches. Oil sample was collected at batches 2, 4 and 6 for analysis of iodine value (IV), peroxide value (PV), free fatty acid (FFA) content and thiobarbituric acid (TBA) value while the fries was kept for sensory quality assessment. Generally, the findings showed that system III was the most effective in retarding oil oxidation as compared to system I and II. This could be clearly observed in analysis of PV and IV, where system III gave the lowest rate of increment. Sensory attributes (yellow colour, hardness, oiliness, rancid smell, curry leaves aroma and overall quality) of the fried fries was found to have no significant (P>0.05) differences between all the systems indicating that the extract did not affect the sensory attributes evaluated.

Key words: Oxidation process, curry leaves extract, palm olein, sensory quality

INTRODUCTION

Palm olein is one of the most widely used frying oil as it offers low cost and greater stability of oil towards oxidation in comparison to other vegetable oils. When oils, particularly unsaturated fatty acids are exposed to high temperature during frying, they oxidize and produce peroxide radicals, unstable molecules with high reactivity. The decomposed volatile compounds of peroxide radicals such as reactive aldehydes, alcohols and ketones, on the other hands are responsible for the rancidity of frying oil (Wasowicz *et al.*, 2004).

Synthetic antioxidants like butylated hydroxyanisole (BHA), butylated hydroxy toluene (BHT) and tertiary butylhydroxyquinone (TBHQ) are often added into lipid products in order to minimize oxidation due to its lower manufacturing cost and high stability towards heat (Stoia & Oancea, 2012). However, the use of synthetic antioxidants has been questioned due to its potential health risk. Recent researches have shown carcinogenic effect and possible toxicity of BHA and BHT. Consistent intake of synthetic anti-oxidants by rats had led to the development of tumour in the fore stomach and other organs (Azizkhani & Zandi 2011; Eskin & Przybylski, 2001).

Murraya koenigii or curry leaves originate from India and had reached Malaysia together with South Indian Immigrant. Curry leaves has been popularly added in cooking to add flavor and aroma, and also used as febrifuge, anti-helmetics, anti-fungal, depressant, anti-inflammatory, blood purifier, kidney pain and vomiting (Purohit *et al.,* 2009). Curry leaves contains high amount of phenolic compounds, showing that it has high antioxidant activity (Huda *et al.,* 2009). Due to this property, extract from curry leaves may show a potential to be used as antioxidant in fat and oil products.

As a consequence, more researches have been done on natural or plant-based antioxidants as an alternative to synthetic antioxidants. Amongst the locally produced herbs and plants, curry leaves is

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one of the most researched plant for antioxidant activity. Researches have revealed that curry leaves contains high amount of polyphenolic compound and has a high antioxidant activity (Wong *et al.*, 2005; Huda *et al.,* 2009). Therefore, this study was conducted to study the effects of curry leaves extract on the physicochemical properties of palm olein and sensory quality of their fried products.

MATERIALS AND METHODS

Curry leaves extraction

The extraction of curry leaves was prepared according to Fatihanim *et al.* (2009) with slight modification at the extraction conditions. One kilogram of curry leaves were obtained from local wet market in Nilai, Negeri Sembilan, Malaysia. The sample was cleaned and washed using running tap water and excessive water was removed using a colander. The leaves were then dried at 45°C for 8 hours using hot oven drying. The sample was ground to fine powder using a domestic blender (Panasonic MX-337N, Japan). The powder was extracted in ethanol under reflux for 4 hours at 50°C, at a 1:10 ratio (w/w) of powder to ethanol. The aqueous extract was filtrated using Whatman No.1 paper before dried using rotary evaporator at 80°C and 50 rpm rotation. The crude extracts were weighed and stored at 0-4°C for further experiments.

Frying experiments

Fries (Tesco Brand) and palm oleins (Seri Murni) were purchased from a supermarket in Nilai, Negeri Sembilan, Malaysia. Frying experiments were carried out in three systems: i) palm olein without curry leaves extract (System I), ii) palm olein with 0.02% concentration of curry leaves extract (System II) and iii) palm olein with 0.04% concentration of curry leaves extract (System III). The frying experiments were conducted in two replications for each system with 1 kg of palm olein was repeatedly fried for six times. Extract of curry leaves were added to palm olein just prior the frying process. The procedure of frying is following Che Man and Irwandi (2000). All the three systems of palm olein were poured into deep-fryer and the temperature was brought up to 180°C. Frying process was started after the temperature had reached 180°C. A batch of 100 g fries were fried for 3 min at 17.5 min intervals and the oil were allowed to equilibrate back to 180°C before frying of the next batch of fries started. The fryers were uncovered during the frying. The samples of cooking oil were collected in batches 2, 4, and 6 (each 100 mL) in storage bottles. All oil samples were stored in the dark at 0°C for further analyses. After frying, fries were removed from the fryer and kept for sensory analysis.

Physicochemical Analysis of Palm Olein

Peroxide value

The method to analyses peroxide value is following Firestones (1993). Five gram of samples was dissolved in 30 mL of acetic acid-chloroform solution. The solution was swirled for 1 minute after the addition of 0.5 mL of saturated potassium iodide. Then, 30 mL of distilled water was added, followed by a few drops of starch solution for freshly processed oils. The solution then was titrated with 0.01N sodium thiosulphate solution gradually at first and drop-wise later until the blue colour disappeared.

Iodine value

AOCS method was used to determine the iodine value of palm olein (Firestones, 1993). Sample of 0.5 g was weighed into 250 mL conical flask. Then, the sample was dissolved in 25 mL Wijs solution. The sample was stored in the dark for 1 hour. Twenty mL of potassium iodide solution and 150 mL distilled water then were added into the solution. The solution later was titrated with 0.1 N sodium thiosulphate until the yellow colour almost disappeared. The titration was continued again until the blue colour disappeared after the addition of 1-2 mL of starch indicator.

Free fatty acid content

The method used to analyse free fatty acid content is following the PORIM method (1995). One and a half gram of sample was dissolved with 25 mL of ethanol. The solution was then boiled in a water bath and allowed to cool. Before titration, 2-3 drops of phenolphthalein were added into solution. The sample was titrated with standard alkali, sodium hydroxide to the first persistent permanent pink colour.

Thiobarbituric acid Value

Pokorny and Dieffenbacher (1989) method was used to determine thiobarbituric acid value of palm olein. One fifth of a gram of sample was accurately weighed into a 25 mL volumetric flask and dissolved in a small volume of 1-butanol and made up to volume with 1-butanol. Then 0.5 mL of the sample solution was transferred to a dry test tube and 5 mL of reagent solution was added. The test tube was closed with a ground-glass stopper, mixed thoroughly and placed in a thermostated water bath (Memmert) at 95°C. The test tube was removed from the thermostated bath after 120 min and cooled under running tap water for about 10 min until it reached room temperature. The absorbance of the reaction solution was measured in a 10 mm cuvette at 530 nm using distilled water in the reference cuvette using UV spectrophotometer (UV-tech).

A reagent blank; a mixture of 1-butanol and TBA reagent was prepared at the same time as sample.

Qualitative Descriptive Analysis (QDA) of fried fries

Hundred grams of the sixth batch of fries were collected from System I, II and III at the end of experiment. The fries were then put on plate and coded with three random digits. Fifteen (15) panellists were selected by asking the potential panelists with a few questions regarding to the product to prevent biasness. They were trained twice prior to sensory evaluation by introducing them to sensory attributes related to fries. Potato fries was used as a reference during the training. Six sensory attributes: yellow colour, hardness, oiliness, rancid smell, curry leaves aroma and overall quality were used during training session. Perceived intensities were scored on 15 cm scale.

Statistical Analysis

All analysis was carried out in triplicate. All data was expressed as mean ± standard deviation (SD) and analysis was performed with a statistical analysis system. Two-way analysis of variance (ANOVA) was used to analyse the experimental data using MINITAB. In order to establish the significance of differences among the mean value at the 0.05 significance level, one way analysis of variance (ANOVA) and Tukey's test were used.

RESULTS AND DISCUSSION

Physicochemical Analysis

Peroxide values

Generally, it was observed that the Peroxide Value (PV) of the three oil systems increased during frying (Table 1). In system I, there was a drastic increase in the formation of peroxides from frying 2 to frying 4 and a subsequent decrease at frying 6. In system II and III, the formation of peroxides generally increased during frying. The oil was exposed to air and high heat (180°C) in this experiment. As a result, the unsaturated acids: oleic and linoleic acids present in the oil reacted with oxygen to form peroxide radicals. These radicals are unstable and are capable of extracting a hydrogen atom from other lipid and thus starting a chain reaction of peroxide formation which consequently increased the PV of the oil. As frying continued, more peroxides were formed. However, peroxides are unstable and can break down to carbonyl and aldehyde compounds. Thus, peroxides formed at frying 6 of system I might have decomposed to secondary oxidation products.

In the systems treated with curry leaves extract, it was generally observed that at 0.02%, the peroxide value was not significantly different ($P>0.05$) as compared to system I. A significant difference could only been seen during frying 6. At frying 6, the PV of system II was significantly ($P<0.05$) higher in comparison to system I. On the other hand, at 0.04% extract addition, the peroxide value was significantly ($P<0.05$) lower in comparison to the control and 0.02%. Generally, the changes in peroxide value were insignificant ($P>0.05$) between all the frying oil systems with different percentage of curry leaves extract addition. Contrary, Fatihanim *et al.* (2009) who reported that increasing the herb concentration could significantly ($P<0.05$) reduce peroxide formation. Inhibition of peroxide formation by curry leave extract was possible via donation of the hydrogen atom from OH group of phenolic compounds to the lipid radical which in turn produces a stable product and thus improving the oxidative stability of the oil towards oxidation.

Table 1. Changes in peroxide and iodine values of palm olein added with curry leaves extract during frying

	System I	System II	System III
	Peroxide value (meq hydroperoxide/ kg oil)		
Frying 2	$5.30\pm2.27^{b}_{A}$	$6.64\pm1.18^{a}_{A}$	$5.93\pm1.97^{a}_{A}$
Frying 4	$13.92\pm0.04^{a}_{A}$	$11.88\pm1.98^{b}_{A}$	$6.62\pm1.14^{a}_{B}$
Frying 6	$7.94\pm0.01^{b}_{A}$	$12.63\pm2.53^{b}_{B}$	$8.62\pm0.59^{a}_{A}$
	Iodine value (g of I_2/100 g oil)		
Frying 2	$62.47\pm0.84^{a}_{A}$	$61.80\pm0.10^{a}_{A}$	$62.73\pm0.38^{a}_{A}$
Frying 4	$61.33\pm0.57^{ab}_{A}$	$61.27\pm0.21^{b}_{A}$	$61.50\pm0.17^{b}_{A}$
Frying 6	$60.33\pm0.21^{b}_{A}$	$60.6\pm0.10^{c}_{AB}$	$60.93\pm0.23^{b}_{B}$

Note: System I, palm olein without curry leaves extract; System II, palm olein with 0.02% curry leaves extract; System III, palm olein with 0.04% curry leaves extract.
Means within each row with different capital letters are significantly ($P < 0.05$) different.
Means within each column with different small letters are significantly ($P < 0.05$) different.

Iodine Value

Iodine value (IV) measures degree of unsaturation in lipid sample with higher IV indicates a higher degree of unsaturation. Table 1 shows the changes in IV of all the three system of palm olein during frying. It was observed that there was a steady decrease in IV of the three oil systems upon deep-frying. In all the systems, a significant (P<0.05) change in IV from frying 2 to frying 6 could be noticed. The decrease in IV of oil after frying was due to the loss of double bonds as the oil becomes more oxidised (Che Man & Tan, 1999). The changes in IV over six times of frying for systems I, II and III were 2.13, 1.2 and 1.8 g of I_2/100 g respectively.

It was observed that there was a steady decrease in iodine value of the three oil systems upon deep-frying. In all the systems, a significant (P<0.05) change in iodine value from frying 2 to frying 6 were found. The decrease in IV of oil after frying was due to the loss of double bonds as the oil becomes more oxidised (Che Man & Tan, 1999). The changes in iodine value over six times of frying for systems I, II and III were shown as 2.13, 1.2 and 1.8 g of I_2/100 g respectively.

Though all the three systems had significant changes in their IV upon frying, system I and II had larger changes as compared to system III. These changes indicated that the rate of oxidation was reduced in system III. However, at frying 2 and 4, the IV of the three oil systems were found to be not significantly (P<0.05) different. Only at frying 6, a significant difference in IV could be observed. The IV of system III was not significantly different from system II but was significantly higher than system I. This showed that the curry leaves extracts were only effective after several frying. This is in support of a report by Fatihanim *et al.* (2009) where it was reported that the curry leaves extracts were only significantly (P<0.05) effective after 24 hours of frying. Therefore, the changes in IV showed that the effectiveness of curry leaves extract against oxidation was in the order: system III > system II > system I.

Free Fatty Acid

Table 2 shows the changes in free fatty acid (FFA) value of palm olein during frying. All the three oil systems showed a progressive increase in FFA value over frying times. FFA value of all the systems (system I, system II and system III) had an increment of 0.18%, 0.17% and 0.12% respectively. This indicated that as concentration of curry leaves extracts increased, the changes in FFA value decreased. However, the result shows no significant difference between free fatty acid value of system I and system II at all frying times. System III on the other hand, had significantly (P<0.05) low FFA value compared to systems I and II during frying. This shows that curry leaves extract was capable in retarding oxidation (29). However, the determination of FFA by titration does not differentiate between acids formed by oxidation and those formed by hydrolysis (Che Man & Tan, 1999). Therefore, the high value of free fatty acid cannot be ascribed to oxidation alone.

Thiobarbituric Acid Test

Thiobarbituric acid (TBA) test measures the amount of secondary oxidation products formed due to decomposition of peroxides. It especially relates to the amount of malondialdehyde formed as a result of peroxide decomposition. These products are responsible for the development of rancid odour and off-flavour of the oil.

Table 2. Changes in free fatty acid (FFA) and thiobarbituric acid (TBA) values of palm olein added with curry leaves extract during frying

	System I	System I	System I
	FFA value (%)		
Frying 2	$0.82\pm0.11^{a}_{A}$	$0.77\pm0.01^{a}_{A}$	$0.57\pm0.00^{a}_{B}$
Frying 4	$0.94\pm0.19^{a}_{A}$	$0.85\pm0.01^{b}_{A}$	$0.63\pm0.11^{a}_{A}$
Frying 6	$1.00\pm0.11^{a}_{A}$	$0.94\pm0.00^{c}_{A}$	$0.69\pm0.10^{a}_{B}$
	TBA value (µmoles malondialdehyde/kg oil)		
Frying 2	$0.78\pm0.01^{a}_{A}$	$2.13\pm0.00^{a}_{B}$	$0.67\pm0.00^{a}_{C}$
Frying 4	$1.09\pm0.01^{b}_{C}$	$2.85\pm0.00^{b}_{A}$	$1.38\pm0.01^{b}_{B}$
Frying 6	$1.42\pm0.01^{c}_{C}$	$2.62\pm0.00^{c}_{A}$	$1.90\pm0.00^{c}_{B}$

Note: System I, palm olein without curry leaves extract; System II, palm olein with 0.02% curry leaves extract; System III, palm olein with 0.04% curry leaves extract.
Means within each row with different capital letters are significantly (P < 0.05) different. Means within each column with different small letters are significantly (P < 0.05) different.

Table 3. Sensory acceptance score for fries fried using palm olein added with curry leaves extract

	Yellow colour	Hardness	Oiliness	Rancid smell	Curry leaves aroma	Overall quality
System I	6.1[ab]	7.3[a]	9.3[a]	5.9[a]	3.0[a]	6.3[a]
System II	5.6[b]	6.3[a]	7.9[a]	5.0[a]	3.8[a]	6.9[a]
System III	7.7[a]	7.5[a]	8.4[a]	5.5[a]	4.3[a]	6.1[a]

It can be generally observed that TBA values increased steadily with frying (Table 2). Throughout the frying, system I consistently had the lowest and significantly (P<0.05) different TBA value among all the systems, whereas system II had the highest TBA value. However, the increments in TBA value of all the three systems from frying 2 to 6 were 0.64, 0.49 and 1.23 μmoles malondialdehyde/kg oil respectively. This showed that system II had the minimal change in TBA value and system III had the maximal change in TBA value. However, this cannot be ascribed to the rate of oxidation. This is because secondary products such as malonadialdehyde were not stable for a long period of time. Malondialdehyde might have decomposed to alcohol and acid, which cannot be detected by a spectrophotometer (Che Man & Tan, 1999). Low result might also occur due to lack of free malondialdehyde as most of them are usually bound to food components and due to interactions between malondialdehyde and food proteins (Tsaknis *et al.,* 1999). Generally, as the peroxide values increased, the values of Thiobarbituric acid also increased. This finding was supported by a report written by Verma and Sahoo (2000) where they found a positive correlation between peroxide value and thiobarbituric acid reactive substances (TBARS) number of chevon during refrigerated storage.

Sensory Analysis of Fried Fries

Among all the oil systems, it was found that there was no significant difference in all sensory attributes; hardness, oiliness, rancid smell, curries leaves aroma and overall acceptance except for yellow colour attribute (Table 3). For yellow colour, system III had the highest score, followed by system I and II. The yellow colour attribute of system III was significantly higher in comparison to system II. However, it was not significantly different from system I. The higher score rated for this attribute in systems III indicate that the fries fried using the oil systems had a darker yellow colour. The darkening of fries fried using system I was due to deterioration of oil and Maillard reaction (Lalas & Dourtoglou, 2003). On the other hand, though system III had been treated with curry leaves, the fries had the darkest colour compared to the other two systems. This is because system III had the highest concentration of curry leaf extracts and thus more naturally occurring pigments in the curry leaves leeched out into the oil (Lee *et al.,* 2004). Fatihanim *et al.* (2009) also reported in their report that the oils containing herb extracts were significantly (P<0.05) darker than the control, and increased significantly (P<0.05) faster compared with BHT and control. Overall quality scores given by the panelists showed no significant different indicating the ability of system II and III (those oil systems with curry leaves extract addition) to minimise deterioration of oil without affecting the sensory attributes of the fries.

CONCLUSION

The findings showed that the addition of 0.04% of curry leaves extract had minimized the changes in PV, IV, Thiobarbithuric value and FFA percentage. The effectiveness of curry leaves extract in retarding and minimizing lipid oxidation is in the order of system III>system II>system I. Qualitative Descriptive Analysis scores showing that the addition of curry leaves extract did not affect the sensory quality attributes.

ACKNOWLEDGEMENTS

This study is funded by Faculty of Science and Technology, Universiti Sains Islam Malaysia, Nilai, Negeri Sembilan. The authors would also like to thank to the staff of the Food Technology Laboratory of Faculty of Science and Technology, Universiti Sains Islam Malaysia for their assistance throughout the study.

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