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# Effect of ultrasound treatment on oxidative stability of sunflower oil and palm oil

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**Abstract**

This study aims to investigate the effect of sonication time (2-120 mins) on lipid oxidation and accelerated storage of ultrasound treated sunflower oil (UTSO) and ultrasound treated palm oil (UTPO). Peroxide values (PV) of UTSO and UTPO were measured to assess the oxidative stability of sunflower oil and palm oil. Accelerated storage of UTSO and UTPO were conducted for 24 days at 60°C with a 6-days-intervals analysis The PV increased gradually with the increasing sonication time and reached the highest PV of 10.25 and 5.67 meq peroxides/kg in UTSO and UTPO, respectively. The UTPO exhibited higher PV (44.67 meq peroxides/kg) than UTSO (19.91 meq peroxides/kg) upon accelerated storage. No significant ($p > 0.05$) difference was observed on the quality of UTSO and UTPO with their controls after 24 days of accelerated storage. Results of this study demonstrated that ultrasound (US) treatment via ultrasonic bath accelerates lipid oxidation process without significant impact on the generation of lipid oxidation by-products during prolonged storage.



## Introduction

Edible oil has been used in many food preparations. Generally, edible oils are high in triacylglycerols with minor compositions such as monoglycerols and diacylglycerols, phospholipids, free fatty acids (FFA), tocopherols, metals, carotenoids, phenolic compounds, and peroxides (Choe and Min, 2006). The commonly used edible oils include sunflower oil (SO) and palm oil (PO). The SO is popular among consumers due to its high amount of monounsaturated fatty acid (MUFA) and polyunsaturated fatty acid (PUFA) (Chowdhury *et al*., 2007). Meanwhile, PO which has high oxidative and thermal stability, provide good frying quality (Azlan *et al*., 2010).

The presence of high amount of PUFA in the structure of triacylglycerol leads to a reduced shelf life (Geleta *et al.*, 2001) in oil rich in PUFA. This is associated to the undesired lipid oxidation that occurs when PUFA is exposed to oxygen, light, and heat (Pingret *et al.*, 2012). This is a major concern in food industry as it could leads to undesired food quality deterioration involving reduction of nutritional level and off-flavours. In an earlier study done by Chemat, Grondin, Costes *et al.* (2004) reported that SO turned cloudy after ultrasound (US) treatment. Therefore, lipid oxidation is one of the concerns for US application.

The US is an energy which is produced by sound waves using high frequency (above 16kHz) (Dolatowski *et al.*, 2007). The use of US treatment in food processing is rising with its ability to provide higher throughput by using lesser energy, maintenance cost and preparation time (Chemat *et al*., 2003; Pingret *et al*., 2012). Recently, US is applied in many food processing such as emulsification, homogenization, cutting, extraction, pasteurization, cleaning, freezing, thawing, cooking, and sterilization of high-lipid-food such as cheese, yogurt, and milk (Chemat, Lagha, AitAmar *et al.*, 2004; Pingret *et al*., 2012). In addition, US has been also used as a slicer in pastry and confectionery (Schneider *et al*., 2008; Chemat *et al.*, 2011).

The US applications are categorized into low energy US (frequencies > 100 kHz, intensities < 1W.cm$^{-2}$) and high energy US (intensities > 1W.cm-2, frequencies: 18-100 kHz). The low intensity US is non-destructive as it utilizes a very low power level where the US waves incapable of altering physical and chemical properties of food. On the other hand, the high intensity US is capable of changing the physical, chemical and mechanical properties of food (Dolatowski *et al*., 2007). However, the major drawback of high intensity US is increased rate of oil deterioration (Hosseini *et al*., 2015). Therefore, US water bath with lower intensity is preferred in this

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study.

In a recent study conducted by Hosseini *et al.* (2015), primary oxidation products of PV and conjugated diene (CD) in sesame oil, olive oil and tallow olein was found elevated with the increasing US intensity but not in SO. Hence, more study is required to understand the effect of US on SO and other edible oils. In contrary to liquid soybean oil, US-treated interesterified soybean oil generated lower PV than untreated sample (Lee *et al*., 2015).

Besides, US is also been utilized widely to enhance crystallization process by inducing smaller crystals formation, reduces time for crystallization induction, enhance production of stable polymorphic form, and produces more elastic and harder materials (Lee *et al.*, 2015). Power US has been utilized to stimulate crystallization of some edible lipids (Chemat, Grondin, Costes *et al.,* 2004). In addition, the US also fasten nucleation rate and controls production and formation of crystals. In a study by Chemat, Grondin, Costes *et al.* (2004), there was a slight modification on chemical composition and development of off flavours compounds such as decadie-2,4-enal, hept-2-enal and hexanal in sonicated oils. The power US had been applied to manufacture ice cream, preserve vegetable and fruit, and crystallize liquid ice and crystallization of food and sugar (Zhang *et al*., 2015). Interestingly, it has been claimed that supercooled crystallization in oil can be induced by US (Kaltsa *et al.*, 2014). Chen *et al*. (2013) asserted that 120 s of US accelerated crystallization in PO which is vital in maintaining the oil product quality.

Undoubtedly, US treatment is effective in inducing physical, functional, structural and chemical modification in foods (Pingret *et al.*, 2012). However, these changes may not be favourable and contribute to quality deterioration. Thus, the use of US in food processing shall be monitored to assure the quality of finished food products. Ideally, US treatment shall maintain the food quality attributes as seen in the study by Chang *et al*. (2015) where the use of US treatment did not alter the meat quality attributes. However, the use of US treatment has reduced protein content in raw whole milk as compared to pasteurized raw whole milk (Bermúdez-aguirre *et al*., 2009). Hence, the use of US treatment in food industry should be studied extensively.

In this study, lipid oxidation products were measured to investigate the effect of sonication time on lipid oxidation in SO and PO. The oxidative stability of US treated SO and PO under accelerated storage was also studied to investigate in the impact of US treatment on the shelf life of treated edible oils via accelerated storage study.

## Materials and methods

### *Materials*

Refined sunflower oil (SunLico Sunflower Seed Oil) and Refined Palm Oil (Buruh Filtered Cooking Oil) were purchased from a hypermarket, Giant, Subang Jaya. All of the chemicals and reagents used were analytical reagent grade. Isooctane (2,2,4-trimethylpentane) was obtained from Fisher Scientific (UK). Sodium thiosulfate pentahydrate and glacial acetic acid were purchased from Merck (Germany). Potassium dichromate and Sodium Dedocyl Sulphate (SDS) were purchased from R&M Chemical (UK). Starch powder and p-anisidine were purchased from Sigma-Aldrich (Germany).

### *Sample preparation*

Briefly, oils (20 mL) were filled into amber bottles with 1cm headspace each. Subsequently, oils in amber bottles were subjected to US treatment in an ultrasonic bath (ELMA Ultrasonic LC130H, frequency: 35 kHz, power: 240 watts, Germany) for various time points.

### *Effect of sonication time on primary oxidation of lipids*

Sample preparation was repeated for time points of 2, 5, 10, 15, 20, 30, 60, 90, and 120 mins. The water in ultrasonic bath was replaced after every sonication time point. Meanwhile, oils without ultrasonic treatment (SO and PO) were used as controls. The resulting samples were subjected to PV analysis. The US treatment on oils was duplicated and PV analysis was triplicated.

### *Accelerated storage of ultrasound treated sunflower oils (UTSO) and ultrasound treated palm oils (UTPO)*

Samples preparation was repeated by subjecting SO and PO to US treatment for sonication time of 10 and 30 mins, respectively. The sonication time were chosen based on the result obtained in Figure 1, where SO and PO with low lipid oxidation product was chosen for accelerated storage study. For accelerated storage, the sonicated oils (UTSO and UTPO) for each sampling day were stored in different amber bottles ($6^{th}$, $12^{th}$, $18^{th}$ and $24^{th}$ day, respectively) to prevent undesirable oxidation and contamination. The US treated oil samples (UTSO and UTSO) were stored in amber bottles with consistent head space. All of the samples were stored in 60$^{o}$C oven (PROTECH) for 24 days (AOCS Recommended Practice CG 5-97 2009). Negative control samples comprising of SO and PO (without US treatment) were also stored under the same storage conditions as US treated samples.

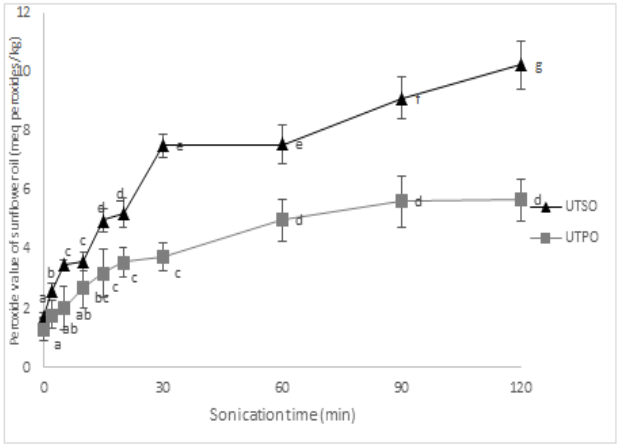


Figure 1. Changes in PV of UTSO and UTPO with different sonication times. The different letters (a-g) indicate significant differences at $p<0.05$ based on Tukey HSD test (n=6) on a peroxide value between sonication time. The controls are SO and PO (at 0 min, without treatment).

The resulting oil samples were stored in a nitrogen atmosphere at 4°C prior to analyses. Samples were analyzed for PV, CD and p-anasidine value (p-AV) and analysis were conducted at six days intervals of 24 days. The accelerated storage and analyses were replicated.

*Determination of peroxide value (PV)*

The peroxide values (PV) were determined according to AOCS official methods (Cg 3-91) (AOCS, 2009). Oils (2.0 g) were dissolved in 3:2 acetic acid-isooctane solutions (50 mL). Briefly, 0.5 mL of saturated KI solution was added by using a volumetric pipette. Samples were shaken for 1 mins and distilled water (30 mL) was added. The samples were titrated with 0.001M sodium thiosulfate solution which was added gradually with vigorous and constant agitation until yellow colour iodine nearly disappears. Then, 10% SDS (0.5 mL) and 1% starch indicator solution (0.5 mL) were added. Titration was continued until blue colour just disappeared. The blank was analyzed in the same treatment and was conducted daily.

*Determination of Conjugated Dienoic Acid (CD)*

The determination of conjugated dienoic acids were according to AOCS Official Method (Ti 1a -64) (AOCS, 2009). Oils (100 mg) were dissolved in 75 mL of isooctane in 100 mL of volumetric flask. Samples were warmed in 50°C water bath (Memmert) for 10 mins to dissolve the sample completely. Samples were then cooled to room temperature for 15 mins. The isooctane was added up to the mark of volumetric flask and samples were swirled. The absorbance was measured at 233nm by using quartz cuvette (1 cm) in UV-Vis spectrophotometer (UvLine 9400–SECOMAM). Isooctane was used for blank. Duplicate readings were obtained and the average value was recorded. The absorbance reading must be between 0.2 and 0.8.

*Measurement of p-Anisidine value*

The p-anisidine values (p-AV) were according to AOCS Official Method (Cd 18-90) (AOCS, 2009). Oils (0.5 ± 0.01 g) were dissolved with isooctane (25 mL) in 25 mL of volumetric flask. The absorbance readings were measured at 350 nm in quartz cuvette with UV-vis spectrophotometer. Then, oil solutions (5 mL) were mixed with 0.25% p-anisidine (1 mL) in glacial acetic acid. The new blank, 5 mL of isooctane added with p-anisidine reagent (1 mL) was used for the second absorbance measurement. The second absorbance readings were measured at 350 nm after 10 mins addition of p-anisidine into oil solutions.

*Total oxidation (TOTOX)*

The PV and p-AV analyses provide a better indication of total oxidation as compared to each test individually. The total oxidation (TOTOX) values of oil samples were calculated by using a formula,

$$\text{TOTOX value} = 2\text{PV} + \text{p-AV}$$

*Statistical analysis*

Experimental results were expressed as mean ± standard deviation of replicate ultrasonic treatment analysis. Statistical analyses were carried using SPS Inc., Chicago, IL). One way analysis of variance and Tukey's test were performed to determine the significant difference of oil quality between control and US treated oil samples.

## Results and discussion

*Effect of sonication time on production of lipid oxidation products*

The rate and extent of lipid oxidation can be determined by measuring formation of hydroperoxides in the US treated oils (UTSO and UTPO) (Rohman *et al.*, 2011). The PV of both UTSO and UTPO increased significantly ($p < 0.05$) as sonication time increased with the maximum PV achieved at 120 mins (Figure 1). Previous studies on enhancement oil crystallization by using US treatment had used about 30s to 60 mins of sonication time (Chemat, Lagha, AitAmar *et al.,* 2004; Chemat, Grondin, Costes *et al*., 2004; Patrick *et al.,* 2004; Lee *et al*., 2015). In this study, sonication time used was extended to 120 mins to identify the ideal sonication time for food

processing without generation of high oxidation products (above 10 meq peroxides/kg) that render the finished product undesirable for consumption.

Both SO and PO without US treatment showed the lowest PV (1.73 meq peroxides/kg and 1.29 meq peroxides/kg respectively) at 0 mins. Interestingly, PV of UTSO (10.25 meq peroxides/kg) was doubled of the PV of UTPO (5.67 meq peroxides/kg) after 120 mins of sonication. This is likely due to the higher composition of PUFA in SO since it is a large source of long-chain unsaturated fatty acids, which is mainly composed of linoleic acid that causes it to be susceptible to lipid oxidation (Edem, 2002; Chowdhury *et al*., 2007; Zhang *et al.*, 2010). As number of double bonds in PUFA elevates, hydroperoxides will become more complex and decomposed easily (Chemat, Grondin, Costes *et al.*, 2004). The lower PV in UTPO after 120 mins might be due to high lipid soluble antioxidants such as vitamin E, carotenoids and ubiquinone in PO, making PO more stable than SO (Edem, 2002; Jacques *et al*., 2008). Therefore, UTSO undergoes lipid oxidation faster than UTPO due to the presence of higher PUFA.

Based on PV, oxidation state is evaluated in three classifications: low (1-5 meq peroxides/kg), moderate (5-10 meq peroxides/kg), and high (above 10 meq peroxides/kg) (Moigradean *et al*., 2012). The low oxidation is observed in UTSO until 15 mins sonication, where further sonication time further induced oxidation to moderation oxidation. Further sonication up to 120 mins rendered it to moderate oxidation state (10.25 meq peroxides/kg). In contrast, UTPO exhibited lower lipid oxidation rate as compared to UTSO.

Among the studied sonication time ranges, 10 and 30 mins are the best sonication time for UTSO and UTPO, respectively. Both of these oils show low oxidation by having PV of 3.60 meq peroxides/kg and 3.74 meq peroxides/kg for UTSO and UTPO, respectively. Therefore, both of the sonication that produce low oxidation products in oils (10 and 30 mins for SO and PO) were selected for accelerated storage study.

The increasing of primary oxidation products were indicated by the increasing PV value in both UTSO and UTPO. This is likely attributed to the cavitation effect generated during US treatment (Chemat, Grondin, Costes *et al*., 2004). The collapse of cavitation bubbles generates many free oxygen species contributing to the increased amount of radicals in US treated oils that induced lipid oxidation. Furthermore, simultaneous decomposition and production of hydroperoxides might be the factors that cause rancidity of UTSO and UTPO. The cavitation induces lipid oxidation through thermal, free radicals production, mechanical forces produced by shock waves and microstreaming or combination any of them (Chemat, Grondin, Costes *et al*., 2004; Hosseini *et al.*, 2015).

Ultrasonic probe and ultrasonic bath were reported to introduce similar ultrasonic degradation in edible oils that resulted undesirable off-flavours and cloudy appearance (Chemat, Grondin, Costes *et al.*, 2004). The recent study suggested that ultrasonic water bath might have weaker sonication power with non-uniform cavitation distribution compared to ultrasonic probe (Dolatowski *et al.*, 2007). Although ultrasonic bath is weaker than ultrasonic probe, but more study is required to understand the effect of this sonication process on the quality changes during prolong storage.

*Accelerated storage of ultrasound treated sunflower oil (UTSO) and ultrasound treated palm oil (UTPO)*

Lipid oxidation is undesirable process that might occur either during processing or storage. Hence, prolonged oxidative stability is vital to the nutritional value and shelf life of edible oils (Akhtar *et al.*, 2012). Oxidative stability of oil refers to the resistance capability of oil towards oxidation within storage and processing (Choe and Min, 2006). In this study, accelerated storage of US treated oils (UTSO and UTPO) were compared with controls, (untreated SO and PO) by measuring PV, CD, p-AV and TOTOX value of the samples.

*Peroxide value*

The PV has been used to measure concentration of hydroxides and peroxides produced during the early lipid oxidation stage. Oils with high PV is unstable and easily become rancid (Zhang *et al.*, 2010; Poiana, 2012). The PV of US treated oils (UTSO and UTPO) increased significantly ($p < 0.05$) from day 0 to 24 of storage with the highest value of 19.91 and 44.66 meq peroxides/kg, respectively on day 24 of storage (Figure 2). Meanwhile, PV showed the highest value of 17.60 and 38.75 meq peroxides/kg in SO and PO (controls) respectively after 24 days of storage.

As oxidation continues, oxygen is integrated into unsaturated fatty acids, hence producing greater hydroperoxides. Principally, the production rate of hydroperoxides and lipid peroxy radicals were influenced by temperature and oxygen availability during storage (Velasco *et al.*, 2005). The autooxidation of oil needs acylglycerols and fatty acids to be in radical states to induce lipid oxidation (Choe and Min, 2006). The oils might contain metals

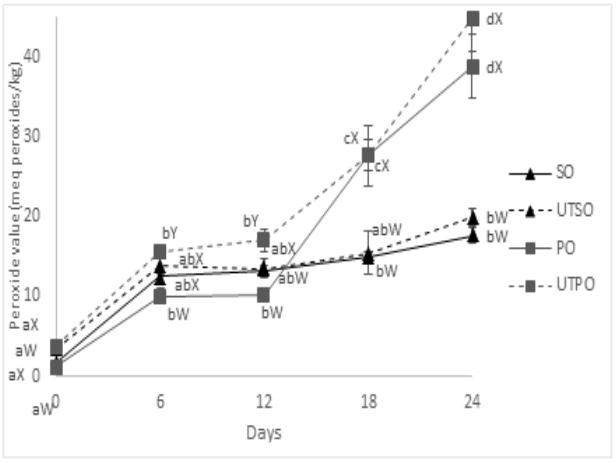


Figure 2. Changes in PV of US treated samples (UTSO and UTPO) and controls (SO and PO) at 60°C under 24 days of accelerated storage (n=4). The different letters (a-d) indicate significant differences on the PV of UTSO, UTPO and controls (SO and PO) from day 0 to day 24. Meanwhile, letters (W-Z) show significant differences on the PV of UTSO, UTPO, SO and PO on day 0, 6, 12, 18, 24 of accelerated storage respectively. Values with same superscripted letters are not significantly different at $p<0.05$ based on Tukey HSD test (n=4)

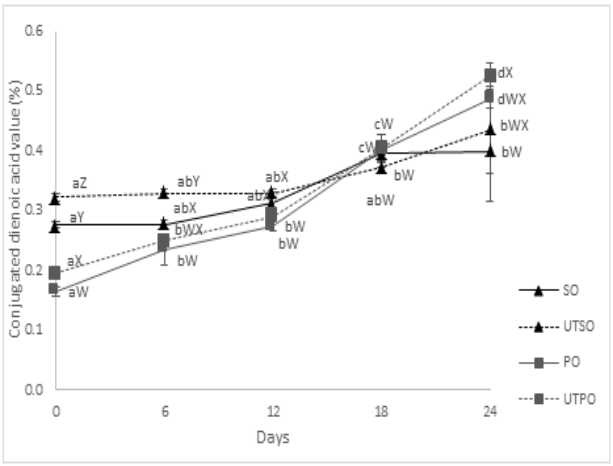


Figure 3. Changes of conjugated CD of US treated samples (UTSO and UTPO) and controls (SO and PO) at 60°C under 24 days of accelerated storage. The different letters (a-d) indicate significantly different on CD in UTSO, UTPO and controls (SO and PO) from day 0 to day 24 of accelerated storage. Meanwhile, different letters (W-Z) show significantly different on CD of treated samples in day 0, 6, 12, 18, and 24 of accelerated storage respectively. Values with same superscripted letters are not significantly different at $p<0.05$ based on Tukey HSD test (n=4).

such as nickel, iron and copper which act as catalysts for lipid oxidation. The main oxidative agents during the storage are oxygen and light (Chemat, Grondin, Costes *et al*., 2004). Surprisingly, US treated edible oils (UTSO and UTPO) showed no significant difference ($p > 0.05$) with their controls, respectively (SO and PO) after 24 days of storage. Therefore, it was deduced that sonication did not enhance the amount of hydroperoxides produced in US treated oils during prolong storage.

The combinations between metals (i.e. copper) and US cavitation produced oxy radical species that initiated the volatile compounds production (Chemat, Grondin, Costes *et al.*, 2004). The initiation of lipid oxidation depends on the speed of reactions between radicals and lipid. During lipid oxidation, hydroxyl radicals react very fast with lipid hence will attack lipid randomly since their reactions are nonspecific. The radicals then initiated the oxidation of chain reaction (Pingret *et al.*, 2013).

A study done by Chemat, Grondin, Costes *et al.* (2004) showed that high power US (20 kHz) generated greater PV (6.33 meq peroxides/kg) in UTSO as compared to untreated sample (5.38 meq peroxides/kg) after 2 mins of sonication. The flavor of edible oils was altered and the compositions were degraded by the US treatment. The PV in The UTSO changed after one month of storage. In the study, PV elevated rapidly along 30 days storage time until a maximum value of about 30 meq peroxides/kg.

During accelerated storage, oils are exposed to thermal oxidation in 60°C with the presence of oxygen (Poiana, 2012). At 0-day of storage, the rancidity of oil after US treatment might be attributed by simultaneous production and degradation of hydroperoxides (Chemat, Grondin, Costes *et al*., 2004). As the length of accelerated storage increased, the amount of hydroperoxides also increased in both US treated oils and controls (Figure 2). The PV of both US treated oils (UTSO and UTPO) and controls (SO and PO) begin to exceed 10 meq peroxides/kg after 6 days of storage. A drastic increased in PV of UTPO was observed after 24 days of storage. Theoretically, UTPO shall has a lower oxidation rate because of its lower amount of unsaturated fatty acids (Akhtar *et al.*, 2012). However, UTPO produced a greater hydroperoxides than UTSO at end of accelerated storage.

The increment of PV values is in accordance to Chemat, Grondin, Costes *et al.* (2004), where there was also no decrement in PV values in refined sunflower oil. The decrease of PV is likely due to the degradation of hydroperoxides into secondary oxidation products such as ketones and aldehydes (i.e. 2-alkenals and dienals) (Pingret *et al*., 2012; Raza *et al.,* 2014). These secondary oxidation products might produce toxic effects and off-flavours in fats and vegetable oils (Pingret *et al.*, 2012; Raza *et al*., 2014). However, PV in this study did not shows any reduction from day 0 to 24 of accelerated storage (Figure 2).

Oil is considered rancid when PV is elevated

(Wannahari and Nordin, 2012). As shown in Figure 2, the PV of UTSO and UTPO increased across accelerated storage period. The length of accelerated storage is proportional to the rancidity of UTSO and UTPO. The result obtained from this study is agreeable with study by Chemat, Grondin, Costes *et al*. (2004) where PV of UTSO also increased after one month of storage. This is because, the rate of oil oxidation is accelerated as the concentration of thermally oxidized compounds elevated.

Undoubtedly, storage at 60ºC favoured the oxidation and formation of PV. This is attributed to the heat provided by high heat treatment that causes hydroperoxides became unstable and favoured the peroxides production. Oil oxidation likely damaged the essential fatty acids, hence producing toxicity, reduce nutritional quality and palatability (Choe and Min, 2006). In this study, US showed no significant effect to the generation of hydroperoxides in UTSO and UTPO during long term storage with no significant ($p > 0.05$) difference observed between UTSO and UTPO with controls (SO and PO).

*Conjugated dienoic acid value*

Similar to the PV, CD is also used to indicate primary oxidation products produced by lipid oxidation. Both PV and CD curves (Figure 2 and Figure 3) shows a similar trend. This finding is supported by Hosseini *et al*. (2015) where the CD value was correlated with PV. It is also observed that CD increased significantly ($p < 0.05$) from day 1 to 24 of accelerated storage (Figure 3). The generation of high amount of CD is attributed to the high percentage of unsaturated fatty acids in oils that contributed to the increased rate of oxidation (Shahidi and Zhong, 2005; Pambou-Tobi *et al*., 2010).

In this experiment, UTSO produced greater CD as compared to UTPO in the early days of accelerated storage (until day 12). This might be due to the presence of greater unsaturated fatty acid composition in SO which has greater susceptibility to lipid oxidation as compared to PO (Akhtar *et al*., 2012). However, CD of UTSO showed no significant difference ($p > 0.05$) with UTPO after 24 days of accelerated storage. By analyzing conjugated dienes in both UTSO and UTPO, it was deduced that US treatment resulted similar primary lipid oxidation products in UTSO and UTPO after prolong storage.

The CD of UTSO and UTPO reached the highest value of 0.44% and 0.53% respectively after 24 days of storage. Whilst, the controls (SO and PO) resulted in a lower CD as compared to US treated oils with a value of 0.40% and 0.49% respectively. Interestingly, the CD of UTSO showed no significant difference ($p > 0.05$) with UTPO at the end of accelerated storage. In brief, US did not enhance primary oxidation products in UTSO and UTPO during storage as the CD generated by US treated oils showed no significant difference ($p > 0.05$) with untreated oils (SO and PO).

*P-anisidine value (p- AV)*

According to Moigradean *et al.* (2012), p-AV measures carbonyl composition in fats or oils. The generation of Schiff base which absorbs at 350 nm is due to the reactiveness of carbonyl bonds in aldehyde towards p-AV amine group. Besides, p-AV is more accurate to measure lipid oxidation because the secondary oxidation products are more stable as compared to primary oxidation products (Akhtar *et al*., 2012). The secondary oxidation products such as ketones, hydrocarbons, aliphatic aldehydes and alcohols cause rancidity in edible oils by producing off-odours or off-flavours (Poiana, 2012).

As shown in Figure 4, p-AV of US treated oils (UTSO and UTPO) increased significantly ($p < 0.05$) from day 0 to 24 of accelerated storage, hence indicating the increment of secondary oxidation products along storage days. Presence of aldehydes might result off-flavours that will induce lipid degradation. The production of off-flavour compounds will make product become unacceptable for consumers and are not allowed to be used in industry for food ingredient.

The UTSO and UTPO reached the highest p-AV (15.64 and 13.09) respectively, after 24 days of storage as shown in Figure 4. Meanwhile, SO and PO showed p-AV of 14.88 and 13.09 after 24 days of storage. From p-AV result, US-treated samples (UTSO and UTPO) showed no significant difference ($p > 0.05$) with controls (SO and PO). Principally, the p-AV assessed both unsaturated and saturated carbonyl compounds in triacylgyerols. Thus, it can be assumed that UTSO and UTPO comprised approximately the same amount of unsaturated and saturated carbonyl compounds after 24 days of storage.

As shown in Figure 4, UTSO showed a greater p-AV as compared to UTPO until 18 days of storage. However, UTPO shows no significant difference ($p > 0.05$) with UTSO after 24 days of storage. The amount of secondary oxidation products produced from primary oxidation products (hydroperoxides) is different in many oils. In rapeseed oil and olive oil, secondary oxidation products were generated quickly after hydroperoxides production. Meanwhile, secondary oxidation products were produced only when hydroperoxides are highly concentrated in SO (Guillen and Cabo, 2002). Although SO and

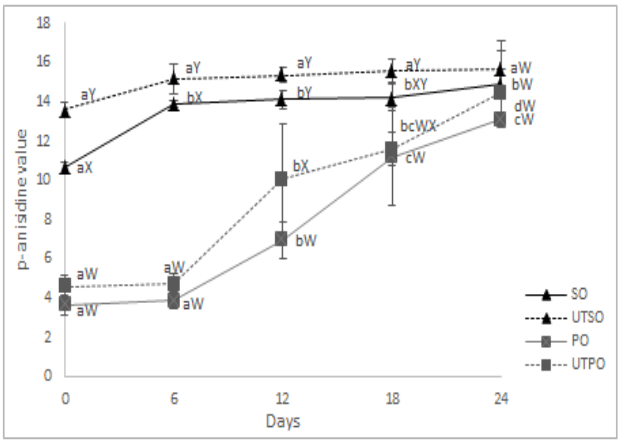


Figure 4. Changes of p-anisidine value (p-AV) in US treated samples (UTSO and UTPO) and controls (SO and PO) at 60°C under 24 days of accelerated storage (n=4). The different letters (a-d), indicates significant differences on p-AV in UTSO, UTPO, and controls (SO and PO) from day 0 to day 24 of accelerated storage. Meanwhile, different letters (W-Z) show significant differences of p-AV of treated samples in day 0, 6, 12, 18 and 24 of accelerated storage. Values with same superscripted letters are not significantly different at $p < 0.05$ based on Tukey HSD test (n=4).

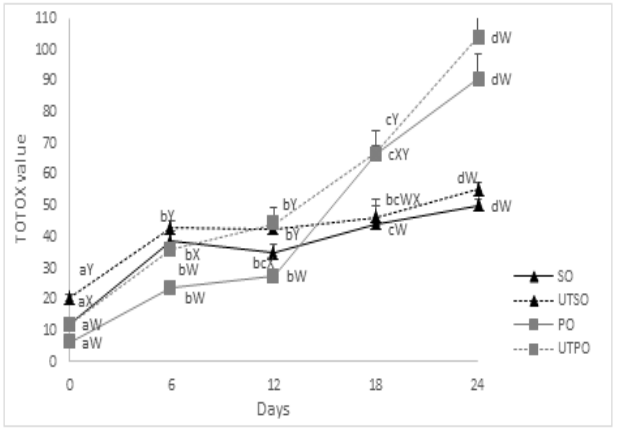


Figure 5. Changes in TOTOX value of US treated samples (UTSO and UTPO) and controls (SO and PO) at 60°C within 24 days of accelerated storage. The different letters (a-d) indicate significant differences in TOTOX value in UTSO, UTPO, SO and PO from day 0 to 24 of accelerated storage. Meanwhile, different letters (W-Z) shows significant differences of TOTOX value of treated samples in day 0, 6, 12, 18 and 24 of accelerated storage respectively. Values with same superscripted letters are not significantly different at $p<0.05$ based on Tukey HSD test (n=4).

PO comprise a different composition of unsaturated fatty acids, respectively, however, US treatment produced no difference in secondary oxidation products by both UTSO and UTPO indicated by p-AV. Hence, it was concluded that UTSO and UTPO have approximately similar amount of substrate for lipid oxidation process, since secondary oxidation products of UTSO and UTPO showed were almost similar after 24 days of storage.

Chemat, Grondin, Costes *et al.* (2004) reported production of off-flavours compounds due to oxidation process such as decadie-2,4-enal, hexanal and hept-2-enal in US-treated oils. In a study by Lee *et al.* (2015), sonicated and non-sonicated samples of interesterified soybean oil and liquid soybean oil showed no significant change of PV after 105 days of storage in 25°C. After transferring to 40°C incubator for 42 days, PV of soybean oil showed higher stability at early stage of storage but eventually showed higher oxidation than interesterified soybean oil. The PV of UTPO in this study elevated faster than UTSO in this study. Similar with this situation, PV of soybean oil elevated faster than interesterified soybean oil even it's initial PV was lower (Lee *et al.,* 2015). In the study, PV only showed significant difference when oils achieved PV greater than 10 meq peroxides/kg. It was interesting to note that PV of sonicated oils showed no significant difference ($p > 0.05$) with non-sonicated oils when PV was lower than 10 meq peroxides/kg. The sonicated soybean oil portrayed a significantly higher PV than non-sonicated sample at 28 to 42 days of storage. It has been claimed that the factors that might influence oxidative stability of sonicated oils were the initial PV of sonicated samples and their chemical constituents (Lee *et al.*, 2015).

*Total oxidation value (TOTOX)*

TOTOX value is the total oxidation indicated by the addition of AV and 2PV. Basically, TOTOX value shows the whole quality and the degradation level of oil. Furthermore, oil with low TOTOX value has good quality of oil (Poiana, 2012).

The p-AV is less specific in determining secondary oxidation of lipid. Therefore, peroxide and anisidine analysis will give better indication of total oxidation as compared to every test individually (Poiana, 2012). The combination of p-AV and PV will indicate oil quality with more accurate, especially for oils with low PV (Pingret *et al*., 2012). The total oxidation (TOTOX) value will indicate the whole oxidative stability which relates to oil deterioration stability. Based on Figure 5, UTSO and UTPO showed significant increased ($p < 0.05$) as days of accelerated storage increased. Thus, it was proposed that total oxidation in UTSO and UTPO increased as days of accelerated storage increased.

The TOTOX value of UTPO (103.80) showed no significant difference ($p > 0.05$) with UTSO (55.46) after 24 days of storage as shown in Figure

5. Interestingly, both US treated oils (UTSO and UTPO) showed no significant difference ($p > 0.05$) with respective controls (SO and PO) after 24 days of storage with TOTOX value of 50.08 and 90.58 respectively after 24 days of storage. This was supported by PV (Figure 2), CD (Figure 3) and p-AV (Figure 4) analyses where oxidation products produced by UTSO and UTPO showed no significant difference ($p > 0.05$) after 24 days of storage. Therefore, it was concluded that US treatment did not enhance total oxidation products in US treated oils during prolong storage.

## Conclusion

The production of hydroperoxides increased with prolonged exposure to the cavitation bubbles during US treatment. It is observed that UTSO is prone to lipid oxidation with formation of more hydroperoxides than UTPO after 120 min of sonication. The accelerated lipid oxidation observed in UTSO and UTPO were attributed to the cavitation oxidation exerted by the US treatment. In comparison, UTPO induced a greater primary oxidation products (PV and CD) than UTSO after 24 days of storage. However, the secondary oxidation products of UTSO showed no significant difference ($p > 0.05$) with UTPO after 24 days of storage which is confirmed by p-AV. Hence, it is concluded that US only fasten lipid oxidation process but did not enhance the amount of secondary oxidation products produced by US treated samples (UTSO and UTPO) during prolong storage. Knowing the drawback of sonication treatment on the quality of edible oil, extensive research should be conducted to minimize the detrimental effect of US treatment on edible oil to enable US application in food processing industry.

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